Two-photon absorption spectroscopy of multisite Gd^{3+} in CaF_2

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The energy levels of Gd^{3+} in the ^6P, ^6I, and ^6D $4f^7$ configuration in cubic, tetragonal, and cluster sites in CaF_2 have been excited by two-photon absorption. The relative two-photon intensities and polarization dependence show behavior which is similar to that previously observed for Gd^{3+}:LaF_3 and Eu^{2+}:CaF_2 and which requires higher-order perturbation theory in the virtual intermediate $4f^6 5d$ configuration.

INTRODUCTION

A systematic investigation of electric dipole two-photon transitions within the $4f^7$ configuration of trivalent and divalent rare-earth (RE) ions in crystals has been reported recently.[1–4] The standard second-order theory for two-photon transitions had to be extended to include higher-order contributions which take into account spin-orbit and crystal-field interactions among the $4f^6 5d$ intermediate states. In this manner two-photon absorption has proved to be a useful spectroscopic tool complementary to one-photon spectroscopy.[5]

We have extended this study to a multisite system, Gd^{3+} in CaF_2. Charge-compensating defects result in different rare-earth site symmetries in this structure. Makovsky[6,7] has identified optical spectra in specimens submitted to various thermal treatments. Studies of the luminescence and absorption spectra have also been reported by Gilfanov and co-workers.[8] Merz[9] observed the thermoluminescence spectrum, as did Schlesinger and Whippey.[10] Zeeman studies were performed by Detrio[11] for the ^6P group. Through these studies the identification, energy, and symmetry of the crystal-field components of the $^6P_{7/2}$, $^6P_{5/2}$ subgroup were definitively established for several sites. Recordings of one-photon spectra for the ^6I configuration were also presented in some of these studies. Crosswhite, Schwiesow, and Carnall[12] correlated several strong one-photon absorption features with the ^6I, ^6D, and higher levels and presented recordings for the ^6G and higher groups. O'Hare and Donlan[13] performed a calculation of the energy-level position of ^6P, ^6I, and ^6D configuration in a cubic crystal field.

In this paper the two-photon spectra are reported for the ^6P, ^6I, and ^6D multiplets in crystals of Gd^{3+}:CaF_2 having cubic and tetragonal sites, as well as sites arising from aggregates of Gd^{3+} ions.

EXPERIMENTAL

We have performed two-photon-absorption (TPA) measurements on Gd^{3+}:CaF_2 samples of various nominal concentrations (0.01, 0.1, 0.2, 1.16, and 1.5 mol %). The 0.2 mol % specimen was obtained from Optovac, Inc., and the others were grown by Merz.[9] The two-photon excitation spectrum of the 1.16 mol % samples were recorded over the range extending from $2\nu_{\text{laser}}=31\,000$ to $41\,200$ cm^{-1}. The remaining samples were studied in selected

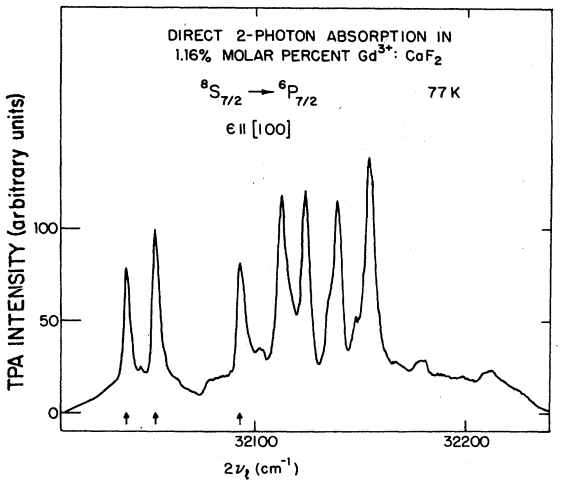

FIG. 1. Two-photon excitation of the $^6P_{7/2}$ levels in 1.16 mol % Gd^{3+}:CaF_2 at 77 K. The polarization of the exciting laser was parallel to the (1,0,0) cubic axis. The experimental trace recordings are not corrected for changes in dye-laser efficiency. Vertical lines indicate lines arising from cubic sites.

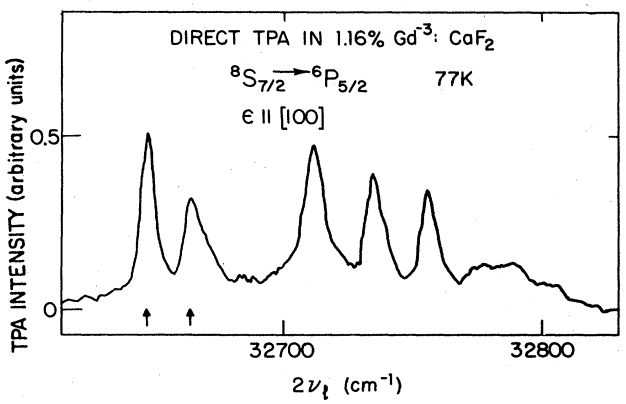

FIG. 2. Two-photon excitation of the $^6P_{5/2}$ levels in Gd^{3+}:CaF_2. All other details are the same as for Fig. 1.

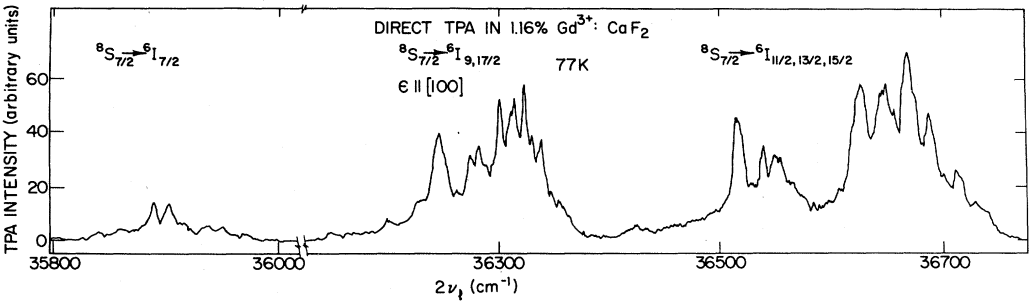

FIG. 3. Two-photon excitation of the ^6I multiplets in Gd^{3+}:CaF_2.

ranges, with emphasis on the range from 31 800 to 32 600 cm^{-1}. Recordings for the 1.16 mol % samples are presented in Figs. 1—4. The vertical scales of these figures are labeled to indicate the TPA intensity on an internally consistent scale in arbitrary units not normalized point by point. Absolute line positions were determined with an accuracy of only ± 5 cm^{-1}, except when noted. The line spacings within a single multiplet are accurate to ± 2 cm^{-1}. Relevant details of the experimental procedure and apparatus have been reported earlier.[1]

RESULTS AND DISCUSSION

The spectra presented in Figs. 1—4 appear concentrated in three well-separated groups along the energy scale. These groups appear to have an overall displacement towards lower energies, compared to similar groupings observed in the Gd^{3+}:LaF_3 case.[1] The three groups are expected to correspond to transitions from the ground state $^8S_{7/2}$ to the ^6P [(32 000—32 800)-cm^{-1} range; see Figs. 1 and 2], ^6I [(35 800—36 800)-cm^{-1} range; see Fig. 3], and ^6D [(39 450—41 200)-cm^{-1} range; see Fig. 4] groupings of multiplets, respectively.

The identification of the energy levels for the ^6P group is facilitated by the clear separation of the subgroups of lines. The lines of the $^6P_{7/2}$ multiplet lie in the (32 000—32 250)-cm^{-1} range and are shown in Fig. 1. The lines belonging to the $^6P_{5/2}$ multiplet lie in the (32 600—32 800)-cm^{-1} range and are shown in Fig. 2. This identification was already performed in the earlier one-photon spectroscopic studies of these multiplets, which also provided an assignment of the spectral lines pertaining to various sites. Transitions to the $^6P_{3/2}$ multiplet proved too weak for detection.

Gilfanov *et al.*[8] and Makovsky[7] found that the occurrence of the various sites in Gd^{3+}:CaF_2 fluorescence spectra was dependent on the concentration of the RE ions. Makovsky identified, among several others, a cubic site labeled C, a tetragonal F^--Gd^{3+} site labeled A, and two sites formed by energetically favored clusters of Gd^{3+} ions, labeled as Q and B. He found that at room temperature only sites A and C are present in the spectrum of crystals of 10^{-4} mol %, with the site A much more intense. At about 0.01 and 0.5 mol %, sites B and Q can be detected. At about 0.1 mol %, site A begins to weaken, as happens to site B at higher concentrations. Only sites C and Q are present at about 2 mol %.

Noting that our concentration values are only nominal, we found, from comparison with Makovsky's results, that for our 0.01 mol % specimen only tetragonal A centers are observed. The 0.1 and 0.2 mol % samples exhibited cubic C sites and cluster Q sites in addition to the tetragonal A ones. The tetragonal A sites are no longer discernible in the 1.16 and 1.5 mol % specimens, for which only the cubic and Q cluster sites remained clearly distinguishable, although the presence of small concentrations of other, not-yet-indentified sites was evident.

The presence of cubic sites in addition to the noncubic ones can be ascertained by considering the number of Stark components in a given J multiplet. For the noncu-

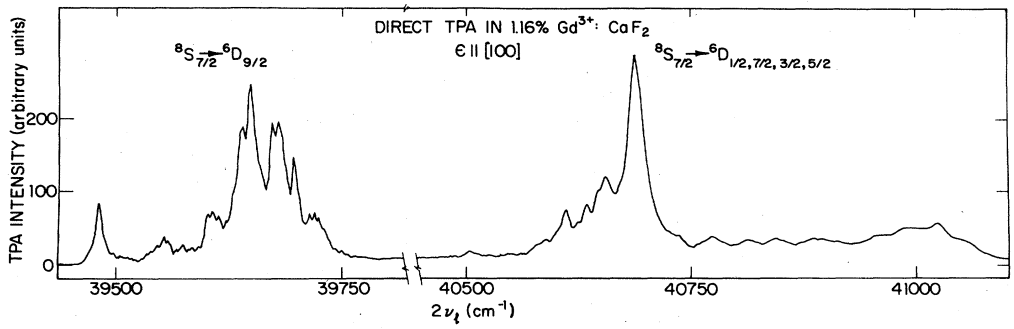

FIG. 4. Two-photon excitation of the ^6D multiplets in Gd^{3+}:CaF_2.

bic fields the $^6P_{7/2}$ and $^6P_{5/2}$ levels are split into 4 and 3 Kramers doublets, respectively, while for the cubic sites the corresponding numbers are 3 and 2. The total number of prominent lines shown in Fig. 1 is in agreement with these assignments. The lines arising from cubic sites, identified by Makovsky,[6,7] which are weak in the one-photon absorption spectrum because of parity-selection rules in the presence of a center of inversion, appear with strength equal to those arising from other sites in the TPA spectra shown in Figs. 1 and 2.

The level positions of all Stark components of the C and A sites were measured to within ± 3 cm^{-1} and agree with those supported by Makovsky.[7] Within this accuracy and in order of increasing energy, the Q-site Stark-level positions, identified by comparison with Makovsky's work[6] but not given numerically in it are, for $^6P_{7/2}$, 32 114, 32 126, 32 143, and 32 159 cm^{-1}; and for $^6P_{5/2}$, 32 703, 32 725, and 32 746 cm^{-1}. TPA spectroscopy thus supplements one-photon spectroscopy in the assignment of individual lines by comparison of specimens with predominant concentrations of the various sites.

With decreasing wavelength of the dye laser, we next encounter the ^6I group. From the known level sequence in the LaF_3 and in other hosts we can assign the observed subgroups of lines to the ^6I levels. The two-photon absorption lines for this configuration are shown in Fig. 3. We expect the first subgroup, encountered within the range from 35 800 to 36 000 cm^{-1}, to correspond to the $^6I_{7/2}$ level. Next we find a subgroup which should correspond to the $^6I_{9/2}$ and $^6I_{17/2}$ multiplets, in the range 36 100—36 400 cm^{-1}. A subgroup which should correspond to the $^6I_{11/2,15/2,13/2}$ multiplets is encountered next in the range 36 400—36 800.

The appearance of broad features, evident also in the reports of Gilfanov *et al.*[8] and of Schlesinger and Whippey,[10] makes the ^6I spectra different from the LaF_3 case, however, and are reminiscent of the TPA observations[2] for Eu^{2+} in CaF_2 and SrF_2. The overall structure of the spectrum closely resembles that obtained by Antic-Fidancev and co-workers in their recently reported one-photon spectrum of Gd_2O_3.[14] Indeed, these workers found the ^6I multiplets grouped in a similar way to our results. They suggested that some of the broad lines they observed could be due to a superposition of several lines. This would be enhanced in the CaF_2 by the occurrence of more than one site, as already evident in the ^6P spectra. Also, as in the Gd_2O_3 study, the number of prominent lines observed does not correspond to the number expected theoretically for the principal sites present.

Considerations similar to the ones above lead to the assignment of the Gd^{3+} ^6D_J subgroups. The observed two-photon spectra are shown in Fig. 4. To our knowledge spectral recordings of these levels have not been reported heretofore for Gd^{3+}:CaF_2. We encounter the $^6D_{9/2}$ multiplet in the (39 450—39 800)-cm^{-1} range, and a large subgroup corresponding to the $^6D_{1/2,7/2,3/2,5/2}$ multiplets, in the range 40 500—41 200 cm^{-1}. The $^6D_{7/2}$ multiplet appears to overlap more than in the Gd_2O_3 case, where they were distinguishable, due to the occurrence of more than one site. No lines stand out prominently above the featured background where the $^6D_{1/2}$, $^6D_{3/2}$, and $^6D_{5/2}$ multiplets would be expected. All Gd^{3+} subgroups assigned in this manner show an overall displacement of their onset towards wavelengths longer than those seen in the LaF_3 host, but less than those found in the spectrum of Gd_2O_3.[14] This is also observed for the $^6P_{7/2,5/2}$ multiplets. A similar assignment has been made in the work of Crosswhite *et al.*[12] for the strongest absorption features exhibited by a specimen with the relatively high concentration of 10% Gd^{3+}. These workers did not discuss the influence of the simultaneous presence of more than one site. A comparison of their results and ours with the calculations of O'Hare and Donlan[13] for a cubic field appears to indicate that the calculated ^6I and ^6D level positions in the latter case are consistently low.

The measured relative intensities of the two-photon transitions for three polarizations of the excitation beam are presented in Fig. 5 on an arbitrary logarithmic scale. The intensity corresponding to a J multiplet or grouping of closely spaced multiplets, integrated over all observed crystal-field components, is represented by each vertical bar for a given polarization of the excitation beam. The overall agreement with the earlier TPA intensity measurements in Gd^{3+}:LaF_3 and Eu^{2+}:CaF_2 presented in the same manner[1,2] is evident.

As found in these earlier studies, the highly forbidden transition $^8S_{7/2} \rightarrow {}^6I_{13/2,15/2,17/2}$ with $\Delta J > 2$, $\Delta L > 2$, and $\Delta S = 1$, requires the inclusion of crystal-field and spin-orbit interactions in the intermediate $4f^6 5d$ configuration. Downer[1] calculated the intensities of two-photon linkages for Gd^{3+} in LaF_3. The importance of similar higher perturbation terms is evident for the cubic, as well as the other sites, of Gd^{3+} in CaF_2. In particular, it should be noted that the intensity of $^8S_{7/2}$ to $^6P_{7/2}$ for linear polarization is considerably more intense than for the other two-photon transitions to the ^6P multiplet. This was explained by Judd and Pooler[15] by incorporating the spin-orbit coupling in the $4f^6 5d$ configuration.

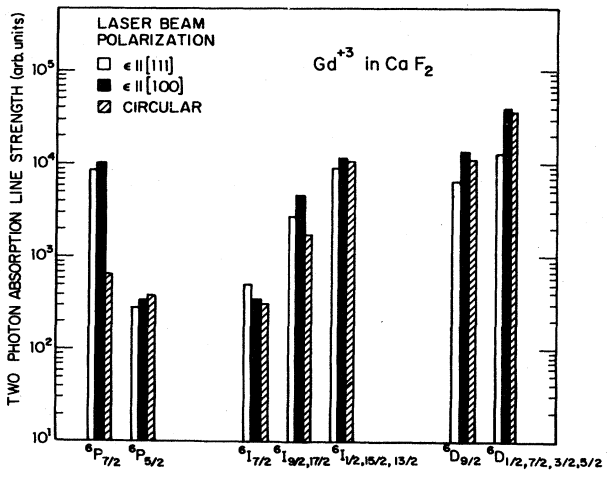

FIG. 5. Relative intensities of the integrated intensities of the various multiplets for three different polarizations of the exciting laser beam. Corrections have been made for changes in dye-laser efficiency.

CONCLUSION

These two-photon absorption studies of Gd^{3+}:CaF_2 have confirmed and enlarged the information previously obtained with one-photon spectroscopy. In particular, the ^6I and ^6D levels have been studied with explicit consideration of the simultaneous presence of various site symmetries. The two-photon intensities for the cubic, tetragonal, and cluster sites all require third- and fourth-order perturbation theory to account for the observed two-photon intensities.

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