### UNIVERSITY OF CALIFORNIA

## SANTA CRUZ

### INFRARED CHARGE DYNAMICS IN COMPLEX MATERIALS

A dissertation submitted in partial satisfaction of the requirements for the degree of

## DOCTOR OF PHILOSOPHY

in

### PHYSICS

by

### Jason N. Hancock

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The Dissertation of Jason N. Hancock is approved:

Professor Zack Schlesinger, Chair

Professor Sue A. Carter

Professor B. Sriram Shastry

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#### Abstract

#### Infrared Charge Dynamics in Complex Materials

by

#### Jason N. Hancock

Here I give a review of work pertaining to optical experiments in condensed matter systems I performed in the Schlesinger lab at UCSC. The introductory chapters give an account of the optical properties of solids and reflectivity analysis methods pertinent to the optical data given in the later chapters. I then discuss the construction of a vacuum chamber extension to a Brüker 66v FTIR spectrometer which I designed and assembled, rendering this state-of-the-art instrument capable of reliably and reproducibly performing reflectivity measurements over a wide range of frequency and temperature. Experiments on  $YbIn_{1-x}Ag_xCu_4$  and  $ZrW_2O_8$  are discussed in the subsequent chapters.

Optical data and analysis on the strongly correlated electron system YbIn<sub>1-x</sub>Ag<sub>x</sub>Cu<sub>4</sub> shows the striking appearance of a well-defined excitation in the mid-infrared as a phase transition is approached at low doping (x < 0.2) and low temperature. Interpretation of this MIR excitation is given in terms of the periodic Anderson model and analysis of the systematic x-dependent changes reveal scaling of the strength and frequency which support our conjecture that this excitation is a consequence of a Kondo resonance near  $E_F$ . Analysis of higher frequency features is also considered and a possible interpretation of trends found there is given.

The second system under consideration is the negative thermal expansion compound  $ZrW_2O_8$ . Our infrared measurements reveal unusual phenomenology in the far-infrared sector of the optical conductivity and we show that reconciliation of these data with those provided by other probes presents a challenge to theory. In addition, we present develop a technique to

model the optical conductivity of phonon systems and apply this technique to  $ZrW_2O_8$ . This analysis reveals the nature of the low frequency ionic motion that is relevant to the unusual negative thermal expansive behavior. For my grandparents,

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In the development of the Brüker 66v vacuum extension described in Chapter 3, special

thanks is due to Darryl Smith and Dave Thayer of UCSC, and Jerry Davis at Davis Machining Products for expert guidance and efforts in the construction of this instrument. In addition, I would like to thank Billy Brown at UCO/Lick Observatory and William Inman at Continental Sales Corporation for their voluntary assistance in constructing the sample and detector mirrors used in this project.

On the YbIn<sub>1-x</sub>Ag<sub>x</sub>Cu<sub>4</sub> project, I would like to thank collaborators John L. Sarrao and Zachary Fisk for expert opinion and for providing excellent single-crystalline samples. At UCSC, Tim McKnew, Sonya Hoobler, Yvonne Rodriguez, and Sean Garner all played roles in helping to acquire the rather expansive set of x- and T-dependent data for the project. Special thanks too to Dimitri Basov, Andy Cornelius, and especially to Dan L. Cox for relevant discussions.

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# Chapter 1

# Introduction

Whenever we are approached with a new problem, we tend to simplify matters at the outset by eliminating variables. In the simplest cases, this is a quite reasonable thing to do, but it seems that nature does not require this conceptual convenience in order to operate. In the early twentieth century it became possible to understand completely the microscopic physics pertinent to the construction of matter, namely that the rules of quantum mechanics and electrodynamics describe the dynamics of the particles underpinning our common experience (photons, electrons, and nuclei). This precision command of material constituents sets up a challenging puzzle, namely how to conceptually bridge the scale gap from  $10^{-9}$  to  $10^{-1}$  meters in the face of necessary complexity resulting from the innumerability of atoms in our experience.

In this thesis, I present a body of work aimed at understanding some material systems using the current techniques of infrared radiation reflectivity measurements. These measurements probe the long wavelength properties of matter and span a range of time scales from the very fast,  $\omega \sim 50,000 \, cm^{-1} \sim 6.2 \, eV$ , corresponding to the most loosely bound core level excitations or the largest known band gaps (diamond), to the very slow ( $\omega \rightarrow 0$  limit) where many processes live (*i.e.* phonons, heavy free carrier relaxation time, the time it takes to make dinner or write a thesis).

The general direction of this thesis is as follows:

Chapter 2 introduces in some depth the optical properties of solids relevant to this work, especially the linear response functions and their properties. Some of these principles are exemplified by two examples at the end of the chapter.

Chapter 3 reads like a manual for anyone interested in reproducing the experimental design of the Brüker 66v reflectivity unit or other practical aspects of doing reflectivity measurements in this lab. The chapter begins by outlining the principle of FTIR spectroscopy, then goes into the details of beam layout for the 66v in preparation for the following discussion of the modification and vacuum chamber construction. The rest of that chapter makes a record of the available infrared materials and detectors and also a detailed procedural account for posterity.

Chapter 4 gives and introduction and outline of some of the known physics of the Kondo effect and moment compensation. This provides background and an opportunity for the reader to appreciate the endeavor of our studies surrounding the phase diagram of  $YbIn_{1-x}Ag_xCu_4$ .

With the generic behavior of Kondo systems sketched out, Chapter 5 discusses the particularly interesting phenomenology of  $YbIn_{1-x}Ag_xCu_4$ , and the strange behavior exhibited there. In addition, we draw on existing theory and present a simply theory to view the results.

Chapter 6 contains with an introductory discussion of phonons and lattice vibrations including the development of a theoretical treatment relevant to optical properties. This is done as a prelude to the modeling presented at the end of Chapter 7.

Chapter 7 presents data and our findings regarding the negative thermal expansion system  $\text{ZrW}_2\text{O}_8$ . We present the optical data, make connections to the results of other experiments, and then use the modeling developed in Chapter 6 to explore the motional dynamics of  $\mathrm{ZrW}_{2}\mathrm{O}_{8}.$ 

Finally, appendix A presents some of the mechanical drawings that were made in the construction of the Brüker 66v reflectivity/vacuum extension project. Appendix B suggests a possible route to viewing some of the low frequency anomalies of the IR spectrum of  $ZrW_2O_8$ .

# Chapter 2

# **Optical Properties of Solids**

# 2.1 Our Working Description of Electrodynamics

This chapter focuses on the description of the macroscopic response of a solid system to electromagnetic radiation. Both radiation and matter are comprised of quantum mechanical entities whose evolution is determined by fundamental laws of nature, as represented for example in the Dirac or Schrödinger equations.

In the energy regime appropriate to the excitations of atoms and solids, as it is for the practical aspects of everyday lives, it is sufficient to account for the quantum mechanical nature of the matter particles (*i.e.* electrons, holes, phonons, magnons,...), while at the same time retaining the classical electromagnetic fields<sup>1</sup>. With this prescription, a minimal substitution  $\mathbf{p} \rightarrow \mathbf{p} + e\mathbf{A}/c$  in the Hamiltonian describing the particle motion completely accounts for the effects of magnetism, and an addition of the appropriate potential describes the electric field

effects.

<sup>&</sup>lt;sup>1</sup>Photon polaritons present a condensed matter exception to this statement, which are outside the scope of most experiments in this field.

The evolution of the classical electromagnetic fields are determined by Maxwell's equations(Griffiths, 1998):

$$\nabla \cdot \mathbf{D} = \rho \tag{2.1}$$

$$\nabla \times \mathbf{H} - \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t} = \mathbf{J}$$
(2.2)

$$\nabla \times \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} = 0 \tag{2.3}$$

$$\nabla \cdot \mathbf{B} = 0. \tag{2.4}$$

which describe fields in the presence of electrically responsive media. The displacement field  $\mathbf{D}$ , and the magnetic field strength  $\mathbf{H}$  are related to the applied fields  $\mathbf{E}$  and  $\mathbf{B}$  through the underlying physics of the medium. Consequently, we can probe the nature of complex material systems by applying electromagnetic fields and observing the response of the system.

In practice, the fields that people are capable of producing and sustaining in an experiment are typically  $|\mathbf{E}| \simeq 1kV/cm$  and  $|\mathbf{B}| \simeq 1T$ . To an electron inside a solid, this feels like a slight tickle, as compared for example to the local fields that are present due to the charged nuclei. The relatively weak applied fields then are usually incapable of altering the nature of the material behavior, and hence the effects which appear second order in the field strength can be very small. Thus a small field expansion of the dependence of  $\mathbf{E}$  and  $\mathbf{B}$  on  $\mathbf{D}$  and  $\mathbf{H}$ usually provides an adequate description of the system response. For quite a large class of such studies, it is sufficient to observe the linear response of a system.

In the case of magnetism, one usually applies an external field  $\mathbf{H}$  and measures the magnetic response through the magnetization  $\mathbf{M} = \chi \mathbf{H}$ . The differential susceptibility  $\chi$  is then commonly reported in the literature.

In the case of electricity, one is interested in the system response to an applied electric field  $\mathbf{E}$ . This can be quantified several ways<sup>2</sup>, but it is common to either quote the dielectric

<sup>&</sup>lt;sup>2</sup>Alternative viewpoints include the index of refraction  $n+ik = \sqrt{\epsilon}$ , the absorption coefficient  $\alpha = 4\pi\sigma_1\mu_1/nc$ ,

function  $\epsilon$ :

$$\mathbf{D} = \epsilon \mathbf{E} \tag{2.5}$$

or the conductivity,  $\sigma:$ 

$$\mathbf{J} = \sigma \mathbf{E}. \tag{2.6}$$

Simultaneously substituting these relations into Maxwell's equations gives the universal relationship:

$$\epsilon = 1 + \frac{4\pi i\sigma}{\omega}.$$
 (2.7)

In most cases, we will be concerned with  $\sigma$ , and in particular  $\sigma_1 = \operatorname{Re} \sigma$ , which is most closely connected to the power absorption–it is the portion of the current, and hence velocity, which is in phase with the electric field, and hence driving force.

 $\sigma$  and  $\epsilon$  relate one vector to another. In general, an applied electric field does not necessarily give rise to a collinear current or polarization. In order to account for this possibility, both  $\sigma$  and  $\epsilon$  are defined as second-rank tensors. The tensorial character of these response functions will arise in the context of deriving conductivity in section 2.6 and in chapter 6 when deriving the optical response of some idealized systems. However, the real systems studied in this thesis (YbIn<sub>1-x</sub>Ag<sub>x</sub>Cu<sub>4</sub>, ZrW<sub>2</sub>O<sub>8</sub>) are cubic, therefore possessing a high enough symmetry that the response tensors are diagonal with the diagonal components equal (*i.e.*  $\sigma^{xx} = \sigma^{yy} = \sigma^{zz}$ and  $\sigma^{xy} = \sigma^{yz} = \sigma^{zx} = 0$ ). To simplify notation in these cases, we will present only one component of the conductivity tensor, called simply  $\sigma_1(\omega) = \text{Re}\sigma_{xx}(\omega) = \text{Re}\text{Tr}\sigma(\omega)$ .

the loss function  $-\text{Im}\frac{1}{\epsilon}$ , the optical mass  $m^* = -\frac{\omega_P^2}{4\pi\omega}\text{Im}\frac{1}{\sigma}$ , and the frequency-dependent scattering rate  $\Gamma = \frac{\omega_P^2}{4\pi}\text{Re}\frac{1}{\sigma}$ .

# 2.2 Conductivity and the Underlying States

The optical conductivity quantifies charge dynamics and is related to the underlying states of a system. At zero temperature, for a cubic system(Mahan, 1990):

$$\sigma_1(\omega) = \frac{\pi}{V\omega} \sum_{n \neq 0} |\langle n | \mathbf{j} | 0 \rangle|^2 (\delta(\hbar\omega - E_n + E_0) + \delta(\hbar\omega + E_n - E_0)).$$
(2.8)

The conductivity gets a contribution at frequency  $\hbar \omega = E_f - E_i$  above the ground state, weighted by the matrix element for the current<sup>3</sup>. The conductivity is then a probe of the energy structure of a system, weighted by a matrix element that involves the charge, but also the symmetry of the underlying states.

# 2.3 Kramer-Krönig Relations, Sum Rules, and the Constraint of Causality

The dynamical response of a material system is subject to the physical requirement that the system must be causal. That means that a system response cannot precede the stimulus that causes it, an intuitive fact which places severe constraints on the possible functions that can represent the response of a real system. The Kramers-Krönig relations are a statement of this constraint in the frequency domain, and they relate the real and imaginary parts of the frequency dependent response. For example, the Kramers-Krönig relations for the conductivity are:

$$\sigma_1(\omega) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\sigma_2(\omega')}{\omega' - \omega} d\omega'$$
(2.9)

$$\sigma_2(\omega) = -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\sigma_1(\omega')}{\omega' - \omega} d\omega'.$$
(2.10)

<sup>&</sup>lt;sup>3</sup>This can be rewritten as the autocorrelation function for the time dependent current.

The Kramer-Krönig relations are not the only consequence of causality. There are other identities that the response functions must obey which are called sum rules(Mahan, 1990). For a system of charges  $q_i$  with masses  $m_i$ , confined to a volume V, the so-called f-sum rule is stated:

$$\int_0^\infty \sigma_1(\omega) d\omega = \frac{\pi}{2V} \sum_{i=1}^N \frac{q_i^2}{m_i}$$
(2.11)

This is a remarkable result, which states that the area under  $\sigma_1(\omega)$  is determined only by the charge and mass of the particles that make up the system, independently of the nature and strength of the interactions between them. We will use this result in Chapter 7 when constraining the effective ionicities appropriate to  $\text{ZrW}_2\text{O}_8$ .

## 2.4 Reflectivity

The experimental results for the conductivity presented in this thesis are produced from measurements of the frequency dependent reflectivity of solid systems. This section discusses how this connection is made.

Infrared radiation detectors are sensitive only to the power, and therefore intensity,  $I \propto |E|^2$ , of radiation incident upon them. The measured quantity in our reflectivity measurements (described in detail in Chapter 3) is the intensity ratio of the reflected to the incident beam  $R = |re^{i\phi}|^2 = r^2$ . This quantity, while easily to measure, is difficult to interpret in its own right due mainly to the highly nonlinear combination of its "atomistic" contributions. That is, the reflectivity is not a simple sum of contributions from physically distinct processes, and it is a highly nonlinear function of the quantities which are made from additive contributions<sup>4</sup>.

We would like to use our measured  $R(\omega)$  to deduce the "atomistic" quantities, that is

<sup>&</sup>lt;sup>4</sup>The nonlinearity in  $R(\omega)$  is intrinsic because the value of this function is bounded from above by 1. The upper bound of 1 is a statement of energy conservation; a surface cannot reflect more light than is incident on it.

the ones which are made of additive contributions from distinct physical mechanisms. These are the linear response functions  $\sigma$  and  $\epsilon$ , introduced above. Applying Maxwell's equations with appropriate boundary conditions leads to the following result for the reflectivity at the surface of a semi-infinite medium:

$$R = \left| \frac{(n+ik) - 1}{(n+ik) + 1} \right|^2.$$
(2.12)

This relates the real and imaginary parts of the index of refraction to the reflected power at an interface. The relation to the response functions is most directly told through the following chain of universal identities:

$$n+ik = \sqrt{\epsilon} \tag{2.13}$$

$$\epsilon = 1 + \frac{4\pi i\sigma}{\omega} \tag{2.14}$$

Unfortunately, a measurement if  $R(\omega)$  at a single frequency does not uniquely determine both the real and imaginary parts of  $\sigma$ , for example. We can, however, balance the information budget and deduce both parts of  $\sigma$  by appealing to the constraint of causality and the Kramers-Krönig relations.

For the reflectivity, the appropriate response function is

$$r(\omega)e^{i\phi(\omega)} = \frac{(n+ik)-1}{(n+ik)+1}$$
(2.15)

here  $\phi(\omega)$  is the phase shift, due to reflection, experienced by an electromagnetic wave of frequency  $\omega$ , and  $r(\omega)$  is the fractional decrease in the electric field strength. These phase and amplitude modulations are related through a set of Kramers-Krönig relations(Dressel & Gruner, 2002; Wooten, 1972; Dresselhaus, 2001):

$$\ln r(\omega) = \frac{2}{\pi} \int_0^\infty \frac{\omega' \phi(\omega') - \omega \phi(\omega)}{\omega'^2 - \omega^2} d\omega'$$
(2.16)

$$\phi(\omega) = -\frac{2\omega}{\pi} \int_0^\infty \frac{\ln r(\omega') - \ln r(\omega)}{\omega'^2 - \omega^2} d\omega'.$$
(2.17)

Using the second of these relations, one can obtain the phase shift upon reflection from the measured reflectivity provided that  $R(\omega)$  is measured over a broad range of frequency. In our experiments, we typically measure the reflectivity over a very broad range:  $40 \, cm^{-1} \leq \omega \leq 50,000 \, cm^{-1}$ . One can then separate the integral into several parts:

$$\phi(\omega) = -\frac{2\omega}{\pi} \left( \int_0^{40 \ cm^{-1}} + \int_{40 \ cm^{-1}}^{50,000 \ cm^{-1}} + \int_{50,000 \ cm^{-1}}^{\infty} \right) \frac{\ln r(\omega') - \ln r(\omega)}{\omega'^2 - \omega^2} d\omega'.$$
(2.18)

The partial integral in the middle is of course straightforward and unambiguous because we know the form of  $r(\omega) = \sqrt{R(\omega)}$  over this frequency range.

The lower interval, too, is relatively easy to account for but relies a bit on experience with the material at hand. In the Drude model of metallic conduction, for frequencies less than the free carrier scattering rate, the reflectivity assumes the relatively simple form  $R(\omega) = 1 - \sqrt{2\omega/\pi\sigma_{\rm dc}}$ , called the Hägen-Rubens relation. In an insulator, for frequencies lower than the first optical excitation, the reflectivity is nearly frequency independent  $R(\omega) = constant$ . Alternatively, one can perform a model fit of the reflectivity in the range of measured data in order to generate a low frequency extrapolation. However, the precise form for the low frequency terminations generally has little influence on the derived optical functions in the range of measured data.

Effective handling of the upper interval of integration requires some experience, and if one is not careful, the effects on the derived optical functions can influence the conclusions drawn from it. For this reason one generally experiments with several high frequency termination protocols and empirically test the robustness of the ultimate conclusions in the face of various high frequency terminations.

The influence of varying the high frequency termination is felt more strongly in the upper edges of the interval over which data is taken. For example, varying the termination protocol at high frequencies  $\omega > 50,000 \, cm^{-1}$  in YbAgCu<sub>4</sub> influences the conductivity around

 $\omega = 20,000 \, cm^{-1}$  by about 5%, while the conductivity around  $\omega = 1000 \, cm^{-1}$  is not noticeably effected.

# 2.5 A Practical Example

Here we will briefly demonstrate some of the features of the body of knowledge of the optical properties of solids which are useful for the analysis of frequency-dependent reflectivity data. The results of this section lead in naturally to the discussion of the next section which presents original work and in addition are a useful groundwork for the derivation of the response functions of the phonons calculation in Chapter 6.

In the Lorentz model of the atom<sup>5</sup>, two charges  $\pm Ze$  are held together by a spring with resonant frequency  $\omega_0$ . In addition, we consider these charges to be inside a viscous medium (damping parameter  $\Gamma$ ). In the presence of an oscillatory electric field, the dielectric function of Lorentz's "atom" is(Dressel & Gruner, 2002; Wooten, 1972)<sup>6</sup>:

$$\epsilon(\omega) = \epsilon_{\infty} + \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\omega_0\Gamma}.$$
(2.19)

 $\epsilon_{\infty}$  here refers to the value of the dielectric constant due to very high frequency contributions, that is the polarizability that is for practical purposes instantaneous due to the "fast" contributions.  $\omega_P^2 = 4\pi n Z^2 e^2/m$  quantifies the overall strength of the response<sup>7</sup>. The corresponding conductivity  $\sigma = \sigma_1 + i\sigma_2$  is,

$$\sigma_1(\omega) = \frac{\omega_p^2}{4\pi} \frac{\omega^2 \Gamma}{(\omega_0^2 - \omega^2)^2 + \omega^2 \Gamma^2}$$
(2.20)

$$\sigma_2(\omega) = \frac{\omega_p^2}{4\pi} \frac{\omega(\omega^2 - \omega_0^2)}{(\omega_0^2 - \omega^2)^2 + \omega^2 \Gamma^2}$$
(2.21)

 $<sup>{}^{5}</sup>$ The most striking success of this early atomic theory was the prediction of the polarization and angular distribution of radiation intensity when light is scattered from atoms in a magnetic field. Zeeman and Lorentz shared the second ever Nobel prize in physics (1902) for the experimental discovery and theoretical explanation of this phenomenon, known as the "normal" Zeeman effect.

 $<sup>^{6}\</sup>mathrm{A}$  generalized derivation of this formula will be given in Chapter 6

<sup>&</sup>lt;sup>7</sup>The area under  $\sigma_1(\omega)$  in Equation 2.20 (and Figure 2.1) is  $\hat{\omega}_P^2/8$ .



Figure 2.1: The optical conductivity for the Lorentz oscillator with two values of damping  $\Gamma = 0.15$  (black) and  $\Gamma = 0.01$  (gray).

The real and imaginary parts of this function are plotted in Figure 2.1. The conductivity  $\sigma_1(\omega)$  is peaked strongly about the resonance frequency  $\omega_0$  of the spring-charge system. Thus  $\sigma_1(\omega)$  is a measure of the absorption by resonances in the system under study.  $\sigma_2$  on the other hand is more closely tied to the phase of the current with respect to the applied field. For  $\omega < \omega_0$ , the current lags the driving field (capacitive), and for  $\omega > \omega_0$ , the current leads the applied field (inductive).

 $\epsilon = \epsilon_1 + i\epsilon_2$  is shown in Figure 2.2. Here,  $\epsilon_1$  addresses the portion of the polarization that is in phase with the applied field and  $\epsilon_2$  is more closely connected to the part of the



Figure 2.2: The dielectric function for the Lorentz oscillator with two values of damping.

polarization out of phase with respect to the driving field. The constant dielectric response  $\epsilon_1$  in the frequency interval below the resonance frequency is due to the residual response of the "fast moving" (*i.e.* high frequency) components. This residue is quantified through quite general considerations leading to the Lyddane-Sachs-Teller relation, which relates the fractional change in  $\epsilon_1$  at high and low frequencies to the strength and position of the resonance.

For completeness, Figure 2.3 shows the reflectivity computed from Equations 2.12, 2.13, and 2.19.

We conclude this example by giving a time-domain interpretation of the optical con-



Figure 2.3: The reflectivity from the Lorentz oscillator with two values of damping.

ductivity  $\sigma$ . First, we note that Ohm's law,

$$\mathbf{J}(\omega) = \sigma(\omega)\mathbf{E}(\omega). \tag{2.22}$$

which is appropriate to the frequency domain, can be used to obtain the current in the time domain:

$$\mathbf{J}(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \sigma(\omega) \mathbf{E}(\omega) d\omega.$$
 (2.23)

If we consider the transient current response of a system to an impulse field at time t = 0, then  $\mathbf{E}(\omega) = constant$  and the time-dependent current is proportional to the Fourier transform of  $\sigma(\omega)$ . Thus, if we know the transient current response  $\mathbf{J}(t)$ , then the optical conductivity,  $\sigma(\omega)$  is simply proportional to the Fourier transform of this transient current, *i.e.*  $\mathbf{J}(\omega)$ . The solid lines of Figure 2.4 show the sum of two Lorentz oscillator terms (Equation 2.20) and the conductivity calculated by taking the Fourier transform of the current obtained by solving the equations of motion of two coupled harmonic oscillators excited by a narrow

pulse of electric field.

### 2.6 An interesting but not-so-practical example

This section presents an original calculation of  $\sigma_1(\omega)$  for a hypothetical system in the spirit of the Lorentz oscillator, namely the torsional oscillator. This problem was originally constructed to force the breakdown of a selection rule which is inherent in the derivation of the Lorentz oscillator<sup>8</sup>. This treatment is purely quantum mechanical and illustrates the use of the Kubo formula for the conductivity, the Kramers-Krönig relations and the optical *f*-sum rule, and a return to the time domain is intended to provide a manner in which to view the physical meaning of the optical conductivity in this case.

In a typical spectroscopic experiment, electromagnetic radiation couples to the charge degrees of freedom of a system whose underlying dynamical behavior is described by a Hamiltonian. In many cases, the behavior of a system near a stable equilibrium can be adequately described by a simple harmonic Hamiltonian, a choice that is often well justified as an expansion in some suitably chosen coordinate about a minimum of a more complicated potential. The potential expansion coordinates are often chosen to be one or more of the Cartesian coordinates x, y, and z, such as is done in the quantum theory of lattice vibrations(Ashcroft & Mermin, 1976).

The coupling of radiation to matter also involves matrix elements of the Cartesian variables and as a result, selection rules arise which forbid optical transitions between vibrational levels which are not adjacent in energy. The effect on spectroscopy is to produce a single peak in the system response at the oscillator's fundamental frequency. The symmetry

<sup>&</sup>lt;sup>8</sup>It was pointed out to the author in correspondence with journal referees that this effect is known to exist and is called "electrical anharmonicity". The literature on this subject is primarily recent and is discussed in the context of *ab initio* calculations sometimes combined with analysis of measured Raman or IR sidebands. This derivation is the first known "textbook example" of the effect.



Figure 2.4: The transient current interpretation of the optical conductivity illustrated. a) A narrow (Gaussian) electric field pulse is applied at t = 0. b) In response to this pulse, a current is set up which oscillates and decays, returning to the original value  $\mathbf{J}=0$  after a long enough time as a result of damping. This plot was made by numerically time evolving the equations of motion for two oscillators. c) The Fourier transform of this transient current,  $\mathbf{J}(\omega)$ , is proportional to  $\sigma$ . The dots represent the conductivity found by numerically transforming b). The red dashed lines show the Fourier transform of the narrow Gaussian pulse in a) and the gray solid lines represent the corresponding Lorentz oscillator line shape.



Figure 2.5: (a) A torsional pendulum. (b) A realization of an analogous quantum mechanical system.

forbidding the transitions to higher energy levels is imposed by the initial choice of Cartesian expansion coordinate, a choice which, in specific situations, could be improved upon toward describing the system dynamics. An example of the latter is a system with inherent curvilinear geometrical constraints.

In this section, we show that for a simple and familiar model system where curvilinear motion is inherent, profound effects on the spectroscopic response functions are realized. We exemplify this principle by studying the dynamical response of a torsional pendulum with charge degrees of freedom (Figure 2.5a).

The quantum mechanical problem which is analogous to the classical torsional pendulum is shown in Figure 2.5b. This situation corresponds to a situation where  $360^{\circ}$  rotations of the particle wavefunction produces a distinct state, which cannot interfere with the unrotated state. The "particle on a pig's tail" system shown in Figure 2.5b can be viewed as a 1D harmonic oscillator, where the x coordinate is wrapped many times around a cylinder. We proceed to investigate the spectroscopic response functions of this harmonic system. The Hamiltonian is

$$H = \frac{L^2}{2I} + \frac{1}{2}I\omega_0^2\theta^2$$
 (2.24)

where I is the moment of inertia and  $\omega_0$  is the resonant frequency of the pendulum. The angular momentum operator L is conjugate to the (unbounded) angular coordinate  $\theta$ , and the Hamiltonian describes a harmonic oscillator.

We exploit extensively Dirac's factorization procedure in order to find the currentcurrent correlation function, and hence the linear response of this model system. The Hamiltonian in quantized form is:

$$H = (a^{\dagger}a + \frac{1}{2})\hbar\omega_0$$

and

$$H|n\rangle = \hbar\omega_0(n+\frac{1}{2})|n\rangle$$

Where  $a^{\dagger}$  and a are the raising and lowering operators of Dirac's theory and  $|n\rangle$  is the *n*th harmonic oscillator state. The spectrum of this system is a ladder of states with rungs separated in energy by  $\hbar\omega_0$ .

The optical conductivity at zero temperature can be written (Mahan, 1990; Shastry, 2004):

$$\sigma_1(\omega) = \frac{\pi}{V\omega} \sum_{n \neq 0} |\langle n | \mathbf{j} | 0 \rangle|^2 (\delta(\hbar\omega - E_n + E_0) + \delta(\hbar\omega + E_n - E_0))$$
(2.25)

The current operator  $\mathbf{j}$  in this formula is the time derivative of the polarization operator,  $\mathbf{j} = \frac{\partial \mathbf{P}}{\partial t} = \frac{i}{\hbar}[H, \mathbf{P}]$ . In a 1D Cartesian harmonic oscillator,  $\mathbf{P}$  connects only those states adjacent in energy, so that at zero temperature, only the  $|0\rangle \rightarrow |1\rangle$  transition would be observed, giving a single delta function peak at the oscillator's natural frequency<sup>9</sup>.

In the torsional oscillator, the polarization operator is a nontrivial function of the angle  $\theta$ , which appears quadratically in the Hamiltonian. This nonlinear dependence of the

 $<sup>^{9}</sup>$ At finite temperature, too, a single peak is observed since again transitions only between states adjacent in n are allowed.
matrix element on the harmonic degree of freedom will permit transitions between states not adjacent in energy. The main effect of this for spectroscopy is that the conductivity will be a series of peaks at integral multiples of the resonant frequency. We will demonstrate this effect below by calculating the spectroscopic matrix elements for this system.

The vector components of the polarization operator are

$$P_x = Qr\cos\theta$$

$$P_y = Qr\sin\theta$$

and the associated current operator can be determined from the Heisenberg equation of motion,

$$j_x = \frac{i}{\hbar} [H, P_x] \tag{2.26}$$

$$= \frac{iQr}{2I\hbar} [L^2, \cos\theta] \tag{2.27}$$

$$= \frac{iQr}{2I\hbar} (L^2 \cos\theta - \cos\theta L^2)$$
(2.28)

$$= \frac{iQr}{2I\hbar} (L^2 \cos\theta - L \cos\theta L + L \cos\theta L - \cos\theta L^2)$$
(2.29)

$$= \frac{iQr}{2I\hbar} (L[L,\cos\theta] + [L,\cos\theta]L).$$
(2.30)

The commutator in this expression is

$$[L, \cos\theta] = -i\hbar(\frac{\partial}{\partial\theta}\cos\theta - \cos\theta\frac{\partial}{\partial\theta})$$
(2.31)

$$= -i\hbar(-\sin\theta + \cos\theta\frac{\partial}{\partial\theta} - \cos\theta\frac{\partial}{\partial\theta})$$
(2.32)

$$= i\hbar\sin\theta \tag{2.33}$$

and so

$$j_x = \frac{iQr}{2I\hbar} (L[L,\cos\theta] + [L,\cos\theta]L)$$
(2.34)

$$= -\frac{Qr}{2I}(L\sin\theta + \sin\theta L).$$
 (2.35)

The matrix elements we will be interested in are of the form

$$\langle n|j_x|m\rangle = -\frac{Qr}{2I}\langle n|(L\sin\theta + \sin\theta L)|m\rangle.$$
 (2.36)

Cribbing the result from the harmonic oscillator theory,

$$L = -i\sqrt{\frac{I\omega_0\hbar}{2}}(a-a^{\dagger}), \qquad (2.37)$$

we can write the current matrix elements in terms of matrix elements of the trigonometric functions of  $\theta$ :

$$\langle n|j_x|m\rangle = -\frac{Qr}{2I}(-i\sqrt{\frac{I\omega_0\hbar}{2}})\langle n|((a-a^{\dagger})\sin\theta + \sin\theta(a-a^{\dagger}))|m\rangle$$
(2.38)

$$= i\frac{Qr}{2I}\sqrt{\frac{I\omega_0\hbar}{2}}(\langle n+1|\sqrt{n+1}\sin\theta|m\rangle - \langle n-1|\sqrt{n}\sin\theta|m\rangle$$
(2.39)

$$+\langle n|\sin\theta\sqrt{m}|m-1\rangle) - \langle n|\sin\theta\sqrt{m+1}|m+1\rangle$$
 (2.40)

$$= i\frac{Qr}{2I}\sqrt{\frac{I\omega_0\hbar}{2}}(\mathbb{S}_{n+1,m}\sqrt{n+1} - \mathbb{S}_{n-1,m}\sqrt{n}$$
(2.41)

$$+\mathbb{S}_{n,m-1}\sqrt{m}-\mathbb{S}_{n,m+1}\sqrt{m+1})$$
(2.42)

where

$$\mathbb{S}_{n,m} = \langle n | \sin \theta | m \rangle \tag{2.43}$$

A nearly identical calculation for the current component  $j_{\mathcal{Y}}$  gives

$$\langle n|j_y|m\rangle = -i\frac{Qr}{2I}\sqrt{\frac{I\omega_0\hbar}{2}}(\mathbb{C}_{n+1,m}\sqrt{n+1} - \mathbb{C}_{n-1,m}\sqrt{n}$$
(2.44)

$$+\mathbb{C}_{n,m-1}\sqrt{m}-\mathbb{C}_{n,m+1}\sqrt{m+1})$$
(2.45)

$$\mathbb{C}_{n,m} = \langle n | \cos \theta | m \rangle \tag{2.46}$$

To take a general approach, we will calculate the matrix elements of the operator

$$\mathbb{E}_{n,m} = \langle n | e^{i\theta} | m \rangle \tag{2.47}$$

and use them to determine those of the trigonometric functions through deMoivre's identity.

Again using a result from the harmonic oscillator theory, and introducing the factor c for notational simplification,

$$\theta = \sqrt{\frac{\hbar}{2I\omega_0}} (a + a^{\dagger}) = c(a + a^{\dagger}), \qquad (2.48)$$

$$\mathbb{E}_{n,m}(c) = \langle n | e^{ic(a+a^{\dagger})} | m \rangle.$$
(2.49)

The trigonometric matrix elements are then

$$\mathbb{S}_{n,m}(c) = \frac{1}{2i} (\mathbb{E}_{n,m}(c) - \mathbb{E}_{n,m}(-c))$$

$$(2.50)$$

$$\mathbb{C}_{n,m}(c) = \frac{1}{2} (\mathbb{E}_{n,m}(c) + \mathbb{E}_{n,m}(-c))$$
(2.51)

To simplify the calculation of  $\mathbb{E}_{n,m}(c)$ , one can invoke the Baker-Campbell-Haussdorf theorem(Harter, 1993):

$$e^{A+B} = e^A e^B e^{-[A,B]/2} (2.52)$$

which holds provided that A and B both commute with their mutual commutator. This is true for a and  $a^{\dagger}$ , so

$$\mathbb{E}_{n,m} = \langle n | e^{ica} e^{ica^{\dagger}} e^{c^2 [a,a^{\dagger}]/2} | m \rangle = \langle n | e^{ica} e^{ica^{\dagger}} e^{c^2/2} | m \rangle.$$
(2.53)

We can now expand the exponentials and operate on the bra and ket multiple times with the a and  $a^{\dagger}$ . Using the identities

$$|m\rangle = \frac{(a^{\dagger})^m}{\sqrt{m!}}|0\rangle \tag{2.54}$$

and

$$\langle n| = \langle 0| \frac{(a)^n}{\sqrt{n!}},\tag{2.55}$$

$$\mathbb{E}_{n,m} = e^{c^2/2} \langle n | e^{ica} \sum_{k=0}^{\infty} \frac{(ic)^k}{k!} (a^{\dagger})^k | m \rangle$$
(2.56)

$$= e^{c^{2}/2} \sum_{k=0}^{\infty} \langle n | e^{ica} \frac{(ic)^{k}}{k!} (a^{\dagger})^{k} \frac{(a^{\dagger})^{m}}{\sqrt{m!}} | 0 \rangle$$
(2.57)

$$= e^{c^2/2} \sum_{k=0}^{\infty} \langle n | e^{ica} \frac{(ic)^k}{k!} \frac{\sqrt{(m+k)!}}{\sqrt{m!}} \frac{(a^{\dagger})^{m+k}}{\sqrt{(m+k)!}} | 0 \rangle$$
(2.58)

$$= e^{c^{2}/2} \sum_{k=0}^{\infty} \langle n | e^{ica} \frac{(ic)^{k}}{k!} \frac{\sqrt{(m+k)!}}{\sqrt{m!}} | m+k \rangle$$
(2.59)

Similarly, the  $e^{ica}$  can be expanded to act on the bra  $\langle n|$ ,

$$\mathbb{E}_{n,m} = \sum_{k=0}^{\infty} e^{c^2/2} \langle n | e^{ica} \frac{(ic)^k}{k!} \frac{\sqrt{(m+k)!}}{\sqrt{m!}} | m+k \rangle$$
(2.60)

$$= e^{c^2/2} \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} \frac{(ic)^l}{l!} \langle n | (a)^l \frac{(ic)^k}{k!} \frac{\sqrt{(m+k)!}}{\sqrt{m!}} | m+k \rangle$$
(2.61)

$$= e^{c^2/2} \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} \frac{(ic)^l}{l!} \langle 0 | \frac{(a)^n}{\sqrt{n!}} (a)^l \frac{(ic)^k}{k!} \frac{\sqrt{(m+k)!}}{\sqrt{m!}} | m+k \rangle$$
(2.62)

$$= e^{c^2/2} \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} \frac{(ic)^l}{l!} \langle 0| \frac{(a)^{n+l}}{\sqrt{(n+l)!}} \frac{\sqrt{(n+l)!}}{\sqrt{n!}} \frac{(ic)^k}{k!} \frac{\sqrt{(m+k)!}}{\sqrt{m!}} |m+k\rangle \quad (2.63)$$

Combining factors and using the orthonormality of the harmonic oscillator states,

$$\mathbb{E}_{n,m}(c) = \frac{e^{c^2/2}}{\sqrt{n!m!}} \sum_{l,k=0}^{\infty} \frac{(ic)^{k+l}\sqrt{(l+n)!(k+m)!}}{l!k!} \delta_{l+n,k+m}$$
(2.64)

$$= \frac{e^{c^2/2}}{\sqrt{n!m!}} \sum_{k=0}^{\infty} \frac{(ic)^{2k+m-n}(k+m)!}{k!(k+m-n)!}$$
(2.65)

$$= \frac{e^{c^2/2}(ic)^{m-n}}{\sqrt{n!m!}} \sum_{k=0}^{\infty} \frac{(-c^2)^k (k+m)!}{k! (k+m-n)!}$$
(2.66)

$$= \frac{e^{c^2/2}(ic)^{m-n}}{\sqrt{n!m!}}S(c^2, m, n)$$
(2.67)

The sum  $S(c^2, m, n)$  is a real function and can be expressed in terms of hypergeometric and gamma functions<sup>10</sup>. This expression can now be used to give the trigonometric matrix elements of  $\theta$  and these are

$$\mathbb{S}_{n,m}(c) = \frac{e^{c^2/2}}{\sqrt{n!m!}} S(c^2, m, n) \frac{(ic)^{m-n} - (-ic)^{m-n}}{2i}$$
(2.68)

$$= \frac{1}{i} \frac{e^{c^2/2}}{\sqrt{n!m!}} S(c^2, m, n) \begin{cases} 0 & m-n \text{ even} \\ (ic)^{m-n} & m-n \text{ odd} \end{cases}$$
(2.69)

 $<sup>(</sup>ic) \qquad m-n \quad \text{odd}$   $10S(c^2,m,n) = {}_1F_1(1+m,1+m-n,-c^2)\frac{\Gamma(1+m)}{\Gamma(1+m-n)} \text{ where } {}_1F_1(x,y,z) \text{ is the Kummer confluent hypergeometric function.}$ 

and

$$\mathbb{C}_{n,m}(c) = \frac{e^{c^2/2}}{\sqrt{n!m!}} S(c^2, m, n) \frac{(ic)^{m-n} + (-ic)^{m-n}}{2}$$
(2.70)

$$= \frac{e^{c^2/2}}{\sqrt{n!m!}} S(c^2, m, n) \begin{cases} (ic)^{m-n} & m-n \text{ even} \\ 0 & m-n \text{ odd} \end{cases}$$
(2.71)

We restrict our attention at this point to the case of zero temperature. In that case, we are interested in transitions from the ground state, so that n = 0:

$$\langle 0|j_x|m\rangle = i\frac{Qr}{2I}\sqrt{\frac{I\omega_0\hbar}{2}}(\mathbb{S}_{1,m} + \mathbb{S}_{0,m-1}\sqrt{m} - \mathbb{S}_{0,m+1}\sqrt{m+1})$$
 (2.72)

This is zero when m is odd. For m even,

$$\langle 0|j_x|m\rangle = i\frac{Qr}{2I}\sqrt{\frac{I\omega_0\hbar}{2}}e^{c^2/2}\sum_{k=0}^{\infty}\frac{(-c^2)^k}{k!i}\Big\{\frac{(k+m)!(ic)^{m-1}}{(k+m-1)!\sqrt{m!}}$$
(2.73)

$$+\frac{(k+m-1)!(ic)^{m-1}\sqrt{m}}{(k+m-1)!\sqrt{(m-1)!}} - \frac{(k+m+1)!(ic)^{m+1}\sqrt{m+1}}{(k+m+1)!\sqrt{(m+1)!}} \Big\} (2.74)$$

$$= i\frac{Qr}{2I}\sqrt{\frac{I\omega_0\hbar}{2}}e^{c^2/2}\sum_{k=0}^{\infty}\frac{(-c^2)^k}{k!i}\frac{(ic)^m}{\sqrt{m!}}\left\{\frac{(k+2m)}{ic}+\frac{c^2}{ic}\right\}$$
(2.75)

$$= i \frac{Qr}{2I} \sqrt{\frac{I\omega_0\hbar}{2}} e^{c^2/2} \sum_{k=0}^{\infty} \frac{(-c^2)^k}{k!i} \frac{(ic)^{m-1}}{\sqrt{m!}} \left\{ k + 2m + c^2 \right\}$$
(2.76)

We can now sum the series, which gives exponentials:

$$\langle 0|j_x|m\rangle = \frac{Qr}{2I}\sqrt{\frac{I\omega_0\hbar}{2}}e^{c^2/2}\frac{(ic)^{m-1}}{\sqrt{m!}}\sum_{k=0}^{\infty}\frac{(-c^2)^k}{k!}\left\{k+2m+c^2\right\}$$
(2.77)

$$= \frac{Qr}{2I}\sqrt{\frac{I\omega_0\hbar}{2}}e^{c^2/2}\frac{(ic)^{m-1}}{\sqrt{m!}}\sum_{k=0}^{\infty}\left\{\frac{(-c^2)^k}{k!}k + \frac{(-c^2)^k}{k!}(2m+c^2)\right\}$$
(2.78)

$$= \frac{Qr}{2I}\sqrt{\frac{I\omega_0\hbar}{2}}e^{c^2/2}\frac{(ic)^{m-1}}{\sqrt{m!}}\left\{-c^2e^{-c^2}+e^{-c^2}(2m+c^2)\right\}$$
(2.79)

$$= \frac{Qr}{2I} \sqrt{\frac{I\omega_0 \hbar}{2}} e^{-c^2/2} \frac{(ic)^{m-1}}{\sqrt{m!}} 2m$$
(2.80)

The analysis of the  $\langle 0|j_y|m\rangle$  matrix element follows similarly. The intensities of the



Figure 2.6: The matrix elements of the torsional oscillator for three values of angular uncertainty. Only the integral values of m are meaningful. Inset: The ground state wavefunctions corresponding to these three uncertainty values.

transitions are determined from

$$|\langle 0|j_x|m\rangle|^2 = \frac{Q^2 r^2}{I} \frac{\hbar\omega_0}{2} e^{-c^2} \frac{m^2}{m!} (c^2)^{m-1} \begin{cases} 1 & m \text{ even} \\ 0 & m \text{ odd} \end{cases}$$
(2.81)

$$|\langle 0|j_y|m\rangle|^2 = \frac{Q^2 r^2}{I} \frac{\hbar\omega_0}{2} e^{-c^2} \frac{m^2}{m!} (c^2)^{m-1} \begin{cases} 0 & m \text{ even} \\ \\ 1 & m \text{ odd} \end{cases}$$
(2.82)

Both the relative and absolute intensities are crucially influenced by the parameter c, which we have not yet supplied a physical interpretation. To this end, we calculate the uncertainty in angular position of the ground state,

$$\Delta \theta^2 = \langle \theta^2 - \langle \theta \rangle^2 \rangle \tag{2.83}$$

$$= c^2 \langle 0|(a+a^{\dagger})^2|0\rangle \tag{2.84}$$

$$= c^2 \langle 0|(aa^{\dagger} + a^{\dagger}a)|0\rangle \qquad (2.85)$$

$$= c^2.$$
 (2.86)

It seems that the parameter which controls the multiple-peak effect is  $\Delta \theta = c = \sqrt{\hbar/2I\omega_0}$ , that is the extent to which the wavefunction covers the circle.

We see that, unlike the Cartesian harmonic oscillator, the transitions between the ground and excited states are allowed for all excited states in the torsional pendulum, and the distribution of intensities is crucially determined by the angular uncertainty. In the "stiff pendulum" limit,  $\omega_0$  is large and  $c \ll 1$ . The ground state wave function in this case subtends a small angle and motion along the periphery of the pendulum is well approximated by the appropriate Cartesian coordinate  $y = r \sin \theta \sim r\theta$ . The  $|0\rangle \rightarrow |1\rangle$  transition is by far the strongest, with the other peak exponentially suppressed both as a function of c and m, thus returning the single peak expected from a simple harmonic oscillator. Conversely, in a floppy pendulum, the perpendicular motion is important to the response and also the matrix elements to higher states become appreciable. The crossover between these limits occurs when the angular uncertainty c becomes comparable to 1 radian.

For values of uncertainty c > 1 radian, the maximum intensity no longer comes from the  $|0\rangle \rightarrow |1\rangle$  transition, but rather the  $|0\rangle \rightarrow |2\rangle$  begins to dominate the oscillator strength. Figure 2.6 shows this in a plot of  $|\langle 0|\mathbf{j}|m\rangle|^2$  versus final state quantum number m for several values of  $\Delta \theta$ .

The system we have considered so far is highly anisotropic. However, if we were to arrange these pendula in a cubic symmetry, or rather if we had a polycrystalline torsional pendulum solid, we could average the diagonal components, in which case the diagonal  $((\sigma_1^{xx} + \sigma_1^{yy})/2)$  optical conductivity is:

$$\sigma_1(\omega) = \frac{\pi}{V\omega} \sum_{m \neq 0} |\langle m | \mathbf{j} | 0 \rangle|^2 (\delta(\hbar\omega - E_m + E_0) + \delta(\hbar\omega + E_m - E_0))$$
(2.87)

$$= \frac{\pi}{V\omega} \frac{Q^2 r^2}{I} \frac{\hbar\omega_0}{2} e^{-c^2} \sum_{m=1}^{\infty} \frac{m^2}{m!} (c^2)^{m-1} (\delta(\hbar\omega - m\hbar\omega_0) + \delta(\hbar\omega + m\hbar\omega_0)) \quad (2.88)$$



Figure 2.7: The conductivity of the torsional pendulum versus frequency for three values of c (and therefore  $\omega_0$ ). Inset: The same data plotted as a function of final state quantum number.

$$= \frac{\pi}{V} \frac{Q^2 r^2}{2I} e^{-c^2} \sum_{m=1}^{\infty} \frac{m}{m!} (c^2)^{m-1} (\delta(\hbar\omega - m\hbar\omega_0) + \delta(\hbar\omega + m\hbar\omega_0))$$
(2.89)

We can integrate the optical conductivity and find the total oscillator strength:

$$\int_{0}^{\infty} \sigma_{1}(\omega) d\omega = \frac{\pi}{V} \frac{Q^{2} r^{2}}{2I} e^{-c^{2}} \sum_{m=1}^{\infty} \frac{m}{m!} (c^{2})^{m-1} \int_{0}^{\infty} \delta(\omega - m\hbar\omega_{0}) d\omega$$
(2.90)

$$= \frac{\pi}{V} \frac{Q^2 r^2}{2I} e^{-c^2} \sum_{m=1}^{\infty} \frac{m}{m!} (c^2)^{m-1}$$
(2.91)

$$= \frac{\pi}{V} \frac{Q^2 r^2}{2I} e^{-c^2} \sum_{n=0}^{\infty} \frac{1}{n!} (c^2)^n$$
(2.92)

$$= \frac{\pi}{V} \frac{Q^2 r^2}{2I} = \frac{\omega_P^2}{8}.$$
 (2.93)

We can also find  $\sigma_2(\omega)$  using the Kramer-Krönig relation (Dressel & Gruner, 2002; Mai, 2004):

$$\sigma_2(\omega) = -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\sigma_1(\omega')}{\omega' - \omega} d\omega'$$
(2.94)

$$= -\frac{1}{\pi} \frac{\omega_P^2}{8} e^{-c^2} \sum_{m=1}^{\infty} \frac{m}{m!} (c^2)^{m-1} \int_{-\infty}^{\infty} \frac{\delta(\omega' - m\omega_0) + \delta(\omega' + m\omega_0)}{\omega' - \omega} d\omega' \quad (2.95)$$

$$= \frac{\omega_P^2}{8} e^{-c^2} \sum_{m=1}^{\infty} \frac{m}{m!} (c^2)^{m-1} \frac{2\omega/\pi}{\omega^2 - (m\omega_0)^2},$$
(2.96)

giving for the complex conductivity  $(\sigma = \sigma_1 + i\sigma_2)$ 

$$\sigma(\omega) = \frac{\omega_P^2}{8} e^{-c^2} \sum_{m=1}^{\infty} \frac{m}{m!} (c^2)^{m-1} (\delta(\omega - m\omega_0) + \delta(\omega + m\omega_0) + i \frac{2\omega/\pi}{\omega^2 - (m\omega_0)^2}) \quad (2.97)$$

Insight into the physical significance of multiple peaks comes by considering the timedependent current which arises from the application of a short electric field pulse  $E(t) \propto \delta(t)$ , as was done in the end of the last section. In this case,  $E(\omega) = E_0 = constant$  and for<sup>11</sup> t > 0,

$$J(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \sigma(\omega) E(\omega) d\omega$$
(2.98)

$$= \frac{E_0}{2\pi} \frac{\omega_P^2}{8} e^{-c^2} \sum_{m=1}^{\infty} \frac{m}{m!} (c^2)^{m-1}$$
(2.99)

<sup>11</sup>For t < 0, J(t) = 0, a consequence of causality that is built-in to the Kramers-Krönig relations.



Figure 2.8: (a) The current response J(t) to an impulse pulse at time t = 0. (b) The same curves as (a), plotted versus the scaled time variable in order to show how the sinusoidal response changes as the pendulum is loosened.

$$\times \int_{-\infty}^{\infty} e^{-i\omega t} (\delta(\omega - m\omega_0) + \delta(\omega + m\omega_0) + i\frac{2\omega/\pi}{\omega^2 - (m\omega_0)^2}) d\omega \quad (2.100)$$

$$= \frac{E_0}{2\pi} \frac{\omega_P^2}{2} e^{-c^2} \sum_{m=1}^{\infty} \frac{m}{m!} (c^2)^{m-1} \cos m\omega_0 t$$
(2.101)

$$= \frac{E_0}{2\pi} \frac{\omega_P^2}{2} e^{-c^2} \frac{1}{2} \left( e^{c^2 e^{-i\omega_0 t} - i\omega_0 t} + e^{c^2 e^{i\omega_0 t} + i\omega_0 t} \right).$$
(2.102)

This current response is shown for three values of c in Figure 2.8. For small values of c, the response of the system is similar to that of a harmonic oscillator, exhibiting nearly sinusoidal oscillations for t > 0. Loosening the pendulum (and increasing the angular uncertainty  $\Delta \theta$ ) effects these dynamics considerably.

While the considerations spelled out here are rather idealized, a reasonable first place

to seek the multiple peak effect in a real system could be in the vibrational spectra of nanotubes. When a chiral nanotube is formed from a graphene sheet, phonons propagating along the graphene lattice basis vectors form a twisting pattern around the nanotube axis. The geometry associated with these vibrational degrees of freedom bear similarities to that of the pig's tail in Figure 2.5b. It is feasible that another realization of this effect could be found in solids which support very soft librational phonon modes.

### 2.7 Conductivity and the Joint Density of States

In this section, we will give a description of the Kubo-Greenwood formula which relates the conductivity to the dispersion of the electrons responsible for conduction. This formalism, derived for band electrons, we later apply to the long-lived excitations of the periodic Anderson model in Chapter 5.

This page follows Dresselhaus, chapter 4(Dresselhaus, 2001). We wish to find the probability rate for a periodic system consisting of an electron in a state  $\vec{\mathbf{k}}$  to make a vertical transition from a filled lower band to a vacant upper band by absorption of a photon of frequency  $\omega$ . Invoking Fermi's Golden Rule, this is

$$W_{\vec{\mathbf{k}}} = \frac{2\pi}{\hbar} |\langle l|H_I|u\rangle|^2 \delta(E_u(\vec{\mathbf{k}}) - E_l(\vec{\mathbf{k}}) - \hbar\omega)$$
(2.103)

Where  $H_I$  is the light-matter interaction Hamiltonian and the  $\delta$ -function expresses energy conservation. The photon momentum has been neglected because it is small (10<sup>-4</sup>) in comparison to typical electron momenta. Each filled single particle state in the lower band must be counted to find the contribution of these states to the conductivity of the system. Accordingly, the total transition rate is an integral over all such transitions

$$W = \frac{2\pi}{\hbar} \frac{2}{(2\pi)^3} \int |\langle l|H_I|u \rangle |^2 \delta(E_u(\vec{\mathbf{k}}) - E_l(\vec{\mathbf{k}}) - \hbar\omega) d^3\vec{\mathbf{k}}.$$
 (2.104)

The light-matter interaction Hamiltonian is

$$H_I = -\frac{e\vec{\mathbf{A}} \cdot \vec{\mathbf{p}}}{mc} \tag{2.105}$$

and we assume for simplicity that the matrix elements do not depend on  $\mathbf{k}$  and can be taken out of the integral. The rate of power absorption can be related to the absorption coefficient, hence  $\epsilon_2$  and  $\sigma_1$ . These considerations generate the Kubo-Greenwood formula:

$$\sigma_1(\omega) = \frac{\pi e^2}{m^2 \omega} \sum_{\ell,\ell'} JDOS_{\ell,\ell'}(\omega) |\mathbf{p}_{\ell,\ell'}|^2$$
(2.106)

where the joint density of states (JDOS) is defined as:

$$JDOS_{\ell,\ell'}(\omega) = \frac{2}{(2\pi)^3} \int_{\Delta E = \hbar\omega} \delta(E_u(\vec{\mathbf{k}}) - E_l(\vec{\mathbf{k}}) - \hbar\omega) d^3\vec{\mathbf{k}}$$
(2.107)

$$= \frac{2}{(2\pi)^3} \int_{\Delta E = \hbar\omega} \frac{dS}{|\nabla_{\mathbf{k}} (E_u(\vec{\mathbf{k}}) - E_l(\vec{\mathbf{k}}))|}$$
(2.108)

These expressions draw a connection between the conductivity and the underlying band structure since the JDOS gives a quantitative measure of the number of electrons that can transit between levels separated by a given frequency  $\omega$ .

To illustrate some working principles related to the joint density of states, consider the  $E(\mathbf{k})$  diagrams shown in Figure 2.9a. Because the vertical separation of the empty upper and filled lower branch have the same frequency for all  $\mathbf{k}$ , there will accordingly be a large contribution to the joint density of states at the separation frequency, as shown in the lower panel. This effect is known as *nesting* and will be important to understanding the peak in the midinfrared conductivity of heavy fermion systems discussed in Chapter 5.

The situation in Figure 2.9b is much different. Each  $\mathbf{k}$  value along the  $\Gamma - X$  direction has a different separation between the upper and lower branches, and hence each  $\mathbf{k}$  value along this line will give an equal contribution to the *JDOS*, but at a different  $\omega$ . In a one-dimensional system, where the only *JDOS* contribution is along the  $\Gamma - X$  direction, then the *JDOS* would



Figure 2.9: Conceptual illustration of the joint-density-of-states through a toy band structure.

be proportional to the top-hat function, which is constant for  $\omega_{low} \le \omega \le \omega_{high}$ , and zero otherwise.

The JDOS for a three-dimensional system would look a bit more like that shown in the bottom of Figure 2.9b. The skew of the JDOS is a result of the three dimensionality of the Fermi surface, and arises as a result of moving off of the  $\Gamma - X$  line and adding all contributions throughout the Brillouin zone. For a nearly isotropic (for example cubic) band structure, points with the same value of  $k = |\mathbf{k}|$  will contribute nearly the same to the JDOS. Since there are more **k**-states per increment of k as k gets larger, there will be a larger contribution to the JDOS integral for large values of k. For the bandstructure in Figure 2.9b, this amounts to a larger JDOS near  $\omega_{\text{high}}$ . Similarly, in Figure 2.9c, the JDOS peak appears nearer  $\omega_{\text{low}}$ .

# Chapter 3

# Instrumentation

In this chapter we discuss in detail a particular method of performing reflectivity measurements which is in widespread use for its speed and ease of use. We will first introduce the principles of Fourier Transform Infrared Spectroscopy (FTIR) and make the introduction of the Brüker IFS 66v/S. This instrument is commercially available and represents the state of the art in FTIR spectrometery. Part of this thesis is the modification of this instrument, which is by default outfitted for room temperature gas-cell/film transmission experiments, for use in infrared reflectivity measurements of condensed matter systems over a wide range of temperature.

## 3.1 Fourier Transform Infrared Spectroscopy (FTIR)

A FTIR spectrometer essentially takes a broadbanded beam of radiation and splits it into two identical copies. The two beams are then recombined, but only after introducing a relative path difference, and hence a relative phase shift, between them. For the purposes of discussion, we will first consider a rather idealized instrument, that can perform the above manipulations without limitation.

Consider the assembly shown in Figure 3.1. The radiation source supplies an "incoherent" electric field which is completely defocused before entering the beam splitter, shown as a red diagonal line. A portion of the parallel rays incident on the beam splitter are reflected upward into the vertical leg of the interferometer, and the rest propagate through to the horizontal leg. After reflection from their respective mirrors, these beams head back toward the beamsplitter, and a portion of the one which was reflected is now transmitted, and vice versa, resulting in recombination of two "copies". The resultant beam is then directed into a detector.

Now consider what happens when we look at the signal in the detector while scanning one of the mirrors. The intensity of the beam component with frequency  $\omega$  at the detector is

$$I(\omega, x) = |\vec{\mathbf{E}}|^2 = |\vec{\mathbf{E}}_1|^2 + |\vec{\mathbf{E}}_2|^2 + 2|\vec{\mathbf{E}}_1||\vec{\mathbf{E}}_2|\cos(\frac{\omega x}{c})$$
(3.1)

where x is the relative path difference between the two beams. If the amplitude of each component does not change in time (the source is stable, or the output of the source does not change appreciably over the time scale of the experiment), then  $\vec{\mathbf{E}}_1 = \vec{\mathbf{E}}_2$  and

$$I(\omega, x) = I_0(\omega)(1 + \cos(\frac{\omega x}{c}))$$
(3.2)

where  $I_0 = |\vec{\mathbf{E}}_1|^2/2$  is the intensity of the beam component of frequency  $\omega$  and is the spectrum of the beam.

The total intensity at the detector is an integral of Eq. (3.2) over all frequencies:

$$I(x) = \int_0^\infty I(\omega, x) d\omega.$$
(3.3)

Using Eq. (3.2), this is

$$I(x) = \int_0^\infty I_0(\omega)(1 + \cos(\frac{\omega x}{c}))d\omega = I_{0,total} + \int_0^\infty I_0(\omega)\cos(\frac{\omega x}{c})d\omega.$$
(3.4)

The first term is independent of x and in practice corresponds to the intensity of the beam at the detector when the relative path difference of the two beams is far from zero (compared to



Figure 3.1: FTIR Illustrated. The green arrows indicate the direction of scanning.



Figure 3.2: (a) An interferogram. The ordinate is measured in number of laser wave pulses of the auxiliary Michelson interferometer. (b) The spectrum resulting from the Fourier transform of the interferogram in (a).

a typical prominent wavelength component present in the beam). Further manipulations show that

$$I(x) = I_{0,total} + \int_0^\infty I_0(\omega) \frac{e^{\frac{i\omega x}{c}} + e^{\frac{-i\omega x}{c}}}{2} d\omega = I_{0,total} + \int_{-\infty}^\infty I_0(\omega) e^{\frac{i\omega x}{c}} d\omega.$$
(3.5)

This states that the part of the signal at the detector that does depend on x is just the Fourier transform of the spectrum of the beam. So if the intensity at the detector as a function of x, called the interferogram of the beam, is known, then one can simply invert the transform and determine the spectral content of the beam. This is the central principle of FTIR spectroscopy. An example of an interferogram is shown in Figure 3.2a and it's corresponding spectrum in shown in Figure 3.2b.

## 3.2 The IFS 66v/S

Figure 3.3 shows the Brüker IFS 66v/S. The beam begins in the source chamber (upper right compartment in Figure 3.3) at one of the two source towers. The source radiation is immediately reflected by a motorized mirror (M1, or source mirror<sup>1</sup>) and is focused on the source aperture (A1) which separates the source and interferometer compartments. Next, a 90° parabolic mirror (M2) then defocuses and directs the beam into the beam splitter (BS). Part of the beam is then reflected into the fixed mirror (M3), and the rest of the beam is transmitted to meet the scanning mirror (M4). After reflection, these two beams then recombine at the beam splitter. Apart from a phase shift, the two portions are ideally equivalent, each having been once transmitted through and once reflected by the beam splitter. The phase shift is introduced by the path length difference in the two arms of the interferometer and is controlled by the position of the scanning mirror (M4).

In order to use the results of the last section in practice, it is necessary to determine <sup>1</sup>This mirror is capable of switching between the two source towers



Figure 3.3: Brüker 66v with vacuum extension assembly attached. The red and faint green lines indicate the beam center and edges throughout the system.

the position of the scanning mirror to very high precision. This is accomplished by a interfering a He-Ne laser along with the broad-banded source. Interference pulses are then counted as the mirror is scanned, each pulse corresponding to a wavelength travel, about  $600\mu$ ! In this way adequate positional tracking precision is attained.

In normal operating mode, the beam emerges from the interferometer chamber (moving to the right, after BS in figure) and is focused by a 90° parabolic mirror (in the position of M5) to a spot halfway across the sample compartment. The beam then continues into the detector compartment (DC) where automated mirror controls can direct the beam to one of two built-in infrared detectors (DTGS-MIR and DTGS-FIR) or out through a port outfitted to couple to an Infrared Laboratories Davidson dewar/bolometer detector.

#### **3.3** Modification for Reflectivity Measurements

So far, the default configuration of the instrument has been outlined. The modification of this configuration for our purposes begins after the beam splitter/interferometer block. We replaced the 90° parabolic mirror by a protected-Al plane mirror (M5). The (parallel ray) beam emerging from the beam splitter/interferometer block is directed 90° by this plane mirror into the sample chamber.

In the sample chamber, a  $45^{\circ}$  diamond-turned parabolic mirror (M6, parent focal length=10", Al stock, protected-Al coating) was inserted to redirect and focus the beam onto a second aperture (A2). This aperture, mounted on a precision XYZ stage, is capable reproducibly switching between a suite of pinhole diameters. This versatility is important because A2 solely determines the beam diameter when it is later focused on the sample.

After the aperture A2, the beam then continues to the sample mirror (M7) which focuses the beam into the sample cryostat (SC) and onto the sample. At this point, a portion of the beam is reflected at the cryostat window. Since this is signal has been modulated by the interferometer, it would be detrimental to the experimental precision if it were to make it into the detector. The freedom associated with the cryostat rotation was used to discard this unwanted reflected beam safely into the chamber wall.

The angle of incidence of the wanted beam on the sample was kept as small as practical and turned out to be about  $10^{\circ}$ , which is considered an acceptable value for this type of experiment(van der Marel et al., 1993). The size of the spot on the sample, as mentioned previously, is determined by the diameter d of the aperture A2. If M7 was a perfect ellipsoidal mirror, and used properly, then the sample spot size would be about 1.2d. Since M7 is toroidal, one expects a slightly larger spot even when used properly, but in practice the smallest spot diameter is so close to this lower limit, measurement of a difference is difficult.

The beam emerging from the sample cryostat is then directed to the detector mirror (M8) and through the detector flange (DF) into one of several detectors.

M7 and M8 were constructed at Continental Sales Corp., a glass grinding facility here in Santa Cruz, specializing in prescription eye glass blanks. William Inman was kind enough to fill our astygmatic prescriptions to make these off-axis toroidal mirrors. The glass blanks were then evaporated with the help of Billy Brown in the UCO/Lick evaporation facility here at the UCSC campus. We are grateful to both William and Billy for their efforts.

The aluminum vacuum chamber extension had to be carefully constructed to meet several design criterion including

- the reproducible placement of the cryostat; a system for easily rotating between windows was also accomplished
- minimal coupling of the optical components to the flexure of the chamber that occurs when the system is evacuated versus vented

- stability against vibration
- the capability to manipulate mirrors inside the vacuum system had to be implemented
- accessibility to all components
- general adjustability and ease of use

Some of the mechanical drawings associated with the modification discussed in this section are disclosed in Appendix A.

## 3.4 Frequency Dependence of Optical Components

One of three Davidson bolometer dewars ( $\omega \leq 240, 700, 5000 \, cm^{-1}$ ) can be coupled directly to the instrument at the detector flange (DF) for measurements at mid- and far-infrared frequencies.

For higher frequencies, one of two specially designed window flanges, housing ZnSe  $(\omega \gtrsim 500 \, cm^{-1})$  or Quartz  $(\omega \gtrsim 2000 \, cm^{-1})$  windows can be mounted to the end of the detector flange (DF) in order to bring the beam outside the vacuum and into one of several photodiode detectors. Steering the beam onto these detectors involves the use of a large elliptic mirror with high focusing power placed about 12" after the detector flange.

Low frequency photodiode detectors experience signal-destroying thermal fluctuations at room temperature. For this reason, a nitrogen cooled "fire hydrant" dewar which houses HgCdTe  $(1000 \, cm^{-1} \lesssim \omega)$  and InSb  $(2000 \, cm^{-1} \lesssim \omega)$  biased-photodiode detectors is used for the low frequency ranges. At higher frequency, gap activation is not possible at ambient temperature and unbiased room-temperature Ge  $(4000 \, cm^{-1} \lesssim \omega)$  or Si  $(8000 \, cm^{-1} \lesssim \omega)$  detectors can be used. All photodiodes mentioned here are used in concert with suitable preamplifiers and pole-filters.



Figure 3.4: Spectra covering the mid and near-IR ranges. The experimental configurations that produced these spectra are outlined in Table B.1. The reflectivity in (a) are for a sample of  $Y_{0.2}Yb_{0.8}InCu_4$ 

Spectrum	Detector	Beam	Cryostat	Chamber	Source
		Splitter	Window	Window	
1	700 range bolometer	T222	White Poly	N/A	Globar
2	HgCdTe (MCT) photodiode	KBr	CsI	ZnSe	Globar
3	InSb photodiode	KBr	CsI	ZnSe	QTH
4	Ge photodiode	$CaF_2$	Quartz	Quartz	QTH

Table 3.1: The experimental configurations used to obtain the spectra shown in Figure 3.4

Just as one must consider the detector best suited for the range of interest, one must also select the appropriate beamsplitter (BS), cryostat window, and source types. The beamsplitters available are CaF<sub>2</sub> (model T602, roughly  $\omega \gtrsim 1000 \, cm^{-1}$ ), KBr (T301,  $\omega \gtrsim 300$  $cm^{-1}$ ), 6 $\mu$  Mylar (T202, 400  $cm^{-1} \gtrsim \omega \gtrsim 40 \, cm^{-1}$ ), or the T222, which is composite Ge/Mylar (400  $cm^{-1} \gtrsim \omega \gtrsim 1 \, cm^{-1}$ ). The cryostat windows are available in a range of materials, but white polyethelene ( $\omega \lesssim 700 \, cm^{-1}$ ), CsI (200  $cm^{-1} \lesssim \omega$ ), KBr (330  $cm^{-1} \lesssim \omega$ ), or Quartz (2000  $cm^{-1} \lesssim \omega$ ) are well suited for most purposes. The two source towers hold one Quartz/Tungsten/Halogen (QTH, 2000  $cm^{-1} \lesssim \omega$ ) source and one Globar (low frequency) source.

### **3.5** Reflectivity Measurements

As with most spectroscopy experiments, reflectivity measurements are made with respect to a suitable reference. For this reason, the sample is mounted (in most cases) inside a brass disk, and polished until the sample and disk surface are smooth, but most importantly, *coplanar* and *flat*. A highly reflective reference metal film such as Ag or Au is then evaporated on a portion of the brass which is very close to the sample. This "sample disk" is then mounted inside the cryostat on a sample mounting surface. The sample mounting surface is not held fast inside the cryostat, but rather it is hinged at one point by a tight-fitting pin holding it against the cold Cu bracket (see Figure 3.5). A metal rod switch arm can be used to manipulate the orientation of the mounting surface, allowing the experimenter to toggle the exposed substrate between the sample or the reference portions of the sample disk. The experimenter then takes a spectrum with the sample exposed, then another with the reference exposed, and numerically divides the two to get the frequency-dependent reflectivity.

The experimenter must take extreme care during the preparation of the sample disk not to polish too much, or else the rounding of the edges of either the brass or the sample could lens the beam, adversely effecting the beampath overall. Equally important is that the sample and brass surface be parallel, or coplanar. This is so that the beam will encounter all optical components after the cryostat (including the detector) in the *same way*. In order to assess whether the sample and reference surfaces are coplanar, a laser alignment procedure is implemented whereby a He-Ne laser beam is bounced off the sample, onto an auxiliary mirror, and across the laboratory, a total distance of about 40'. One then can trace the laser beam spot on the wall, switch the exposed portion of the disk to the reference, and see if the beam moves significantly. In this way, we can reduce systematic uncertainty associated with the accuracy and precision of the reflectivity measurements that involve the sample cryostat.



Figure 3.5: The cryostat with a mounted sample.

## Chapter 4

# Kondo Systems

### 4.1 Strongly Correlated Electron Systems

What is an electron? We think we understand pretty well every thing that we possibly can understand about a *single* electron that is relevant to the behavior of solids. That is, we know that when this particular piece of the universe is sufficiently isolated from all other things, we measure that the charge is e, the mass is m, the gyromagnetic ratio is around 2, and that the dynamics of the electron are governed by the rules of quantum electrodynamics, and in many cases of interest a much less sophisticated description can tell us what we want to know.

But given all of the knowledge of the behavior of a single electron, one can reasonably ask, "is it possible, and furthermore practical, to deduce the properties of a collection of electrons in terms of the properties of a single electron?". The answer to this question is an open subject, although there are some definite ideas about it(Anderson, 1972). In practice, so far we have a resounding no.

Studying the emergent behavior of many-electron systems is the duty and pleasure of

the condensed matter physicist and presents one of the greatest challenges to science and human exploration of the known universe. The difficulty lies mainly in finding a manageable treatment of electronic interactions, which seem to also provide much the rich diversity of material behavior, leading to competing instabilities giving rise to a diverse landscape of material behaviors marked by charted material phases (superconductivity, some magnetic states, charge-ordered, metallic phases, ...), and a multitude of unexplored phases (non-Fermi liquid, Fulde-Ferrell-Larkin-Ovchinikov phases, magnon condensate, ...), and probably even more phases which are as yet undiscovered.

This chapter is devoted to describing aspects of the current understanding of a class of interacting electron systems, residing on the boundary of metallic and magnetic paradigms, which are generically termed Kondo systems. The paradigm for this class of behavior begins with a wide-band metal that coexists with localized magnetic moments. An introduction to the phenomenology and microscopic physics of this type of system is presented as a backdrop to the presentation of the original contributions to that body of knowledge which center on their infrared response. First, Landau-Fermi liquid theory is outlined, then a historical introduction to the Kondo effect, then phenomenology of Kondo systems and the Anderson impurity model, then heavy fermion materials and the role of the periodic Anderson model in the description of their phenomenology.

The next chapter presents data related to the electrodynamics of  $YbIn_{1-x}Ag_xCu_4$ and our systematic studies of its unexplained phase diagram. There we will use some results of the periodic Anderson model in order to make a quantitative connection concerning specific aspects of the measured electrodynamic response.

### 4.2 Landau-Fermi Liquid Theory

A great practical advance in the direction of conceptually controlling the complexity of matter is the development of the theory of the Fermi gas. This model uses the simple quantum mechanics of a particle-in-a-box as a starting point for understanding the transport and magnetic properties of metallic systems. The excitations of the systems are then indexed though a geometrical construction in momentum space called a Fermi sphere, which is the central paradigm for metallic behavior.

Landau(Landau & Lifshitz, 1980) made an important extension of the ideas of Fermi and a path toward exploring the effects of interactions of the electrons in the limit of low energy. He postulated that for interactions that are not too strong, and for excitations that are not too high in energy, the states of the Fermi gas would remain in a one-to-one correspondence with those of the interacting system. This allows one to retain the quantum numbers of the Fermi gas and watch the continuous evolution of the effective energy levels as the interaction strength is turned up from zero. With the interaction on, referring to the single particle excitations as *electrons* is inaccurate, since in general the observables associated with these excitations can be very different from those of electrons in free space. These excitations are instead called *quasiparticles*. The quasiparticle concept can be developed further, by making allowance for the dependence of an excitation on the presence of other excitations. These notions together describe what is called the Fermi liquid, or sometimes the Landau-Fermi liquid, and is the central paradigm for understanding the behavior of "conventional" metals. In fact, one often says that a metal is conventional if the Landau theory applies.

It is important to emphasize that while the Landau-Fermi liquid (LFL) provides a practical way of thinking about many aspects of condensed matter phenomena, behavior beyond the LFL is not only expected, but common. Local magnetism and superconductivity are examples of behavior that lie beyond the scope of LFL theory.

We proceed to describe in some detail the history and phenomenology of the Kondo effect until section 4.9 where we introduce the quasiparticles of the periodic Anderson model and discuss the nature of the low energy excitations which are related to the observed phenomenology of heavy fermion systems.

### 4.3 The Kondo Effect

The liquefaction of helium lead to the discovery many physical effects in the early twentieth century, and among these was the earliest vestiges of what is now known as the Kondo effect. In 1934, de Haas *et al*(de Haas et al., 1934) revealed an unexpected peculiarity of the low temperature resistivity in a Au sample. Before revealing the peculiarity, let us look at what we might expect to happen to the resistivity in a metallic system with a high carrier concentration.

The resistivity of so called "noble metals" (*e.g.* Au, Cu, Ag, Al) is associated with deviations of the charge-derived crystalline potential from perfect periodicity. This most commonly occurs in these systems through either the presence of defects, or by the deviations associated with thermal lattice vibrations, or by the presence of other electronic excitations. Matheissen's rule, which states that scattering rates for independent scattering mechanisms should simply add, permits us to consider these three contributions to the resistivity independently.

Charged impurities set up a static field of scattering centers which depends only very weakly on temperature and so one expects that it will provide a temperature-independent contribution to the resistivity. In fact the value of the low-temperature resistance of a metallic system relative to its high temperature value, called the residual resistivity ratio (sometimes RRR), is frequently quoted as a figure of merit for sample purity. Alternatively, phonon scattering can be a sizable source of electron scattering. The population of phonon levels is strongly temperature dependent and so the contribution of the lattice influence to the resistivity is expected to be strongly T-dependent. In the Debye model, when Umplapp scattering is negligible, the resistivity due to phonons varies<sup>1</sup> as  $T^5$ .

A third source of scattering in metals is electron-electron scattering which gives, according to the Landau-Fermi Liquid theory, a  $T^2$  contribution to the resistivity<sup>2</sup>.

Since all of these contributions increase or stay constant with temperature, no combination of these scattering processes alone could provide a nonmonotonic temperature dependence of the resistivity, so the expected behavior of "cold gold" is that dR/dT > 0 for all Tdown to T = 0. And indeed, this trend is observed at room temperature and continues down to very low temperatures. So it came at some surprise when de Haas *et al*(de Haas et al., 1934) observed in 1934 a deviation from this expectation as a minimum in the resistivity around 1K! It is now known that the resistance minimum is an effect of the presence of *magnetic* impurities which were most likely Fe in de Haas' sample.

More expansive experiments revealed a correlation between the depth of the resistance minimum and the appearance of a Curie-Weiss moment in the magnetic susceptibility as magnetic impurities were deliberately introduced. Kondo(Kondo, 1964) made this observation which motivated him to carry out a calculation of the scattering rate of Zener's s-d model(Zener, 1951). The s-d model is a Hamiltonian description of a Fermi gas of electrons which couple antiferromagnetically to a localized magnetic moment. Kondo revealed that in the third order perturbation theory in this coupling, the carrier scattering rate of the s-d model contained contributions logarithmic in temperature which could describe the low temperature upturn

<sup>&</sup>lt;sup>1</sup>This result is attributed to Felix Bloch and is sometimes called the Bloch  $T^5$  law(Ashcroft & Mermin, 1976). <sup>2</sup>This form is understood by considering the phase space available to scattering of electrons. These scattering events conserve momentum, but are additionally restricted by the Pauli exclusion principle. The presence of the (filled) Fermi surface to the low energy **k**-states severely constrains the phase space available to these scattering events.

in resistivity and make a quantitative connection to aspects of the impurity-concentrationdependent minimum.

Most surprising was the revelation that the theory which explains so well the resistance minimum experiences divergences in physical quantities<sup>3</sup> which are calculated within perturbation theory. The perturbation expansion is valid at high temperature but breaks down below a temperature  $T_K$ , characteristic of the theory. Crossing over this boundary into the low temperature regime is what is known as the Kondo problem(Hewson, 1993). The theoretical development of the Kondo problem from proposal to solution is an interesting story whose pursuit helped introduce concepts of scaling(Anderson & Yuval, 1969; Anderson et al., 1970), renormalization group(Wilson, 1980; Krishnamurthy et al., 1980a; Krishnamurthy et al., 1980b), numerous numerical techniques(Jarrell, 1995; Georges et al., 1996), etc. into the lexicon of theoretical physics but also rekindled and advanced other ideas such as the diagonalization technique of the Bethe ansatz(Bethe, 1931; Andrei, 1980; Wiegmann, 1980) and the 1/N expansion(Witten, 1978; Bickers et al., 1987). Unfortunately, these interesting developments lie outside the scope of this thesis. The reader is referred to Hewson's book(Hewson, 1993) and Wilson's review article(Wilson, 1980) for discussion of the historical development of the Kondo problem.

# 4.4 The Anderson Model and the Phenomenology of Kondo Systems

In this section we discuss some of the physics of Kondo phenomena and introduce the concept of the Kondo resonance.

 $<sup>^{3}</sup>$ Most notably are the zero temperature resistance, specific heat, and magnetic susceptibility.

The s-d model has the Hamiltonian:

$$\mathcal{H} = \sum_{\mathbf{k},\sigma} \epsilon_{\mathbf{k}} c^{\dagger}_{\mathbf{k},\sigma} c_{\mathbf{k},\sigma} + \sum_{\mathbf{k},\mathbf{k}'} J_{\mathbf{k},\mathbf{k}'} (S^{+} c^{\dagger}_{\mathbf{k},\downarrow} c_{\mathbf{k}',\uparrow} + S^{-} c^{\dagger}_{\mathbf{k},\uparrow} c_{\mathbf{k}',\downarrow} + S^{z} (c^{\dagger}_{\mathbf{k},\uparrow} c_{\mathbf{k}',\uparrow} - c^{\dagger}_{\mathbf{k},\downarrow} c_{\mathbf{k}',\downarrow})).$$
(4.1)

The first term is the kinetic energy and creates a Fermi sea of a band of conduction states.  $S^{\pm}$ and  $S^z$  address the spin components of a localized magnetic impurity (spin 1/2), which can be either up or down. The second terms describe the magnetic scattering of the conduction states with ( $S_z$  term), or without ( $S^+$  and  $S^-$  terms) a spin flip, keeping the total spin conserved. Kondo(Kondo, 1964) treated this second term in perturbation theory to describe the resistance minimum due to magnetic spin scattering.

One must realize that the quantum rotor of the *s*-*d* model is actually the spin of another electron and that the Heisenberg-like coupling is a result of an exchange interaction. In principle, processes where this localized orbital is emptied or doubly occupied, in addition to simply having its spin reoriented, could be included. The more general Hamiltonian which encompasses all of the physics of the *s*-*d* model but also allows a variable occupation of the local orbital is the Anderson model<sup>4</sup>:

$$\mathcal{H} = \sum_{\mathbf{k},\sigma} \epsilon_{\mathbf{k}} c^{\dagger}_{\mathbf{k},\sigma} c_{\mathbf{k},\sigma} + \sum_{\sigma} \epsilon_{f} f^{\dagger}_{\sigma} f_{\sigma} + U n_{f,\uparrow} n_{f,\downarrow} + \sum_{\mathbf{k},\sigma} (V_{\mathbf{k}} f^{\dagger}_{\sigma} c_{\mathbf{k},\sigma} + V^{*}_{\mathbf{k}} c^{\dagger}_{\mathbf{k},\sigma} f_{\sigma}).$$
(4.3)

The first term is the kinetic energy of the conduction electrons and is responsible for the formation of the Fermi sphere as introduced in Section 4.2. The second term is the

$$J = \frac{|V|^2}{\epsilon_f} + \frac{|V|^2}{\epsilon_f + U}.$$
(4.2)

 $<sup>^{4}</sup>$ If the f level is not broadened so much that it distributes weight on both sides of the Fermi level, then the Anderson model can be mapped into the s-d model through a Schrieffer-Wolf transformation:

This exchange energy has a physical interpretation as the energy associated with three (virtual) events; for simplicity, consider the first term. A down spin conduction electron "swaps" places with an up-spin electron in the localized orbital, giving one factor of V. The up spin conduction electron then "propagates" in the local orbital, giving  $\epsilon_f$  as an energy denominator. The conduction electron is then put back in the original state with a factor of V<sup>\*</sup>. The second term can be understood similarly by considering a process where a hole exchanges spin with the empty level at  $\epsilon_f + U$ .(Scalletar, 2003)



Figure 4.1: The density of states for the Anderson Hamiltonian (in the Kondo limit) with V = 0.

energy of the a singly occupied localized orbital, and  $-\epsilon_f$  is the energy position of this level with respect to the Fermi level. U is the on-site repulsion of f electrons, and so represents the energy cost for doubly occupying the local orbital. This term is responsible for the formation of a net magnetic moment at high temperatures (or in the absence of hybridization)(Anderson, 1961). This can happen if the Fermi level lies between  $\epsilon_f$  and  $\epsilon_f + U$ , so that a singly occupied f orbital is the lowest energy configuration, provided that V = 0. The last term is called the *hybridization* term and mixes the conduction and f states, an action with profound effects on the observable properties of the magnetic-impurity/metallic system.

Figure 4.1 shows the bare density of states (the basis) for single particle excitations of this model, with V = 0. One effect of a nonzero V is to broaden the f level, as can be seen by Fermi's Golden Rule. This is conveniently done by assuming a constant density of states, and a **k**-independent hybridization:

$$\Delta = \pi \sum_{\mathbf{k}} |V_{\mathbf{k}}|^2 \delta(\epsilon_{\mathbf{k}} - \epsilon_f) = \pi N(E_F) |V|^2$$
(4.4)

In the next section we discuss the more profound consequences of the inclusion of the hybridization term.

### 4.5 Effects of Hybridization

In this section we discuss the emergence of the many body Kondo resonance at the Fermi level through the discussion of the time-evolution of the non-hybridized system under the action of the hybridization. This will set the stage for the discussion of the physics behind the optical data taken on the Kondo lattice system  $YbIn_{1-x}Ag_xCu_4$ .

To begin, consider the many body state corresponding to the ground state of the Anderson model<sup>5</sup> with V = 0 (see Figure 4.1 and Equation 4.3). We will be interested here in the case where  $\epsilon_f \ll E_F$  and  $\epsilon_f + U \gg E_F$ , called the Kondo limit. For definiteness, we will let the orbital degeneracy of the singly occupied level N = 2, corresponding to a spin  $\frac{1}{2}$  impurity.

The two species of particles, c and f, will act independently since there is no term in the Hamiltonian to mix them when V = 0. The conduction electrons will form a Fermi sea with a well defined Fermi surface and their elementary excitations will form a continuum of sharp (long lived) excitations which will dominate the transport properties, a result their itinerant nature. In addition, these electrons will provide a Pauli-paramagnetic (*i.e.* temperature independent) contribution to the magnetism due to their continuous spectrum.

Conversely, the localized f electrons will give negligible contribution to the transport dynamics but will have a substantial effect on the magnetism. This is due primarily to the action of the on-site U term, which prevents double occupancy of this local level<sup>6</sup>, leaving one unpaired local spin in the ground state and hence a net magnetic moment. This partially filled

<sup>&</sup>lt;sup>5</sup>We will assume that T = 0 in this section.

<sup>&</sup>lt;sup>6</sup>This is specific to the case of interest,  $\epsilon_f < E_F$  and  $\epsilon_f + U > E_F$ . Other cases are include the empty orbital, mixed valent, and doubly occupied regimes.
orbital then acts as a quantum rotor, giving a Curie-type ( $\chi \sim 1/T$ ) susceptibility contribution.

Introduction of the hybridization term mixes the conduction and f electron states and influences this situation greatly. The hybridization term does not commute with the number operator for f electrons  $n_f = f^{\dagger} f$  and so this f occupancy is no longer a good quantum number, a fact which we depended on to justify our expectation of a Curie term in the susceptibility. Transport properties are also greatly effected by the mixing through a renormalization of the carrier mass.

To appreciate the complexity that the hybridization introduces, imagine now that our initial state (with V = 0) is allowed to evolve under the action of the full Anderson Hamiltonian with  $V \neq 0$ , starting at t = 0.

If a measurement of any microscopic property is performed an *extremely* short time later, then of course nothing will have changed and the physical properties will be those of the unhybridized system<sup>7</sup>.

However, if the system is allowed to evolve for a time of order  $t \sim \hbar/V$ , then the influence of the hybridization term will appear as the amplitude for two other type of states becomes appreciable. These states are identical to the ground state, except that a conduction electron is either swept into the unoccupied portion of the local orbital, or the orbital is emptied and a conduction electron is created. If measurements are performed at one particular time  $t \sim \hbar/V$  in the evolution of an ensemble of systems, then a finite fraction of this experimental sampling will return microscopic properties corresponding to any of the states shown in the bottom tiers of Figure 4.2, as well as the original state shown in the top.

Further time evolution will create an amplitude for more holes in the conduction band<sup>8</sup>

$$U(t)|\psi_0\rangle = (1 + (\frac{-i}{\hbar})\int_0^t dt_1 H_{hyb}(t) + (\frac{-i}{\hbar})^2 \int_0^t dt_1 \int_0^{t_1} dt_2 H_{hyb}(t_1) H_{hyb}(t_2) + \dots)|\psi_0\rangle$$
(4.5)

<sup>&</sup>lt;sup>7</sup>This is the quantum Xeno effect(Griffiths, 1994).

 $<sup>^{8}</sup>$ What is being described here is the effect of a time evolution operator for the (here interaction picture) hybridization term on the ground state



Figure 4.2: Possible states reached under the repeated action of hybridization.

and generate an infinite regression of states with particle-hole excitations, so after a long time the state of the system will be a grand linear combination of all particle-hole excitations and configurations of the local orbital, all of which are present with appreciable amplitude.

The dynamical evolution of the ground state of the unhybridized hamiltonian under the action of the hybridization term forces the system to accrue finite overlap with states that would otherwise be highly excited. This connection to high energy states through the hybridization creates a cooperative effect on the energy structure which is especially pronounced near the Fermi level. Diagonalizing the Hamiltonian requires the inclusion of excitations of very high energy, the highest being of order the system bandwidth, an energy scale which accordingly bears some importance to the low energy properties of the system.



Figure 4.3: The influence of hybridization on the density of states. The f level broadens and a narrow resonance in the vicinity of the Fermi level appears.

This spreading of the low lying states over Hilbert space under the action of the full Anderson impurity Hamiltonian is so extreme in fact that one finds that the ground state with V = 0 is orthogonal to the ground state with  $V \neq 0$  when the thermodynamic limit is taken(Guinea et al., 1997; Anderson, 1967). This is a special case of a more general result called Anderson's orthogonality catastrophe(Anderson, 1967; Mahan, 1990) which stems from the localized nature of the impurity orbital and is intimately related to the breakdown of perturbation theory of the impurity models.

#### 4.6 The Kondo Resonance

An important effect of hybridization on the energy structure of the local moment plus metal system is to concentrate a small amount of state density into an extremely narrow band very near the Fermi level (Fig 4.3), called the Kondo, or Abrikosov-Suhl resonance. It is important to realize that these states are no longer the non-interacting single particle levels of the Fermi gas, but instead correspond to many body levels of the system. In this many-body picture, the formation of the peak in the density of states near  $E_F$  translates into the existence of large number of low-lying excitations above the ground state. The scale for the onset of these excitations is a small energy,  $T_K$ , which depends on model parameters<sup>9</sup>, and in practice is between 0.1 and 1000 K.

#### 4.7 Magnetism and Kondo Crossover

We mentioned earlier that the hybridization term does not commute with the number operator for f electrons  $n_f = f^{\dagger} f$ , destroying the "goodness" of the f occupancy as a quantum number, a fact which is depended on in the theory of Curie paramagnetic (local moment) susceptibility.

In the absence of hybridization, we indeed expect Curie 1/T behavior, with the susceptibility diverging<sup>10</sup> as  $T \to 0$ . The conduction electrons on the other hand, give a *T*-independent contribution which, being independent of the local orbital, simply adds to the Curie contribution.

What happens when  $V \neq 0$ ? Interestingly, the conduction electrons screen out the net moment of the localized orbital, forming a state whose average spin is zero(Anderson & Yuval, 1969). This state is known as the Kondo singlet, and is shown schematically in Figure 4.4<sup>11</sup>.

$$T_K = \frac{B}{2\pi} e^{\frac{3}{4} + \gamma} \sqrt{2DOS(E_F)|J|} e^{-\frac{1}{2DOS(E_F)J}}$$
(4.6)

<sup>&</sup>lt;sup>9</sup>In the theory of the Anderson impurity model,  $T_K$  is related to the model parameters, in the Kondo limit, by

<sup>,</sup> where  $\gamma = 0.577216...$  is the Euler-Masceroni constant and J is given (Bickers et al., 1987) by the Schrieffer-Wolf transformation, Eq. 4.2.

<sup>&</sup>lt;sup>10</sup>Within the local moment/Curie formalism, the finite field  $(H \neq 0)$  or any other degeneracy breaking effects would prevent this occurrence.

<sup>&</sup>lt;sup>11</sup>The oscillatory behavior of the spatial correlation function is a feature common to the charge (Friedel) oscillations about a potential impurity, but in the Kondo case this oscillation happens in the spin sector. This behavior also occurs in the (closely related) magnetic Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction, whereby localized moments are correlated through a superexchange interaction involving a conduction electron.



Figure 4.4: Schematic illustration of the Kondo screening cloud. In (a), V = 0 and the local spin and Fermi sea act independently, so the spin correlation function follows closely the local orbital wavefunction, giving local paramagnetism. In (b), the hybridization  $V \neq 0$  and the "goodness" of the orbital occupancy as a quantum number is ruined. Locally, the spin in this case is screened by the electrons of the Fermi sea, and the spin-spin correlation function reflects this fact with a spatial oscillation with wavevector  $2k_F$ . The overall spin state is singlet.



Figure 4.5: The susceptibility of a Kondo resonance. The high temperature Curie-Weiss behavior crosses over into a temperature independent Pauli-paramagnetic form with a characteristic temperature scale  $T_K$ . In the cases of higher angular momentum, a peak develops in the susceptibility. These results are taken from the calculations of Rajan(Rajan, 1983) using the Bethe ansatz solution to the Coqblin-Schrieffer model for J=1/2 and J=7/2.

We mentioned above that a characteristic energy scale  $T_K$  arises in the theory of the *s*-*d* model. As the scale below which perturbation theory breaks down, it is not surprising that this quantity plays the role of a crossover temperature, dividing the realms of high and low temperature behavior. Figure 4.5 shows the calculated susceptibility of the J = 1/2 and J = 7/2 Kondo (*s*-*d* and Coqblin-Schrieffer models). In each, at high temperature, the susceptibility behaves as a localized moment, with Curie-Weiss behavior,  $\chi \propto 1/(T + \Theta_W)$ , with the Weiss temperature  $\Theta_W$  closely related to  $T_K$ . This form is essentially that of a localized moment that is coupled to its environment via an antiferromagnetic exchange interaction of order  $T_K$ . For  $T < T_K$ , the Kondo singlet forms and the free-moment behavior is quenched by the screening influence of the conduction electron sea. So at the lowest temperatures, the susceptibility becomes temperature independent.

Interestingly, in the s-d model, calculated thermodynamic quantities are universal

The competition of the Kondo mechanism, which destroys magnetism, and the RKKY mechanism, which can favor either long range magnetic order or spin glassiness, is a currently active research topic (Schroder et al., 2000).

functions<sup>12</sup> of  $T/T_K$ . While this remarkable scaling does not strictly carry over to the case of a lattice of localized moments, in practice much of the behavior of the lattice systems is controlled by the Kondo temperature. In the next chapter, we will use  $T_K$  as a single variable quantifier of the effects of hybridization in the low temperature phase of YbIn<sub>1-x</sub>Ag<sub>x</sub>Cu<sub>4</sub>.

#### 4.8 Heavy Fermions

So far we have discussed some of the theoretical aspects of magnetic impurities embedded in a host metal. What happens then if we are faced with a situation in which a periodic lattice of localized moments hybridizes with a conduction sea? Such a case is manifest experimentally in rare-earth metallic compounds such as YbAgCu<sub>4</sub>, a member of a class of compounds called *heavy fermions*.

The heavy fermi systems of interest here are typified by Fermi liquid behavior<sup>13</sup>, and the quantities associated with the carrier mass are greatly enhanced over the bare electron values. These include the zero temperature value of the dc magnetic susceptibility  $\chi(\omega = T = 0)$ , linear specific heat (Sommerfeld) coefficient  $\gamma$ , and the A coefficient<sup>14</sup> of the temperature dependent resistivity,  $\rho_{dc} \propto AT^2$ .

In heavy fermion systems, the hybridization between the local moments and the conduction electrons is a controlling influence, and the hybridization between conduction electrons and local moments is manifest in the magnetic susceptibility, which can follow the predictions

<sup>&</sup>lt;sup>12</sup>In general, they may also depend on the magnetic degeneracy N = 2J + 1. In the rare earth system  $YbIn_{1-x}Ag_xCu_4$ , N = 8 is appropriate, since the spin-orbit interaction leads to a  $j = \frac{7}{2}$  configuration of the  $f^{13}$  orbital. The case chosen here for the sake of simple discussion of the Kondo phenomenology is N = 2, appropriate to a crystal-field split *d*-orbitals containing one electron.

 $<sup>^{13}</sup>$ Many other competing instabilities observed in practice include superconducting, long range magnetic, and non-Fermi liquid phases (Stewart, 1984; Degiorgi, 1999)  $^{14}$  The Kadowaki-Woods ratio  $\frac{A}{\gamma^2} = 1.0\,10^{-5}\mu\Omega cm/(mol\,K/mJ)^2$  (Kadowaki & Woods, 1986) is an empirically

<sup>&</sup>lt;sup>14</sup>The Kadowaki-Woods ratio  $\frac{A}{\gamma^2} = 1.0 \, 10^{-5} \mu \Omega cm/(mol K/mJ)^2$  (Kadowaki & Woods, 1986) is an empirically discovered result which holds remarkably well of heavy fermions as well as many metallic transition metal systems.

of impurity models very well<sup>15</sup>.

#### 4.9 Quasiparticles in the Periodic Anderson Model

The physics unique to heavy fermion systems are believed to be encompassed by the periodic Anderson model (PAM), sometimes referred to as the Anderson lattice model. In this section we will derive the effective dispersion relations for low energy quasiparticles of this model. The treatment follows Hewson(Hewson, 1993) chapter 10 very closely and the derivation of the quasiparticle dispersion is taken originally from Edwards(Edwards, 1988). The earliest reference to dispersion relations of this type to describe the physics of these materials is given by Varma(Varma, 1976). This mathematical interlude is necessary to make a connection between the phenomenology of the optical data and the theory of the Anderson lattice.

The Anderson model generalizes to a lattice model by making the relative phase of the hybridization at each site a rigid parameter. The Hamiltionian is

$$\mathcal{H} = \sum_{\mathbf{k},\sigma} \epsilon_{\mathbf{k}} c^{\dagger}_{\mathbf{k},\sigma} c_{\mathbf{k},\sigma} + \sum_{i,\sigma} \epsilon_{f} f^{\dagger}_{i,\sigma} f_{i,\sigma} + U \sum_{i} n_{f,i,\uparrow} n_{f,i,\downarrow} + \sum_{i,\mathbf{k},\sigma} (V_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}_{i}} f^{\dagger}_{i,\sigma} c_{\mathbf{k},\sigma} + V^{*}_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}_{i}} c^{\dagger}_{\mathbf{k},\sigma} f_{i,\sigma})$$

$$(4.7)$$

where  $\epsilon_f$  is the f level position,  $\epsilon_{\mathbf{k}}$  describes the conduction band, U is the on-site electronic repulsive energy, and  $V_{\mathbf{k}}$  is the hybridization. The positions  $\mathbf{R}_i$  locate the f-orbital centers,  $c_{\mathbf{k}}$ and  $f_i$  destroy an electron of wavevector  $\mathbf{k}$  and an f electron at site i, respectively.

The Green's function of this Hamiltonian is, quite generally,

$$G_{\mathbf{k},\sigma}^{ff}(\omega) = \frac{1}{\omega - \epsilon_F - \epsilon_{f,\mathbf{k}} - \Sigma_{\sigma}(\omega,\mathbf{k}) - |V_{\mathbf{k}}|^2 / (\omega - \epsilon_{\mathbf{k}})}.$$
(4.8)

 $\Sigma_{\sigma}(\omega, \mathbf{k})$  here is the proper self energy of the on-site repulsive interaction. This energy is zero if U = 0. This quantity is difficult to calculate(Tahvildar-Zadeh et al., 1999; Jarrell, 1995;

<sup>&</sup>lt;sup>15</sup>The generalization of the *s*-*d* model to arbitrary magnetic degeneracy N gives rise to the Coqblin-Schrieffer model(Coqblin & Schrieffer, 1969). In practice, numerical calculations of this model(Rajan, 1983) are used to fit susceptibility data and deduce a Kondo temperature(Cornelius et al., 1997).

Vidhyadhiraja et al., 2003; Georges et al., 1996; Millis & Lee, 1987), so to get a handle on the low lying excitations, we apply a useful approximation regarding its momentum and energy dependence in the vicinity of the Fermi level. We assume that the self-energy can be expanded around the Fermi surface  $\omega = \epsilon_F$  and  $\mathbf{k} = \mathbf{k}_F$ ,

$$\Sigma(\omega, \mathbf{k}) = \Sigma^{R}(\epsilon_{F}, \mathbf{k}_{F}) + (\mathbf{k} - \mathbf{k}_{F}) \cdot \nabla_{\mathbf{k}_{F}} \Sigma^{R}(\epsilon_{F}, \mathbf{k}_{F}) + (\omega - \epsilon_{F}) \left(\frac{\partial \Sigma^{R}(\epsilon_{F}, \mathbf{k}_{F})}{\partial \epsilon_{F}}\right) + \cdots$$
(4.9)

The imaginary part of  $\Sigma$  has been left out because it is of higher order<sup>16</sup>.

Combination of these relations and an algebraic reduction give the same Green's function (GF) as 4.8 with U = 0, but with a renormalization of the *f*-level position and hybridization strength by the on-site repulsion U. The *f*-electron and *c*-electron Green's functions with the interaction non-zero have the same form as when the interaction is equal to zero, but the model parameters have different values. Thus,

$$\tilde{G}_{\mathbf{k},\sigma}^{ff}(\omega) = \frac{1}{\omega - \epsilon_F - \tilde{\epsilon}_{f,\mathbf{k}} - |\tilde{V}_{\mathbf{k}}|^2 / (\omega - \epsilon_{\mathbf{k}})}.$$
(4.10)

The quasiparticle dispersion are those values of  $\epsilon$  and **k** that make the Green's function large. Since the GFs here are real, the finite lifetime of the excited states is ignored, essentially assumed long lived, and the poles of the GF give the quasiparticle dispersion. This gives

$$\epsilon^{\pm} = \frac{\epsilon_F + \tilde{\epsilon_f} + \epsilon_{\mathbf{k}} \pm \sqrt{(\epsilon_F + \tilde{\epsilon_f} - \epsilon_{\mathbf{k}})^2 + 4\tilde{V}^2}}{2}.$$
(4.11)

as the momentum-energy relation for the low lying excitations of the PAM. These dispersion relations are shown in Figure 4.6. These dispersions provide a handle on the quasiparticle character of the PAM and will be referred to often in the next chapter as the PAM dispersion relations.

These dispersion relations allow us access to the **k** dependence of the Kondo resonance, given that we know the underlying **k** dependent band states and the dispersion of  $\tilde{V}_{\mathbf{k}}$  and  $\tilde{\epsilon}_{\mathbf{k}}$ .

 $<sup>^{16}\</sup>Sigma^{I} \sim (\omega - \epsilon_{F})^{2}$  around the Fermi surface; this is for the same reason that the resistivity  $\rho_{dc} \propto const. + T^{2}$  as mentioned in the section on Landau-Fermi liquid theory.



Figure 4.6: The dispersion relations of the periodic Anderson model, Equation 5.9. The darkened portion of the lower band indicates filled quasiparticle states.

In practice, we will take these to be constant. For  $\tilde{\epsilon}_{\mathbf{k}}$ , this means that the localized orbital is very localized, and does not extend outside of one unit cell.  $\tilde{V}_{\mathbf{k}} = constant$  on the other hand is merely a simplifying assumption, in general, one expects there to be angular dependence to this quantity.

### Chapter 5

# $\mathbf{YbIn}_{1-x}\mathbf{Ag}_{x}\mathbf{Cu}_{4}$

This chapter presents results for the optical study of this Kondo lattice system. We begin by presenting the phenomenology of  $YbIn_{1-x}Ag_xCu_4$  in the *x*-*T* plane, then presenting the *x* and *T*-dependent optical conductivity and reflectivity. A feature which appears at 2000  $cm^{-1}$  in YbInCu<sub>4</sub> is then analyzed in detail in terms of a particular excitation which arises in the context of the periodic Anderson model (PAM), and a model is developed for use with fitting the measured conductivity. Through this comparison, we are able to positively identify the 2000  $cm^{-1}$  feature as an excitation of the Kondo resonance in the context of the PAM.

# 5.1 Phenomenology of $YbIn_{1-x}Ag_xCu_4$ and the Valence Transition in $YbInCu_4$

Figure 5.1 shows a schematic representation of the phase diagram of  $YbIn_{1-x}Ag_xCu_4$ . This system is of marked interest because unlike the paradigmatic/generic Kondo systems discussed in the previous chapter, where  $T_K$  is uniquely determined for a given system, the low



Figure 5.1: Schematic phase diagram of  ${\rm YbIn}_{1-x}{\rm Ag}_x{\rm Cu}_4.$  Lighter shading indicates a larger  $T_K.$ 

doping region of YbIn<sub>1-x</sub>Ag<sub>x</sub>Cu<sub>4</sub> displays a first order phase transition, across which the effective  $T_K$  value changes by over an order of magnitude. In YbInCu<sub>4</sub> (x=0) at high temperature ( $T > T_v = 42 K$ ), the magnetic response exhibits a Curie-Weiss form with magnitude appropriate to j = 7/2 moment of Yb and a small Weiss temperature(Svechkarev et al., 1999)  $\Theta_W \sim -13 K$ , which constrains the effective Kondo temperature appropriate in this high temperature range to be comparably small in magnitude.

Lowering the temperature through the first order phase transition has dramatic effects on both the spin and charge response. For  $T < T_v$ , the magnetic susceptibility drops considerably into a temperature independent (Pauli paramagnetic) form, with a magnitude indicating a dramatic increase in the Kondo temperature. In concert the carrier concentration increases markedly and the resistance drops(Sarrao et al., 1996). Extensive experimentation has revealed substantial changes in specific heat(Sarrao et al., 1998; Felner & Nowik, 1986; Hauser et al., 1996), elastic constants(Sarrao et al., 1998; Kindler et al., 1994), single-particle (photoemission)(Dallera et al., 2002; Joyce et al., 1996; Weibel et al., 1993; Lawrence et al., 1994; Reinert et al., 1998), two-particle (optical)(Garner et al., 2000; Hancock et al., 2004a; Antonov et al., 2000; Marabelli & Bauer, 1993) and neutron(Lawrence et al., 1997) spectroscopies.

Changes associated with the phase transition in YbInCu<sub>4</sub> are generally interpreted as an effective screening of the localized Yb 4f moments in the low temperature phase. This is associated with an order of magnitude increase in Kondo coupling scale ( $T_K \sim 17 K$  for  $T > T_v$ ;  $T_K \sim 300 K$  for  $T < T_v$ ). Universal scaling observed(Immer et al., 1997; Sarrao, 1999) in the *B-T* plane was shown(Dzero et al., 2002; Mushnikov et al., 2003) to support the scenario of a transition-induced screening of the Yb moment.

Doping Ag on the In site serves to stabilize the low temperature phase, driving the phase transition temperature upward (Sarrao et al., 1996) and blending the low and high tem-

perature phases. For x=0.5 and x=1.0, a single Kondo temperature is adequate to describing the hybridization physics. Experimentally, the transition becomes less sharp with doping and it is estimated (Sarrao et al., 1996) that the transition disappears completely at the critical concentration  $x_c=0.2$ . Concentration values  $x > x_c$  display behavior more typical of heavy fermion systems, where coherent heavy metallic quasiparticles responsible for the low energy physics have an enhanced mass as high as  $m^* \simeq 50m_e$ .

#### 5.2 Experimental Details

We have measured the reflectivity of single crystals of a sequence of samples of  $YbIn_{1-x}Ag_xCu_4$  with compositions x = 0, 0.3, 0.5, 0.75 and 1.0. Our measurements cover the frequency range from  $40 \, cm^{-1}$  to  $50,000 \, cm^{-1}$  with detailed temperature dependent data taken between  $40 \, cm^{-1}$  and  $23,000 \, cm^{-1}$ . Each sample was mounted into a recess custom-machined into a brass disk. Each disk was polished (minimally) such that a smooth, flat sample surface sits parallel to a similarly flat, polished portion of the brass mounting disk. Ag film was then evaporated on the bare brass surface, creating a reference mirror for use in the temperature dependent reflectivity measurements. Soon after evaporation, the sample disk was mounted inside a continuous-flow He<sup>4</sup> cryostat with a custom switching mechanism designed to expose either Ag or sample surfaces to the beam. To insure that the reference mirror and sample disk. Frequency dependent spectra were then taken using a combination of Fourier transform and grating spectrometers. At each temperature and composition, spectra were taken for Ag and sample exposed through the cryostat window and the the ratio at each frequency used to determine the reflectivity  $R(\omega)$ .

In addition to the temperature dependence, room temperature reflectivity spectra

were also taken in the range 12,  $500 \ cm^{-1} < \omega < 50,000 \ cm^{-1}$  with an optical setup which does not involve the use of a reference mirror. The spectra taken by this method and those spectra taken using the cryostat (and with Ag reference) generally agree well in the region of overlap  $(12, 500 \ cm^{-1} < \omega < 23,000 \ cm^{-1})$ . Through this comparison, we estimate the uncertainty of the absolute value of the reflectivity in the temperature dependent measurements to be less than 1%.

A Kramers-Krönig transform is applied to the measured reflectivity in order to determine the frequency dependent reflection phase shift(Dressel & Gruner, 2002; Wooten, 1972). The magnitude and phase of the reflectivity are then used in order to determine the dynamical conductivity  $\sigma_1(\omega)$  (and the dielectric function  $\epsilon_1(\omega)$ ).

For the purposes of the transform, Hagen-Rubens terminations  $(1 - R(\omega) \propto \sqrt{\omega})$  are used below  $40 \ cm^{-1}$ . At high frequency (above  $50,000 \ cm^{-1}$ ) each reflectivity spectrum is extrapolated to a common value of 0.08 at  $120,000 \ cm^{-1}$  and then continued as a constant to  $200,000 \ cm^{-1}$ . Between  $200,000 \ cm^{-1}$  and  $400,000 \ cm^{-1}$ , an  $\omega^{-2}$  form is used for  $R(\omega)$  to represent the non-constant reflectivity expected as a result of deep core level excitations(Wooten, 1972). At still higher frequencies, the free-electron form  $\omega^{-4}$  is assumed.

We have experimented with a number of termination protocols including other common values and coalescence frequencies as well as constant extrapolations above 50,000  $cm^{-1}$ . These show convincingly that our results regarding trends in the x and  $T_K$  dependence of  $\sigma_1(\omega)$  below 10,000  $cm^{-1}$  are not significantly influenced by any of the extrapolations above 50,000  $cm^{-1}$ . The conductivity above 10,000  $cm^{-1}$  but below 20,000  $cm^{-1}$  is influenced by the detailed extrapolation by about 5% for reasonable extrapolation protocols.

In YbInCu<sub>4</sub>, where a first-order phase transition occurs at finite temperature, we have been careful to control the potential hysteresis effects [ref] usually associated with first order phase transitions by keeping the thermal cycling through the phase transition to a minimum while collecting the optical data. We found that hysteresis effects are observable in the infrared spectrum, and are especially pronounced in the frequency range  $1000 < \omega < 7000 \, cm^{-1}$  (see Figure 5.2). For this reason, our data for several ranges were retaken on fresh samples, ensuring that these effects are controlled.

#### 5.3 Optical Results

#### **5.3.1** T and x dependence

Figure 5.2 shows the frequency-dependent reflectivity and infrared conductivity  $\sigma_1(\omega)$ of YbInCu<sub>4</sub> at temperatures below and above the  $T_v \simeq 42K$  phase transition temperature. At high temperature (250 K),  $\sigma_1(\omega)$  consists of a narrow free-carrier (Drude-like) contribution clearly seen in the far-infrared spectrum, due to the presence of mobile carriers. This is consistent with Hall(Figueroa et al., 1998) and resistivity(Sarrao et al., 1996) measurements.  $\omega \simeq 6000 \, cm^{-1}$  marks a clear onset of a set of strong interband transitions extending upward into the visible spectral range.

At the lowest temperature (20 K), a significant decrease in conductivity in the interband region ( $\omega > 4000 \, cm^{-1}$ ) accompanies a substantial increase in the conductivity below  $4000 \, cm^{-1}$  in the form of a well-defined peak centered around  $2000 \, cm^{-1}$ . The development of this peak is highly correlated with the phase transition ( $T_V=42 K$ ) and is a prominent and essential feature of the low-T phase of YbInCu<sub>4</sub>. The connection between this peak and the physics of hybridization is an important theme of the present work.

Figure 5.3 shows optical data for the x=0.3 system. Trends similar to those in low temperature YbInCu<sub>4</sub> are apparent, with a depletion of weight around  $8000 \, cm^{-1}$ , accommodated



Figure 5.2: Reflectivity and optical conductivity  $\sigma_1(\omega)$  for YbInCu<sub>4</sub>.



Figure 5.3: Reflectivity and optical conductivity  $\sigma_1(\omega)$  for YbIn<sub>.7</sub>Ag<sub>.3</sub>Cu<sub>4</sub>.

by a replenishing at lower frequencies. Vestiges of the  $2000cm^{-1}$  peak persist at temperatures as high as 300 K, an energy scale much higher than the extrapolated value of the phase transition temperature for this composition  $T_V(\sim 100K)$ , but still lower than the Kondo scale appropriate to the low temperature phase  $T_K \sim 360K$ .

Figure 5.4 shows the similar plots for  $YbIn_{0.5}Ag_{0.5}Cu_4$ . The behavior displayed by the conductivity shows behavior more typical of a heavy fermion system, with moderate temperature dependence and spectral weight which is approximately conserved below 0.5 eV.

Figure 5.5 shows the similar plots for  $YbIn_{0.25}Ag_{0.75}Cu_4$ . The  $2000 \, cm^{-1}$  feature seems to be present even at high temperature, but masked by the free carrier Drude contribution. The temperature dependence of the conductivity features above  $10,000 \, cm^{-1}$  appears to be mainly a redshifting of the  $14000 \, cm^{-1}$  hump as temperature is increased.

Figure 5.6 shows the similar plots for YbAgCu<sub>4</sub>. The moderate temperature dependence of the spectral weight and deep minimum in conductivity around  $100 \, cm^{-1}$  is again typical of heavy fermion systems. The conductivity features around  $10,000 \, cm^{-1}$  have nearly disappeared.

There seems to be a continuous evolution of the  $2000 \, cm^{-1}$  feature, activated by crossing the valence transition at low x, and the more familiar phenomenology found in the low frequency response of the heavy fermi system YbAgCu<sub>4</sub>. We now look at the xdependent systematics at low temperatures.

#### 5.3.2 Low temperature x dependence

Figure 5.7 profiles the x dependence of  $\sigma_1(\omega)$  at low temperatures. The 2,000 cm<sup>-1</sup> peak in YbInCu<sub>4</sub> undergoes a complex shifting behavior as x is increased, blueshifting slightly when x=0.3, then redshifting upon further doping, reaching a minimum peak frequency when



Figure 5.4: Reflectivity and optical conductivity  $\sigma_1(\omega)$  for YbIn<sub>0.5</sub>Ag<sub>0.5</sub>Cu<sub>4</sub>.



Figure 5.5: Reflectivity and optical conductivity  $\sigma_1(\omega)$  for YbIn<sub>0.25</sub>Ag<sub>0.75</sub>Cu<sub>4</sub>.



Figure 5.6: Reflectivity and optical conductivity  $\sigma_1(\omega)$  for YbAgCu<sub>4</sub>.



Figure 5.7: Infrared conductivity  $\sigma_1(\omega)$  versus  $\omega$  at 20 K for the five x values studied. Also shown are the components of a Lorentzian-Drude fit as described in the text. The dashed vertical lines are a guide to the eye and correspond to the center frequencies of the fit components when x=0.

x=0.75, before blueshifting again as x continues to 1. The strength of this feature is also influenced by x in a nontrivial way, discussed further below.

At higher frequency, the large hump feature centered on  $11,000 \, cm^{-1}$  in YbInCu<sub>4</sub> monotonically blueshifts and decreases in overall strength as x is increased. Further, inflection points around  $6000 \, cm^{-1}$  and  $9000 \, cm^{-1}$  redshift slightly upon doping to the x=0.3 and x=0.5systems. These inflection points are not discernable for x=0.75, but reappear at low frequency  $(3000 \, cm^{-1} \text{ and } 5500 \, cm^{-1})$  in the x=1 system.

The x-dependent profiling of the low temperature conductivity is an important part of our experimental results, allowing clear identification of systematic changes of the low temperature electrodynamics as a function of an external control parameter. The discussion begins with identification of systematic trends in the  $2000 \, cm^{-1}$  feature followed by a discussion of interband features in a later section.

### 5.4 The $2000 \, cm^{-1}$ Resonance

The most striking feature of the data presented in the previous section is the feature in the vicinity of  $2000 \, cm^{-1}$ , especially at low doping where a dramatic temperature dependence is displayed below the valence transition. As discussed, the occurrence of the phase transition in YbInCu<sub>4</sub> can be viewed as a sudden and drastic increase in the Kondo temperature as temperature is lowered below 42 K. The sudden appearance of the prominent  $2000 \, cm^{-1}$  feature then invites us to consider this feature as a consequence of Kondo resonance formation. Later sections consider this possibility in the context of the low energy behavior of the periodic Anderson model, introduced previously at the end of Chapter 4. We will use these dispersions in developing a model approach toward exploring the optical conductivity of the PAM.

In this section, we quantify the x dependent trends in Figure 5.7 and draw important



Figure 5.8: (a) The characteristic frequencies,  $\omega_{pk}$  (triangles) and  $\omega_{th}$  (boxes), and (b) the Kondo temperature as a function of x. (c) The spectral weights,  $n(4000 \, cm^{-1})$  (boxes) and  $n(6000 \, cm^{-1})$  (circles) and the results of a combined Drude/Lorentz fitting (triangles) of the low frequency conductivity. (d) The low temperature susceptibility (open circles) and Sommerfeld coefficient (solid circles) as a function of x.  $T_K$  in (b) is related to  $\chi(0)$  in (d). Spectral weights are computed assuming a band mass of  $4m_e$ .

conclusions through the comparison to previously published thermodynamic data. The inferred relationships are then explored below where we consider an interpretation based on the periodic Anderson model.

Figure 5.8a shows the frequency of the  $2000 \, cm^{-1}$  feature versus x as determined in two ways. The black triangles mark the frequency of the peak in  $\sigma_1(\omega)$  (also marked in Figure 5.7). Alternatively, a threshold frequency can be extracted from a fit of the conductivity to a calculation based on the low energy dispersion of the periodic Anderson model (PAM), discussed below in Section 5.5.

In addition to examining the frequency of the peak as a function of x, we can also look at the strength of the  $2000 \, cm^{-1}$  feature. We quantify this characteristic through the spectral weight, defined as the integrated intensity of  $\sigma_1(\omega)$  over a low frequency interval:

$$n(\omega) = \frac{2m}{\pi e^2} \int_{0^+}^{\omega} \sigma_1(\omega') \mathrm{d}\omega'$$
(5.1)

where *m* represents a bare band mass. The lower limit is chosen to be nonzero  $(0^+ = 50 \, cm^{-1})$ in order to exclude from the strength estimate the comparatively minute contribution of the free carrier (Drude) response. The upper limit of integration is chosen to encompass the  $2000 \, cm^{-1}$ peak without including the *x*-dependence of the high frequency interband contributions. Neither integration limit is critical; in fact a lower limit of 0 and upper limits between anywhere between  $3000 \, cm^{-1}$  and  $8000 \, cm^{-1}$  produce similar *x* dependence.  $n(4000 \, cm^{-1})$  and  $n(6000 \, cm^{-1})$  are shown in Figure 5.8c.

As an alternative to this simple integral calculation of the strength, we can fit the complex conductivity ( $\sigma = \sigma_1 + i\sigma_2$ ) with a sum of Lorentzian and Drude response functions(Dressel & Gruner, 2002; Wooten, 1972):

$$\sigma(\omega) = \sum_{j} \frac{\omega_{P,j}^2}{4\pi} \frac{\omega}{i(\omega_j^2 - \omega^2) + \omega\Gamma_j}.$$
(5.2)

The constituents of the fits include: one narrow Drude (D1,  $\Gamma \sim 10 - 40 \, cm^{-1}$ ) contribution to represent the free carrier peak, a wide Drude (D2,  $\Gamma > 800 \, cm^{-1}$ ), and a Lorentz oscillator (L1) in the vicinity of the 2000  $cm^{-1}$  feature which we discuss below relate to the Kondo resonance. There are in addition two Lorentz oscillators (L2 and L3, around 7,300  $cm^{-1}$  and 11,000  $cm^{-1}$ for x=0) to represent the infrared interband conductivity, and two wide Lorentz oscillators at ultraviolet frequencies ( $\omega > 30,000 \, cm^{-1}$ ) representing the conductivity in that range. These fit components are labeled in Figure 5.7a.

Previous work(Tahvildar-Zadeh et al., 1999) has explicitly demonstrated that the calculated lineshape of the optical signature of the Kondo resonance is intrinsically non-Lorentzian, and furthermore demonstrated the viability of fits which combine Drude and Lorentz terms to represent the Kondo resonance. The combination of the contributions D2 and L1 reasonably fit the conductivity in the range of the  $2000 \, cm^{-1}$  peak. The strength from that combination is shown by the triangles in Figure 5.8c. This determination of the strength exhibits an xdependence similar to the simpler integral representations of the strength. This makes one confident that the n versus x dependence shown here is an essential characteristic of the data, and independent of any of the detailed choices we have made in the analysis. n determined by the methods discussed here is presented in Figure 5.8c.

It is interesting to compare the x-dependent trends inferred from previously published thermodynamic measurements with those from our optical data. Figure 5.8b shows the Kondo temperature of low-T phase YbIn<sub>1-x</sub>Ag<sub>x</sub>Cu<sub>4</sub> as deduced by Cornelius *et al*(Cornelius *et al.*, 1997) from fitting the measured magnetic susceptibility to the numerically calculated result of the  $j = \frac{7}{2}$  Coqblin-Schreiffer model(Cornelius *et al.*, 1997; Rajan, 1983). Figure 5.8d shows that the trend in the x dependence of  $\chi(T = 0)^1$  generally agrees with the corresponding trend in the Sommerfeld coefficient  $\gamma$ , implying a Wilson ratio within 10% of the value ( $\mathcal{R} = \frac{8}{7}$ ) expected for a  $j = \frac{7}{2}$  Anderson impurity(Hewson, 1993; Cornelius *et al.*, 1997). Thus the  $T_K$ values inferred from the susceptibility analysis reasonably represent the effective energy scale relevant to the onset of strong-coupling Kondo physics within the low temperature phase.

The complicated x dependence of  $T_K$  is not understood, and may be the result of an interplay of band structure, chemical pressure, screening, disorder, and other many-body effects. While resolving the detailed cause of this complex x dependence presents a subject for future work, out focus here is the relationship between the x dependence of  $T_K$  and that of the optical data; the similar form of the x dependent electrodynamic (Figures 5.8a and 5.8c) and thermodynamic quantities (Figures 5.8b and 5.8d) indicates a common source. We show below

<sup>&</sup>lt;sup>1</sup>In the N-fold degenerate Anderson impurity model, the value of the low temperature susceptibility is related (Hewson, 1993) simply to the Kondo temperature  $T_K$  by  $\chi(0) = (g\mu_B)^2 j(j+1)w_N/3k_B T_K$ , where  $w_N$  is given by Equation 5.18.

that this is rooted in the strongly correlated electron physics of hybridization by constructing a model for the conductivity from the dispersion relations of the PAM.

#### 5.5 PAM Dispersion

We can make progress toward eliciting the relationships suggested in Figures 5.8 by examining an interpretation of the 2000  $cm^{-1}$  feature in the context of the periodic Anderson model (PAM). Complementary to the work of other authors(Tahvildar-Zadeh et al., 1999; Jarrell, 1995; Vidhyadhiraja et al., 2003; Georges et al., 1996; Zlatic & Freericks, 2001; Freericks & Zlatic, 2003a; Freericks & Zlatic, 2003b), which focus the rigorous techniques of many-body theory directly toward the underlying Hamiltonian, we will invoke a simplified approach by analyzing in detail the implications of the effective low energy (near- $E_F$ ) PAM dispersion relations(Edwards, 1988; Hewson, 1993). These dispersion relations ( $\epsilon^+$  and  $\epsilon^-$  in Figure 5.9) present a unifying picture in which to view much of the low energy phenomenology of heavy fermion materials including the mass enhancement, aspects of magnetism, and transport measurements(Millis & Lee, 1987; Cox et al., 1986). In Figure 5.9, the vertical extent of the plot is of order 1 eV and the (singly occupied) f-electron level is below the bottom plot boundary. The light dashed lines indicate the bare (unhybridized) conduction electron dispersion.

In a system with no hybridization, the conduction electrons are the dominant influence on the transport properties such as thermopower and resistivity, while at the same time provide a temperature-independent Pauli-paramagnetic contribution to the magnetic susceptibility. The *f*-electrons, on the other hand, are localized and as a result contribute very little to the transport properties, but play a major role in magnetism, contributing a Curie 1/T term to the susceptibility. Inclusion of the hybridization and on-site Coulomb repulsion terms complicates this independent particle picture considerably and the new eigenstates become nontrivial



Figure 5.9: The PAM dispersion relations, showing the optical transitions. Vertical arrows indicate possible optical transitions. The horizontal dashed lines represent  $E_F$  and  $\tilde{\epsilon_f}$ . The light diagonal line represents the unrenormalized dispersion of the conduction carriers.

admixtures of the states of pure f and conduction electron character.

The PAM quasiparticle dispersion relations provide a venue through which to explore the effects of nonzero hybridization on the phase space of excitations. At energies far from the chemical potential, the upper and lower bands,  $\epsilon^+$  and  $\epsilon^-$ , follow closely the unrenormalized free carrier dispersion. There the main effect of the interaction and hybridization is to provide a channel for relaxation of the conduction states, *i.e.* a broadening of the spectral function along the dispersion curves. At lower energies, these relaxation effects are reduced by the phasespace-constraining presence of a filled Fermi sea, however, renormalization also opens the Fermi surface ( $k_F^{(bare)} \rightarrow k_F$  and the bands flatten) to accommodate the *f*-electron weight projected up to the Fermi level. This reorganization of the bands in the vicinity of the Fermi level is due to many-body interactions, the strength of which is characterized by the parameter  $\tilde{V}$ . The resultant narrow peak in the density of states, called the Kondo, or Abrikosov-Suhl, resonance<sup>2</sup> is central to the understanding of heavy fermion and mixed-valent phenomenology(Degiorgi, 1999; Hewson, 1993; Jarrell, 1995).

From the point of view of optical probes, a key effect of renormalization on the optical response is to create the possibility for vertical transitions from filled states below  $E_F$ , across a *direct* gap, and into unoccupied levels above  $E_F$ , as illustrated by the vertical arrows of Figure 5.9. The threshold for these transitions (short arrow) occurs at a frequency  $\omega = 2\tilde{V}$ , where  $\tilde{V}$  is the hybridization strength renormalized by the on-site *f*-electron repulsion. This energy scales with the Kondo temperature as(Coleman, 1987; Cox, 2003; Millis & Lee, 1987; Millis et al., 1987; Grewe, 1984)

$$\tilde{V} = \sqrt{T_K B} \tag{5.3}$$

where B is a model parameter related to the conduction electron bandwidth. At threshold, the nesting condition for the upper and lower bands is met  $(\nabla_{\mathbf{k}}\epsilon^+ = \nabla_{\mathbf{k}}\epsilon^-)$ , leading to a very high joint density of states for vertical quasiparticle transitions and hence a strong peak in the conductivity.

At frequencies larger than the threshold frequency there are two distinct contributions to the conductivity: one originating from levels inside the unrenormalized Fermi surface ( $k_{<}$ below); the other from the states occupied as a result of renormalization, *i.e.*, outside the unrenormalized Fermi surface ( $k_{>}$  below). An example of two such transitions with the same frequency  $\omega$  are indicated by dashed arrows in Figure 5.9. Transitions involving both of these sets of quasiparticles are important and must be counted independently in the determination of the total optical conductivity, as discussed further below.

<sup>&</sup>lt;sup>2</sup>Strictly speaking, there appears a peak in the DOS in the impurity case. The periodic system differs in that an additional *indirect* gap within this peak is present (Georges et al., 1996).

## 5.6 Infrared Frequency Scales in the Heavy Fermi Response

In addition to the threshold frequency, another, higher frequency scale appears which is relevant to the electrodynamic response. This higher frequency scale corresponds to the vertical transition (long arrow, Figure 5.9) which occurs from states on the Fermi surface (*i.e.* the locus of points which divides the set of occupied and unoccupied  $\mathbf{k}$  states). Vertical transitions involving higher  $\mathbf{k}$  states cannot occur because both initial and final states are unoccupied when  $k > k_F$ , and hence one expects a drop in the conductivity at this frequency. For a linearly dispersing conduction band, direct calculation reveals that the frequency of the last allowed transition is equal to

$$\Omega_{FS} = \frac{\tilde{V}^2 + \tilde{\epsilon_f}^2}{\tilde{\epsilon_f}}.$$
(5.4)

The identification of  $\tilde{\epsilon_f}$  with  $T_K$  (discussed further below), together with Equation 5.3 implies that this scale is of order the conduction electron bandwidth, B. For high energy transitions, band edge final states can be reached and the linear approximation to the conduction band is likely to become poor. Quasiparticle transitions in this frequency range may be influenced by the details of the underlying band structure.

We have already mentioned that there is a finite-frequency onset for vertical transitions in the optical response transition discussed above. This occurs at a low frequency  $\omega = 2\tilde{V}$  with a sharp cusp.

Here we point out that one expects there to be a second, higher energy scale at which there is an abrupt reduction in conductivity. This occurs because as the initial state wavevector crosses the Fermi surface from within, filled initial quasiparticle states are no longer available. Therefore there should be a reduction of the conductivity at a frequency that corresponds to the vertical transition frequency of the Fermi wavevector.

Within the approximation scheme spelled out above, this "last transition" frequency occurs at

$$\omega = \frac{\tilde{V}^2 + \tilde{\epsilon_f}^2}{\tilde{\epsilon_f}} \simeq \frac{\tilde{V}^2}{\tilde{\epsilon_f}} \sim B \tag{5.5}$$

This energy is of order the bandwidth so it is likely that our simplistic, linear-dispersing view of the band structure will break down at such a large frequency. Nevertheless, one expects that there will exist *some* feature representing this quasiparticle depletion effect on the electrodynamics. We will return to this point in subsequent sections.

#### 5.7 Modeling, Kubo-Greenwood Analysis

With these considerations of the phase space for optical transitions in mind, we can proceed with an analysis using the Kubo-Greenwood formula(Dressel & Gruner, 2002):

$$\sigma_1(\omega) = \frac{\pi e^2}{m^2 \omega} \sum_{\ell,\ell'} JDOS_{\ell,\ell'}(\omega) |\mathbf{p}_{\ell,\ell'}|^2$$
(5.6)

where  $|\mathbf{p}_{\ell,\ell'}|$  denotes the dipole matrix element connecting electronic bands  $\ell$  and  $\ell'$ , and  $JDOS_{\ell,\ell'}(\omega)$  is the corresponding joint density of states. Applying this formula to hybridizing quasiparticles (as though they were electrons) allows an exploration of the phenomena of the mid-infrared conductivity in the context of the PAM. In that case, the two relevant bands are  $\epsilon^+$  and  $\epsilon^-$ , which in this model approach leads to:

$$\sigma_{pam}(\omega) = \frac{e^2}{4\pi^2 m^2 \omega} \int_{\Delta \epsilon = \omega} \frac{dS}{|\nabla_{\mathbf{k}}(\epsilon^+ - \epsilon^-)|} |\mathbf{p}_{+,-}|^2$$
(5.7)

where  $|\mathbf{p}_{+,-}|$  is the matrix element for transitions between the two bands under consideration. In the case of a spherical Fermi surface, the integrand is constant and equation (5.7) simplifies to

$$\sigma_{pam}(\omega) = \frac{e^2}{4\pi^2 m^2 \omega} \sum_{k'=k_<,k_>} \frac{4\pi k^2 |\mathbf{p}_{+,-}|^2}{|\partial_k(\epsilon^+ - \epsilon^-)|} \bigg|_{k=k'}$$
(5.8)

It is useful to consider the case of constant optical matrix elements  $|\mathbf{p}_{+,-}|$ , meaning that every filled **k** state transits to the corresponding upper band state with equal probability. One can now obtain a model lineshape from Equation 5.8 using the explicit PAM dispersion relations(Grewe, 1984; Hewson, 1993; Millis & Lee, 1987)

$$\epsilon^{\pm} = \frac{E_F + \tilde{\epsilon_f} + \epsilon_{\mathbf{k}} \pm \sqrt{(E_F + \tilde{\epsilon_f} - \epsilon_{\mathbf{k}})^2 + 4\tilde{V}^2}}{2},\tag{5.9}$$

where  $E_F$  is the Fermi level,  $\tilde{V}$  is the renormalized hybridization strength and  $\tilde{\epsilon_f}$  is the *f*-level position renormalized by on-site *f*-electron repulsion. This latter quantity defines the scale of the low-energy physics and is commonly identified with the impurity Kondo temperature,  $T_K$ (discussed further below).

Putting Equation 5.9 into 5.8, the conductivity takes the form:

$$\sigma_{pam}(\omega) = \frac{2e^2 |\mathbf{p}_{+,-}|^2}{m^2 |\nabla \epsilon_{k_F}|^3 \pi} \frac{(E_F + \tilde{\epsilon_f})^2 + \omega^2 - 4\tilde{V}^2}{\sqrt{\omega^2 - 4\tilde{V}^2}}$$
(5.10)

for  $2\tilde{V} < \omega < \frac{\tilde{V}^2 + \tilde{\epsilon_f}^2}{\tilde{\epsilon_f}}$  and

$$\sigma_{pam}(\omega) = \frac{e^2 |\mathbf{p}_{+,-}|^2}{m^2 |\nabla \epsilon_{k_F}|^3 \pi} \frac{(E_F + \tilde{\epsilon_f} - \sqrt{\omega^2 - 4\tilde{V}^2})^2}{\sqrt{\omega^2 - 4\tilde{V}^2}}$$
(5.11)

for  $\omega > \frac{\tilde{V}^2 + \tilde{\epsilon_f}^2}{\tilde{\epsilon_f}}$ . Figure 5.10a shows this lineshape for two sets of  $\tilde{V}$  and  $\tilde{\epsilon_f}$  values.

The rather idealized lineshape generated by these considerations is extremely sharp and a meaningful comparison with the data requires addressing the effects of relaxation, which were thus far neglected in our treatment. To this end, we convolute this idealized lineshape with a Lorentzian function, keeping the half width  $\Delta$  as an adjustable parameter when performing fits to the measured conductivity. Examples of fits produced using this procedure are shown in Figure 5.10b.



Figure 5.10: (a) The idealized conductivity (Equations 5.10 and 5.11) for  $\tilde{V} = 93 \, meV$  and  $\tilde{\epsilon_f} = 9 \, meV$  (solid) and  $\tilde{V} = 40 \, meV$  and  $\tilde{\epsilon_f} = 2.5 \, meV$  (dashed). Inset contrasts the lineshapes derived with constant matrix elements  $|\mathbf{p}_{+,-}|$  (Equations 5.10 and 5.11), and those with the coherence factors discussed in the text. (b) The same idealized conductivity curves as (a), Lorenztian broadened with widths  $\Delta_0 = 0.16 \, eV$  and  $\Delta_{0.75} = 0.125 \, eV$  for comparison to the measured conductivity of  $\mathrm{YbIn}_{1-x}\mathrm{Ag}_x\mathrm{Cu}_4$  with x=0 and x=0.75, respectively.

The broadening parameter  $\Delta$  addresses the finite width of the spectral function along the dispersion curves of Figure 5.9, and therefore provides a measure of the statistical time over which a typical quasiparticle decays. The numerical values for  $\Delta$  obtained from our fits range from  $0.12 \, eV$  to  $0.17 \, eV$ , with an associated time scale for decay in the range  $\tau = \hbar/\Delta = 5.4 \, ps$ to  $3.8 \, ps$ , respectively. These lifetimes estimates are in good agreement with the quasiparticle lifetime of members of this class of materials (YbAgCu<sub>4</sub>), as measured directly by Demsar *et al* in pump-probe experiments(Demsar et al., 2003) of electron-hole relaxation lifetime. The extraction of this parameter from the conductivity data is a meaningful consistency check on the method developed here.

We now take a moment to consider the possible influence of **k**-dependent matrix elements associated with the composite nature of the hybridized quasiparticles on the electrodynamic response. The hybridizing quasiparticles are composite admixtures of excitations with both f and conduction electron character. The regions of the dispersion which are flatter correspond to quasiparticles with a large amplitude of f admixture whereas regions which follow more closely the bare conduction dispersion are dominated by conduction character. Generally speaking transitions among the bare states are not all equally probable (*i.e.*  $|\mathbf{p}_{cc}| \neq |\mathbf{p}_{cf}| \neq |\mathbf{p}_{ff}|$ ). Thus one expects that the optical transition rate for quasiparticles may exhibit some dependence on **k**, which goes beyond our earlier assumptions.

One can obtain a relatively simple model with **k** dependence by assuming transitions among bare states only occur between conduction electron initial and final states ( $|\mathbf{p}_{cc}| \neq$  $0, |\mathbf{p}_{cf}| = |\mathbf{p}_{ff}| = 0$ ), and using that to calculate transition rates between the hybridized quasiparticle bands. To model the non-constant admixture of states, we use the coherence factors of the resonant level model(Cox et al., 1986; Cox, 2003) (aka Fano-Anderson(Mahan, 1990)),

$$u_{\mathbf{k},\sigma} = \frac{1}{\sqrt{1 + (\frac{\tilde{V}}{\tilde{\epsilon_f} - \epsilon^+})^2}}, \quad v_{\mathbf{k},\sigma} = \frac{1}{\sqrt{1 + (\frac{\tilde{V}}{\tilde{\epsilon_f} - \epsilon^-})^2}}.$$
(5.12)

The approach follows as before however the *JDOS* integral (Eqn. 5.7) picks up a factor  $u_{\mathbf{k},\sigma}^2 v_{\mathbf{k},\sigma}^2 = \tilde{V}^2/\omega^2$  associated with these coherence factors. One thus obtains a model conductivity similar to Equations 5.10 and 5.11, but with  $|\mathbf{p}_{+,-}|^2$  replaced by  $|\mathbf{p}_{cc}|^2 \tilde{V}^2/\omega^2$ . The most significant effect of the inclusion of coherence factors is that the conductivity at high frequency should fall to zero much more quickly than in the constant matrix element case(Cox, 2003). The line shapes with and without coherence factors are contrasted in the inset of Figure 5.10.

This approach may be too nuanced because in a general mixed valent system, bare fto-conduction state transitions can be appreciable, and in fact are expected to be important in YbIn<sub>1-x</sub>Ag<sub>x</sub>Cu<sub>4</sub>. This is because the conduction band states are derived primarily from Cu-In-Ag p and d orbitals(Antonov et al., 2000), whereas the f electrons sit on Yb sites. This physical displacement between the underlying orbital states is manifest in the banded states through nonvanishing dipole transition matrix elements,  $|\mathbf{p}_{fc}|(\text{Cox}, 2003)$ . Thus, in YbIn<sub>1-x</sub>Ag<sub>x</sub>Cu<sub>4</sub>, transitions involving the flatter portions of the quasiparticle dispersion, which are dominated by f-like character, can be expected to provide a considerable contribution to the optical strength, thus we feel that Equations 5.10 and 5.11 are more applicable to YbIn<sub>1-x</sub>Ag<sub>x</sub>Cu<sub>4</sub>.

### **5.8** Discussion, $T_K$ Scaling

We now analyze the x dependent frequency of the  $2000 \, cm^{-1}$  feature (Figure 5.8a), and its relationship to the Kondo temperature  $T_K$  (Figure 5.8b). Figure 5.11 shows  $\omega_{pk}$ , the maximum of the conductivity, and the threshold frequency  $\omega_{th}$ , determined from the fit described above, plotted versus the square root of the Kondo temperature. The complex x


Figure 5.11: Plot of  $\omega_{pk}$  and  $\omega_{th}$  versus  $\sqrt{T_K}$ . The dotted lines represent Eq. (5.3) and the slopes are  $1.6 eV^{\frac{1}{2}}$  and  $1.1 eV^{\frac{1}{2}}$ .

dependence of  $\omega_{th}$  and  $\omega_{pk}$  (Figure 5.8) simplifies considerably when we plot these quantities as a function of  $T_K$  (Figure 5.11). The emergence of a functional relationship between these quantities implies that the frequency of the  $2000 \, cm^{-1}$  peak is controlled by the same physics that underlies the thermodynamic behavior. The square root dependence is evidence that hybridization physics plays a dominant role.

With that in mind, the modeling developed in the previous section can be used to extract an estimate for the band parameter B (Equation 5.3) by associating the threshold frequency,  $\omega_{th}$ , with its PAM value,  $2\tilde{V}$ . The slope of the line through the  $\omega_{th}$  values in Figure 5.11, together with Equation 5.3, directly gives  $B = 0.30 \, eV$ . This value of B reflects the rate at which the frequency increases with  $T_K$ . This can be compared with expectations based on density of states, as well as the rate at which the strength decreases with  $T_K$ , as discussed below.

Within the approach developed in Section 5.7 the relationship between  $T_K$  and the strength of the  $2000 \, cm^{-1}$  feature (n) can be addressed. We can obtain a closed-form result from our model calculation if we set the two sphere areas in (5.8) equal to  $4\pi k_F^2$ . This approximation<sup>3</sup> avoids the effects of bare band structure details while including the influence of the strong cusp at  $2\tilde{V}$ , which originates from the many-body physics of the PAM. Solving for the wavevectors  $k_{>}$  and  $k_{<}$  using the condition  $\epsilon^+ - \epsilon^- = \omega$ , and substituting the result into 5.8, we obtain a model strength:

$$n_{pam} = \frac{2m}{\pi e^2} \int_{2\tilde{V}}^{\Omega_{FS}} \sigma_{pam}(\omega) d\omega$$
(5.13)

$$\simeq \frac{4|\mathbf{p}_{+,-}|^2 k_F}{\pi^2} \ln\left(\frac{V}{\tilde{\epsilon_f}}\right). \tag{5.14}$$

This is essentially the area under the curves of Figure 5.10a. Using Equation 5.3 and introducing

<sup>&</sup>lt;sup>3</sup>In regards to the  $T_K$  dependence, this approximation is equivalent to assuming that  $E_F$  is the largest energy scale in the problem.



Figure 5.12: Scaling relations for the strength of the  $2000 \, cm^{-1}$  feature with  $T_K$ . Dark circles represent  $n(4000 \, cm^{-1})$  and open circles represent  $n(6000 \, cm^{-1})$  (a) shows the result of fitting the measured dependence with Equation 5.15, and (b) shows the same data fit with Equation 5.19.

the parameter c, defined by  $T_K = c \,\tilde{\epsilon_f}$ , we can express  $n_{pam}$  in terms of  $T_K$ :

$$n_{pam} \simeq \frac{4|\mathbf{p}_{+,-}|^2 k_F}{\pi^2} \ln\left(c\sqrt{\frac{B}{T_K}}\right).$$
(5.15)

Figure 5.12a shows a least squares fit of this logarithmic scaling relationship to the data.

The factor c relates the renormalized f level position at low energies and the Kondo temperature,  $T_K$ . The value of c is unambiguous in the Fermi liquid theory of the N(=2j+1)fold degenerate Anderson impurity model where,

$$\tilde{\epsilon_f} = \frac{T_K}{c} = k_B T_L \frac{N^2 \sin(\pi/N) \cos(\pi/N)}{\pi(N-1)}$$
(5.16)

 $and^4$ 

$$T_K = w_N T_L. \tag{5.17}$$

 $w_N$  is the generalized Wilson number (Hewson, 1993) given by

$$w_N = \frac{e^{1+C-\frac{3}{2N}}}{2\pi\Gamma(1+\frac{1}{N})}.$$
(5.18)

For the  $j = \frac{7}{2}$  moment of Yb, N = 8 and  $c \simeq 0.66$ .

Using this value of  $c \simeq 0.66$  and fitting the measured result to Equation 5.14 gives  $B = 0.35 \, eV$  and  $0.45 \, eV$  for  $n(4000 \, cm^{-1})$  and  $n(6000 \, cm^{-1})$  (Eq. 1), respectively. We consider these to be a reasonable agreement given the simplicity of our approach. These values of B, which are determined by the amount that n goes up when  $T_K$  goes down, are similar in size to our previous estimate of the parameter  $B = 0.30 \, eV$  determined from the amount that  $\omega_{th}$ goes down as  $T_K$  goes down. Therefore, in addition to the agreement of experiment and theory regarding the *direction* of the  $T_K$  dependence of n and  $\omega_{th}$ , the *sensitivity* of the dependence of n and  $\omega_{th}$  on  $T_K$  are in reasonable agreement with each other. In addition, the numerical values for B are reasonable bandwidths for the InAgCu d-orbital derived band states(Ibach &

 $<sup>{}^{4}</sup>T_{L}$  here is a common alternative definition of the Kondo temperature (Rajan, 1983; Cornelius et al., 1997) and is related to the Kondo temperature  $T_{K}$  by (Hewson, 1993) 5.17

Luth, 1995) of YbIn<sub>1-x</sub>Ag<sub>x</sub>Cu<sub>4</sub>. Thus we conclude that the observed dependences of both nand  $\omega_{th}$  on  $T_K$  is consistent with the predictions of the periodic Anderson model in magnitude as well as direction.

An alternative strength estimate can be made using the coherence factor model of the conductivity, introduced in detail above. In that case, we replace  $|\mathbf{p}_{+,-}|^2$  by  $|\mathbf{p}_{cc}|^2 \tilde{V}^2 / \omega^2$  in Equation 5.7 and repeat the steps which produced Equation 5.15, giving a theoretical strength

$$n_{pam} = \frac{|\mathbf{p}_{cc}|^2 k_F}{\pi^2} \frac{c^2 B - T_K}{c^2 B + T_K}.$$
(5.19)

Again using c = 0.66, fits to the data would yield *B* estimates 0.17 eV and 0.19 eV, for  $n(4000 cm^{-1})$  and  $n(6000 cm^{-1})$ , respectively. These values are in order-of-magnitude agreement with the band parameter estimates made above. This functional form is fit for comparison to the data in Figure 5.12b. As discussed at the end of section 5.7, the *f*-to-conduction electron transition matrix elements are important for this system and the  $n(T_K)$  given by equation 5.19 is more appropriate for YbIn<sub>1-x</sub>Ag<sub>x</sub>Cu<sub>4</sub>.

#### 5.9 Discussion, High Frequency Interband Transitions

We now consider the x-dependent trends in the high frequency ( $\omega > 6000 \, cm^{-1}$ ) conductivity. We will use the language introduced in Figure 5.7 (Section 5.3.1) associated with Lorentzian fitting of the conductivity data, focussing our attention on the features L2 and L3. In Figures 5.13a and 5.13b we show the center frequency and strength of these high energy excitations as a function of x. This measured x-dependence can inform our understanding of the nature of the underlying states associated with these transitions and the density of states near  $E_F$ .

In a textbook picture of metals and semiconductors, an important effect of doping is



Figure 5.13: (a) The center frequencies of the transitions L2 and L3 from (Figure 5), and (b) the strengths of the corresponding Lorentzian fit components are shown as a function of doping, x. A band-structure picture which we use to interpret the trends in (a) and (b) is shown for (c) YbInCu<sub>4</sub> and (d) YbAgCu<sub>4</sub>. The dashed lines illustrate **k**-conserving transitions which we associate with L1, L2 and L3, respectively. (L1 is the Kondo resonance excitation.)

to add or remove electrons from a set of band states, thereby influencing the position of  $E_F$ . In YbIn<sub>1-x</sub>Ag<sub>x</sub>Cu<sub>4</sub>, increasing x from 0 to 1 corresponds to the net removal of 2 electrons (per formula unit) from the system, hence we expect the Fermi level to move downward in energy as x is increased. In this scenario, optical features involving transitions from filled states just below  $E_F$  tend to weaken and move upward as x is increased and these states are emptied<sup>5</sup>. The dashed arrow of Figure 5.13c illustrates one such transition, which we identify with L3. In this scenario, the width of the feature when x=0 suggests bandwidths of order  $\sim 1 eV$ , and the threshold for these transitions, approximately  $7000 cm^{-1}$  ( $\sim 0.9 eV$ ) when x=0, gives an indication of the overall energy position relative to  $E_F$ . Furthermore, the amount of shift with doping implies that the density of states in the near- $E_F$  region of the band structure is approximately  $2/0.58 eV \sim 3.5 e^- eV^{-1}/f.u$ . Both of these numbers are quite reasonable for conduction bands in rare earth and transition metal systems(Ibach & Luth, 1995).

With this rigid band interpretation as a backdrop describing the salient relationships between L3 and x, the correlated electron effects discussed in previous sections occur in addition. The renormalization discussed there dresses these bare states and the renormalized region of the band structure, including the Kondo resonance, tracks  $E_F$ , which moves downward with increasing x.

We now turn to the systematics of the feature L2. This feature redshifts with x by an amount similar in magnitude to the shift of L3 (Figure 5.13a). However, the narrowness and nearly x-independent strength of L2 does not lend as easily to a simple band interpretation. When considering an identification of the component L2, we point out the significant temperature dependence in the frequency region associated with L2, as shown before in Figures 5.2, 5.3 and 5.6. The temperature dependent interplay of spectral weight contained in the frequency

<sup>&</sup>lt;sup>5</sup>Similarly, optical features involving final states just above  $E_F$  may strengthen as x is increased and new final states become available.

intervals of L1 and L2 naturally lead one to speculate that perhaps the same correlated electron physics controlling L1 may also be relevant to L2. One is thus lead toward the question of whether the presence of the feature L2 represents a further phenomenon associated with hybridization physics.

We noted in Section 4.9 that in addition to the strong peak in the PAM conductivity associated with renormalized band nesting, a second feature could appear at higher frequencies associated with the initial state energy crossing  $E_F$ . In a linearly dispersing band model, this change occurs around the conduction electron bandwidth frequency (Equation 5.4). In a more realistic bandstructure, the filling fraction and band curvature details could influence the frequency and magnitude of this conductivity change. In particular, if the transition final states are band edge states, then significant shifting with doping concentration could result.

With these considerations, it is reasonable to suggest that L2 represents a conductivity feature arising from Fermi surface quasiparticles. The narrowness can then be attributed to the very long lifetime of the initial state (because it occurs on the Fermi surface), and weak xdependence of the strength arises because the energy structures responsible for the associated transitions track the x dependent Fermi level, as opposed to becoming filled or depleted with x. The culmination of the identifications suggested in this section are presented at a light and heavy doping concentration in Figures 5.13c and 5.13d, respectively.

#### 5.10 Discussion, The Phase transition of YbInCu<sub>4</sub>

The physical mechanism of the phase transition in the lightly doped system remains elusive, however, progress has been made in understanding aspects of the phase transition. In previous sections, we have analyzed in detail the low temperature conductivity in terms of PAM renormalizations of few-band models. We now discuss the how this picture identifying optical transitions may be related to the interesting phenomenology displayed by  $YbIn_{1-x}Ag_xCu_4$ including the phase transition at the low x.

The Kondo volume collapse(Allen & Martin, 1982) (KVC) model, which describes the complex interplay of the system volume, hybridization, Kondo temperature, and f level occupation, seems adequate to describe the valence transition in elemental Ce(Allen & Martin, 1982; Haule et al., 2004). This model, however, seems insufficient to quantitatively describe the phase transition in YbInCu<sub>4</sub>, as evidenced mainly by the smallness of the volume change at the transition. Some authors(Sarrao et al., 1998; Cornelius et al., 1997; Figueroa et al., 1998) have argued that a quasigap, or region of low density of states, exists in the bare band structure located just above the Fermi level in YbInCu<sub>4</sub>, and is important to the phase transition. This description is qualitative, but addresses the change in carrier density as well as the changes related to Kondo physics. In this approach, the presence of a quasigap makes the Kondo temperature very sensitive to the placement of the Fermi level and can help induce the phase transition in manner akin to the KVC model, but with the importance placed on the density of states dependence, rather than the volume.

It is of interest to ask what consequences a quasigap scenario could have for the optical data in YbInCu<sub>4</sub>, where the conductivity in the range of  $8000 \, cm^{-1}$  (L2 in the fits) drastically displaces to lower frequency forming the Kondo resonance excitation (L1) discussed above. In the picture outlined in Figure 5.13c, an upward shift in the Fermi level off of the bare band edge and into the quasigap could have drastic consequences for the optical response, possibly forcing the contribution L2 to shift to very high frequency, as the renormalized portion of the upper band is forced across the gap in response to a small shift in  $E_F$ . This possible interpretation of the temperature dependence indicates that further theoretical work directed toward investigating the generic physics of the PAM and the fate of the Kondo scenario in the

context of rapidly varying band structure is needed to understand the complex temperature dependence of YbInCu<sub>4</sub>.

Theoretical work on the Falicov-Kimball model(Zlatic & Freericks, 2001; Freericks & Zlatic, 2003a; Freericks & Zlatic, 2003b) attempts make a quantitative connection to the experiment using a particular many-body model which features a first-order phase transition. Aspects of this modeling seem promising, in particular the prediction of substantial temperature dependence of the high frequency optical conductivity, however this model does not yet explicitly include the effects of hybridization. It is possible that a minimal model that describes the first order phase transition and also includes the Kondo physics may require and extension of the periodic Anderson model to include Falicov-Kimball-type interaction.

Our results show that  $T_K$  scaling is present in the low temperature finite-frequency dynamics of YbIn<sub>1-x</sub>Ag<sub>x</sub>Cu<sub>4</sub> and can be addressed in the context of local-moment models. Furthermore, our data provide numerical estimates of key parameters necessary for the construction of a minimal theoretical model of the valence transition as well as pointing out salient features of the underlying bandstructure. Further work may be directed toward greater understanding of this low-T scaling as well as unexplained temperature-dependence of lightly doped YbIn<sub>1-x</sub>Ag<sub>x</sub>Cu<sub>4</sub>.

# Chapter 6

# Modeling Optical Phonon Response

#### 6.1 Motivation and Modeling Ansatz

This chapter focuses on how the charged ion cores of a solid contribute to the optical response. We develop a method used to calculate the spectrum of excitations of these ionic motions relevant to optical probes. Because of their large mass, the time scale of ionic motion tends to be very long compared to that of electrons, corresponding to frequencies typically less than 1000  $cm^{-1}$ . The very large masses of the ions also have a hindering effect on the total integrated optical response when compared to their electronic counterparts, thereby reducing the integrated response as well.

In the next section we wish to find the normal modes of a set of coupled oscillators. The motivation here is to introduce notation relevant to section 6.3, where we calculate the dynamical conductivity of one unit cell of a crystal subject to periodic boundary conditions,



Figure 6.1: An optical phonon oscillation at finite wavevector.

given that the positions, ionicities, masses, and spring constants of the atoms in the cell are provided. Such an exercise is of interest because a solution of the equations of motion of this system will capture the long-wavelength dynamics of a infinite lattice of unit cells.

Figure 6.1 illustrates a snapshot of a lattice vibration corresponding to an optical phonon living at a finite wavevector, about  $\frac{1}{4}$  of the way out to the Brillouin zone edge,  $k = \pi/a$ . Infrared wavelengths, which are of interest here, correspond to wavevectors which are much closer to the zone center (typically 0.00001 of the way to the zone edge). For these modes, the internal oscillations of each cell will be very nearly in phase with its neighbors, and the bonds connecting (say) cell i - 1 to cell i will be stressed in almost exactly the same manner as the corresponding bonds connecting cell i to cell i + 1. This observation allows us to identify the dynamical properties of a single unit cell, subjected to periodic boundary conditions, with those of the full lattice at long wavelengths. Using the results of this chapter, combined with our optical experiments in the next chapter, will allow us to infer basic things about the lattice vibrations of the negative thermal expansion compound  $\text{ZrW}_2\text{O}_8$ .

## 6.2 Derivation of the Normal Modes

The equations of motion of the N charges in the unit cell can be written

$$\left(\widetilde{\mathbf{m}}\frac{d^2}{dt^2} + \widetilde{\mathbf{b}}\frac{d}{dt} + \widetilde{\kappa}\right)\overrightarrow{\mathbf{r}} = 0$$
(6.1)

$$(-\omega^2 \widetilde{\mathbf{m}} - \imath \omega \widetilde{\mathbf{b}} + \widetilde{\kappa}) \overrightarrow{\mathbf{r}} = 0$$
(6.2)

where  $\vec{\mathbf{r}}$  is a 3*N*-dimensional vector specifying the displacements from equilibrium,  $\tilde{\mathbf{m}}$  is the mass matrix,  $\tilde{\mathbf{b}}$  is a damping matrix and  $\tilde{\kappa}$  is the stiffness matrix which determines the coupling of the charges to each other through effective spring-type force laws.

In order to find the normal modes of the system, we wish to find a Hermitian matrix whose eigenvalues determine the oscillation frequencies. This can be done by noting that  $\tilde{\mathbf{m}}$  is diagonal and so  $\tilde{\mathbf{m}}^{-\frac{1}{2}}$  is well defined. Multiplying on the left by  $\tilde{\mathbf{m}}^{-\frac{1}{2}}$ ,

$$\left(-\omega^{2}\widetilde{\mathbf{m}}^{\frac{1}{2}} - \imath\omega\widetilde{\mathbf{m}}^{-\frac{1}{2}}\widetilde{\mathbf{b}} + \widetilde{\mathbf{m}}^{-\frac{1}{2}}\widetilde{\kappa}\right)\overrightarrow{\mathbf{r}} = 0$$

$$(6.3)$$

Noting that  $\widetilde{\mathbf{m}}^{\frac{1}{2}}\widetilde{\mathbf{m}}^{-\frac{1}{2}} = \widetilde{\mathbf{m}}^{-\frac{1}{2}}\widetilde{\mathbf{m}}^{\frac{1}{2}} = 1$ ,

$$(-\omega^2 - \imath\omega\widetilde{\mathbf{m}}^{-\frac{1}{2}}\widetilde{\mathbf{b}}\widetilde{\mathbf{m}}^{-\frac{1}{2}} + \widetilde{\mathbf{m}}^{-\frac{1}{2}}\widetilde{\kappa}\widetilde{\mathbf{m}}^{-\frac{1}{2}})\widetilde{\mathbf{m}}^{\frac{1}{2}}\overrightarrow{\mathbf{r}} = 0$$
(6.4)

or more compactly,

$$\widetilde{\mathbf{A}} \, \overrightarrow{\mathbf{u}} = \mathbf{0}. \tag{6.5}$$

Here,  $\widetilde{\mathbf{A}}$  is the (Hermitian) matrix in parenthesis of Eq. (6.4) and  $\overrightarrow{\mathbf{u}} = \widetilde{\mathbf{m}}^{\frac{1}{2}} \overrightarrow{\mathbf{r}}$ . This rescaling of the coordinates allows us to diagonalize the real symmetric (i.e. Hermitian) matrix  $\widetilde{\mathbf{A}}$ , which can be done to a basis of real orthonormal eigenvectors. Each term in  $\widetilde{\mathbf{A}}$  deserves special attention. The first term is constant. The second term is diagonal, but in general non-constant. We invoke a greatly simplifying assumption that  $\widetilde{\mathbf{m}}^{-\frac{1}{2}}\widetilde{\mathbf{b}}\widetilde{\mathbf{m}}^{-\frac{1}{2}} = \Gamma$ . This assumption is common and states that all ions in the unit cell feel the same viscous damping force. The

last term is a numerical matrix, defined as  $\widetilde{\Omega} = \widetilde{\mathbf{m}}^{-\frac{1}{2}} \widetilde{\kappa} \widetilde{\mathbf{m}}^{-\frac{1}{2}}$ , and depends only on the known masses and spring constants and so can be diagonalized on a computer.

This is a useful thing to do since the matrix  $\widetilde{\mathbf{U}}$  that diagonalizes  $\widetilde{\Omega}$ , allowing a full solution of the equations of motion.

$$\widetilde{\Lambda} = \widetilde{\mathbf{U}}^{-1} \widetilde{\Omega} \widetilde{\mathbf{U}} \tag{6.6}$$

also diagonalizes  $\widetilde{\mathbf{A}}$ .

.

$$\widetilde{\Lambda}' = \widetilde{\mathbf{U}}^{-1} \widetilde{\mathbf{A}} \widetilde{\mathbf{U}} = \widetilde{\mathbf{U}}^{-1} (-\omega^2 + \imath \omega \Gamma + \widetilde{\Omega}) \widetilde{\mathbf{U}}$$
(6.7)

$$= -\omega^2 + \imath \omega \Gamma + \widetilde{\mathbf{U}}^{-1} \widetilde{\Omega} \widetilde{\mathbf{U}}$$
(6.8)

$$= -\omega^2 + \imath \omega \Gamma + \widetilde{\Lambda} \tag{6.9}$$

# 6.3 Derivation of Optical Response

In this section we wish to relate the normal modes found above to the optical response functions<sup>1</sup>. In the presence of an externally applied field  $\vec{\mathbf{E}}$ , the equations (6.1) and (6.2) generalize to

$$\left(\widetilde{\mathbf{m}}\frac{d^2}{dt^2} + \widetilde{\mathbf{b}}\frac{d}{dt} + \widetilde{\kappa}\right)\overrightarrow{\mathbf{r}} = \widetilde{\mathbf{Z}}e\overrightarrow{\mathbf{E}}(t)$$
(6.10)

$$(-\omega^2 \widetilde{\mathbf{m}} - \imath \omega \widetilde{\mathbf{b}} \frac{d}{dt} + \widetilde{\kappa}) \overrightarrow{\mathbf{r}} = \widetilde{\mathbf{Z}} e \overrightarrow{\mathbf{E}}(\omega).$$
(6.11)

Here, the diagonal matrix  $\widetilde{\mathbf{Z}}$  contains the effective ionicities for each charge in the unit cell and e is the proton charge (e > 0).

As before, we multiply both sides on the left by  $\widetilde{\mathbf{m}}^{-\frac{1}{2}}$ ,

$$(-\omega^2 - \imath\omega\widetilde{\mathbf{m}}^{-\frac{1}{2}}\widetilde{\mathbf{b}}\widetilde{\mathbf{m}}^{-\frac{1}{2}} + \widetilde{\mathbf{m}}^{-\frac{1}{2}}\widetilde{\kappa}\widetilde{\mathbf{m}}^{-\frac{1}{2}})\widetilde{\mathbf{m}}^{-\frac{1}{2}}\overrightarrow{\mathbf{r}} = \widetilde{\mathbf{m}}^{-\frac{1}{2}}\widetilde{\mathbf{Z}}e\overrightarrow{\mathbf{E}}$$
(6.12)

 $<sup>^{1}</sup>$ The author would like to gratefully acknowledge valuable discussions with Onuttom Narayan(Narayan, 2003) and Frank Bridges(Bridges, 2003) in arriving at this derivation.

$$\widetilde{\mathbf{A}}\widetilde{\mathbf{m}}^{-\frac{1}{2}}\overrightarrow{\mathbf{r}} = \widetilde{\mathbf{m}}^{-\frac{1}{2}}\widetilde{\mathbf{Z}}e\overrightarrow{\mathbf{E}}.$$
(6.13)

The matrix  $\widetilde{\mathbf{A}}$  can be inverted, and we can solve for  $\overrightarrow{\mathbf{r}}$ :

$$\vec{\mathbf{r}} = \tilde{\mathbf{m}}^{-\frac{1}{2}} \tilde{\mathbf{A}}^{-1} \tilde{\mathbf{m}}^{-\frac{1}{2}} \tilde{\mathbf{Z}} e \vec{\mathbf{E}}.$$
(6.14)

We can use this result to find the electric dipole moment in terms of the electric field via

$$\overrightarrow{\mathbf{p}} = \widetilde{\mathbf{Z}}e\,\overrightarrow{\mathbf{r}} \tag{6.15}$$

giving

$$\overrightarrow{\mathbf{p}} = \widetilde{\mathbf{Z}} e \widetilde{\mathbf{m}}^{-\frac{1}{2}} \widetilde{\mathbf{A}}^{-1} \widetilde{\mathbf{m}}^{-\frac{1}{2}} \widetilde{\mathbf{Z}} e \overrightarrow{\mathbf{E}}.$$
(6.16)

Comparing this equation with the definition of the polarizability tensor

$$\overrightarrow{\mathbf{p}} = \widetilde{\alpha} \, \overrightarrow{\mathbf{E}}, \tag{6.17}$$

we can make the identification

$$\widetilde{\alpha} = \widetilde{\mathbf{Z}} e \widetilde{\mathbf{m}}^{-\frac{1}{2}} \widetilde{\mathbf{A}}^{-1} \widetilde{\mathbf{m}}^{-\frac{1}{2}} \widetilde{\mathbf{Z}} e.$$
(6.18)

In terms of the eigendata, the inverse of  $\widetilde{\mathbf{A}}$  is

$$\widetilde{\mathbf{A}}^{-1} = \widetilde{\mathbf{U}}\widetilde{\Lambda'}^{-1}\widetilde{\mathbf{U}}^{-1} \tag{6.19}$$

giving for  $\widetilde{\alpha}$ 

$$\widetilde{\alpha} = \widetilde{\mathbf{Z}} e \widetilde{\mathbf{m}}^{-\frac{1}{2}} \widetilde{\mathbf{U}} \widetilde{\Lambda'}^{-1} \widetilde{\mathbf{U}}^{-1} \widetilde{\mathbf{m}}^{-\frac{1}{2}} \widetilde{\mathbf{Z}} e.$$
(6.20)

The columns of  $\widetilde{\mathbf{U}}^{-1}$  in this expression are made of the eigenvectors of  $\widetilde{\Omega}$  and the total, frequency-dependent dipole depends on contributions from all of the normal modes. In order to express (6.20) as a sum of contributions of each of these normal modes, we write the above matrix equation as sums over indices, invoking the Einstein summation convention:

$$\alpha_{\mu\varphi} = e^2 \widetilde{Z}_{\mu\nu} \widetilde{m}_{\nu\xi}^{-\frac{1}{2}} \widetilde{U}_{\xi\rho} \widetilde{\Lambda'}_{\rho\tau}^{-1} \widetilde{U}_{\tau\sigma}^{-1} \widetilde{m}_{\sigma\theta}^{-\frac{1}{2}} \widetilde{Z}_{\theta\varphi}.$$
(6.21)

We now introduce the matrices  $\widetilde{\mathbf{a}}$  and  $\widetilde{\mathbf{b}}$ 

$$\alpha_{\mu\varphi} = e^2 \underbrace{\widetilde{Z}_{\mu\nu} \widetilde{m}_{\nu\xi}^{-\frac{1}{2}} \widetilde{U}_{\xi\rho}}_{\tilde{\mathbf{a}}} \widetilde{\Lambda'}_{\rho\tau}^{-1} \underbrace{\widetilde{U}_{\tau\sigma}^{-1} \widetilde{m}_{\sigma\theta}^{-\frac{1}{2}} \widetilde{Z}_{\theta\varphi}}_{\tilde{\mathbf{b}}} = e^2 a_{\mu\rho} \widetilde{\Lambda'}_{\rho\tau}^{-1} b_{\tau\varphi}.$$
(6.22)

Since  $\tilde{\Lambda'}_{\rho\tau}^{-1}$  is diagonal, we can write the last expression as

$$\alpha_{\mu\varphi} = e^2 a_{\mu\rho} \widetilde{\Lambda'}_{\rho}^{-1} b_{\rho\varphi}.$$
(6.23)

Then a contribution of mode j is the jth term when this sum is written out. Using the general expressions relating the optical response functions,

$$\chi_e(\omega) = N\alpha(\omega) \tag{6.24}$$

$$\epsilon = 1 + 4\pi\chi_e(\omega) \tag{6.25}$$

$$\epsilon = 1 + \frac{4\pi i \sigma(\omega)}{\omega} \tag{6.26}$$

$$\sigma(\omega) = i\omega\chi_e(\omega) \tag{6.27}$$

one can generate the response functions of the model system. One finds in particular that the absorptive conductivity tensor is

$$\sigma_{1\mu\varphi}(\omega) = Re[iN\omega\alpha_{\mu\varphi}(\omega)] = Ne^2 a_{\mu\rho} \frac{\Gamma\omega^2}{(\widetilde{\Lambda}_{\rho} - \omega^2)^2 + \Gamma^2\omega^2} b_{\rho\varphi}.$$
(6.28)

# 6.4 The *f*-Sum Rule for Phonons

We now discuss the implications of the theory developed in the previous sections to the integrated conductivity, the spectral weight. Integrating Equation (6.28) over frequency(Wooten, 1972),

$$\int_0^\infty \sigma_{1\mu\varphi}(\omega)d\omega = Ne^2 a_{\mu\rho}b_{\rho\varphi} \int_0^\infty \frac{\Gamma\omega^2 d\omega}{(\omega_\rho^2 - \omega^2)^2 + \Gamma^2 \omega^2}$$
(6.29)

where  $\omega_{\rho} = +\sqrt{\Lambda_{\rho}}$  denotes the eigenfrequency of the  $\rho$ th normal mode. In the limit of small damping, the denominator can be factored and the major contributions to the integral are from  $\omega \simeq \omega_{\rho}$ ,

$$\int_0^\infty \sigma_{1\mu\varphi}(\omega)d\omega = Ne^2 a_{\mu\rho}b_{\rho\varphi}\Gamma \int_0^\infty \frac{\omega^2 d\omega}{(\omega_\rho^2 - \omega^2)(\omega_\rho^2 + \omega^2) + \Gamma^2 \omega^2}$$
(6.30)

$$= \frac{Ne^2 a_{\mu\rho} b_{\rho\varphi} \Gamma \omega_{\rho}^2}{4\omega_{\rho}^2} \int_0^\infty \frac{\omega^2 d\omega}{(\omega_{\rho}^2 - \omega^2)(\omega_{\rho}^2 + \omega^2) + \Gamma^2 \omega^2}$$
(6.31)

$$= \frac{Ne^2 a_{\mu\rho} b_{\rho\varphi} \Gamma}{4} \frac{2}{\Gamma} \arctan\left(2\frac{\omega - \omega_{\rho}}{\Gamma}\right)\Big|_{0}^{\infty}$$
(6.32)

$$= \frac{\pi}{2} N e^2 a_{\mu\rho} b_{\rho\varphi}. \tag{6.33}$$

If we further sum over all contributions to the conductivity from each of the normal modes (complete the sum over  $\rho$ ), we get

$$\int_0^\infty \sigma_{1\mu\varphi}(\omega)d\omega = \frac{\pi}{2}Ne^2 a_{\mu\rho}b_{\rho\varphi}$$
(6.34)

$$= \frac{\pi}{2} N e^2 \widetilde{Z}_{\mu\nu} \widetilde{m}_{\nu\xi}^{-\frac{1}{2}} \widetilde{U}_{\xi\rho} \widetilde{U}_{\rho\sigma}^{-1} \widetilde{m}_{\sigma\theta}^{-\frac{1}{2}} \widetilde{Z}_{\theta\varphi}$$
(6.35)

$$= \frac{\pi}{2} N e^2 \widetilde{Z}_{\mu\sigma} \widetilde{m}_{\sigma\theta}^{-1} \widetilde{Z}_{\theta\varphi}$$
(6.36)

$$= \frac{\pi}{2} N e^2 \mathbf{Z} \mathbf{m}^{-1} \mathbf{Z}$$
(6.37)

Taking the trace of the integrated conductivity tensor then concludes the derivation of the f-sum rule for phonons:

$$\int_{0}^{\infty} \sigma_{1\mu\mu}(\omega) d\omega = \frac{\pi}{2} N e^{2} \operatorname{tr}(\mathbf{Zm}^{-1}\mathbf{Z})$$
(6.38)

$$= \frac{\pi}{2} N e^2 \sum_{\text{atoms } i} \frac{Z_i^2}{m_i}$$
(6.39)

This is a remarkable result: the diagonal integrated conductivity is *completely independent* of the coupling between the atoms. Equation (6.38) is a specific realization of a general result(Mahan, 1990) for the integrated conductivity which says that *all* charge degrees of freedom must be included in the sum. In principle these would include the electronic excitations which, because of their small masses, give a large contribution to the integrated spectral weight. In a band insulator, where the onset for electronic motion occurs at a high energy scale relative to that associated with ionic motion, partitioning of the integral is common practice, provided the electron-phonon coupling is small enough. We will use this result in a following section to constrain the effective ionicities of the ions in the negative thermal expansion system  $ZrW_2O_8$ .

#### 6.5 Positional Uncertainties

This section presents a slight digression from the optical properties of a lattice system and shows how to obtain the quantum mechanical uncertainty in position of an atom in the lattice from the eigenvectors and eigenvalues. This may be of use for making a connection between the modeling, the optical data, and the results of other experiments such as X-ray diffraction data.

Once the dynamical matrix has been diagonalized, and the motions of the ions are decoupled, one can quantize the system by writing the classical Hamiltonian for the system<sup>2</sup>:

$$\mathcal{H} = \frac{p_i^2}{2m_i} + \frac{1}{2} x_i \mathcal{M}_{ij} x_j \tag{6.40}$$

then decoupling the degrees of freedom through the formalism discussed above,

$$\mathcal{H} = \frac{1}{2}\dot{v}_i^2 + \frac{1}{2}\omega_i^2 v_i^2 \tag{6.41}$$

$$\rightarrow \quad \frac{1}{2}V_i^2 + \frac{1}{2}\omega_i^2 v_i^2 \tag{6.42}$$

 $<sup>^{2}</sup>$ The author would like to gratefully acknowledge Trieu Mai<br/>(Mai, 2004) who began this calculation in his derivation of the pair distribution function for this problem.

where V denotes the momentum operator conjugate to v. Here

$$\mathbf{v} = \mathbf{U}^{-1}\mathbf{m}^{-\frac{1}{2}}\mathbf{r} \tag{6.43}$$

$$\mathbf{V} = \mathbf{U}^{-1}\mathbf{m}^{-\frac{1}{2}}\mathbf{p} \tag{6.44}$$

The observable  $v_i$  corresponds physically to the amplitude of vibration of the system of the normal mode i.

This Hamiltonian is the familiar harmonic oscillator Hamiltonian, with the well known quantization rules arising from Dirac's raising and lowering operator formalism:

$$v_i = \sqrt{\frac{\hbar}{2\omega_i}} (a_i + a_i^{\dagger}) \tag{6.45}$$

$$V_i = -i\sqrt{\frac{\hbar\omega_i}{2}}(a_i - a_i^{\dagger}) \tag{6.46}$$

$$a_i | n_1 n_2 \cdots n_i \cdots n_{3N} \rangle = \sqrt{n_i} | n_1 n_2 \cdots n_i - 1 \cdots n_{3N} \rangle$$

$$(6.47)$$

$$a_i^{\dagger}|n_1n_2\cdots n_i\cdots n_{3N}\rangle = \sqrt{n_i+1}|n_1n_2\cdots n_i+1\cdots n_{3N}\rangle$$
(6.48)

$$\mathcal{H}|n_1\cdots n_{3N}\rangle = \sum_i (n_i + \frac{1}{2})\hbar\omega_i |n_1\cdots n_{3N}\rangle.$$
(6.49)

We now want the positional uncertainty of a single atom in the lattice. This involves inverting the unitary diagonalizing transformation and writing the single atom coordinate in terms of sums over normal mode coordinates.

The coordinate for the ith Cartesian component is

$$r_i = U_{ij} m_j^{-\frac{1}{2}} v_j$$
 (6.50)

$$= U_{ij}\sqrt{\frac{\hbar}{2m_j\omega_j}(a_j + a_j^{\dagger})}$$
(6.51)

We wish to find the "quantum ellipsoids"<sup>3</sup> of the ionic positions. These are the surfaces of equal probability for finding each if the ions about their equilibrium positions. To lowest order, these will be ellipsoids which are directed in a manner determined by the local ionic environment.

<sup>&</sup>lt;sup>3</sup>This term arises from thermal ellipsoids.

To illustrate the complexity involved in this calculation, consider a particle whose xyplanar motion is stiffly constrained about the point (x, y) = (0, 0) but is given a softer harmonic restoring force in the z direction. The region of space with highest probability of finding the particle takes the form of a long, narrow ellipsoid oriented parallel to the z axis. The radius of the ellipsoid would be  $\sqrt{\langle x^2 \rangle + \langle y^2 \rangle}$ , which is small, and the length would be  $\sqrt{\langle z^2 \rangle}$ , which is big.

If the coordinate system were not so cleverly chosen, one can see that finding the dimensions of this ellipsoid would present some trouble. If the easy axis of motion were instead chosen to be along the  $\langle 111 \rangle$  direction, and we simply calculated  $\langle x^2 \rangle$ ,  $\langle y^2 \rangle$ ,  $\langle z^2 \rangle$  and naively following the identification protocol which so successfully worked before, one (wrongly) deduces that the locus of high probability points is in the shape of a sphere.

The problem at hand is then to find the isoprobabilistic locus of points for a system of arbitrary complexity. We will do this by calculating the expectation value of the matrix

$$\langle R_{\mu\nu} \rangle = \langle r_{\mu}r_{\nu} \rangle \tag{6.52}$$

within the eigenstates of the Hamiltonian. Here  $\mu$  and  $\nu$  refer to different Cartesian components of the same ion. When this matrix is diagonalized, the eigenvectors point along the principle axes of the ellipsoid, and the eigenvalues give the uncertainties values along each of these axes.

For general ionic coordinate components,

$$r_{\mu}r_{\nu} = U_{\mu j}\sqrt{\frac{\hbar}{2m_{j}\omega_{j}}}U_{\nu k}\sqrt{\frac{\hbar}{2m_{k}\omega_{k}}}(a_{j}+a_{j}^{\dagger})(a_{k}+a_{k}^{\dagger})$$
(6.53)

$$= \frac{\hbar}{2} U_{\mu j} U_{\nu k} \frac{1}{\sqrt{m_j m_k \omega_j \omega_k}} (a_j + a_j^{\dagger}) (a_k + a_k^{\dagger})$$
(6.54)

and so we will be interested in matrix elements of the form

$$\langle n_1 \cdots n_{3N} | (a_i + a_i^{\dagger}) (a_j + a_j^{\dagger}) | n_1 \cdots n_{3N} \rangle.$$
 (6.55)

These will be nonvanishing only if there are the same number of creation and annihilation operators for every state. We are left then with only

$$\langle n_1 \cdots n_{3N} | (a_i a_j + a_i a_j^{\dagger} + a_i^{\dagger} a_j + a_j^{\dagger} a_j^{\dagger}) | n_1 \cdots n_{3N} \rangle = \langle n_1 \cdots n_{3N} | (a_i a_j^{\dagger} + a_i^{\dagger} a_j) | n_1 \cdots n_{3N} \rangle$$

At this point we restrict attention to zero temperature. This implies the system is in its ground state and that the matrix elements are simply

$$\langle 0_1 \cdots 0_{3N} | a_i a_j^{\dagger} | 0_1 \cdots 0_{3N} \rangle = \delta_{ij}$$
(6.56)

and the coordinate product expectation value is

$$\langle r_{\mu}r_{\nu}\rangle = \frac{\hbar}{2}U_{\mu j}U_{\nu k}\frac{1}{\sqrt{m_{j}m_{k}\omega_{j}\omega_{k}}}\delta_{jk}$$
(6.57)

$$= \frac{\hbar}{2} U_{\mu k} U_{\nu k} \frac{1}{m_k \omega_k} \tag{6.58}$$

$$= \frac{\hbar}{2} U_{\mu k} U_{k\nu}^{-1} \frac{1}{m_k \omega_k}$$
(6.59)

$$= \frac{\hbar}{2} U_{\mu k} \frac{1}{m_k \omega_k} U_{k\nu}^{-1}$$
(6.60)

$$= \frac{\hbar}{2} (\widetilde{\mathbf{U}}\widetilde{\mathbf{m}}^{-1}\widetilde{\boldsymbol{\Lambda}}^{-\frac{1}{2}}\widetilde{\mathbf{U}}^{-1})_{\mu\nu}.$$
(6.61)

To find the uncertainty ellipsoid of atom i, we then just find the  $3 \times 3$  matrix corresponding to the three components of  $\vec{\mathbf{r}}_i$  and diagonalize it to produce the principle axes and associated uncertainty widths.

# 6.6 Numerical Solution of the Dynamical Matrix

The use of the speed and power of present computing technology can provide access to numerical solutions of models of high complexity. This section outlines the numerical solution of a classical mass-and-spring model of the negative thermal expansion system  $ZrW_2O_8$ . The calculation finds the dynamical conductivity for comparison with experiment. The optical phonon modes are determined for  $\mathbf{k} = 0$  by considering a unit cell (44 atoms =132 total degrees of freedom) subject to periodic spatial boundary conditions as described in the beginning of this chapter. The unit cell is set up using the positions of the seven distinct ions Zr, W1, W2, O1, O2, O3, and O4 given by Auray, Quarton, and LeBlanc(Auray et al., 1995). The 12 equipoint transformations (rotations plus translations) of the  $P2_13$  space group are then applied to these seven ions in order to generate more ionic positions of the lattice. These positions are translated back appropriately in the event that they lie outside the primary unit cell. This procedure generates all 44 of the atomic coordinates in one unit cell ZrW<sub>2</sub>O<sub>8</sub>, which consist of 4 Zr, 4 W1, 4 W2, 4 O1, 4 O2, 8 O3, and 8 O4 atoms.

The program then determines the equations of motion by calculating the potential energy of the unit cell with 27 different spring constants linking nearest neighbors with compressive springs ( $\alpha$ -type springs) which contribute a potential energy term of the form

$$V_{comp} = \frac{1}{2} k_{ij} (\delta \vec{\mathbf{r}_i} - \delta \vec{\mathbf{r}_j})^2$$
(6.62)

or by angle-fixing springs ( $\beta$ -type), which contribute

$$V_{bend} = \frac{1}{2} b_{ij} \Delta \theta_{ij}^2 = \frac{1}{2} b_{ij} \arcsin\left(\frac{\delta \vec{\mathbf{r}}_i \times \delta \vec{\mathbf{r}}_j}{|\delta \vec{\mathbf{r}}_i| |\delta \vec{\mathbf{r}}_j|}\right)^2 \tag{6.63}$$

to the potential energy. Each bond type must be included by hand, so a searching procedure was used to speed up this process. For example, if we wish to include an  $\alpha$  bond between neighboring Zr and O atoms, we could set up the program to index a particular Zr ion and search through the list of O3 and O4 ions and ask if each of these is inside a thin spherical shell with radius equal to the nearest neighbor Zr-O distance (Zr-O3; 2.092 Å, Zr-O4; 2.051 Å). If this condition is true, a term of type 6.62 is added to the potential energy.

The potential energy function generated is a complicated function of over 200 terms with the spring constants and displacement coordinates (132 in all) kept variable. The equations of motion are then derived from the potential energy through Lagrange's equations of motion(Marion & Thornton, 1980),

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_j} = \frac{\partial L}{\partial q_j}.$$
(6.64)

These equations are then Taylor expanded about their equilibrium positions, retaining terms linear in the displacements, and the stiffness matrix  $\tilde{\kappa}$  is generated. This symbolic calculation is computationally intensive and can take up to 6 hours<sup>4</sup>. The matrix is then saved as a text file which can later be read back into *Mathematica*.

With this matrix and the mass information known, one can easily generate the normal mode eigenvectors and frequencies and a number of calculations could be done from this information. To compare the results to our data, we determine the dynamical conductivity from the eigendata in the manner described in sections 6.2 and 6.3. Figure xx shows a comparison of the calculated optical conductivity to the measured data for the parameter set listed in the caption. Also shown is an estimate of the density of states told by the

 $<sup>^4\</sup>mathrm{On}$  a Powerbook G4 laptop computer, with a 1GHz processor.

# Chapter 7

# $\mathbf{ZrW}_2\mathbf{O}_8$

This chapter presents the current results of our optical study of the negative thermal expansion (NTE) compound  $ZrW_2O_8$ . This compound is most unusual among materials in that the NTE effect is large, isotropic, and extremely robust: the thermal expansion coefficient  $\alpha < 0$  over a very large temperature range, and even survives the structural phase transition at T = 440 K. These characteristics enhance our interest in both the fundamental physics of  $ZrW_2O_8$ , and the potential applications of such a substantial NTE effect, which are widespread(Sleight, 1998). A defining feature of  $ZrW_2O_8$  is the existence of a 1-fold coordinated oxygen site for each WO<sub>4</sub> tetrahedron. This terminal, or unconstrained(Ernst et al., 1998), oxygen creates a structural openness along the high-symmetry  $\langle 111 \rangle$  axes and is thought to be influential in the low-energy dynamics and crucial to the phenomenon of NTE in  $ZrW_2O_8$ , point out the strange low frequency behavior, explore the implications of the energy spectrum as told by the peaks in the optical conductivity, and use modeling in order to understand as fully as possible the nature of the phonons in  $ZrW_2O_8$ . Appendix B presents a rather speculative, alternative viewpoint

on the nature of the lowest frequency peaks in  $ZrW_2O_8$  in terms of rotational tunneling.

#### 7.1 Background, Motivation, and Outlook

Thermal expansion phenomena generally come from anharmonic phonon dynamics (Ashcroft & Mermin, 1976). For ZrW<sub>2</sub>O<sub>8</sub>, analysis of temperature dependence(Ramirez & Kowach, 1998; Ernst et al., 1998; David et al., 1999; Mittal & Chaplot, 1999) indicates that the low energy region should be of primary importance. For example, in the Grüneisen approach to thermal expansion(Ashcroft & Mermin, 1976), a constant  $\alpha(T)$  is possible if the phonons primarily responsible for thermal expansion have energy  $\hbar\omega \leq k_B T$ . In ZrW<sub>2</sub>O<sub>8</sub>, the onset of NTE occurs at around  $T \simeq 15 K$ , increasing in magnitude until around 50 K, above which  $\alpha$  takes the essentially temperature independent value(Ernst et al., 1998; David et al., 1999)  $-8.7 \times 10^{-6} K^{-1}$ . Hence, information regarding the nature of phononic excitations at low energies is an important step toward a detailed understanding of the unusual phenomenon of NTE in ZrW<sub>2</sub>O<sub>8</sub>.

To probe the low-energy phonon dynamics we use temperature dependent infrared spectroscopy covering the range from  $5000 \, cm^{-1}$  to  $16 \, cm^{-1}$  (600-2 meV), which encompasses all the optic phonons of  $\text{ZrW}_2\text{O}_8$ . We find that the phonon-related peaks in the infrared spectra extend to unusually low energy (~  $3 \, meV$ ), and that there is strong and unusual temperature dependence in the low-energy region, reflecting evidence of unconventional and anharmonic behavior. We suggest that understanding the mechanism of NTE and understanding the exotic nature of the infrared spectra from  $\text{ZrW}_2\text{O}_8$  are two essentially similar problems, both rooted in exotic low energy dynamics.

# 7.2 Competing Theories

One of the central unresolved issues for  $ZrW_2O_8$  has to do with the nature of the lattice motion responsible for NTE. While earlier work has emphasized the role of transverse oxygen vibration(Mary et al., 1996; Evans et al., 1996; Pryde et al., 1996; Ramirez & Kowach, 1998; Ernst et al., 1998; David et al., 1999) for the mechanism of NTE, Cao *et al*(Cao et al., 2002; Cao et al., 2003) have proposed a model, based on XAFS data, in which translation of WO<sub>4</sub> tetrahedra along  $\langle 111 \rangle$  directions plays an important role. Using eigenvector calculations together with our data, we infer that transverse oxygen motion, in the form of libration, tends to be accompanied by translation within each low-energy mode (thus they are essentially inseparable). This mixing is permitted by lattice symmetry and is prominent due to the unconstrained oxygen and the associated openness of the structure along the high-symmetry  $\langle 111 \rangle$  direction axes, and it appears to be essential to the nature of the low-frequency IR spectra. This mixing may also be crucial to the mechanism of the NTE: while the transverse oxygen motion provides the thermal motion that contracts the lattice, the presence of a translational component in each low-energy mode provides a source of frustration that inhibits lattice instabilities that could destroy NTE.

#### 7.3 Experiment

High purity single-crystal samples were grown at Lucent using a layered self-flux technique(Kowach, 2000). Our measurements of the specular reflectivity cover the frequency range from 15 to  $5000 \, cm^{-1}$  and the temperature range 20 to  $300 \, K$ . The optical conductivity,  $\sigma_1(\omega)$ , is determined from the reflectivity via a Kramers-Krönig transform with carefully chosen upper and lower terminations. For the acentric  $P2_13$  structure of  $\text{ZrW}_2\text{O}_8$  one expects a total of 132



Figure 7.1: a) The reflectivity and b) real part of the conductivity,  $\sigma_1(\omega)$ , is shown for the entire optic phonon region for T = 300 K (dashed) and T = 20 K (solid).

modes: 3 acoustic modes, 32 triplets of IR optical phonons, 11 doublets and 11 singlets, associated with the irreducible representations 33T + 11E + 11A(Ravindran et al., 2000; Ravindran et al., 2001; Chen et al., 2001). Our results are broadly consistent with earlier work(Ravindran et al., 2000; Ravindran et al., 2001; Chen et al., 2001; Yamamura et al., 2002; Ravindran et al., 2003) for the higher frequency parts of the phonon spectrum, and complementary in our emphasis on the low frequency range.



Figure 7.2: The optical data in the frequency interval below  $200 \, cm^{-1}$  at the lowest and highest temperatures measured.



Figure 7.3: a) The real part of the conductivity,  $\sigma_1(\omega)$ , is shown for the entire optic phonon region. The inset shows the low frequency region for temperatures of 20, 80(dotted) and 240 K. b) and c) show  $\sigma_1(\omega)$  for T=20, 60, 80, 100, 120, 140, 160, 180, 200, 220, 240, 260 and 300 K in two low  $\omega$  regions, along with neutron density of states in (b).

# 7.4 Reflectivity and Conductivity

Figure 7.3a shows the real part of the optical conductivity,  $\sigma_1(\omega)$ , versus frequency. The infrared active optical phonon modes, which generally appear as peaks in  $\sigma_1(\omega)$ , are sufficiently dense that they tend to merge together into clusters in  $\text{ZrW}_2\text{O}_8$ . The upper cluster is associated with bond stretching motion (including the  $\nu_3$  modes of the WO<sub>4</sub> tetrahedra) and the middle cluster (180-400 cm<sup>-1</sup>) with bond bending modes (*e.g.*,  $\nu_2$  modes). Below these two clusters there are additional infrared features, shown in the inset, which we associate with librational and translational motion of WO<sub>4</sub> tetrahedra, as discussed below. Unlike the generic modes of the upper clusters, the modes in this region are specific to the  $\text{ZrW}_2\text{O}_8$  structure, and it is in this lower region that one expects to find modes relevant to the mechanism of NTE.

### 7.5 Peculiarities below $150 \, cm^{-1}$

The set of peaks in the region below  $150 \, cm^{-1}$  are unusual in several respects. As shown in Fig. 7.3b and 7.3c, many of the peaks in this region are approximately equal in strength, extend to unusually low energy, and exhibit striking temperature dependence. They tend to sharpen and grow in strength as the sample is cooled; they exhibit swept, asymmetric (Fano) lineshapes, and in some cases substantial dependence of both strength and peak frequency on temperature.

#### 7.5.1 Continuum Background and Lineshape Asymmetry

Many of the peaks in the region below  $150 \, cm^{-1}$  have intrinsic asymmetry which is especially apparent at low temperature. This asymmetry is a feature reminiscent of the Briet-Wigner/Fano line profile, which results from considering the effects of interaction between a discrete level and a continuous background on the matrix elements relevant to spectroscopic probes. Within that framework, the sense of asymmetry of many of these peaks (a dip below background on the high energy side) indicates that the interaction here is with states of primarily higher energy(Fano, 1961; Damascelli et al., 1997). Furthermore, the presence of the asymmetry indicates that the background in the conductivity is intrinsic, and not an experimental artifact.

Fano lineshapes have been reported and analyzed in detail in the Kondo insulator system FeSi(Damascelli et al., 1997). In that work, the strongly correlated electronic states provide a continuous background with which the phonons interact (mix), providing the underlying framework which gives rise to the Fano line profile. In  $ZrW_2O_8$ , the electronic band gap is large(Muthu et al., 2002), ~ 2.8 eV, making itinerant electrons an unlikely source of background in this system.

It is conceivable, however, that mobile ions (e.g. oxygen) can provide a strongly damped free carrier contribution to the conductivity in open framework structures (Zheng et al., 2003), and hence the appearance of a conductivity background. Ionic conductivity in  $\text{ZrW}_2\text{O}_8$ is strongly suggested by microwave ( $\omega < 3 \text{ cm}^{-1}$ ) frequency dependent dielectric measurements at elevated temperatures (Evans et al., 1996). However at room temperature, these data support the suppression of ionic transport. Extrapolating this trend to low temperatures, one expects the ionic conductivity to decrease further as temperature is lowered. This expected temperature dependence is however opposite to the temperature dependence of the background in the frequency interval of our experiments ( $\omega > 15 \text{ cm}^{-1}$ ). Precision experimentation crossing the "terahertz gap" ( $3 < \omega < 15 \text{ cm}^{-1}$ ) and elucidating the nature of the low frequency spectral weight transfer may help resolve the role of ionic transport in this system.

Asymmetric line shapes have also been observed (Gupta & Katiyar, 2001) in thin fer-

roelectric oxide films and suggested to be a consequence of the relaxation of the q=0 selection rule induced by defects, which is further amplified by the large polarizability in those systems. Alternatively, in a clean system, coupling of the zone center phonons to phonons at other **k**-vectors can occur in a symmetry allowed, momentum conserving interaction. Such an interaction could project weight from the continuum of states existing at points throughout the Brillouin zone (*e.g.* at finite wavevector) back to the zone center<sup>1</sup> (and zero wavevector).

Asymmetric line shapes and unusual temperature dependence have also been observed by Foster *et al* in the soft-mode ferroelectric PbTiO<sub>3</sub>(Foster et al., 1993). These authors are able to describe their Raman data using an approach based on the energy levels of an effective (Landau-Ginzberg), strongly anharmonic potential which describes the soft mode transition. These compelling results point to anharmonicity as the culprit giving rise to the non-Lorentzian lineshapes, but without the need to invoke a phonon picture explicitly.

In our high quality single crystals, the appearance of the background and asymmetric lineshapes of the phonon region strongly suggest that beyond-harmonic dynamics play a major role in the low frequency dynamics of  $ZrW_2O_8$ .

#### 7.5.2 Temperature Dependence

The largest peak frequency shifts are observed for the broad  $28 cm^{-1}$  mode, which shifts from about 27 to  $29.5 cm^{-1}$  (+8%), and the  $88 cm^{-1}$  mode, which shifts from about 91.5 to  $86 cm^{-1}$  (-6%). These shifts are unusually large and are beyond the scope of purely harmonic phonon models. The pervasiveness of strong temperature dependence throughout this low frequency region reflects the exotic character of the low energy dynamics which is clearly evident in the IR spectra.

<sup>&</sup>lt;sup>1</sup>In the language of many-body theory, the  $\mathbf{k}=0$  phonon spectral function would not be a simple set of sharp peaks with nothing in between, but rather would have a more smeared out distribution as a result of anharmonic influences.



Figure 7.4: The temperature dependence of Batman<sup>TM</sup>'s head a) for temperatures  $T \ge 80 K$ , and b) for T = 20, 60 and 80 K. c) shows the temperature dependence of the integral of  $\sigma_1(\omega)$  between the dashed bars in a) and b).

In addition to the significant temperature-dependent shifting of the modes around 29  $cm^{-1}$  and 90  $cm^{-1}$ , there are substantial changes in the strength and definition of all the peaks below  $150 cm^{-1}$ . All peaks  $40 cm^{-1}$  and above seem to sharpen and increase strength as temperature is lowered. In addition, the conductivity background seems to increase monotonically as temperature is decreased.

The conductivity around the lowest peaks differs in this behavior. Figure 7.4 shows a close up view of the three lowest peaks, which we refer to as Batman<sup>M</sup>'s head (one head, two ears). Figure 7.4c shows the temperature dependence of the integral of  $\sigma_1(\omega)$  in three different frequency intervals. These intervals are chosen to encompass the spectral weight associated with each of the 20, 28, and  $40 \, cm^{-1}$  peaks.

The low frequency "ear" peak exhibits the most striking temperature dependent behavior, reaching a clear maximum<sup>2</sup> around T = 80 K. Around room temperature, the low ear mode disappears almost completely. This interesting effect of nearly depleting the strength of an excitation is quite unusual. We note that 300 K corresponds to an energy scale nearly 10 times that of the  $20 cm^{-1}$  mode. In the conventional quantum theory of the Lorentz oscillator, the oscillator strength of an optical excitation is independent of temperature. The complex temperature depedence of the  $20 cm^{-1}$  mode could indicate that anharmonic effects have significantly influenced the otherwise equal-spaced harmonic ladder of states, and that these effects are very important at the 11th ladder rung. We revisit this point in Appendix B.

#### 7.6 Implications of Energy Levels

Because all triplets (T representation) are dipole active in the acentric structure of  $ZrW_2O_8$ , our experiments are in principle sensitive to 96 of the 129 optical phonon modes. With

<sup>&</sup>lt;sup>2</sup>A plot of the maximum of the conductivity versus T shows very similar behavior.



Figure 7.5: The optical conductivity and time-of-flight density-of-states for  $ZrW_2O_8$ .

the zone center values of the majority of the optical phonon branches told by our spectroscopic results, we can explore the connection with other experimental results already present in the literature. This will lead to some definite conclusions while opening up new questions concerning the applicability of conventional phonon models to the low frequency dynamics of  $ZrW_2O_8$ .

#### 7.6.1 IR data and DOS

Figure 7.5 shows the density of states (DOS) from the time-of-flight neutron scattering results of Ernst*et al*(Ernst et al., 1998) together with the infrared data. The DOS is an average

over all  $\mathbf{k}$  vectors in the Brillouin zone, while the conductivity probes only the zone center phonon branch intercepts ( $\mathbf{k}=0$ ). If the optical phonon branches are weakly dispersing, then we expect that the major differences between these two quantities arise from the matrix elements that express the coupling of different experimental probes (*i.e.* neutrons versus photons) to the system.

In the case of the DOS, as with all spectroscopic experiments, there are matrix element effects present which in this case depend on the different coupling of the neutrons (through scattering lengths and Debye-Waller factors) to the Zr, W, and O nuclei(Lovesey, 1984; Ernst et al., 1998). However, it is believed(Ernst et al., 1998) that for  $ZrW_2O_8$ , the true DOS and the matrix-element-weighted DOS are not very different, on account of the similarity of the coupling of the different ions to neutrons<sup>3</sup>.

The dominant difference between  $\sigma_1(\omega)$  and the DOS enters through the matrix elements relevant to the optical data. These depend crucially on the distribution of charge and mass among the Zr, W, and O ions as well as symmetry character of the optical phonon modes. With these differences in mind, we proceed to analyze different parts of the spectra in detail.

#### Upper cluster

In Figure 7.5, both the DOS and conductivity break up into two clusters. As mentioned above, the cluster above  $600 \, cm^{-1}$  arises from bond stretching motion(Ravindran et al., 2001), and in particular, stretching of the rigid W-O bond. One can understand the total number of modes in the upper cluster (area under the DOS data in this region) in terms of counting of the degrees of freedom associated with this type of motion. There are 8 WO<sub>4</sub> tetrahedra per unit cell, each with 4 strong W-O bonds whose compression involves high frequency motion.

<sup>&</sup>lt;sup>3</sup>However, Ernst *et al*(Ernst *et al.*, 1998) believe that the oxygen contribution to the DOS is weighted more heavily in the data of Figure 7.5 and 7.6. Furthermore, the integral over the measured DOS is not identically 132, indicating a potential discrepancy between the time-of-flight DOS and the true DOS.
This gives 32 degrees of freedom associated with the highest frequencies of the system<sup>4</sup>, *i.e.* the upper cluster. Experimentally, the area of the DOS above  $700 \, cm^{-1}$  indeed rounds off to 32.

#### Low cluster

The lowest group of phonon peaks is compared to the DOS data in Figure 7.6. The most striking disparity between these data sets is the appearance of a peak in the conductivity around  $2.2 \, meV$ , in a region where the DOS appears smooth, and below the edge of the lowest optical phonon appearing in the DOS data  $(3 \, meV)$ . This anomalous discrepancy brings attention to the  $2.2 \, meV \, \sigma_1(\omega)$  peak. We will show below in a comparison of our data to the measured specific heat data that the appearance of this excitation cannot be interpreted as due to the zone center intercept of a weakly dispersing optical phonon branch.

It is however, worth mentioning that this energy does appear in the molecular dynamics calculations of Mittal *et al*(Mittal et al., 2003) for the isostructural compound  $HfW_2O_8$ . These calculations show that the lowest phonon branch, most closely associated with acoustic phonons, has zero energy at zero wavevector and energy  $\sim 2 \, meV$  at the zone boundary. Any *N*-fold increase in the unit cell volume, or disruption of translational invariance could fold the zone boundary endpoints back to the center, making a phonon-like excitation observable by our infrared experiments. X-ray and neutron experiments, however, are unable to refine this hypothetical/speculative cell multiplication, and no superlattice reflection peaks have been reported so far. Simple phonon peak counting of our data are inconclusive in the detection of superstructure, and we cannot address the influence of defects on the low frequency dynamics at this time.

Putting the 2 meV peak aside for the moment, we note that the temperature depen-

<sup>&</sup>lt;sup>4</sup>This viewpoint is vindicated by the modeling described below, in which a very stiff W-O bond gives 32 modes in the upper cluster, given by 32=8T + 2A + 4E. Changing the model parameters to give a stiff Zr-O bond but weak W-O give 24 modes in the upper cluster. These correspond to the 6 Zr-O bond stretching modes (T + A + E) of each of the 4 ZrO<sub>6</sub> octahedra.



Figure 7.6: The optical conductivity and time-of-flight density-of-states for ZrW<sub>2</sub>O<sub>8</sub>.

dence of the  $3 \, meV$  hump in  $\sigma_1(\omega)$  follows reasonably well the temperature dependent DOS data reported by Ernst *et al*(Ernst et al., 1998). The redshift of DOS with decreasing temperature was ascribed in that work as a result of anharmonicity in the lowest frequency phonon modes. The optical spectral weight seems to redshift similarly, and the peak around  $3 \, meV$  has a similar width in both data sets, facts which lend naturally toward an identification of the peaks in the vicinity of  $3-4 \, meV$  in the DOS and  $\sigma_1(\omega)$ . This identification constrains the symmetry of the motion responsible for this peak to involve a three dimensional aspect, since infrared probes are only sensitive to phonons belonging to the T (three dimensional) representation.

With a conventional phonon interpretation, keeping in mind that infrared probes are sensitive only to zone center triplets, and assuming that the optical phonon branches are weakly dispersing, the infrared data should be able to put a lower bound on the integrated DOS in a given region. To do this, we simply count the peaks in a given region, multiply by 3, and account appropriately for the 3 acoustic branches when the frequency interval of interest includes low frequencies<sup>5</sup>. This estimate will inevitably be low, since optical probes are not sensitive to branches which are doublet or singlet at the zone center, while the neutrons does count these branches.

Following this procedure, the integrated DOS (number of modes) expected below 80  $cm^{-1}$  is  $5\times3+3=18$ . The integral of the DOS in this region is only 5, indicating that the conventional picture of weakly dispersing phonon mode branches is insufficient to describe the details of both the DOS and optical data in this frequency region. Continuing this procedure to higher frequencies, the infrared estimate gives at least  $8\times3+3=27$  modes below  $150 cm^{-1}$ , and  $23\times3+3=72$  modes below  $600 cm^{-1}$ . The integral of the DOS up to  $150 cm^{-1}$  is about 20 and the integral to  $600 cm^{-1}$  is about 88. The overestimate of the DOS implied by the optical

<sup>&</sup>lt;sup>5</sup> "Low" here means lower than the Debye frequency, or the zone edge intercept of the acoustic branch. For Pb, this is approximately  $70 \, cm^{-1}$ . Specific heat measurements constrain the Debye frequency of  $\text{ZrW}_2\text{O}_8$  to be about  $66 \, cm^{-1}$ .

data at low frequencies leads us to conclude that below  $150 \, cm^{-1}$ , optical probes reveal more peaks than could be expected based on the density of states alone. We proceed to further explore the connections of our optical data to data associated with other probes.



Figure 7.7: a) A fit to the specific heat with a lowest infrared mode at  $28.5 \, cm^{-1}$  ( $3.5 \, meV$ ) is shown by the solid lie (through the specific heat data). The dashed curves show the excess specific heat generated by failed attempts to fit C(T) with a lowest optic mode at 20 or 24  $cm^{-1}$ , respectively. b) a(T) data (open squares) is shown along with a fit based on a two Einstein mode model.

## 7.6.2 IR Data and Specific Heat

It is informative to consider the relationship between our IR data and the specific heat data of Ramirez and Kowach(Ramirez & Kowach, 1998). For the fit shown in Figure 7.7a, we have placed an Einstein mode at each measured peak frequency in  $\sigma_1(\omega)$  with triplet weight, except for the  $20 \, cm^{-1}$  mode, which is omitted, and the wide hump around  $3.5 \, meV$ , which we represent with an Einstein mode at  $28.5 \, cm^{-1}$  with a spectral weight of 2.6 oscillators per unit cell<sup>6</sup>. Attempts to include an Einstein mode at the frequency of the lowest peak in  $\sigma_1(\omega)$ , or to move the  $28.5 \, cm^{-1}$  mode to lower frequency leads to a sizable overestimate of C(T), shown by the dashed curves in Figure 7.7. This fitting leads us to conclude that the  $20 \, cm^{-1}$ 

<sup>&</sup>lt;sup>6</sup>In addition, we have included a Debye contribution  $\Theta_D = 62 \, cm^{-1}$ , a value which is determined by the value of the flat portion of the  $C(T)/T^3$  plot at temperatures below the main peak.

peak in  $\sigma_1(\omega)$  does not contribute extensively to the specific heat with triplet weight. A similar conclusion was suggested by comparison of  $\sigma_1(\omega)$  and the time-of-flight DOS in section 7.6.1.

We therefore conclude that the  $20 \, cm^{-1}$  peak in  $\sigma_1(\omega)$  does not correspond to the zone-center endpoint of an ordinary optical phonon branch and that the broad  $28 \, cm^{-1}$  peak is the signature of the lowest optical phonon of  $\text{ZrW}_2\text{O}_8$ . The total spectral weight in the peaks between 28 and  $100 \, cm^{-1}$  is in agreement with the results of our phonon eigenvector calculations, discussed below, and the peaks in this region are in reasonable correspondence with zone-center intercepts of optical phonon dispersion relations calculated for the isostructural compound HfW<sub>2</sub>O<sub>8</sub>(Mittal et al., 2001; Mittal et al., 2003) as well as neutron DOS peaks(Ernst et al., 1998). The  $20 \, cm^{-1}$  peak stands out among the others in that it diminishes substantially below 80 K (the others grow) and is clearly irreconcileable with neutron DOS and C(T). These two features may suggest a low-density defect with an extremely large dipole matrix element. However, for defect densities of order  $10^{18}/cm^3$ , an absorption coefficient of  $\alpha \sim 1-50 \, cm^{-1}$  is expected (Sievers, 2004). For  $\text{ZrW}_2\text{O}_8$ ,  $\alpha \sim 500 \, cm^{-1}$  in the range of the  $20 \, cm^{-1}$  mode, making a defect source for this excitation unlikely. Further theory is needed to ascertain the origin of this marked absorption, and its possible connection with the unusual lattice dynamics of the bulk compound.

#### 7.6.3 IR Data and Grüneisen Formalism

Focusing further on energetics, one can let the infrared spectra provide a context in which to explore the origins of the temperature dependence of the lattice parameter, a(T). Similar to earlier work(Ernst et al., 1998; David et al., 1999), we approach this by associating negative Grüneisen parameters ( $\gamma$ ) with Einstein mode frequencies. We calculate a(T) using a bulk modulus of 72 GPa(Jorgensen et al., 1999) and assuming triplet weight(Ashcroft & Mermin, 1976). Starting with the frequency of the lowest optic mode from our data (at 28  $cm^{-1}=3.5 meV$ ), we find that associating a large negative Grüneisen parameter to this mode alone does not allow a good fit to a(T), however, a good fit can be obtained simply by including a second Einstein mode at higher frequency, as shown in Figure 7.7b) for  $\gamma=-20$  at  $28 cm^{-1}$ and  $\gamma=-7$  at 88  $cm^{-1}$ . The lower energy corresponds to the lowest energy optical phonon in ZrW<sub>2</sub>O<sub>8</sub>, which is so low it cuts through the acoustic phonon dispersion and may thereby acquire mixed character(Mittal et al., 2003); the higher energy corresponds to the strongly temperature dependent peak near 88  $cm^{-1}$  (Figure 7.4). While this 2-mode approach provides the minimal context in which a good fit can be obtained, one can also do more nuanced fits involving additional modes. One can use Grüneisen parameters for modes above 40  $cm^{-1}$  from pressure dependent Raman measurements of Ravindran et al.(Ravindran et al., 2001) and add an additional term for the 28  $cm^{-1}$  mode. In that more nuanced approach good fits to a(T)can be obtained when the  $\gamma$ 's of the two lowest optic modes add to about -20.

## 7.7 Structure

It is worth taking a section to describe in detail the  $\text{ZrW}_2\text{O}_8$  structure. The cubic  $\text{ZrW}_2\text{O}_8$  lattice can be constructed from "kabobs" consisting of one Zr and two WO<sub>4</sub> tetrahedra, as shown in Figure 7.8. The tetrahedra are skewered so that they do not eclipse, but rather form a star of David when viewed down the kabob axis, as indicated in the figure.

In the lattice, the kabobs come in four distinct orientations, corresponding to the body diagonals of a cube (*i.e.* the four tetrahedral directions, see Figure 7.9b). However unlike the body diagonals of a cube, the kabobs never cross, that is, the sticks don't intersect. Instead, they are offset from each other in a manner resembling a spiral staircase with a four-step pitch. This imposes a chirality, or sense of twist, to the cubic lattice. Also, kabobs of parallel



Figure 7.8: Three views of a "kabob", which can be used to build the structure of  $ZrW_2O_8$ . The dashed lines indicate the octahedron made from the corners of WO<sub>4</sub> tetrahedra on neighboring kabobs.



Figure 7.9: a) The nature of a low frequency triplet mode is shown in terms of WO<sub>4</sub> tetrahedra and Zr-centered octahedra via a time sequence. As the tetrahedra rotate clockwise, they translate downward along the  $\langle 111 \rangle$  axis, which is shown by the dark line. The two lowest-frequency optic mode are similar, but in the other one the  $\langle 111 \rangle$  axis octahedron (white) rotates opposite the tetrahedra. The unconstrained oxygen lies on the  $\langle 111 \rangle$  axis. b) The pair of tetrahedra shown in (a) couples to other tetrahedra as shown. There are eight WO<sub>4</sub> tetrahedra in a unit cell organized in pairs on  $\langle 111 \rangle$  axes (dark lines) which are offset in a spiral-staircase configuration as shown. (Illustration by Alison Kendall)

orientation form a triangular lattice when projected onto a plane perpendicular to them.

It has been suggested that the retention of cubic symmetry to very low temperature in this system is a result of a sort of frustration which is inherent in the lattice structure. The frustration then stabilizes the cubic structure in a manner akin to the way frustration effects can stabilize a disordered phase in magnetic systems with triangular, kagome, pyrochlore, or spinel geometries(Ramirez, 1994). The appearance of tetrahedral and triangular symmetry in this structural analysis of the  $ZrW_2O_8$  system suggests a possible mechanistic origin for the soft-mode-inhibiting frustration(Ramirez, 2001; Cao et al., 2002; Ramirez, 2004).

## 7.8 Phonon Modeling

To attempt to draw a connection between our measured optical dynamics and underlying atomic motion, we have numerically simulated the dynamics of one unit cell of zirconium tungstate modeled as a mass-and-spring system with periodic boundary conditions with the theory developed in the previous chapter. First we will justify the choice spring constants and ionicities for the ion cores, then we will discuss the robust results which followed from that study.

## 7.8.1 Relative Strengths of the Zr-O versus the W-O Bonds

We find in our modeling that the WO<sub>4</sub> bond is far more stiff than the Zr-O bond, a conclusion experimentally brought out by Cao *et al*, that can be understood in a simple way which involves an analysis of the electron budget in the bonding chemistry (*a la* Pauling(Pauling, 1960)) of ZrW<sub>2</sub>O<sub>8</sub>. The Zr<sup>+4</sup> ions (4/unit cell) each sit inside nearly-regular octahedral cages of O ions<sup>7</sup> (see Figure 7.10). Since there are 6 (very nearly) equivalent directions for the 4

<sup>&</sup>lt;sup>7</sup>The bonding character of the Zr-O bonds are  $sp^3d^2$  hybrid orbitals, the simplest linear combinations of spherical harmonics which have octahedral symmetry.



Figure 7.10: Bonding chemistry of  $\text{ZrW}_2\text{O}_8$ . Zr shares its 4 valence electrons with the 6 surrounding O, with each O receiving 2/3 of an electron. For these constrained O to receive 2  $e^-$  total, they must pull an additional 4/3 of an electron from the neighboring W. For the W to reach its formal valence, the neighboring unconstrained O must receive 2 electrons in addition. Conclusion: there are approximately twice as many electrons involved in the W-O bond as are in the Zr-O bond.

electrons to bond, then there is on average 2/3e involved in each Zr-O bond, giving these bonds a strength of 2/3. If the O atoms are to form  $O^{-2}$  ions, then the O atom must pull an additional 4/3e from the W ions. The W ions come in two types, which locally see nearly the same structural environment. This environment is nearly tetrahedral, consisting of 3 strictly equivalent W-O bonds (each containing 4/3e) and a fourth shorter bond to the unconstrained oxygen. For the W then to take its formal valence +6, the bond to the unconstrained oxygen must then be very strong<sup>8</sup>, containingabout2e. Since the number of electrons involved in a bond determines its resilience to distortion, we can say something about the relative magnitudes of the bond strengths for each of these bond types. From these considerations, we then expect that the W-O bond is significantly stronger than the Zr-O bond. This conclusion is experimentally brought out by the local structure studies of Cao et al. (Cao et al., 2002; Cao et al., 2003), and further enforced by the appearance of precisely 32 modes in the upper cluster of the DOS data of Ernst et al(Ernst et al., 1998) as discussed above in section 7.6.1.

## 7.8.2 Spring Constant Considerations

The spring constants left as free parameters in the dynamical matrix include compression ( $\alpha$ -type) springs between all nearest-neighbor pairs less than  $3\mathring{A}$  apart, but also angle-fixing ( $\beta$ -type) contributions with the metal ions as the angle vertex. One formula unit of ZrW<sub>2</sub>O<sub>8</sub> consists of one Zr, two distinct W (called W1 and W2), and four groups of O (one O1, one O2, three O3, and three O4)<sup>9</sup>. Inclusion of bending and stretching bonds for each distinct pair of nearest neighboring atoms results in 27 distinct nearest neighbor bonds. A simplification in the modeling is made right off by noticing that many of the strictly speaking inequivalent bonds

<sup>&</sup>lt;sup>8</sup>The fact that the W-O distance associated with this unconstrained oxygen is indeed the shortest(Auray et al., 1995) indicates that this bond is stronger than the W-constrianed O bond(Pauling, 1960; Sleight, 2004). <sup>9</sup>The convention for this naming is not consistent throughout the literature. We follow the convention of

Auray, Quarton, and LeBlanc(Auray et al., 1995) whose crystallographic data was used in our modeling.

are nearly identical. For example, the  $\text{ZrO}_6$  cage in the structure is only slightly acentric, which strictly speaking groups the 6 O ions into two distinct classes (three O3 and three O4). However, each O ion is 2-fold coordinated by a W and a Zr with comparable bond distances, so we make the simplifying assumption that the spring constants derived from the orbital chemistry about the O3 and O4 sites is the same. Similar approximations are made for the two W ions, which have very similar local environments. With these approximations, we are left with only 7 bonds, described in Table 7.1.

We can constrain the magnitude of the bond strengths by a combination of considerations. If we set all bonds associated with Zr equal to 0, this leaves only unlinked tetrahedra. This will force many modes to zero, corresponding to the free rotation and translation of the 8 tetrahedra per unit cell. The excitations of this unlinked system that persist at nonzero frequency are associated with the internal vibrations of the WO<sub>4</sub> tetrahedra, a trait which influences the electrodynamics of all WO<sub>4</sub>-containing solids. We have made a comparison with the infrared data of Barker *et al*(Barker, 1964) on the system CaWO<sub>4</sub> in order to estimate the spring parameters appropriate to the WO<sub>4</sub> tetrahedra.

Taking the opposite viewpoint and setting all of the WO<sub>4</sub>-related bonds equal to zero delivers a set of 4 ZrO<sub>6</sub> octahedra in the unit cell. Experience with transition metal oxide (TMO) tetrahedra is readily available from the extensive work on Ruddlesden-Popper TMO systems such as cuprate superconductors, soft-mode ferroelectrics, and CMR manganates. In these systems, there are generally IR active modes around  $300 \, cm^{-1}$  and  $700 \, cm^{-1}$ , generally identified as the  $\nu_3$  eigenmodes calculated for free octahedra(Harter, 1993).

Further, in the case of hexaflouride molecules,  $XF_6$  octahedra, where X=(S, U, Pt, Np), a mass-spring model as been used successfully to describe the optical (Raman) data(Harter, 1993). In these analyses, the F-F compressional strength is approximately 1/5 of the X-F

Symbol	Linkage	Type	Value
ZO	Zr-O	compression	$3.15 \mathrm{N/m}$
OOZ	$O-O$ ( $ZrO_6$ )	compression	$0.6 \mathrm{N/m}$
b	O-Zr-O $(90^\circ)$	angular	$5.25 \text{ mN/}^{\circ}$
ZOW	Zr-O-W (171° or $153^{\circ}$ )	angular	$1.64 \text{ mN/}^{\circ}$
WO	W-O (constrained O)	compression	9.02  N/m
wou	W-O (unconstrained O)	compression	$13.52 \mathrm{~N/m}$
OOW	$O-O(WO_4)$	compression	$2.25 \mathrm{~N/m}$
owo	O-W-O	angular	$27.3 \text{ mN}//^{\circ}$

Table 7.1: Spring parameters used in the modeling. In the program, the output is in  $cm^{-1}$  and the masses are in *amu*. For compressive-type springs, to convert from the program units to N/m, multiply by  $1.50328 \times 10^{-6}$ . For bending springs, multiply program values by  $2.62371 \times 10^{-8}$  to convert to N/°.

compressional bond strength. In addition, the F-X-F bending strength is similar in magnitude to the F-F compressional strength in  $SF_6$ , but negligible for the larger  $UF_6$  molecules. We have considered this experience in our choice of spring constant values.

#### 7.8.3 Ionic Constraints

It is worthwhile to note however that a great body of work exists on the extension of the ionic model to accommodate changes due to notably the shell model of Dick and Overhauser(Dick & Overhauser, 1958) and also the considerations of Szegti(Szigeti, 1949) in distinguishing the charges relevant to optical response versus the computation of Madelung energy. However, for the sake of simplicity, we choose to use an ionic model for computing the optical strength of the computed lattice vibrations.

Information concerning the ionicities of the Zr, W and O ions is available in the optical data. One can show through quite general considerations that the integrated conductivity of a system of N particles of mass  $m_i$  and charges  $Z_i e$  is equal to(Dressel & Gruner, 2002):

$$\int_0^\infty \sigma_1(\omega) d\omega = \frac{\pi e^2}{2V} \sum_{i=1}^N \frac{Z_i^2}{m_i}.$$
(7.1)

In the case of the phonon conductivity of ZrW<sub>2</sub>O<sub>8</sub>, this can be stated

$$\int_{0}^{1000cm^{-1}} \sigma_1(\omega) d\omega = \frac{\pi e^2}{2a^3} \left(4\frac{Z_{Zr}^2}{m_{Zr}} + 8\frac{Z_W^2}{m_W} + 32\frac{Z_O^2}{m_O}\right)$$
(7.2)

Where the upper cutoff is chosen to include only ionic contributions to the conductivity. In the three dimensional space of effective charges  $Z_O$ ,  $Z_{Zr}$ , and  $Z_W$ , Equation 7.2 constrains the values of these three quantities to lie on the surface of an ellipsoid. In addition, the requirement of charge neutrality

$$Z_{Zr} + 2Z_W + 8Z_O = 0, (7.3)$$

describes a plane through the origin and a further constraint. The effective ionicities, which are necessary to calculate the optical response functions from the equations of motion, are now constrained to within one parameter. We choose  $Z_{Zr}=+3.7$ ,  $Z_W=+5.6$ , and  $Z_O=-1.9$ , which is in reasonable agreement of electronic band structure calculations(Ouyang et al., 2002) and formal valence expectations(Pauling, 1960).

#### 7.8.4 Modeling Results

With the above physical considerations for the spring constants and ionicities of the Zr, W, and O ions in  $\text{ZrW}_2\text{O}_8$ , our modeling attempts capture salient features of the measured conductivity data, while at the same time bringing out some unexpected results. We present the results of a typical parameter set in Tables 7.2 and 7.3, which follows from the spring parameters in Table 7.1. Analysis of the degeneracies in this table indicates that the space group factorization 132=33T + 11A + 11E is respected by our calculation, and further that our nearest-neighbor model includes enough interaction to reach this group-theoretical lowest symmetry.

Figure 7.11 shows the integral of the density of states (DOS) of Ernst *et al*(Ernst et al., 1998). The two clusters separated by a gap in the DOS data of Figure 7.5 appear as

Mode	$\omega \ (cm^{-1})$	$\omega_P \ (cm^{-1})$	Mode	$\omega \ (cm^{-1})$	$\omega_P \ (cm^{-1})$
1	0	0	34	170.93	51.581
2	0	0	35	170.93	51.581
3	0	0	36	170.93	51.581
4	34.4487	0	37	182.535	126.26
5	34.4487	0	38	182.535	126.26
6	34.4487	0	39	182.535	126.26
7	37.61	0	40	186.63	0
8	51.0257	109.073	41	186.63	0
9	51.0257	109.073	42	200.042	58.8114
10	51.0257	109.073	43	200.042	58.8114
11	62.6136	0	44	200.042	58.8114
12	62.6136	0	45	209.7	106.742
13	64.0709	0	46	209.7	106.742
14	73.5985	21.3725	47	209.7	106.742
15	73.5985	21.3725	48	223.27	9.58222
16	73.5985	21.3725	49	223.27	9.58222
17	80.5873	1.74275	50	223.27	9.58214
18	80.5873	1.74275	51	236.073	0
19	80.5873	1.74275	52	247.517	13.1999
20	92.7326	3.36756	53	247.517	13.1999
21	92.7326	3.36756	54	247.517	13.1998
22	92.7326	3.36756	55	251.447	0
23	96.9843	0	56	251.447	0
24	96.9843	0	57	256.832	35.8383
25	106.213	9.40507	58	256.832	35.8383
26	106.213	9.40507	59	256.832	35.8379
27	106.213	9.40508	60	257.383	0
28	124.039	18.1933	61	354.85	196.689
29	124.039	18.1933	62	354.85	196.689
30	124.039	18.1933	63	354.85	196.687
31	139.651	0	64	370.791	0
32	161.146	0	65	373.192	0
33	161.146	0	66	373.192	0

Table 7.2: Frequencies and oscillator strengths of Modes 1-66 for the parameters in Table 7.1. Modes 1-3 are acoustic modes, which for k=0 describe translation of the lattice as a whole.

Mode	$\omega \ (cm^{-1})$	$\omega_P \ (cm^{-1})$	Mode	$\omega \ (cm^{-1})$	$\omega_P \ (cm^{-1})$
67	380.327	12885.9	100	482.778	0
68	380.327	12885.9	101	823.652	0
69	380.327	12885.8	102	823.652	0
70	390.198	826.896	103	825.671	187.422
71	390.198	826.896	104	825.671	187.422
72	390.198	826.905	105	825.671	187.422
73	393.361	0	106	844.113	173.848
74	393.361	0	107	844.113	173.848
75	397.202	0	108	844.113	173.846
76	398.66	3025.88	109	846.485	3812.61
77	398.66	3025.88	110	846.485	3812.61
78	398.66	3025.91	111	846.485	3812.61
79	407.717	2138.27	112	846.81	0
80	407.717	2138.27	113	846.81	0
81	407.717	2138.29	114	851.672	0
82	423.922	0	115	851.672	0
83	423.922	0	116	851.672	0
84	423.922	0	117	857.898	0
85	445.17	0	118	859.984	33.6052
86	445.17	0	119	859.984	33.6052
87	452.223	31.8423	120	859.984	33.6052
88	452.223	31.8423	121	866.86	0
89	452.223	31.8424	122	867.325	1205.2
90	460.291	0	123	867.325	1205.2
91	460.291	0	124	867.325	1205.21
92	460.291	0	125	952.583	127.716
93	470.69	29.4216	126	952.583	127.716
94	470.69	29.4216	127	952.583	127.716
95	470.69	29.4216	128	962.915	0
96	476.268	318.637	129	965.502	0
97	476.268	318.637	130	965.502	0
98	476.268	318.638	131	965.502	0
99	482.778	0	132	980.566	0

Table 7.3: Frequencies and oscillator strengths of Modes 67-132. A small field along the  $\langle 111 \rangle$  direction was applied to slightly break the degeneracy within a triplet. This is why sometimes the third member of a triplet appears to have a slightly different oscillator strength.

two steps separated by a plateau when represented as an integral. The total integral of this DOS data is only 120 modes/unit cell, which is 11 short of the number expected from simply counting the number of degrees of freedom of the ideal structure (132/unit cell). In this data set, there are 32 modes in the upper cluster and the remainder fall into the lower cluster, below  $400 \, cm^{-1}$ .

An extremely robust result of our modeling is that the upper cluster contains 32 modes whenever the W-O to Zr-O bond strength is of order unity or larger. In accord with the physicality of this hierarchy of bond strength as discussed in section 7.8.1, and by Cao *et al*(Cao et al., 2002; Cao et al., 2003), we believe that this is indeed the case and that 32 modes is an appropriate number for the upper cluster. As a result, we feel that the underestimate of the total integrated DOS of Ernst *et al* does not effect the upper cluster. For this reason, we have also presented integrated DOS shifted upward by the integral deficit (11 modes).

Also in this plot is the integrated DOS from our model. This is defined as the number of eigenfrequencies, determined from the calculation, which are less than frequency  $\omega$  (see Table 7.2). While this quantity, in the context of our model, is not strictly speaking the true DOS, which represents the distribution of **k**-dependent mode eigenvalues, it does represent the distribution of zone center intercepts of the phonon eigenvalues (*i.e.* **k**=0 phonons). Since most of the modes here are optical and are therefore expected to be weakly dispersing(Ashcroft & Mermin, 1976; Ernst et al., 1998), a meaningful comparison can be made. The reasonable agreement between the measured DOS and the distribution of zone center eigenvalues of a model calculation based on physically motivated parameter values indicates that our model captures the salient elements of the phonon spectrum.

The highest mode in the upper cluster is singlet for any reasonable choice of parameters and the sense of the eigenvector is the maximal compression of W-O and Zr-O bonds. In the



Figure 7.11: The integral of the DOS as measured by Ernst *et al* (short dashes, as reported; long dashes, shifted by 11 modes/unit cell) and as calculated by our model (solid red line). Horizontal lines, from top down, indicate: the total degrees of freedom (132), the total integral of the measured data (132-11=121), and the total minus the upper cluster (132-32=100).

language of pure octahedra and tetrahedra, this is the pure  $A_{1g}$  (in-phase radial stretch) beating of these polyhedra with their centers fixed in space<sup>10</sup>.

The eigenvectors in the upper cluster are prominently characterized by bond compression, while below  $400 \, cm^{-1}$  the eigenvectors show mostly bond bending. Below both of these clusters, however, in the region below  $150 \, cm^{-1}$ , are modes which, to a surprisingly high degree, respect the resilience of both of these bonds types and feature the motion of octahedra and tetrahedra which remain relatively undistorted throughout a mode cycle. Figure 7.9a shows an example of one of these modes chosen from a strongly dipole active triplet, with a mode frequency  $\omega = 51 \, cm^{-1}$ .

While the number of modes in the upper cluster (32) is in good agreement with the number in the measured DOS, a glaring failure of our ionic model is in capturing relative in-

<sup>&</sup>lt;sup>10</sup>A back of the envelop calculation tells us that the frequency of this mode is approximately  $\omega_{max} = \sqrt{(wo + zo)/m_O}$ .



Figure 7.12: The integral of  $\sigma_1(\omega)$  as measured (dotted black line) and as calculated by our model (solid red line). The grey lines show the integrated conductivity calculated for free  $\text{ZrO}_6$  octahedra (long dashes) and free WO<sub>4</sub> tetrahedra (short dashes) in the same geometry as  $\text{ZrW}_2\text{O}_8$ , and with the parameters stated in Table 7.1.

tegrated oscillator strength of the upper and lower clusters. Figure 7.12 shows the integrated conductivity calculated from the modeling program with the parameters of Table 7.1. Experimentally, the ratio of strength of the upper to lower cluster is about 3:4, whereas our ionic model predicts a ratio closer to 1:4. Such a failure of the ionic model is treated in simple models of Szigeti(Szigeti, 1949) and Dick and Overhauser(Dick & Overhauser, 1958).

Mechanisms of NTE based on transverse thermal motion of oxygens in two-fold coordination (W-O-Zr) have been widely considered (Sleight, 1998; Mary et al., 1996; Evans et al., 1996; Pryde et al., 1996; Ramirez & Kowach, 1998; Ernst et al., 1998; David et al., 1999), however, Cao et al. (Cao et al., 2002; Cao et al., 2003) have proposed an alternative model, based on XAFS data, in which translation of WO<sub>4</sub> tetrahedra along the high-symmetry  $\langle 111 \rangle$ axes plays a key role. Ultimately the discussion of mechanism centers on the eigenvectors of the relevant phonon modes. For the range below about  $120 \, cm^{-1}$  our calculation generates 24 optic modes; of which 21 are associated with triplets. The two lowest energy modes are triplets at 34 and  $51 \, cm^{-1}$  respectively, in reasonable correspondence with the data. The eigenvectors for these modes exhibit a mixture of librational and translational motion, as illustrated in Figure 7.9a. A suitable choice of eigenvector within the triplet degeneracy manifold is required to clarify the motion in this way. For the mode shown, clock-wise rotation about the  $\langle 111 \rangle$  axis is accompanied by downward translation of the two tetrahedra along the  $\langle 111 \rangle$  axis<sup>11</sup>, giving rise to a sense of motion akin to that seen in a Wilberforce pendulum.

This mixing of translational and rotational (librational) motion is intimately related to the underconstrained nature of the  $ZrW_2O_8$  structure, in which each tertrahedron has an unconnected (terminal) oxygen at its (111) axis apex(Ramirez & Kowach, 1998). Because there are no strong second bonds for this unconstrained oxygen, translations of WO<sub>4</sub> tetrahedra along (111) axes do not involve significant bond compression and therefore project to very low frequency. There they tend to mix with the low frequency librational motion, and it is through this mixing that these low energy modes can acquire a dynamic dipole moment (since the WO<sub>4</sub> tetrahedra carry net charge). Our observation of non-zero dipole moment for many low energy modes indicates that this mixing is pervasive. Thus the richness of the low frequency infrared spectra is connected to the existence of the unconstrained oxygen and the related openness along the high symmetry (111) directions, which is a defining feature of the  $ZrW_2O_8$  structure and critical to NTE(Ramirez & Kowach, 1998; Ernst et al., 1998; David et al., 1999; Mittal & Chaplot, 1999; Allen & Evans, 2003).

<sup>&</sup>lt;sup>11</sup>For most parameter choices, this is one of the two lowest energy modes. In the other the  $\langle 111 \rangle$ -axis octahedra rotates opposite to the two tetrahedra. Two singlet modes with purely translational motion (along the  $\langle 111 \rangle$ -axes) also occur at relatively low frequencies which are sensitive to weak next-nearest-neighbor interactions.

## 7.9 Rotational Tunneling

Regarding the origins of anharmonicity in  $ZrW_2O_8$ , we note that, in the context of simple harmonic picture, the uncertainties in the circumferential oxygen position would be substantial. Using the frequency of the lowest optic mode  $(28 \, cm^{-1})$  one gets a theoretical (full width) uncertainty in the ground state of  $\Delta \theta = \sqrt{2\hbar/m_0 r^2 \omega} \simeq 14^\circ$  with a corresponding circumferential uncertainty  $\Delta(r\theta) \simeq 0.4$  Å. These increase to about 40° and 1.2 Å by room temperature. Such large values suggest a possible origin of anharmonicity and motivate consideration of the relevance of configurational tunneling or rotation to the low energy dynamics. Tunneling, rotation and configurational exchange phenomenon have been observed in systems with a similar 3-fold rotation axis involving methyl-group tetrahedra (Prager & Heidemann, 1997; Dimeo, 2002), where the breakdown of the harmonic approximation for low-energy librational motion has been carefully studied. For methyl-group tetrahedra such as CH<sub>3</sub>I the lowest librational mode frequency is typically  $80 \, cm^{-1}$ , about 3 times higher than  $\rm ZrW_2O_8$ . That most of this difference can be accounted for by the hydrogen-oxygen mass difference suggests a roughly comparable confining potential to lowest order. The potential relevance of finite barrier phenomena and large oxygen excursions to the the low-energy dynamics of  $\rm ZrW_2O_8$  is explored in greater detail in appendix B.

We have provided evidence for highly unusual low-energy phonon dynamics in  $\text{ZrW}_2\text{O}_8$ as reflected in our infrared spectra. We infer that the lowest optic modes in  $\text{ZrW}_2\text{O}_8$  tend to have a mixed librational and translational character in which the unconstrained oxygen plays an essential role, and it is likely that these modes play a central role in the mechanism of negative thermal expansion. While further work is needed to fully elucidate the mechanism of NTE in  $\text{ZrW}_2\text{O}_8$ , the present works shows that both librational and translational motions are operative: the transverse oxygen motion associated with libration provides NTE, while translational component within each mode frustrates a displacive (soft-mode) transition that would otherwise remove the unique structural environment in which these mixed phonon modes exist.

## Appendix A

# **Mechanical Drawings**

This Appendix presents some of the mechanical drawings made in the construction and design of the 66v/S vacuum extension described in section 3.3 and shown in Figure 3.3. The order follows roughly the Poynting vector of the beam, until full absorption after the detector window.



Figure A.1: The plane mirror mount M5.



Figure A.2: The base of the XYZ stage which holds the aperture A2.



Figure A.3: These mounts were made for the mirrors M7 and M8 for use in the evaporation chamber as well as for permanent use with the instrument.



Figure A.4: The mirrors M7, M8, and the aperture A2 sit on this aluminum "table". The "table" has three "legs", with positions chosen carefully to decouple the flexure of the main chamber from the optic component positions. These are shown as circles. The long slots are for depth adjustment of M7 and M8. A shorter slot was milled later for adjustability of the aperture position.



Figure A.5: This is the detector mating flange (DM in Figure 3.3). The angle here was chosen very carefully to give the best focal properties. The round end (right side of drawings on left) is made to accept a Davidson/bolometer dewar flange that came with the instrument. We had to customize aspects of this pre-existing system to fit our dewars, but also to make window flanges which allow the beam to leave the instrument.



flange for 5000cm-1 detector

Figure A.6: These Davidson/bolometer dewars related pieces are specially designed to accept the three slightly different dewars.



Figure A.7: This "window pane" piece can hold either a ZnSe or Quartz window in window flanges, similar to those shown in the previous figure.



Figure A.8: This is a drawing done in the final stages of construction showing almost all of the parts together, including the vacuum enclosure. The pieces of the vacuum enclosure follow below.



Figure A.9: The bottom of the main vacuum chamber.



Figure A.10: The majority of the top of the main vacuum chamber. The large hole is for the cryostat.



Figure A.11: The narrow piece of the top of the main vacuum chamber that sits nearest the instrument.



Figure A.12: This piece orients vertically and connects the main and narrow top pieces shown in the last two figures.



Figure A.13: The detector side of the main vacuum chamber. Later a large hole was drilled to allow the beam to exit through the detector mating flange (Figure A.5) and the appropriate hole pattern was also drilled.



Figure A.14: This piece mounts the main vacuum chamber against the side of the 66v.



Figure A.15: This piece is the end furthest from the instrument. A window was made to cover it (next figure), allowing visibility into the main vacuum chamber.


Figure A.16: This is the window for the end of the instrument. It is made of Lexan, a durable plastic used for Nalgene bottles and the transparent barriers between the front and back seats of police cars.



Figure A.17: This is the chamber side opposite the detector side. The hole is an access window. A plexiglass window with an o-ring groove covers it (the hole pattern was later made eight holes, instead of the four shown).



Figure A.18: This rather specialized piece sits on top of the instrument and holds the rotary motion feedthroughs above the mirrors they manipulate. This piece and the Lexan window for the chamber end were outsourced to Jerry Davis and his CNC shop, Davis Machining Products.





ed 80 tpi



Figure A.20: These are the same as the previous figure, but for the other two mirror screws.

## Appendix B

# On the Possibility of a Rotational Tunneling Effect in an Oxide

This appendix entertains the possibility that a rotational tunneling effect (RTE) could occur in an oxide. First, the experimentally well-established effect in methyl group (CH<sub>3</sub>containing) molecular crystals is outlined in the context of theory. Next, the application of these results to the hypothetical situation where the H atoms are replaced by O atoms is considered, including the caveat presented by the difference in nuclear spin. We then attempt to use a modified RTE theory to describe the low frequency optical data for  $ZrW_2O_8$  presented in chapter 7.

#### B.1 RTE in Methyl Molecular Crystals

The rotational tunneling effect is well documented (Prager & Heidemann, 1997; Press, 1981; Dimeo, 2002) in CH<sub>3</sub>-containing molecular crystals through a variety of experiments



Figure B.1: The CH<sub>3</sub>I complex discussed in the introduction of the RTE. The angle  $\theta$  describes the orientation about the C-I axis, as indicated by the arrow.

including inelastic neutron scattering, NMR, and infrared measurements. In these systems, exemplified here by the system  $CH_3I$ , a simple model called the single particle model is quite successful at describing the energy spectrum. In the single particle model, the orientation of the  $CH_3I$  group (see Figure B.1) is quantified by a single angle  $\theta$ , describing the orientation of the rigid methyl group about the C-I axis.

The Hamiltonian describing the orientational degree of freedom  $\theta$  is given by:

$$\mathcal{H} = \frac{L^2}{2I_H} + V(\theta) \tag{B.1}$$

where  $L = -i\hbar \frac{\partial}{\partial \theta}$  is the angular momentum operator and  $I_H \propto m_H$  is the moment of inertia of the CH<sub>3</sub>I group about the high symmetry ( $C_3$ ) axis. The potential  $V(\theta)$  describes the confining influence of the crystalline environment on the orientation of the methyl group.

The  $C_3$  symmetry of the methyl group allows us to represent the potential as a Fourier series:

$$V(\theta) = \sum_{j=1}^{\infty} \frac{V_{3j}}{2} (1 - \cos(3j\theta + \alpha_j))$$
 (B.2)

In practice, the lowest order coefficients in the expansion are dominant, and

$$V(\theta) = \frac{V_3}{2}(1 - \cos 3\theta) + \frac{V_6}{2}(1 - \cos(6\theta + \alpha))$$
(B.3)

adequately describes the energy levels of a host of many methyl complexes (for an extensive list, see "Rotational Tunneling and Neutron Spectroscopy: A Compilation" (Prager & Heidemann, 1997)). The parameter  $\alpha$  addresses the asymmetry of the potential about its minima. For these systems,  $V_3$  is typically of order  $40 \ meV$  ( $320 \ cm^{-1}$ ), but values in the range  $7 - 150 \ meV$ ( $56 \ cm^{-1}$ - $1200 \ cm^{-1}$ ) are observed.  $V_6$  is usually a small fraction(Dimeo, 2002) of  $V_3$ , typically  $0-0.15 \ V_3$ .

The energy level spacing plays a key role in the experimental determination of the coefficients and observation of the RTE. For a potential which supports several bound states, the barrier height is large, and the spacing between the lowest and first excited states is, to first order in  $V_3$ :

$$\omega_0 = 3\sqrt{\frac{V_3}{2I_H}} \tag{B.4}$$

This parameter quantifies the curvature at the bottom of the potential and represents the frequency at which the molecule would twist back and forth if the motion was classical and excursions from equilibrium were small compared to  $120^{\circ}$ . From a theoretical point of view, this approximation becomes increasingly good as  $V_3$  increases and the harmonic approximation of the well bottom becomes better and better.  $\omega_0$  is  $10 \, meV \ (80 \, cm^{-1})$  for CH<sub>3</sub>I with a barrier height of  $V_3 = 40 \, meV \ (320 \, cm^{-1})$ .

The origin of the RTE is the inevitable breakdown of the harmonic approximation. This breakdown is guaranteed by the fact that that a 120° rotation of the molecule produces an energetically equivalent state. This is a quality that the harmonic potential does not possess, and therefore the harmonic approximation must inevitably fail for large enough excursions from equilibrium.

The experimental crux of the RTE is the ability to sense when the harmonic approximation to the restoring potential becomes poor. To understand this in detail, we will consider the case where  $V_3$  is finite, and where  $\alpha_j$  and all other  $V_{3j} = 0$ :

$$\mathcal{H} = \frac{L^2}{2I_H} + \frac{V_3}{2}(1 - \cos 3\theta)$$
(B.5)

The barrier height is  $V_3$  and the potential has three minima, corresponding to the three distinct, but energetically equivalent, orientations of the methyl group. We will diagonalize this exemplary Hamiltonian in the free rotor basis.

The limit  $V_3 = 0$  in Eq. B.5 gives the Hamiltonian of a free rotor. The solution is similar to the familiar particle-in-a-box and the eigenstates are plane waves in the coordinate  $\theta$ :

$$\psi_m(\theta) = \langle \theta | m, \text{FR} \rangle = \frac{1}{\sqrt{2\pi}} e^{im\theta}$$
 (B.6)

with  $m = 0, \pm 1, \pm 2, \cdots$ . These states have energy  $E_m = \hbar^2 m^2 / 2I_H$ . The ground state here is nondegenerate (singlet), and every excited state is doubly degenerate (doublet). We will use these states as a basis to diagonalize the Hamiltonian with  $V_3 \neq 0$  below<sup>1</sup>.

In the opposite limit, where  $V_3$  is large, the three minima are separated by a large energy barrier, and so effectively decouple. Since the potentials are equivalent, a "single particle" would have the same energy in any one of these. As mentioned above, the high barrier limit is also the limit where the harmonic approximation to the well minima becomes very good. The states in this limit accordingly form triplets<sup>2</sup> with energy  $(n + \frac{1}{2})\hbar\omega_0$ . At intermediate values

$$|n, \frac{2\pi}{3}, \mathrm{HO}\rangle = |n, 1, \mathrm{HO}\rangle + e^{i2\pi/3}|n, 2, \mathrm{HO}\rangle$$
 (B.7)

$$+e^{i4\pi/3}|n,3,\mathrm{HO}\rangle$$
 (B.8)

$$|n,0,\mathrm{HO}\rangle = |n,1,\mathrm{HO}\rangle + |n,2,\mathrm{HO}\rangle + |n,3,\mathrm{HO}\rangle$$
 (B.9)

$$|n, -\frac{2\pi}{3}, \mathrm{HO}\rangle = |n, 1, \mathrm{HO}\rangle + e^{-i2\pi/3}|n, 2, \mathrm{HO}\rangle$$
 (B.10)

$$+e^{-i4\pi/3}|n,3,\mathrm{HO}\rangle$$
 (B.11)

<sup>&</sup>lt;sup>1</sup>Degeneracy arises from a symmetry operator which commutes with the Hamiltonian. In this case, the symmetry operator is the parity operator which mirrors the particle on the  $\theta$  axis. That is,  $P_{\theta}|\psi(\theta)\rangle = |\psi(-\theta)\rangle$ . One may then diagonalize the degenerate manifold of states with respect to the symmetry operator. Alternatively, we could diagonalize with respect to the  $2\pi$  rotation operator, which give the states in EquationB.15.

<sup>&</sup>lt;sup>2</sup>The symmetry operator  $\mathcal{R}(2\pi/3)$  commutes with the Hamiltonian and the diagonalization with respect to this operator leads to a linear combination of the "well"-indexed states:



Figure B.2: Level diagram of the potential  $\frac{V_3}{2}(1 - \cos 3\theta)$  versus the barrier height  $V_3$  with the moment of inertia appropriate to CH<sub>3</sub>I. In the low barrier limit, the eigenstates are free rotor doublets (D) and  $\mathcal{H}|n\operatorname{FR}\rangle \propto n^2|n\operatorname{FR}\rangle$ . At large barrier height, the low energy eigenstates are harmonic oscillator triplet (T) states (index j) and  $\mathcal{H}|n\operatorname{HO}\rangle \propto (n + \frac{1}{2})|n\operatorname{HO}\rangle$ . The solid vertical line represents the empirically determined barrier height of CH<sub>3</sub>I.

System	Crystal Structure	$V_3$	$V_6$
$CH_3F$	$P2_{1}/c$	26.6meV	0
$CH_{3}I$	Pnma	41.0meV	_
CH <sub>3</sub> COCOCH <sub>3</sub>	$P2_1/n$	129meV	30 meV
$(CH_3COO)_2Mn \cdot 4H_2O$	$P2_{1}/c$	7.4meV	—

Table B.1: Rotational tunneling parameters of some methyl group molecular solids. Taken from Prager and Heidemann, 1997.

of the barrier  $V_3$ , the crossover between the harmonic states at low energy and the free rotor states at high energy is roughly marked out by the barrier height. That is, for energies higher than the barrier, the states are free-rotor-like and for energies lower than the barrier the states are more harmonic-like. With increasing barrier height, doublet rotor wavefunctions evolve continuously into banded triplet harmonic oscillator wavefunctions. The manner in which the levels rearrange themselves to is depicted in Figure B.2. Every third doublet,  $|3m, \pm, FR\rangle$  splits into two singlets, one approaching the doublet below  $|3m-1, \pm, FR\rangle$  and the other approaching the one above,  $|3m + 1, \pm, FR\rangle$ , as the barrier height is increased.

#### B.2 Numerical Solution of the Rotor + Potential Hamil-

### tonian

We now show how to numerically solve for the energy levels of the Hamiltonian. The matrix elements of the full Hamiltonian (Equation B.2) with respect to this basis are:

$$\langle n|\mathcal{H}|m\rangle = \frac{\hbar^2 n^2}{2I_H} \delta_{n,m} + \frac{1}{2\pi} \int_0^{2\pi} \sum_{j=0}^{\infty} (1 - \cos\left(3j\theta + \alpha_j\right) e^{i(m-n)\theta} d\theta$$
(B.12)

$$= \frac{\hbar^2 n^2}{2I_H} \delta_{n,m} + \sum_{j=1}^{\infty} V_{3j} (2\delta_{n,m} - e^{-i\alpha_j} \delta_{m,n-3j} - e^{i\alpha_j} \delta_{m,n+3j}).$$
(B.13)

and  $\mathcal{R}(2\pi/3)|n,\varphi,\mathrm{HO}\rangle = e^{i\varphi}|n,\varphi,\mathrm{HO}\rangle.$ 

In our example choice of parameters, these matrix elements are:

$$\langle n|\mathcal{H}|m\rangle = \frac{\hbar^2 n^2}{2I_H} \delta_{n,m} + V_3 (2\delta_{n,m} - \delta_{m,n-3} - \delta_{m,n+3}).$$
 (B.14)

With these matrix elements in hand, we can find the energy levels for a given barrier height in our example Hamiltonian, Equation B.5, by diagonalizing a large block of the Hamiltonian with *Mathematica*. Fortunately, with modern laptop computers (ca. 2004), one can diagonalize a sparse matrix of order 100 in less than one second.

It is common practice to compare the results of such a calculation to an experimental determination of the energy structure, such as spectroscopy. This is commonly done in the context of rotational tunneling for the single particle model(Dimeo, 2002), but also frequently occurs in the more contemporary study of molecular magnetism(Gatteschi & Sessoli, 2003).

#### **B.3** Rotational Tunneling in an Oxide

The above discussion describes the well-established theory of the vibrational spectrum of molecular crystals containing  $CH_3$  groups. We now endeavor to consider the extension of this description to crystals which contain  $XO_3$  subunits, where X is any atom chemically capable of forming such a group. There are four effects that one can readily distinguish upon such a replacement in the theory outlined thus far.

First, the chemistry of the substitution could influence the magnitude of the confining potential  $V(\theta)$ . One is tempted to build expectations of these effects based on experience with the bonding character of oxygen versus hydrogen. However, a generic understanding of this change may not be possible, given the variety of confining potentials occurring among CH<sub>3</sub> systems, which indicates that the barrier height depends crucially on the chemical environment of the molecular group. We will therefore adopt an empirical approach that a measured spec-



Figure B.3: Same as Figure B.2, except that the moment of inertia was scaled by 16, as would be the case if the mass of H were increased to the mass of O.

trum will reveal the size of the molecular confining potential rather than attempting to build an expectation based on complicated chemistry details.

Second, the mass of a typical oxygen atom is 16 times that of a hydrogen atom. This mass increase affects a proportional increase in moment of inertia<sup>3</sup>, tending to decrease the level spacing by a factor of  $\sqrt{16} = 4$ . Figure B.3 shows the energy levels versus barrier height assuming the mass effect were the only player.

Third, the chemistry of the oxygen versus hydrogen bond is likely to significantly effect the size of the tetrahedron in question. In methyl complexes, the C-H distance is approximately 1.1 Å. X-O distances will typically be larger than this, increasing the moment of inertia and having the same effect as an additional mass increase over the factor of 16 due to the mass alone.

<sup>&</sup>lt;sup>3</sup>The replacement of X by C does not effect the moment of inertia.



Figure B.4: Same as Figure B.3, except with the additional wave function constraint  $\psi(0) = \psi(2\pi/3)$ . This constraint incorporates the higher symmetry introduced by the indistinguishability of the corner atoms and has the important effect of thinning the number of levels.

The fourth major effect arises from the difference of the nuclear spin of O versus H. The nuclear spin of  $O^{16}$  is zero. This isotope is by far the most abundant, comprising 99.9757% of all O found on earth. In contrast, the most abundant (99.9885%) isotope of H is H<sup>1</sup>; the H<sup>1</sup> nucleus is a single proton with spin 1/2. The presence of a nuclear spin is crucial to the experimental signature of the RTE through neutron scattering, but also plays a deeper role on the energy spectrum.

In the case of H, the spin 1/2 nucleus provides a quantum number that we can use to label the different orientations. For example, in the case of a very high barrier, the configuration  $|\uparrow\downarrow\uparrow\rangle$  is degenerate with, but distinguishable from, the state  $|\uparrow\uparrow\downarrow\rangle$ . These two states are also related by the symmetry operation performed by a 120° rotation.

In the case of a molecule with three  $O^{16}$  atoms, things are a bit different. A  $120^{\circ}$ 

rotation does not produce a distinct state because with O, there is no nuclear spin degree of freedom to distinguish these states. A 120° rotation of the molecule is in fact equivalent to a double exchange of identical bosons and hence the resultant wavefunction must be identically the same. The effect of this identical particle issue is to influence the degeneracy of the energy levels.

It seems reasonable to attempt to use the single particle model, but we should consider a modification to the single particle potential  $V(\theta)$  to account for the indistinguishability of the O atoms. This is done by restricting the initial basis states of the free rotor Hamiltonian to respect the identical particle symmetry<sup>4</sup>. For the free rotor states  $\psi_m(\theta)$ , only wavefunctions which are left invariant under a 120° rotation can be considered, since this rotation is equivalent to exchanging two bosons, twice. So for the single particle model appropriate to oxygen,

$$\psi_m(\theta) = \langle \theta | m, \text{FR} \rangle = \frac{1}{\sqrt{2\pi}} e^{im\theta}$$
 (B.15)

with  $m=0, \pm 3, \pm 6,...$  With this new basis, which respects the indistinguishability of the different orientations of and XO<sub>3</sub> group, calculation of the energy levels follows as before. A calculation similar to the one done for H is shown in Figure B.4.

#### **B.4** Experimental Outlook

We mentioned earlier that the classical vibration frequency arising from a high barrier potential is given by Equation B.4. This frequency can be observed as a sideband to a high frequency molecular excitation in a spectroscopic experiment. In the language of solid state physics, this frequency would be identified with a librational phonon and a signature could be observable at this frequency in a Raman or infrared spectroscopy experiment.

 $<sup>^4{\</sup>rm The}$  author would like to thank Onuttom Narayan (Narayan, 2004) for valuable input in approaching the implications of the O substitution presented in this section.



Figure B.5: A WO<sub>4</sub> tetrahedron.

It is natural to discuss where one may hope to find an oxide RTE, and in particular, in ZrW<sub>2</sub>O<sub>8</sub>. There are no known chemical considerations(Pickett, 2004) which prevent this possibility and so we will pursue this notion to the fullest extent possible within the context of the simple theory outlined so far. In Chapter 7 we discussed the structure of ZrW<sub>2</sub>O<sub>8</sub> as consisting of rigid WO<sub>4</sub> tetrahedra sitting in a  $C_3$  symmetric environment. If the restoring potential and bond lengths were to remain the same under the replacement of H with O, the effect of the substitution of O for H would be to lower the first librational frequency by a factor of  $\sqrt{I_H/I_O} = 1/4$ , giving a frequency of order  $2.5 \, meV \, (20 \, cm^{-1})$  for the confining potential CH<sub>3</sub>I (40  $meV=320 \, cm^{-1}$ ).

However, there is a significant difference in the moment of inertia arising from the large W-O distance in  $\text{ZrW}_2\text{O}_8$  compared with the C-H distance in CH<sub>3</sub>I. In the case of CH<sub>3</sub>I, the kinetic energy scale is  $\hbar^2/2I_H=654\mu eV$ . The analogous scale for WO<sub>4</sub> is  $I_H/I_O =$  $(1)(1.1\text{\AA})^2/(16)(1.8\text{\AA})^2 \simeq 1/43$  times smaller, giving  $\hbar^2/2I_O=15\mu eV$  for the relevant kinetic energy scale. With the difference in bond lengths under consideration, the first librational frequency would be a factor of  $\sqrt{I_H/I_O} = 1/6.5$  smaller.

Several features of the low frequency conductivity of  $ZrW_2O_8$  invite the consideration of RTE phenomena. First is the "counting problem". In Section 7.6.1, we showed that the



Figure B.6: The potential  $V(\theta) = \frac{V_3}{2}(1 - \cos 3\theta)$  with the reduced coordinate range  $-\pi/3 < \theta < \pi/3$  appropriate for O. Here  $V_3 = 13.4 \, meV = 108 \, cm^{-1}$ . Also plotted are the energy levels of this potential calculated with a moment of inertia  $I_O$  appropriate for oxygen. The  $|0\rangle \rightarrow |n\rangle$  transition energies are compared to the optical conductivity in Figure B.7

number of peaks in  $\sigma_1(\omega)$  below  $150 \, cm^{-1}$ , when interpreted conventionally, far exceeds the number expected based on the neutron density of states data(Ernst et al., 1998). One may ask then if these unusually low frequency peaks then all represent the electromagnetic response signature of a set of oscillations that contribute only a few modes worth of strength to the density of states. The similar sharp peaks below  $150 \, cm^{-1}$  occur in the sequence 20, 40, 61, 72, 92, 98, and  $126 \, cm^{-1}$ . The first three peaks of this sequence appear to mimic the "Balmer series" one expects from a harmonic ladder with resonant frequency  $\omega_0 = 20 \, cm^{-1}$ . The momentary tightening and then rarefying of the peak spacing as one moves up in frequency suggests that an effective potential which describes these energy levels might be represented by that discussed in the previous sections of this appendix and shown in Figure B.6.

We now compare the optical transitions of the single particle model to the low fre-



Figure B.7: An attempt to fit the low frequency conductivity of  $\text{ZrW}_2\text{O}_8$  with an O-adjusted version of the single particle model developed in this appendix. The barrier height used in this calculation is  $13.4 \, meV$  with a kinetic parameter  $\hbar^2/2I=65.4 \, \mu eV$ .

System	$I \left[ \operatorname{amu} \mathring{A}^2 \right]$	$\frac{\hbar^2}{2I} [\mu eV]$
$CH_3X$	3.19	654
$WO_4$	136.8	15.2
Fit	33.2	65.4

Table B.2: Moments of inertia and kinetic parameters for the RTE.

quency ( $\omega < 150 \, cm^{-1}$ ) conductivity peaks of ZrW<sub>2</sub>O<sub>8</sub>. Figure B.7 shows an attempt to do this by comparing the calculated  $|0\rangle \rightarrow |n\rangle$  transition frequencies of the simplified Hamiltonian B.5 to the 8 lowest sharp peaks in  $\sigma_1(\omega)$  of ZrW<sub>2</sub>O<sub>8</sub> at low temperature. The best agreement between the measured peak positions and single particle model occurs for the barrier height  $V_3 = 13.4 \, meV \, (108 \, cm^{-1})$  and a kinetic energy parameter  $\hbar^2/2I = 0.065 \, \mu eV$ .

The determination of the barrier height is constrained most fully by the pair of peaks<sup>5</sup> near 90  $cm^{-1}$ . Incidentally, the higher of these peaks displays a severe temperature dependent shift, redshifting by about  $7 cm^{-1}$  as temperature is dropped from room temperature to 20 K. In the RTE interpretation of this fit, this peak arises from transitions to a final state that sits on the very edge of the barrier.

The determination of the kinetic parameter  $\hbar^2/2I$  is made in the fit at fixed barrier height by adjusting the number of peaks in the spectrum. Remarkably, a two parameter fit to the single particle model represents the lowest 8 peaks in the spectrum of  $\text{ZrW}_2\text{O}_8$ . The moment of inertia found in this fit is 10 times that for CH<sub>3</sub>I, indicating that these energy levels could arise from a heavy version of a methyl-group system. However, this moment of inertia is still a factor of 4.3 too small to account for the full moment of inertia of the WO<sub>4</sub> tetrahedra in  $\text{ZrW}_2\text{O}_8$ .

 $<sup>{}^{5}</sup>$ This is done with the restricted basis set which accounts for the modified wavefunction symmetry imposed by the nuclear spin. Using the unrestricted basis gives additional transition frequencies, without affecting the existing ones.

#### B.5**Evaluation of Appendix B**

This unconventional view of the low frequency phonon spectrum produces a reasonablelooking fit in a physically motivated model considering the nuclear spin and rotational spectrum of WO<sub>4</sub> tetrahedra. It also addresses the "counting problem" mentioned above in that it this extreme anharmonicity obfuscates the mode counting interpretation of the neutron DOS<sup>6</sup>, and also introduces the breakdown of the zone-center phonon-branch intercept interpretation of the  $\sigma_1(\omega)$  peaks in a natural way.

While the gross overestimate of the moment of inertia for the  $WO_4$  tetrahedron produced by the considerations of this appendix (Table B.2) indicates that a simple RTE model alone does not account for the dynamics of  $ZrW_2O_8$ , the success of this model in fitting the peaks of  $ZrW_2O_8$  does, however, suggest that an effective potential theory may be a useful direction toward understanding the slow lattice dynamics relevant to NTE in  $ZrW_2O_8$ . It is conceivable that appropriate inclusion of the coordinated motion of the 8  $WO_4$  plus 4 Zr per unit cell in the formation of a symmetry-allowed low frequency triplet mode may effect the effective mass of the "single particle" in such a model.

While the theoretical basis of the RTE notion developed here is far from firm, one could address the importance of a rotational effect by an isotopic substitution of  $O^{17}$ , with nuclear spin 5/2, for the far more abundant  $O^{18}$  in an effort. This would introduce extra degeneracy in the RTE scenario and changes would be expected in the IR spectra as well as specific heat and probably neutron data as well. Large and unintuitive isotope effects are already known to exist in the microwave and far-infrared spectra of light atom materials (Kirby et al., 1970) where tunneling<sup>7</sup> is known to be important. Further work may be expected to reveal the degree

 $<sup>^{6}</sup>$ ...and similarly with the specific heat. The Einstein mode analysis typically performed on specific heat data and repeated in section 7.6.2 assumes a harmonic ladder of states in the partition function of the derivation and uses this fact to perform a geometric series summation. Harmonic ladder breakdown at the 4th ladder rung may have important effects even on the low temperature specific heat. <sup>7</sup>The reference addresses off-center Li<sup>+</sup> dopant tunneling in KCl:Li<sup>+</sup>.

RTE present in this oxide system.

## Bibliography

- Allen, J. & Martin, R. 1982, Phys. Rev. Lett., 49, 1106
- Allen, S. & Evans, J. S. O. 2003, Phys. Rev. B, 68, 134101
- Anderson, P. W. 1961, Phys. Rev., 124, 41
- Anderson, P. W. 1967, Phys. Rev., 164, 352
- Anderson, P. W. 1972, Science, 177, 393
- Anderson, P. W. & Yuval, G. 1969, Phys. Rev. Lett., 23, 89
- Anderson, P. W., Yuval, G., & Hamann, D. R. 1970, Phys. Rev. B, 1, 4464
- Andrei, N. 1980, Phys. Rev. Lett., 45, 379
- Antonov, V. N., Galli, M., Marabelli, F., Yaresko, A. N., Perlov, A. Y., & Bauer, E. 2000, *Phys. Rev. B*, 62, 1742
- Ashcroft, N. W. & Mermin, N. D. 1976, Solid State Physics, Saunders College
- Auray, M., Quarton, M., & LeBlanc, M. 1995, Acta Cryst., C51, 2210
- Barker, A. S. 1964, *Physical Review*, 135, 742
- Bethe, H. 1931, Z. Phys., 71, 205
- Bickers, N., Cox, D., & Wilkins, J. 1987, Phys. Rev. B, 36, 2036
- Bridges, F. 2003, personal communication

Cao, D., Bridges, F., Kowach, G. R., & Ramirez, A. P. 2002, Phys. Rev. Lett., 89, 215902/1

- Cao, D., Bridges, F., Kowach, G. R., & Ramirez, A. P. 2003, Phys. Rev. B, 68, 14303
- Chen, B., Muthu, D. V. S., Liu, Z. X., Sleight, A. W., & Kruger, M. B. 2001, Phys. Rev. B, 64, 214111/1
- Coleman, P. 1987, Phys. Rev. Lett., 59, 1026
- Coqblin, B. & Schrieffer, J. R. 1969, Phys. Rev., 185, 847
- Cornelius, A. L., Lawrence, J. M., Sarrao, J. L., Fisk, Z., Hundley, M. F., Kwei, G. H., Thompson, J. D., Booth, C. H., & Bridges, F. 1997, *Phys. Rev. B*, 56, 7993
- Cox, D., Tannous, C., & Wilkins, J. 1986, Phys. Rev. B, 33, 2132
- Cox, D. L. 2003, personal communication.
- Dallera, C., Grioni, M., Shukla, A., Vanko, G., Sarrao, J., Rueff, J., & Cox, D. 2002, Phys. Rev. Lett., 88, 196403
- Damascelli, A., Schulte, K., van der Marel, D., & Menovsky, A. A. 1997, *Phys. Rev. B*, **55**, R4863
- David, W. I. F., Evans, J. S. O., & Sleight, A. W. 1999, Europhys. Lett., 46, 661
- de Haas, W. J., de Boer, J., & van den Berg, G. J. 1934, Physica, 1, 1115
- Degiorgi, L. 1999, Rev. Mod. Phys., 71, 687
- Demsar, J., Averitt, R. D., Ahn, K. H., Graf, M. J., Trugman, S. A., Kabanov, V. V., Sarrao, J. L., & Taylor, A. J. 2003, *Phys. Rev. Lett.*, **91**, 027401
- Dick, B. G. & Overhauser, A. W. 1958, Phys. Rev., 11, 90
- Dimeo, R. M. 2002, Am. J. Phys., 71, 885
- Dressel, M. & Gruner, G. 2002, *Electrodynamics of Solids: Optical Properties of Electrons in Matter*, Cambridge University Press
- Dresselhaus, M. 2001, MIT Open Courseware, Solid State Physics, pp Part II, Optical Prop-

erties of Solids

- Dzero, M., Gor'kov, L., Fisk, Z., & Zvezdin, A. 2002, Physica B, 312-313, 321
- Edwards, D. M. 1988, in *Narrow Band Phenomenon*, NATO ASI Series, p. 23, Plenum, New York
- Ernst, G., Broholm, C., Kowach, G. R., & Ramirez, A. P. 1998, Nature, 396, 147
- Evans, J. S. O., Mary, T. A., Vogt, T., Subramanian, M., & Sleight, A. W. 1996, Chem. Mater., 8, 2809
- Fano, U. 1961, Phys. Rev., 124, 1866
- Felner, I. & Nowik, I. 1986, Phys. Rev. B, 33, 617
- Figueroa, E., Lawrence, J., Sarrao, J., Fisk, Z., Hundley, M., & Thompson, J. 1998, Solid State Commun., 106, 347
- Foster, C. M., Grimsditch, M., Li, Z., & Karpov, V. G. 1993, Phys. Rev. Lett., 71, 1258
- Freericks, J. K. & Zlatic, V. 2003a, Phys. Stat. Sol. B, 236, 256
- Freericks, J. K. & Zlatic, V. 2003b, Rev. Mod. Phys., 75, 1333
- Garner, S. L., Hancock, J. N., Rodriguez, Y. W., Schlesinger, Z., Bucher, B., Sarrao, J. L., & Fisk, Z. 2000, Phys. Rev. B, 62, R4778
- Gatteschi, D. & Sessoli, R. 2003, Angewandte Chemie Int. Ed., 42, 268
- Georges, A., Kotliar, G., Krauth, W., & Rozenberg, M. 1996, Rev. Mod. Phys., 68, 13
- Grewe, N. 1984, Z. Phys. B, 56, 111
- Griffiths, D. J. 1994, Introduction to Quantum Mechanics, Prentice Hall
- Griffiths, D. J. 1998, Introduction to Electrodynamics, Prentice Hall
- Guinea, F., Bascones, E., & Calderon, M. J. 1997, in F. Mancini (ed.), Lectures on the Physics of Highly Correlated Electron Systems, AIP Conference Proceedings, pp 1–82, American Institute of Physics, Woodbury, New York

Gupta, S. & Katiyar, R. S. 2001, Journal of Raman Spectroscopy, 32, 885

- Hancock, J. N., McKnew, T., Schlesinger, Z., Sarrao, J. L., & Fisk, Z. 2004a, Phys. Rev. Lett., 92, 186405
- Hancock, J. N., Turpen, C. A., Schlesinger, Z., Kowach, G. R., & Ramirez, A. P. 2004b, Phys. Rev. Lett., 93, 225501
- Harter, W. G. 1993, Principles of Symmetry, Dynamics, and Spectroscopy, Wiley
- Haule, K., Oudovenko, V., Savrasov, S., & Kotliar, G. 2004, cond-mat/0403086
- Hauser, R., Naber, L., Schaudy, G., Bauer, E., Hilscher, G., Kindler, B., & Assmus, W. 1996, *Czech. J. Phys.*, 46, 2543
- Hewson, A. C. 1993, The Kondo Problem to Heavy Fermions, Cambridge University Press
- Ibach, H. & Luth, H. 1995, Solid State Physics: An Introduction to the Principles of Materials Science, Springer
- Immer, C., Sarrao, J., Fisk, Z., Lacerda, A., Mielke, C., & Thompson, J. 1997, Phys. Rev. B, 56, 71
- Jarrell, M. 1995, Phys. Rev. B, 51, 7429
- Jorgensen, J. D., Hu, Z., Teslic, S., Argyriou, D. N., Short, S., Evans, J. S. O., & Sleight, A. W. 1999, Phys. Rev. B, 59, 215
- Joyce, J., Andrews, A., Arko, A., Bartlett, R., Blythe, R., Olson, C., Benning, P., Canfield, P., & Poirier, D. 1996, Phys. Rev. B, 54, 17515
- Kadowaki, K. & Woods, S. B. 1986, Solid State Comm., 58, 507
- Kindler, B., Graf, R., Ritter, F., Assmus, W., & Luthi, B. 1994, Phys. Rev. B, 50, 704
- Kirby, R. D., Hughes, A. E., & Sievers, A. J. 1970, Phys. Rev. B, 2, 481
- Kondo, J. 1964, Prog. Theor. Phys., 32, 37
- Kowach, G. R. 2000, J. Cryst. Growth, 212, 167

- Krishnamurthy, H. R., Wilkins, J. W., & Wilson, K. G. 1980a, Phys. Rev. B, 21, 1003
- Krishnamurthy, H. R., Wilkins, J. W., & Wilson, K. G. 1980b, Phys. Rev. B, 21, 1044
- Landau, L. D. & Lifshitz, E. M. 1980, Statistical Physics, v. 2, Pergamon Press
- Lawrence, J., Kwei, G., Canfield, P., DeWitt, J., & Lawson, A. 1994, Phys. Rev. B, 49, 1627
- Lawrence, J., Shapiro, S., Sarrao, J., & Fisk, Z. 1997, Phys. Rev. B, 55, 14467
- Lindley, D. 2004, Phys. Rev. Focus, 14, 21
- Lovesey, S. W. 1984, *Theory of Neutron Scattering from Condensed Matter*, Oxford University Press
- Mahan, G. D. 1990, Many-Particle Physics, Plenum Publishing Corp.
- Mai, T. T. 2004, personal communication
- Marabelli, F. & Bauer, E. 1993, Journal of Applied Physics, 73, 5418
- Marion, J. & Thornton, S. 1980, Classical Dynamics of Particles and Systems, McGraw-Hill
- Mary, T. A., Evans, J. S. O., Vogt, T., & Sleight, A. W. 1996, Science, 272, 90
- Millis, A. J., Lavagna, M., & Lee, P. A. 1987, Phys. Rev. B, 36, 864
- Millis, A. J. & Lee, P. A. 1987, Phys. Rev. B, 35, 3394
- Mittal, R. & Chaplot, S. L. 1999, Phys. Rev. B, 60, 7234
- Mittal, R., Chaplot, S. L., Kolesnikov, A. I., Loong, C. K., & Mary, T. A. 2003, Phys. Rev. B, 68, 54302
- Mittal, R., Chaplot, S. L., Schober, H., & Mary, T. A. 2001, Phys. Rev. Lett., 86, 4692
- Mushnikov, N., Goto, T., Yoshimura, K., & Zhang, W. 2003, Physica B, 334, 54
- Muthu, D. V. S., Chen, B., Sleight, A. W., Wrobel, J. M., & Kruger, M. B. 2002, Solid State Commun., 122, 25

Narayan, O. 2003, personal communication

- Narayan, O. 2004, personal communication
- Ouyang, L., Xu, Y.-N., & Ching, W. Y. 2002, Phys. Rev. B, 65, 113110
- Pauling, L. 1960, The Nature of the Chemical Bond and the Structure of Molecules and Crystals, Cornell University Press
- Pickett, W. E. 2004, personal communication
- Prager, M. & Heidemann, A. 1997, Chem. Rev., 97, 2933
- Press, W. 1981, Single Particle Rotations in Molecular Crystals, Springer
- Pryde, A. K. A., Hammonds, K. D., Dove, M. T., Heine, V., Gale, J. D., & Warren, M. C. 1996, J. Phys. Cond. Matt., 8, 10973
- Rajan, V. 1983, Phys. Rev. Lett., 51, 308
- Ramirez, A. P. 1994, Annual Review of Materials Science, 24, 453
- Ramirez, A. P. 2001, in N. P. Ong (ed.), More is Different: Fifty Years of Condensed Matter Physics, Princeton Series in Physics, pp 255–264, Princeton University Press, Princeton, NJ
- Ramirez, A. P. 2004, personal communication
- Ramirez, A. P. & Kowach, G. R. 1998, Phys. Rev. Lett., 80, 4903
- Ravindran, T. R., Arora, A. K., & Mary, T. A. 2000, Phys. Rev. Lett., 84, 3879
- Ravindran, T. R., Arora, A. K., & Mary, T. A. 2001, Journal of Physics: Condensed Matter, 13, 11573
- Ravindran, T. R., Arora, A. K., & Mary, T. A. 2003, Phys. Rev. B, 67, 64301
- Reinert, F., Claessen, R., Nicolay, G., Ehm, D., Hufner, S., Ellis, W., Gweon, G., Allen, J., Kindler, B., & Assmus, W. 1998, *Phys. Rev. B*, 58, 12808
- Sarrao, J. 1999, Physica B, 259-261, 128

- Sarrao, J., Immer, C., Benton, C., Fisk, Z., Lawrence, J., Mandrus, D., & Thompson, J. 1996, *Phys. Rev. B*, 54, 12207
- Sarrao, J., Ramirez, A., Darling, T., Freibert, F., Migliori, A., Immer, C., Fisk, Z., & Uwatoko, Y. 1998, Phys. Rev. B, 58, 409
- Scalletar, R. 2003, personal communication
- Schroder, A., Aeppli, G., Coldea, R., Adams, M., Stockert, O., Lohneysen, H. v., Bucher, E., Ramazashvili, R., & Coleman, P. 2000, *Nature*, 407, 351
- Shastry, B. S. 2004, personal communication
- Sievers, A. J. 2004, personal communication
- Sleight, A. W. 1998, Current Opinion in Solid State and Materials Science, 3, 128
- Sleight, A. W. 2004, personal communication
- Stephens, T. November 18, 2004, UCSC Press Release
- Stewart, G. 1984, Rev. Mod. Phys., 56, 775
- Svechkarev, I., Panfilov, A., Dolja, S., Nakamura, H., & Shiga, M. 1999, J. Phys.: Cond. Mat., 11, 4381
- Szigeti, B. 1949, Trans. Faraday Soc., 45, 155
- Tahvildar-Zadeh, A., Jarrell, M., Pruschke, T., & Freericks, J. 1999, Phys. Rev. B, 60, 10782
- van der Marel, D., Kim, J. H., Feenstra, B. J., & Wittlin, A. 1993, Phys. Rev. Lett., 71, 2676
- Varma, C. M. 1976, Rev. Mod. Phys., 48, 219
- Vidhyadhiraja, N., Smith, V., Logan, D., & Krishnamurthy, H. 2003, J. Phys.: Cond. Mat., 15, 4045
- Weibel, P., Grioni, M., Malterre, D., Dardel, B., Baer, Y., & Besnus, M. 1993, Z. Phys. B, 91, 337
- Wiegmann, P. B. 1980, Sov. Phys. JETP Lett., 31, 392

Wilson, K. G. 1980, Rev. Mod. Phys., 47, 733

Witten, E. 1978, Nucl. Phys. B, 145, 110

Wooten, A. 1972, Optical Properties of Solids., Academic Press

- Yamamura, Y., Nakajima, N., Tsuji, T., Koyano, M., Iwasa, Y., Katayama, S., Saito, K., & Sorai, M. 2002, *Phys. Rev. B*, 66, 014301/1
- Zener, C. 1951, Phys. Rev., 81, 440
- Zheng, N., Bu, X., & Feng, P. 2003, Nature, 426, 428
- Zlatic, V. & Freericks, J. K. 2001, Acta Phys. Polon. B, 32, 3253