

Two-photon spectroscopy in  $\text{GdAlO}_3$ 

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Two-photon absorption spectroscopy is used to study  $f \rightarrow f$  transitions of the  $\text{Gd}^{3+}$  ion in pure  $\text{GdAlO}_3$  crystals. This technique allows us to observe the electronic transitions far in the ultraviolet without background as opposed to conventional spectroscopy. We observed several transitions that violated the angular-momentum selection rules  $\Delta J \leq 2$ .

Two-photon spectroscopy has been shown to be useful in obtaining complementary information to that obtained from the conventional one-photon spectroscopy due to the difference in the selection rules.<sup>1</sup> With the development of tunable dye lasers, two-photon spectroscopy became a powerful tool for the investigation of sharp  $4f \rightarrow 4f$  transitions of rare-earth ions in solids in the ultraviolet spectra.<sup>2</sup> In the present paper, the observation of direct two-photon  $f \rightarrow f$  transitions of the  $\text{Gd}^{3+}$  ion in pure  $\text{GdAlO}_3$  crystals is reported. To our knowledge this is the first observation of sharp lines in two-photon spectra in pure crystals. This ion has a very special level structure in relation to all other rare-earth ions because its first excited state is  $32000 \text{ cm}^{-1}$  above the ground state.<sup>3</sup> Two-photon transitions were induced between the  $^8S_{7/2}$  ground state and the  $^6P$  and  $^6I$  excited states of the  $f$  configuration. As a result of the shielding of  $4f$  levels by  $5s$  and  $5d$  the former do not form band structures and very sharp lines are measured even in pure crystals. Gadolinium orthoaluminate belongs to the family of rare-earth aluminum oxides that crystallize in a slightly distorted orthorhombic perovskite structure ( $Pb_{nm}-D_{2h}^{16}$ ). Its structure can be regarded as a perfect cube with eight distorted octahedra of oxygen in each vertex, and a  $\text{Gd}^{3+}$  ion displaced slightly within the  $xy$  plane in the center. The local symmetry of the  $\text{Gd}^{3+}$  ion in the gadolinium aluminate is  $C_3$ .<sup>4</sup> These crystals were grown from high-temperature solution technique.<sup>5</sup> During the growing of these crystals, color centers can be formed.<sup>6</sup> We verified the existence of these centers in our samples by using one-photon spectroscopy techniques. The blue fluorescence of color centers was used to monitor the two-photon absorption of the  $\text{Gd}^{3+}$  energy levels, as indicated in the energy-level diagram in Fig. 1.

The laser used in two-photon spectroscopy was a homemade pulsed dye laser of the modified Littman type,<sup>7</sup> pumped by the second harmonic of a Nd:YAG laser (YAG is yttrium aluminum garnet). Typical characteristics of this dye laser are 500-kW peak power,  $0.1\text{-cm}^{-1}$  linewidth,<sup>7</sup> and 10-Hz repetition rate. The luminescence of the color center was collected at  $90^\circ$  from excitation. The completed rejection of laser radiation was done by employing color filters with a transmission range of  $24000 \pm 1000 \text{ cm}^{-1}$ . A homemade data-acquisition system based on a PC-XT microcomputer was used to control the experiment. The details of our experimental apparatus have been described elsewhere.<sup>8</sup> Conventional

luminescence spectroscopy was employed to measure the emission spectra of the color centers. By using conventional optical absorption the presence of the color centers was not detected. Its presence was only observed when the luminescence spectrum was measured by exciting the  $^6P$  levels of the  $\text{Gd}^{3+}$  ion (Fig. 2). The luminescence occurs through the color centers showing the coupling between it and the  $\text{Gd}^{3+}$  ion. Direct fluorescence from the  $^6P$  was not observed. The lifetime of the color centers band was measured by means of temporal resolution spectroscopy. The lifetime is about  $10 \mu\text{sec}$ .

Although the  $\text{Gd}^{3+}$  ion transitions are allowed for one-photon spectroscopy,<sup>9</sup> two-photon absorption spectroscopy is the ideal technique to study this ion. Besides the facility of using visible tunable dye lasers, the other advantage of this technique is that two-photon absorption is only allowed for the ion levels, being forbidden for the crystal excitonic band. As a consequence of it the electronic transitions in the ultraviolet of gadolinium can be seen in the two-photon spectroscopy without the background as op-

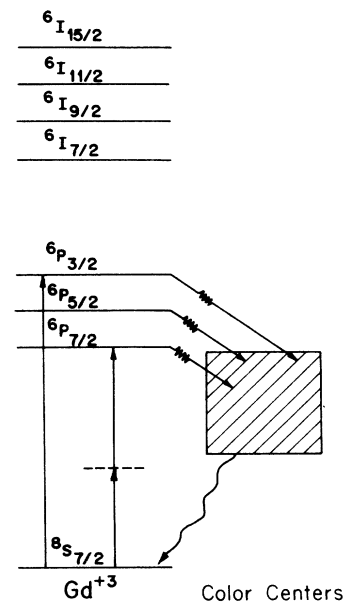


FIG. 1. Schematic diagram of the energy level of our sample of  $\text{GdAlO}_3$  showing one- and two-photon excitation of  $^6P_J$  and subsequent decay by fluorescence of color centers.

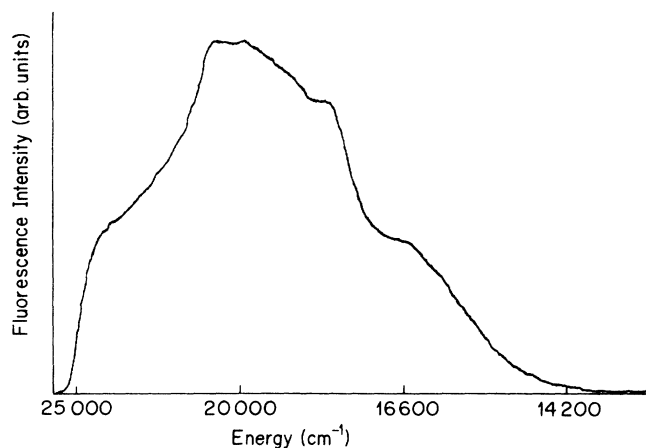


FIG. 2. Fluorescence spectra of color centers in  $\text{GdAlO}_3$  at 300 K excited with a broadband excitation around  $31\,900\text{ cm}^{-1}$ .

posed to conventional spectroscopy.

Two photons from a dye laser are simultaneously absorbed and produce a blue fluorescence in which intensity increases with the square of the laser power. This quadratic behavior is the most evident signature that a two-photon process takes place. Figure 3 shows the two-photon linear polarized absorption spectrum of the  ${}^8S_{7/2} \rightarrow {}^6P_{7/2}$  transitions of the  $\text{Gd}^{3+}$  ion. All the transitions between the ground state and the four Kramers doublets were observed, as predicted by group theory for the  $C_s$  symmetry. These transitions can be explained in quantitative detail when third-order terms referring to spin-orbit interactions are introduced.<sup>10</sup> There are strong anomalies with respect to the predictions of a second-order theory.

The  ${}^8S_{7/2} \rightarrow {}^6P_J$  ( $J = \frac{5}{2}, \frac{3}{2}$ ),  ${}^8S_{7/2} \rightarrow {}^6I_J$  ( $J = \frac{7}{2}$ ) transitions were observed in the two-photon absorption spectra. Second-order theory permits the transitions, but it is not able to explain the strong line intensity of the observed two-photon spectrum. Their number is according to the prediction of group theory for the site symmetry and ener-

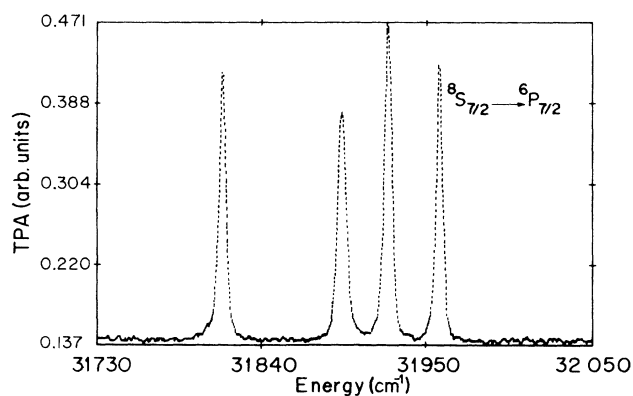


FIG. 3. Two-photon absorption spectra of the electronic transition of  $\text{Gd}^{3+}$  in  $\text{GdAlO}_3$ . The absorption in this spectra corresponds to the  ${}^8S_{7/2} \rightarrow {}^6P_{7/2}$  transition. The sample was at room temperature. The energy represents 2 times the laser frequency.

TABLE I. Stark-component energies of the  $\text{Gd}^{3+}$  ion observed by two-photon absorption in pure  $\text{GdAlO}_3$ .

| Multiplet     | Observed components ( $\text{cm}^{-1}$ ) |
|---------------|--|
| ${}^6P_{5/2}$ | 32 450                                   |
|               | 32 500                                   |
|               | 32 540                                   |
| ${}^6P_{3/2}$ | 33 060                                   |
|               | 33 100                                   |
| ${}^6I_{7/2}$ | 35 630                                   |
|               | 35 650                                   |
|               | 35 700                                   |
|               | 35 750                                   |

gies measured of these excited states are summarized in Table I.

The remaining  ${}^8S_{7/2} \rightarrow {}^6I_J$  ( $J = \frac{15}{2}, \frac{17}{2}$ ) transitions measured by us exhibit enormous discrepancies with the second-order perturbation theory: selection-rule violation and anomalously strong intensities. The second-order perturbation theory predicts zero intensity for  ${}^8S_{7/2} \rightarrow {}^6I_J$  ( $J = \frac{15}{2}, \frac{17}{2}$ ) because the selection rule allows only transitions with  $\Delta J \leq 2$  for two-photon absorption. In Fig. 4 we show the two-photon absorption spectra of the electronic transitions from the ground state  ${}^8S_{7/2}$  to the  ${}^6I_{15/2}$ . These transitions that should be forbidden by this theory are stronger than the allowed transitions. The two-photon-absorption-signal scale in both Figs. 3 and 4 are the same and are in arbitrary units. The discrepancies with second-order theory were explained previously with the introduction of third-order terms involving crystal interactions.<sup>10</sup> The inclusion of a third-order term in the perturbation theory may allow transition with  $\Delta J$  up to six.<sup>11</sup> Therefore, these high-order terms explain our observation of the anomalous intensity of the  ${}^8S_{7/2} \rightarrow {}^6I_J$  ( $J = \frac{15}{2}, \frac{17}{2}$ ) two-photon absorption.

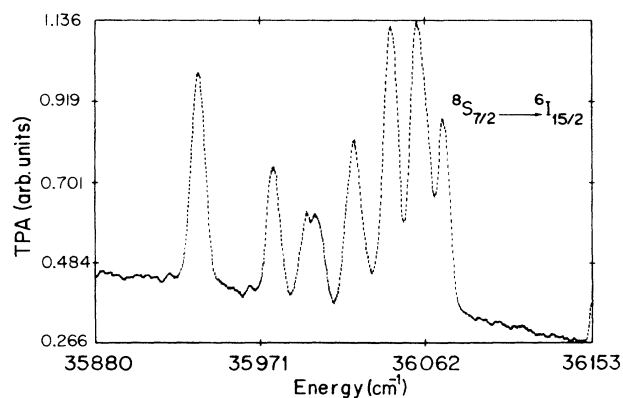


FIG. 4. Two-photon absorption spectra of the electronic transition of  $\text{Gd}^{3+}$  in  $\text{GdAlO}_3$ . The absorption in this spectra corresponds to the  ${}^8S_{7/2} \rightarrow {}^6I_{15/2}$  transition. The sample was at room temperature. The energy represents 2 times the laser frequency.

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