

TWO-PHOTON EXCITATIONS OF HIGHER 5d STATES IN $\text{Ce}^{3+}:\text{CaF}_2$

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The investigations of 4f→5d two-photon transitions of Ce^{3+} in CaF_2 from 33 900 to 50 500 cm^{-1} is presented. At the low-energy end, the observed two-photon excitation spectrum for a 0.003% sample consists of a broad vibronic band arising from transitions to the second 5d orbital of the C_{4v} cerium center, a transition which is dipole allowed but not observed in one-photon absorption. At higher cerium concentrations, the band shows a contribution from O_h centers. Two-photon transitions to two other higher 5d orbitals constitute the high-energy end of the spectra.

The 4f→5d near-UV transitions in $\text{Ce}^{3+}:\text{CaF}_2$ are dipole allowed in one-photon absorption (OPA) but are first order parity forbidden for two-photon absorption (TPA). However, odd-crystal field parity mixing relaxes this restriction and a TP transition from the 4f ground state to the lowest 5d state has been observed.¹ In this paper we report on TP excitation measurements to the higher 5d states. The two-photon transitions were measured by monitoring the Ce^{3+} fluorescence (3100-3550 Å) following excitation by a 5-nsec pulse from a tunable dye laser. The experimental apparatus is similar to that used before,¹ except for additional scattered-light-rejecting filters.

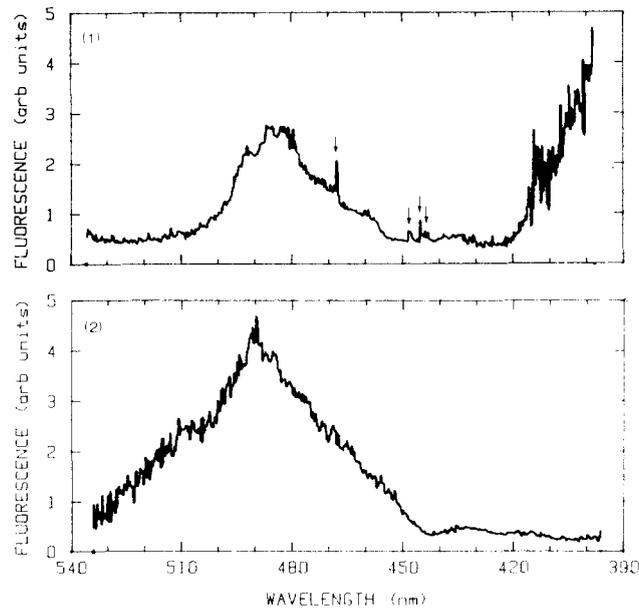
In the low-concentration samples, the dominant site symmetry of the Ce^{3+} ion is C_{4v} . The crystal-field and spin-orbit interactions completely remove the orbital degeneracy. Of the five expected 5d bands, only four, labelled B, E, F and G with peaks around 3090, 2020, 1954 and 1873 Å are observed in the OPA spectrum, with the fifth corresponding to a transition to the second 5d level predicted to peak around 2600 Å. Two "cluster bands", C and D, which originate from absorption by clusters of two or more cerium ions, with peaks around 2407 and 2135 Å are also observed.² At 4 K and for low Ce^{3+} concentration, the OP spectrum of the B band consists of a sharp no-phonon line at 3132 Å and is accompanied by a vibrational sideband which shows both one- and multiphonon contributions, all attributable to the C_{4v} -center transitions. At concentrations over 0.05%, the O_h -center no-phonon line and its prominent vibrational satellite (490 cm^{-1} apart) start to appear in the high-energy side

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of the B band, and becomes dominant for the 0.1-1% concentration range.³ The TP spectrum of the B band for 0.003% Ce³⁺:CaF₂ at 6 K consists of the C_{4v}-center no-phonon line, its one-phonon vibrational sideband which has some features in common with the OPA spectra, and multiphonon contributions. The TP cross section has a dependence on laser polarization which is consistent with C_{4v} site symmetry for the no-phonon transition, but is isotropic for the multiphonon sideband, where the superimposed contributions from different vibrations with, in general, different symmetries (both even and odd vibrational modes may appear for the noncentrosymmetric C_{4v} center) average out angular variations.¹ The B band TP spectrum for a 0.1% sample shows additional features in the multiphonon sideband which have a polarization anisotropy consistent with O_h site symmetry, but absent are the O_h-center no-phonon line and its 490-cm⁻¹ symmetric vibrational satellite. For the O_h centers, the 4f→5d TP transitions become "allowed" due to coupling with odd-parity phonon modes, which have been found to preserve the expected polarization anisotropy.⁴

With this behavior of the B-band TP spectra in mind, we now turn to the analysis of TP spectra arising from transitions to higher 5d states as displayed in Figs. 1 and 2. The most prominent feature in both spectra is the broad vibronic band at the low-energy end, which we attribute to a TP transition to the second 5d level, a transition not observed in OPA. The TP cross section shows a strong polarization anisotropy consistent with O_h site symmetry over the entire band for the 0.1% sample, but is isotropic for the 0.003% sample. This difference, together with the differences in shape, spectral width and peak position of the band in the two samples, and the close parallelism of the present situation with that discussed earlier for the high-energy end of the B band, lead us to conclude that for the 0.003% sample, the C_{4v}-center multiphonon transitions mainly contribute to the strength of the second 5d band, while for the 0.1% sample, the superimposed contributions from O_h centers dominate. The 5d level of the O_h center involved here is presumably the Jahn-Teller-coupling split higher e_g level. We estimate a value of 7500 cm⁻¹ for this splitting, which is rather large, though smaller than the value of 10Dq (17 000 cm⁻¹).

The second 5d band peaks around 4820 Å which is different from the predicted value, but overlaps the corresponding position of the cluster band C. However, this cannot be a cluster band since: (i) we monitor the fluorescence over the single Ce³⁺-ion emission band and it is unlikely that the cerium-ion clusters will also fluoresce in the same spectral range; (ii) the cluster band D is not observed in the TP excitation spectra; and (iii) the polarization anisotropy is completely different for the two concentrations.



Two-photon excitation spectra of 0.003% (Fig. 1) and 0.1% (Fig. 2) $\text{Ce}^{3+}:\text{CaF}_2$ at 80 K. The dye laser beam is incident along the [100] axis and is linearly polarized along the [010] axis of the CaF_2 host.

The 4100-3960 Å range of the TP excitation spectra corresponds to the E band and part of the F band. These bands are vibronic in nature and there is no polarization anisotropy of the TP cross section for these bands. Above 3960 Å, the filters start to transmit scattered dye laser light prohibiting any meaningful measurements. In the 5900-5400 Å range there is little TP signal. A number of sharp resonance lines (marked by arrows in Fig. 1) appear between 4690 and 4400 Å only in the TP spectrum of the 0.003% sample. The measured 400-μsec fluorescence lifetime of these transitions indicates that they probably arise from TP transitions in some other rare earth ion, which are always present in small amounts.

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