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Excited-State Exchange Broadening of Optical Transitions in $PrCl_3$

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We have observed an anomalous broadening of two fluorescence lines in $PrCl_3$. The new effect is observed only when the terminal state is a magnetic doublet and only at low temperatures ($T < 100$ K). However, the effect is seen far above any transition or ordering temperature. The broadening can be, at least partially, suppressed by application of a large magnetic field. The effect is almost certainly a cooperative phenomenon arising from an interaction between ground- and excited-state ions.

In previous papers[1,2] we have investigated the properties of $PrCl_3$ and $Pr_{0.01}La_{0.99}Cl_3$. In the course of this work we observed an unexpected behavior of the fluorescent linewidths which we report in this Letter.

The experimental setup is the same as described in Refs. 1 and 2 except that a superconducting magnet was used to obtain the magnetic field data. The $^3P_0(\mu = 0)$ level was pumped with the pulsed dye laser (4 nsec pulse width) from the $^3H_4$ ground state (excitation ~488 nm). Fluorescence of the $^3P_0$ to the $^3F_2$ and $^3H_6$ manifolds was observed[3,4] (Fig. 1). In hexagonal $PrCl_3$ and $LaCl_3$ (site symmetry C_{3h} or $\bar{3}$) the levels with $\mu = 1$, 2 are doublets while those with $\mu = 0$, 3 are nondegenerate.

The anomaly that attracted our interest is displayed in the upper (solid) curve in Fig. 2 which is a plot of linewidth versus temperature of the $^3P_0$-$^3F_2$ emission (645 nm) in $PrCl_3$. Theories based on ion-phonon interactions predict a monotonic decrease in linewidth with decreasing temperature.[5] Indeed, the data (curve 2) for $Pr_{0.01}La_{0.99}Cl_3$ are monotonic. If a large magnetic field splits the Zeeman components, the linewidth as a function of temperature of these components changes as seen in curve 3. The maximum reduction of width occurs when the two components are fairly well separated[6] and further increase of the field to 90 kG has no effect.

In Fig. 3 we show the linewidth as a function of temperature for transitions to $^3H_6$ in $PrCl_3$.[7] The 619-nm transition in zero field (curve 1) does not display the dramatic increase of linewidth at lower temperatures. Note, however, that at 20 K its width is more than double that in dilute crystals (curve 2). In the latter, we see that there is significant phonon broadening even at 50 K so that a minimum, such as observed in the 645-nm line, would be effectively masked. In a magnetic field the linewidth of the 619-nm emission in $PrCl_3$ becomes about as narrow as it is in the

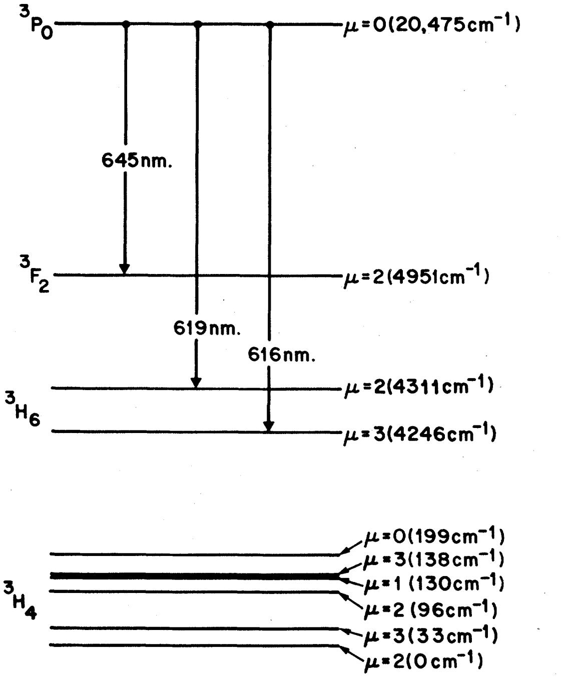

FIG. 1. Partial energy-level diagram of $Pr_{0.01}La_{0.99}Cl_3$. We display only those levels of interest. The energy of each level is shown at the right. (The energies and hence transition wavelengths change slightly in $PrCl_3$.)

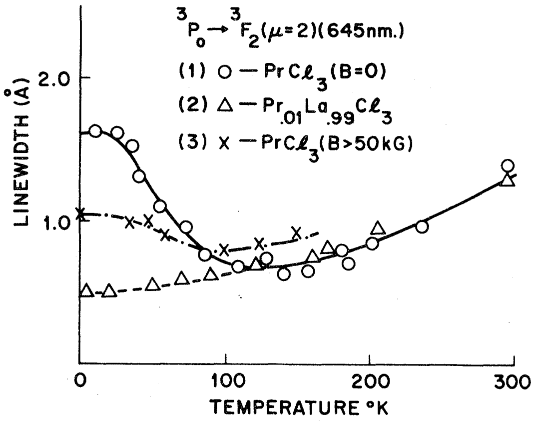

FIG. 2. Linewidth versus temperature of 645-nm emission. The solid curve, 1, is for $PrCl_3$ in zero magnetic field. The middle curve, 2, is the linewidth of each Zeeman component in a magnetic field of 60 kG (the data actually refer to a different crystal from 1). The lowest curve displays the linewidth as a function of temperature in $Pr_{0.01}La_{0.99}Cl_3$. Magnetic fields do not affect the linewidth in dilute crystals.

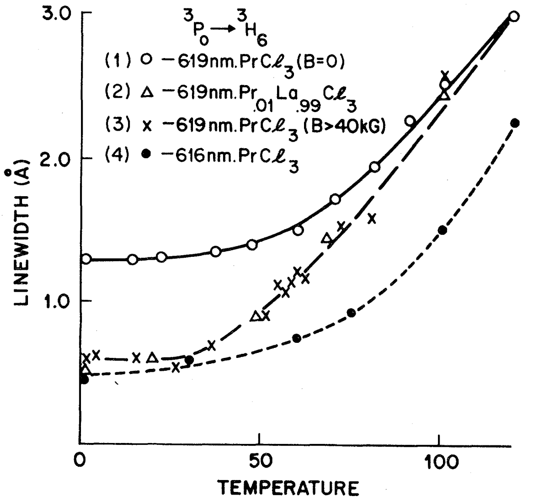

FIG. 3. Linewidth versus temperature of 619- and 616-nm emissions. These linewidth-versus-temperature plots 1, 3, and 4 all refer to $PrCl_3$. In the dilute crystal, 2, the 619-nm emission is almost identical to curve 3. The 616-nm emission in the dilute crystals is nearly the same as curve 4.

dilute crystal. This is in contrast to the 645-nm emission where the Zeeman components narrowed to a point intermediate between that of $PrCl_3$, $B=0$, and that of the dilute crystal.

We will characterize the behavior of the concentrated crystals by introducing a "narrowing parameter" ϵ defined as $\epsilon = \Delta\nu_0 - \Delta\nu_B$, where $\Delta\nu_0$ is the linewidth when $B=0$ and $\Delta\nu_B$ is the linewidth for large[6] magnetic fields. Then we find that for $PrCl_3$, $^3P_0 \to {}^3F_2$, $\epsilon = 1.3 \pm 0.2\ \mathrm{cm}^{-1}$, and for $^3P_0 \to {}^3H_6(\mu=2)$, $\epsilon = 1.8 \pm 0.2\ \mathrm{cm}^{-1}$. For all transitions in dilute crystals and for nonmagnetic levels in $PrCl_3$, ϵ is zero. The nonmagnetic level of $^3H_6$ has the same linewidth in dilute and concentrated crystals.

We have also investigated the analogous transitions in the very similar crystals $PrBr_3$ and $Pr_{0.01}La_{0.99}Br_3$. In all cases, the results were qualitatively identical to those observed in the chlorides and ϵ was 0.7 cm^{-1} and 1.7 cm^{-1} for the analogous transitions to $^3F_2$ and $^3H_6$, respectively.

Certain characteristics of the magnetic-field narrowing are reminiscent of what one could expect for a strain-broadened line. Suppose we have a doublet $|i\rangle$, $|i'\rangle$, and a strain potential energy V_s such that $a \equiv \langle i|V_s|i\rangle = \langle i'|V_s|i'\rangle$ and $b \equiv \langle i|V_s|i'\rangle$. At zero field the linewidth is given by[8] $\langle a^2 + b^2\rangle^{1/2}$. However, if we apply a magnetic field such that $g\beta B \gg \langle b^2\rangle^{1/2}$, the linewidth is reduced to $\langle a^2\rangle^{1/2}$, that is, only the diagonal component of strain contributes. Any attempt to interpret our results strictly in this framework suffers from several fatal flaws. For one we would have to explain why the diagonal part of V_s does not influence the nondegenerate states more. Also it is very difficult to understand why b should be larger in concentrated crystals than in dilute (in fact, we would expect the reverse to be true.)

We will show that the experimental observations can be explained, at least qualitatively, by the existence of an exchange interaction between excited magnetic levels and magnetic sublevels of the ground $^3H_4$ manifold. Of course, such an interaction will immediately account for the difference between concentrated and dilute crystals. A two-ion spin Hamiltonian[9] for axial crystals may be written as

$$\mathcal{H} = {\sum}'_{ij}(K_0^{ij}\vec{J}^{(i)}\cdot\vec{J}^{(j)} + K_z^{ij}J_z^{(i)}J_z^{(j)} + g_J^{(i)}\beta\vec{B}\cdot\vec{J}^{(i)}), \qquad (1)$$

where $\vec{J}^{(i)}$ and $\vec{J}^{(j)}$ are the angular momenta of ions i and j, $g_J^{(i)}$ is the Lande g factor of ion i, $\vec{B}$ is the external magnetic field, and the crystal c axis is in the z direction. Culvahouse, Schinke, and Pfortmiller[10] have shown that $K_0 = \pm 2.44\ \mathrm{cm}^{-1}$ and $K_z = \pm 1.79\ \mathrm{cm}^{-1}$ for the ground-state–ground-state nn interaction of Pr^{+++} in Pr:$LaCl_3$. Thus one would expect splittings of several cm^{-1} in the ground state. Similar splittings would be expected in the excited states since the exchange field would be comparable.

The coefficients K_0 and K_z may include the effects of magnetic dipole interactions, electric quadripole-quadripole interactions, isotropic and anisotropic exchange, and virtual-phonon exchange. The magnetic-dipole term is readily calculable, but can be shown to be very small (<0.005 cm^{-1}). An estimate of electric quadripole-quadripole interaction in our case, using parameters scaled from $PrAlO_3$[11] but using $PrCl_3$ wave functions, indicated that $\langle \mathcal{H} \rangle_{EQQ} < 0.1$ cm^{-1}, which is again too small. The virtual-phonon exchange could contribute significantly to K_0 while exchange can be significant in both K_0 and K_z.

The temperature dependence of the broadening may be attributed to the different interaction strengths between the thermally populated levels of the $^3H_4$ manifold and the excited states. For instance, recognizing that the matrix elements of J_z are all proportional to g_z while both $\langle J_x \rangle$ and $\langle J_y \rangle$ are zero, we can calculate the temperature-dependent interaction by multiplying the interaction strength of each level by its Boltzmann factor and summing. Taking the energies in $^3H_4$ from Fig. 1 with $g_z(\mu=2)=1.0$, $g_z(\mu'=2')=-4.33$, and $g_z(\mu=1)=1.6$, we find that the resultant[12] is fairly small for temperatures above 200 K, but increases rapidly with decreasing temperature below ~140 K. Thus, the linewidth of the 645-nm line initially decreases on cooling as the lifetime of the terminal state increases, but then increases below ~140 K as the net exchange splitting exceeds the phonon-broadened linewidth.

The magnetic field can influence the linewidth in several ways. First, we can, in principle, describe the effects of exchange as an equivalent field which can split the magnetic states even in zero external magnetic field.[13] Since $PrCl_3$ was not ordered at temperatures accessible to us, there is a random and an average component to the equivalent field. If the average splitting is of the same order as the random part, the two fields contribute to the linewidth. When an external field splits the line, however, only the random splitting contributes to an inhomogeneous width. Also, as we saw in the discussion of strains above, the magnetic field can quench the off-diagonal terms so long as $g\beta B$ is greater than the off-diagonal interaction. Thus, depending on whether the exchange splittings are dominantly diagonal or off-diagonal terms in the Hamiltonian for the excited state, all or part of the exchange broadening may be quenched. This could explain the difference in the high-field width of the 619-nm line (same as in the dilute sample) and the 645-nm line (high-field width greater than in the dilute case).

In conclusion, we have observed anomalous behavior in linewidths of optical transitions in Pr halides which we believe are indicative of an excited-state exchange process.[14] This effect occurs far above any transition or ordering temperature (for optical effects in the ordered regime see Wickersheim, and Meltzer and Moos[15]) and could be useful in studying cooperative phenomena and exciton dispersion in concentrated crystals.

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[6] Our operational definition of "well separated" or alternatively "in high magnetic fields" is that the ratio of the valley amplitude to peak amplitude of the split Zeeman components is <0.15.

[7] Considerable effort was expended on eliminating various, possibly spurious effects such as gain narrowing, reabsorption, and spatial diffusion. No phase transition occurs in $PrCl_3$ above 0.8 K; see J. H. Colwell, B. W. Mangum, and U. B. Utton, Phys. Rev. 181, 842 (1969).

[8] For simplicity we assume that there is no correlation between a and b, and $\bar{a}=\bar{b}=0$.

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[12] If the amplitude of such a sum is somewhat arbitrarily equated to the difference between the 0-K intercepts of the linewidths in the dilute and concentrated crystals in Fig. 2, then the predicted variation of the linewidth with temperature below 100 K will be indistinguishable

from curve 1 of Fig. 2.

[13] From this point of view the linewidth broadening could also be treated as an unresolved Davydov splitting.

[14] This behavior of the linewidth is not directly related to the more common effect of exchange narrowing of magnetic resonance spectra for several reasons, the foremost being the absence of another large interaction that exchange can average out or narrow.

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Evidence for Percolation-Controlled Conductivity in Amorphous As_xTe_{1-x} Films

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The compositional dependence of the dc conductivity of As_xTe_{1-x} films with $0.3<x<0.78$ was measured. The resistivity over the entire compositional range investigated could be described with an effective-medium percolation theory. No adjustable parameters enter into this first analytical description of the compositional variation of a transport property in an amorphous multicomponent semiconductor.

Over the last decade, the electronic transport properties of amorphous semiconducting chalcogenides have been studied extensively. However, in spite of measurements of dc and ac conductivity, thermopower, Hall coefficient, photoconductivity, and high-field conductivity over a wide temperature range, no agreement exists on the theoretical description of the conduction process. In respect to As-Te based glasses, a controversy has recently developed between the Cohen, Fritzsche, and Ovshinsky (CFO)[1] model on the one hand and the small-polaron model[2] on the other. This paper reports the results of a study of the compositional dependence of the dc conductivity of As_xTe_{1-x}. The choice of this system was based on the following considerations: Relative to other arsenic chalcogenides,[3,4] As_xTe_{1-x} exhibits few tendencies for chemical ordering since like bonds (As-As, Te-Te) and unlike bonds (As-Te) have similar bond energies[5]; absence of short-range order is also indicated by thermodynamic data on liquid As_2Te_3,[6] and by the smooth monotonic compositional variation of both the glass transition temperature[7,8] and the nearest-neighbor separation[9]; and finally, the electrical conductivities of the pure components differ by 3 orders of magnitude, which, as discussed by Landauer,[10] allows sensitive tests of various possible mathematical descriptions of the compositional dependence of the conductivity.

Generally, an evaporated specimen has a more random structure than a quenched one, since the latter retains the short-range order of the liquid. Because of this and the reported difficulties in quenching As_xTe_{1-x},[9] steady-state sublimation of As_2Te_3 was chosen to prepare the samples. Small changes in the substrate temperature were used to vary the composition which in each case was analyzed with an electron microprobe. More details are reported elsewhere.[11]

In order to check for the absence of contact and layering effects, specimens with two and four coplanar electrodes, as well as with sandwich configurations, were evaporated onto one and the same wafer. In almost all evaporation runs, the resistivity computed from devices of various geometries agreed within the experimental error of 15% in determining dimension and resistance. Wafers containing specimens outside this range were discarded. The conductivity σ was found to be independent of thickness, which together with the absence of contact effects indicated that true bulk resistivities were measured.

Most specimens showed a slight curvature in the $\ln\sigma$ versus $1/T$ plot. The room-temperature activation energy varied approximately linearly with composition and ranged from about 0.38 eV (30 at.% As) to 0.48 eV (80 at.% As). These values are about 0.03 eV lower than those reported for bulk specimens in this composition range.[12] In the so-called Stuke plot,[13] the specimens fell within the experimental scatter on the line measured for quenched As-Te-I specimens (Quinn and Johnson[14]). The room-temperature resistivity —on a *linear* scale— as a function of composition is shown in Fig. 1. The open circles denote experimental results. The dotted lines represent calculations based on effective-medium