Γ point between the top of the valence band and the lowest antibonding *d* bands in the Oguchi calculation, the latter states have negative dispersion. Thus one would not expect to see emission from the bands at Γ but rather from the indirect minimum at X, a transition of only 0.7 eV. In addition to this quantitative discrepancy between our measurements and the $X\alpha$ calculation, another unresolved problem is the short carrier lifetime of this material. Nonradiative recombination or transitions to intermediate levels, possibly the *d* bands, are the dominant relaxation processes in CdCr$_2$Se$_4$. Like the deep levels in semi-insulating GaAs:Cr, the *d* bands in the gap may have the effect of shortening carrier lifetimes but to a much greater extend in this stochiometric material.

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Two-Photon Absorption as a New Test of the Judd-Ofelt Theory

M. Dagenais,[a] M. Downer, R. Neumann,[b] and N. Bloembergen
Gordon McKay Laboratory, Division of Applied Sciences, Harvard University,
Cambridge, Massachusetts 02138
(Received 15 December 1980)

Observation by fluorescence detection of direct two-photon absorption within the 4*f* configuration of the Gd^{3+} ion following excitation with a continuous-wave laser is reported. Quantitative intensity measurements test assumptions behind the Judd-Ofelt theory of lanthanide transition intensities in a new way, and significant discrepancies are found. The discrepancies indicate that the radial integrals $\langle 4f|r|5d\rangle$ vary markedly for different J multiplets, and that ligands significantly influence two-photon intensities.

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Kaiser and Garrett[1] observed direct two-photon absorption for the first time by exciting a $4f^n \to 4f^{n-1}5d$ transition in a lanthanide ion with a pulsed ruby laser. Few subsequent studies of two-photon absorption, however, have explored the parity-allowed transitions within the $4f^n$ configuration of lanthanides.[2,3] In the present work we report observation of direct two-photon $f \to f$

transitions in the Gd^{3+} ion in a LaF_3 host, using continuous-wave (cw) dye-laser excitation. To our knowledge, this represents the first experiment in two-photon solid-state spectroscopy done exclusively with cw lasers. The purpose of this Letter is to show that quantitative measurements of relative two-photon absorption cross sections provide a new test of the method of Judd and Ofelt[4,5] for calculating oscillator strengths of $f \rightarrow f$ transitions in lanthanide ions.

Figure 1 shows the experimental arrangement. A cw dye laser (Coherent Inc. Model 599-21), operating broadband with Rhodamine-6G, is pumped by an 18-W argon-ion laser. A small fraction of the dye-laser power is sent into a monochromator for frequency calibration. A linearly polarized beam of several hundred milliwatts is focused into a sample crystal, the temperature of which could be varied between 4 and 300 °K. The LaF_3 crystal, which contained 0.5% Gd^{3+}, was purchased from Optovac, Inc. It was mounted with its c axis either parallel or perpendicular to the direction of beam propagation. The experiment has also been performed in another arrangement in which the sample and cryostat were placed inside the dye-laser cavity. An increase in laser intensity of an order of magnitude was obtained. The data reported here were taken with the sample outside the cavity. This simplifies the operation and adjustments.

Two-photon transitions were induced between the ${}^8S_{7/2}$ ground state of Gd^{3+} and the lowest-lying excited multiplets ${}^6P_{7/2}$ at 32 230 cm^{-1}, ${}^6P_{5/2}$ at 32 790 cm^{-1}, and ${}^6P_{3/2}$ at 33 360 cm^{-1} above the ground state. The relevant intermediate states, which belong mostly to the $4f^{n-1}5d$ configuration, lie about 100 000 cm^{-1} above the ground state. This fact, in combination with $4f \rightarrow 5d$ oscillator strengths of only about 10^{-3}, makes two-photon absorption cross sections prohibitively small for direct absorption measurements. In order to achieve the required sensitivity, therefore, uv fluorescence from one-photon decay back to the ground state was monitored at right angles to the laser beam with a suitably filtered EMI 9635 photomultiplier tube. With three Corion solar-blind filters, we achieved a rejection ratio against scattered light larger than 10^{12}, and a very good signal-to-noise ratio. The observed fluorescence is emitted almost entirely from the lowest-energy crystal-field component of the ${}^6P_{7/2}$, since higher-lying ${}^6P$ levels decay to this level through rapid, nonradiative processes. Fluorescence yield of this lowest level, on the other hand, approaches unity, since, because of the large energy gap separating it from the ground state, radiative decay dominates. Nevertheless, to check that fluorescence following excitation of different excited states was not selectively quenched, which would lead to erroneous measurement of relative transition intensities, single-photon absorption and fluorescent spectra were taken with a Cary 14 spectrophotometer and found to yield identical relative intensities to all of the ${}^6P_J$ and ${}^6I_J$ excited $4f$ states (except for an inconclusive result with the ${}^6P_{3/2}$, which was too weak to be observed by direct one-photon absorption).

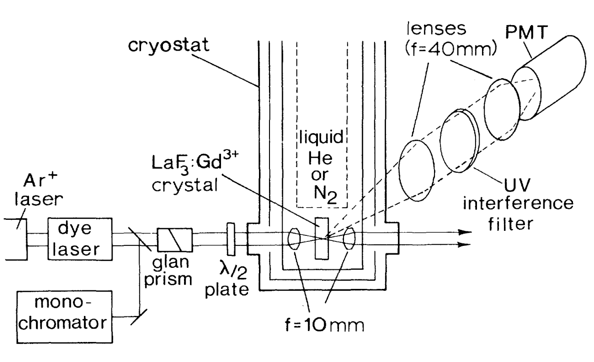

FIG. 1. Schematic diagram of the experimental arrangement.

Two-photon intensity measurements were made at both liquid-nitrogen and liquid-helium temperatures. As suspected, no temperature dependence was observed, since the ground-state splitting is less than 0.3 cm^{-1}, so that all Stark components are essentially equally populated even at 4 °K. Level positions for the two-photon transitions were checked at liquid-helium temperature, and found to agree within the resolution of our monochromator (± 1 cm^{-1}) with those reported by Schwiesow and Crosswhite.[6] The expected temperature dependence of the level positions[7] was confirmed. Crystal-field splittings of the ${}^6P$ multiplets were fully resolved, as shown by the experimental curves in Fig. 2. The observed linewidths of 1–2 cm^{-1} in this figure arise from a convolution of the laser linewidth (0.3 cm^{-1}) with itself and with the transition linewidths, which are homogeneously broadened at 77 °K. Measurements at 4 °K on the ${}^6P_{7/2}$ state with a single-mode dye laser (~ 1 MHz width) yielded transition linewidths of 7 GHz for the three lowest crystal-field components (see Fig. 3), and a linewidth of 21 GHz for the highest. This last component is homogeneously broadened because of spontaneous emission of phonons. Fluorescence line narrow-

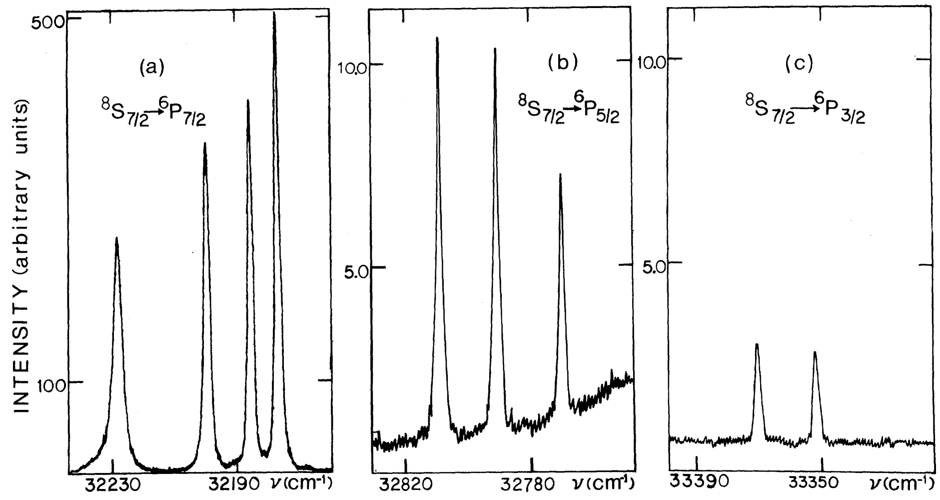

FIG. 2. Observed uv fluorescence intensity at 77 °K following two-photon absorption with incident light linearly polarized perpendicular to c axis from the $^8S_{7/2}$ ground state to the (a) $^6P_{7/2}$, (b) $^6P_{5/2}$, and (c) $^6P_{3/2}$ excited states. Note that the vertical scale in (a) is different. The indicated scales measure the relative intensities.

ing following two-photon excitation, which is in progress in our laboratory, should help to eliminate inhomogeneous contributions to the width. The ground-state splitting of 8 GHz[8] might then be resolved.

Axe[9] showed that for photons of the same frequency and polarization, the Judd-Ofelt method gives the integrated line strength S for a two-photon transition from a ground state with components $|f^n\psi JM\rangle$ to an excited state with components $|f^n\psi'J'M'\rangle$ in the form

$$S=c\Omega_2\langle f^n\psi J\| U^{(2)}\| f^n\psi'J'\rangle^2. \qquad (1)$$

c is a polarization dependent factor equal to 1 for linearly polarized light and $\frac{3}{2}$ for circularly polarized light. Ω_2 contains integrals over the radial parts of the $4f^n$ and $4f^{n-1}5d$ wave functions, and is analogous to the phenomenological T_2 parameter in Judd's theory of one-photon intensities,[4] in which the role of the second photon is replaced by the noncentrosymmetric part of the crystal field.

Equation (1) assumes that total angular momentum J is a good quantum number. Effective spherical symmetry is then obtained by summing over all components of each J multiplet. Our calculation of the effect of J mixing of the free-ion $4f^7$ levels by the crystal field $V=\sum_{k,q}B_{kq}C_{kq}$, by using coefficients B_{kq} determined from a phenomenological fit of crystal-field term splittings,[10] indicates that it is negligible. If we assume, as is customary, that Ω_2 has the same value for all excited states, then Eq. (1) shows that, for a given polarization, the relative integrated intensities of two-photon transitions to states $|f^n\psi'J'\rangle$ should be given by the ratios of the quantities $\langle \mathrm{g.s.}\| U^{(2)}\| f^n\psi'J'\rangle^2$. These quantities have been calculated for most lanthanides by using atomic intermediate-coupling wave functions,[10] and the appropriate ratios for the $^8S_{7/2}\to{}^6P_{7/2}$, $^6P_{5/2}$, $^6P_{3/2}$ transitions in Gd^{3+} are shown in Table I. This

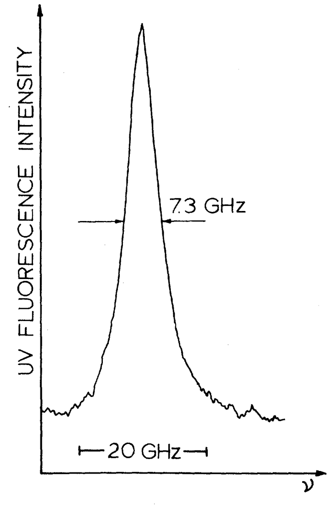

FIG. 3. Observed fluorescence at 4.2 °K following two-photon absorption from the $^8S_{7/2}$ ground state to the second-lowest-energy crystal-field component of the $^6P_{7/2}$. The laser was operating in single mode.

TABLE I. Calculated and experimental ratios of integrated intensities for three two-photon transitions in Gd^{3+} with incident light linearly polarized perpendicular and parallel to crystal c axis.

Intensity ratios	Calculated[a]	Experimental Polarization perpendicular to c axis	Experimental Polarization parallel to c axis
$S(^6P_{7/2})/S(^6P_{5/2})$	2.3	58 ± 5	83 ± 5
$S(^6P_{5/2})/S(^6P_{3/2})$	29.4	5.4 ± 0.4	>15
$S(^6P_{7/2})/S(^6P_{3/2})$	68.8	320 ± 10	>900

[a] Ratios of the quantities $\langle \text{g.s.} \| U^{(2)} \| f^7 \psi' J \rangle^2$, as calculated in Ref. 10 for the states indicated.

table also illustrates, however, the serious discrepancies between this theory and the experimental results, considerably larger than discrepancies normally encountered in single-photon intensity data. We believe the reason is that two-photon absorption experiments uniquely test a prediction of the Judd-Ofelt method which does not involve phenomenological parameters. They are, therefore, more sensitive to the physical assumption on which the method rests.

Among these assumptions use of the closure relation for arriving at Eq. (1) may be questioned, although in our opinion the large number of intermediate $4f^{n-1}5d$ states justifies the replacement of individual energy denominators by a common average denominator. A violation of the assumption of effective spherical symmetry, arising, for example, from interaction of the $4f$ electrons with the ligands, would be expected to show up as a polarization dependence of the integrated intensities. Measurements of the variations of the intensities of individual crystal-field components with the direction of the electric field with respect to the crystallographic axes have been made. There are sizable variations both in the c plane, as well as for $E \parallel c$ axis. The anisotropy of the integrated intensity of the $J = \frac{7}{2}$ and $\frac{5}{2}$ multiplets is much smaller. There is practically no variation in the c plane, and the difference between $E \parallel c$ and $E \perp c$ axis is less than 20%. The $J = \frac{3}{2}$ intensity is quite small for $E \parallel c$, as shown in Table I. In addition, measurements with light circularly polarized around the c axis show significant deviations from the polarization dependence predicted in Eq. (1), indicating a need for a theory of two-photon absorption which takes ligand-field effects into account. These data will be reported in more detail elsewhere.

In addition, the radial integrals $\langle 4f | r | 5d \rangle$ contained in Ω_2 may vary for different $4f^n$ states. We note, in support of this suggestion, that theoretical fits to measured crystal-field splitting are often markedly improved if different sets of crystal-field parameters are used for different multiplets.[11] This indicates that the charge distribution of the $4f$ electrons, and presumably the small overlap of the $4f^n$ and $4f^{n-1}5d$ wave functions as well, can depend on the nature of the state. Judd,[12] in fact, has used the effect of the contraction of the $4f^n$ wave function by attractive exchange intereactions to explain a number of discrepancies in crystal-field analysis.

State dependence of the radial integral $\langle 4f | r | 5d \rangle$ would, of course, influence T_2 as well as Ω_2. Our results, however, would not contradict single-photon intensity data, since more than 95% of the single-photon intensity of the $^8S_{7/2} \to {}^6P_{7/2}, {}^6P_{5/2}$ transitions is magnetic dipole in nature,[13] and thus unaffected by this integral.[14]

Two-photon absorption data can significantly augment our knowledge of lanthanide wave functions. Studies of the ^6D_J states of Gd^{3+}, which have large values of the relevant $U^{(2)}$ matrix element, should be of considerable interest. We have searched for the two-photon transitions to the $^6I_{7/2,9/2,11/2}$ states without success, in agreement with calculated values of the $U^{(2)}$ matrix element[10] more than an order of magnitude smaller than those to the $^6P_{3/2}$ state.

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(a)Present address: GTE Research Laboratory, Waltham, Mass. 02254.

[b]On leave from Physikalisches Institut, D-6900 Heidelberg, Federal Republic of Germany.

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[14]It has been pointed out to us that fuller treatment of the spin-orbit interaction in calculating the $U^{(2)}$ matrix element may be required, since the transitions in question are spin forbidden.

Two-Dimensional Localization in Thin Copper Films

L. Van den dries, C. Van Haesendonck, and Y. Bruynseraede
Laboratorium voor Vaste Stof-Fysika en Magnetisme, University of Leuven, B-3030 Leuven, Belgium

and

G. Deutscher[a]
Department of Physics and Astronomy, Tel-Aviv University, Ramat-Aviv, Tel-Aviv, Israel

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Resistance measurements have been made on low-resistivity thin Cu films (50–500 Å) between 1 and 20 K. A logarithmic temperature dependence of the resistance is observed. For a resistance per square of $R < 20\ \Omega/\square$, good agreement is obtained with the localization theory. The amplitude of the resistance variation and its large magnetic-field dependence exclude possible Coulomb-interaction effects predicted by Altshuler *et al.* as the main source of the observed behavior.

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Based on the scaling ideas of Thouless,[1] Abrahams *et al.*[2] recently predicted that in a thin metallic film, electronic states should become localized at low temperatures, resulting in a logarithmic increase of the resistance as the temperature is lowered.[3] Experimental studies of this effect have been reported in ultrathin (and presumably granular) Au-Pd films[4] and in inversion layers.[5] The resistance per square $R_\square$ of these samples was typically 1000 $\Omega/\square$ or more. Although the results did show the predicted ln$T$ dependence, the magnitude of the effect was only a half to a quarter of that predicted by the theory. Similar problems have arisen in the study of one-dimensional (1D) localization in highly disordered[6] and amorphous[7] systems and have been attributed by Thouless[8] to a linear temperature dependence of the electron-phonon scattering time characteristic of highly disordered two-level systems.[9] An alternative interpretation of these results in terms of the Coulomb interaction has been proposed by Altshuler, Aronov, and Lee.[10]

We report for the first time on measurements of 2D localization in clean metallic (copper) films, with a mean free path of the order of the film thickness and a resistance per square of the order of 10 $\Omega/\square$. The resistance of these films shows the expected logarithmic increase at low temperatures. The strength of the effect is in agreement with the localization theory but disagrees strongly with the theory of Altshuler *et al.*, in view of the Hartree correction which becomes very important for clean films. Slightly thinner films, approaching the discontinuity limit, show a weaker effect, similar to what was observed by Dolan and Osheroff.[4] However, in this limit it is quite difficult to distinguish between the predictions of the localization and the Coulomb theory.