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Fluorescence line narrowing of trivalent praseodymium in lanthanum trifluoride single crystal—Phonon-induced relaxation

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Phonon-induced relaxation of Pr^{3+}:LaF_3 is studied by a fluorescence-line-narrowing technique at temperatures from 4 to 50 °K. For temperatures exceeding 15 °K the theory fits the data within the experimental error. For the lowest temperatures, however, mechanisms other than phonon-induced relaxation must contribute to the linewidth. Several such mechanisms are discussed.

The phonon-induced relaxation of trivalent praseodymium in lanthanum trifluoride single crystals was studied by Yen, Scott, and Schawlow.[1] Their work established that the temperature dependence of the linewidth and energy of the transitions studied could be explained in terms of one-phonon and two-phonon (Raman) assisted relaxation of the levels. However the resolution of their experiments was limited by a large strain broadening (16 GHz), so that the homogeneous linewidths at low temperature of the narrowest lines could not be determined. Several years ago Szabo[2] demonstrated a new technique, fluorescence line narrowing, for studying the homogeneous linewidths of Cr^{3+} in Al_2O_3 (ruby) in the presence of a large strain broadening. This technique has been extended to rare-earth ions in glasses by Riseberg,[3] to organic molecules in molecular-crystal hosts by Personov *et al.*,[4] and to rare-earth ions in single crystals by Delsart.[5] In this work, the phonon-induced relaxation of Pr^{3+}: LaF_3 is studied from 4 to 50 °K using this fluorescence-line-narrowing technique.

The theory of phonon-induced relaxation has been summarized by Yen *et al.*[1] and will not be repeated here in detail. The homogeneous linewidths of transitions are determined primarily by processes which affect the lifetime of the two levels involved. The limiting lifetime is that due to radiative transitions coupling the level of interest to all others at lower energy, accompanied by emission of a photon. In addition, there are a number of nonradiative processes. Those of immediate interest are (i) absorption or (ii) emission of one *phonon* accompanied by a transition to adjacent level (direct process), (iii) simultaneous absorption and emission of two phonons accompanied by a transition between two levels (Raman process), (iv) emission of many phonons accompanied by a transition to a lower energy level, and (v) cooperative transitions between nearby ions which result in cross relaxation. (i), (ii), and (iii) serve to couple levels whose energy separation is less than the maximum phonon energy of the host crystal. (iv) and (v) are not so restricted. The rate of these processes vary widely, determined in part by the details of the phonon spectrum, the temperature, and the separations of the energy levels involved. Obviously, at low temperatures, the phonon occupation is limited to low energies ($\hbar\omega_{\text{phonon}} \lesssim kT$), so that for levels separated by an energy of several kT the absorption of a phonon and transition to a higher level is unlikely. As a result, the lowest level in each manifold of states has the longest lifetime of that manifold, and is the sharpest spectral line of that group. However, if the next-lower-lying level is separated by only a few times the maximum phonon energy of the host or less, the higher level will relax by multiphonon emission (iv) before it can radiate; i.e., there is no luminescence from that level.[6]

From studies of Pr^{3+}: LaF_3 single crystals in several laboratories,[1,7–9] the two prominent fluorescent levels of this system are $^1D_2$(16872 cm^{-1}) and $^3P_0$(20 927 cm^{-1}). Since the $^1D_2$ level was accessible to the Rhodamine 6G dye laser, the fluorescence from it was studied. Several properties of this level should be noted. The energy gap from $^1D_2$ to the next-lower level is some 6000 cm^{-1}, so that multiphonon emission probability should be 10^{-4} sec^{-1},[6] compared to the radiative lifetime of 10^3 sec^{-1}.[10] Fluorescence occurs to the lowest level of $^3H_5$ but not to the lowest level of $^3H_6$. As a result the $^1D_2 \rightarrow {}^3H_5$ transition should be the narrower. The energy gap between $^3H_5$ and the next-lowest level ($^3H_4$) is some 1600 cm^{-1}, which leads to a multiphonon rate of 10^5 sec^{-1}.[6] This will lead to a line broadening of less than 1 MHz. (The radiative decay rate of $^3H_5$ to $^3H_4$ is 10^1 sec^{-1}.[10])

The levels of interest are shown in Fig. 1. The absorption spectrum near 5900 Å shows two sharp lines plus a number of broader transitions.[7] The 5917-Å π absorption is very strong with less than 1% transmission at 4 °K for a 0.05-at.% Pr^{3+} sample 4 mm thick. The 5925-Å σ transition is much weaker, with an absorption of 5% under the same conditions. The luminescence from $^1D_2$ at temperatures less than 10 °K originates from the 16 872.4-cm^{-1} level. There are two sharp fluorescence

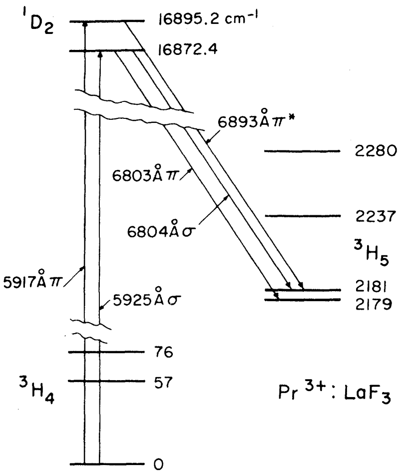

FIG. 1. This figure shows the energy levels of interest in these experiments. Only the lowest-lying crystal-field-split levels of each manifold of states are shown. The transitions are labeled by approximate wavelength. The levels are labeled by energy/hc or wave number.

lines (labeled σ, π) at ~6804 Å, separated by approximately 2 cm^{-1}. As the temperature is increased, the 16 895.2 cm^{-1} level of $^1D_2$ is thermally populated, and one sharp fluorescence line originates from this level (labeled π^*). On excitation of $^1D_2$ by absorption of 5880-Å laser light (absorbed by the phonon bands)[1] the fluorescence transitions appear as in Fig. 2 for three different temperatures. The left-hand line is the π transition. The right-hand line is the σ transition, and the middle line at higher temperatures is the π^* transition. The separation of the two $^3H_5$ levels was measured to be 59.1 ± 1 GHz (π - σ). The π^* transition was higher in frequency than π by 620 ± 6 GHz, compared to a $^1D_2(16895.2) - {}^1D_2(16872.4)$ separation of 684 GHz.[7] These lines are *inhomogeneously* broadened to a total full width at half-maximum (FWHM) of 5 GHz at 4 °K because the excitation was not site selective.

The absorption linewidth of the 5917-Å π transition is shown in Fig. 3. The parameters which summarized the linewidth as a function of temperature were derived from a fit of the theory of Ref. 1 to the data. Because of the small absorption, similar results could not be obtained for the 5925-Å σ transition. However, the main contribution to the 5925-Å σ linewidth at low temperature is the direct-process (i) absorption of a 23-cm^{-1} phonon and a transition to the upper $^1D_2$ level. The direct process (ii) occurs at exactly the same rate for the upper level. As a result, the linewidth of the 5925-Å σ transition can be calculated from the 5917-Å π transition data. At 4 °K the homogeneous linewidth of $^1D_2(16872)$ is calculated to be 2.0 MHz. We note that this is buried in a strain-broadened absorption width of 6.5 GHz.

The fluorescence line narrowing measurements were made as shown schematically in Fig. 4. A single-frequency cw dye laser at 5925 Å was focussed on the sample in a cryostat and the resulting emission was recollimated by the same lens and analyzed by a scanning Fabry-Perot interferometer. An interference filter was used to isolate the three lines near 6800 Å from the luminescence at other wavelengths. The samples, 0.05-at.% and 1-at.% Pr^{3+} in LaF_3 were obtained from Optovac, Inc. When the $^1D_2(16872)$ level was excited at 10 °K, the emission in the neighborhood of 6800 Å was as shown in Fig. 5. The π transition narrows from 5 GHz of Fig. 2 to approximately 1.35 GHz. The σ transition narrows to 1.8 GHz. We thus observe a significant fluorescence line narrowing when $^1D_2(16872)$ is excited resonantly. The π line shape lies between Lorentzian and Gaussian.

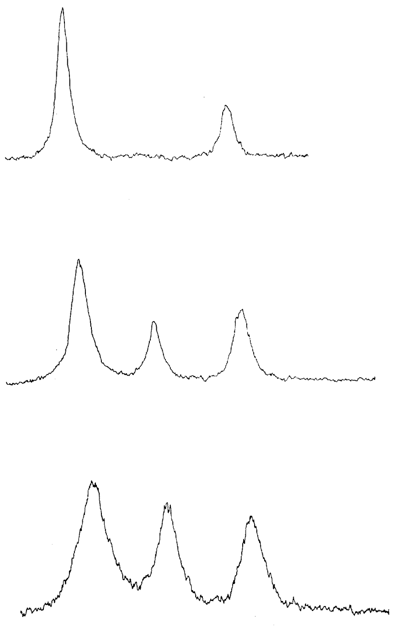

FIG. 2. Fluorescence originating from $^1D_2$ levels at 16 872 and 16 895 cm^{-1} to $^3H_5$ levels at three temperatures (7.3, 20.8, 27.0 °K, top to bottom) is shown. The $^1D_2$ level was excited by light at 5880 Å which is absorbed in the phonon bands of that level. As a result all Pr^{3+} ions contribute to the linewidth. The left-hand π peak is separated from the right-hand σ peak by 59.1 ± 1 GHz. The middle π^* peak is higher in frequency than the π peak by 620 ± 6 GHz. Frequency increases towards the left. (These measurements were obtained using a scanning Fabry-Perot interferometer of interorder spacing 5.3 cm^{-1}. This accounts for the overlap of the π^* line.)

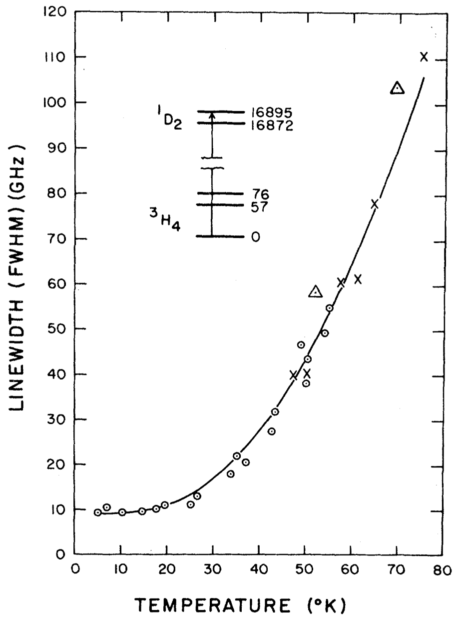

FIG. 3. Absorption linewidth of the $^3H_4 \rightarrow {}^1D_2$(16 895 cm^{-1}) transition is given vs temperature. The theory of phonon-induced relaxation (Ref. 1) when fitted to the data yielded

$$\Delta\nu_{5918\,\text{Å}} = 6.3 + 2.7\ [p(22)+1] + 50p(57) + 125p(76) + 7200\,(T/\Theta_D)^7\ \xi_6\,(\Theta_D/T)\ \text{GHz},$$

where

$$\Theta_D = 300\ ^\circ\text{K},\ p_{ij}(\bar{\nu}_{ij}) = [\exp(hc\bar{\nu}_{ij}/kT)+1]^{-1}.$$

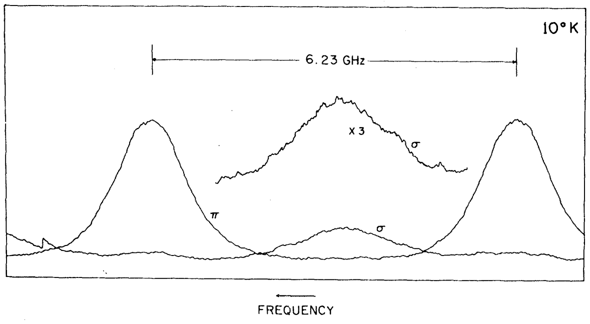

FIG. 5. Line-narrowed fluorescence from Pr^{3+} : LaF_3 at 10 °K. The linewidth of the π transition is 1.35 GHz. The linewidth of the σ transition is 1.8 GHz. The interorder separation of the scanning Fabry-Perot interferometer 6.23 GHz. The finesse was 120. An aperture lens detector combination (74 MHz) was used to correct for imperfect collimation of the light.

The linewidths as a function of temperature are shown in Fig. 6. The equations for the direct and Raman processes were fitted to the data by using the known energy levels and by adjusting the multipliers to obtain a satisfactory fit. The parameters are correct to within 15%. From these results, the linewidth at 4 °K of the π transition is calculated to be 200 MHz instead of the observed 1.0 GHz. Because of this large discrepancy an attempt was made to determine the width of the $^1D_2$ level. The 5925-Å σ transition absorption saturates at a very low incident light level when excited with a monochromatic source at 4 °K. The recovery time from this saturation was measured by varying the time between blocking the exciting light and unblocking it and by monitoring the luminescence passed by a low-pass filter at 6300 Å. The population of the $^1D_2$ level and consequently the absorption is proportional to this luminescence. At 4 °K the recovery time from saturation was 0.5 sec.[11] If the luminescence is plotted as a function of incident power the graph departs from a linear function at an incident power of 5×10^{-7} W (or 3×10^{11} photons/sec), for a 2- mm-diam laser beam focussed with a 7.5-cm focal length lens. The focal volume was ~ 1.3×10^{6} cm^3, and contained ~ 1.2×10^{13} Pr^{3+} ions. Of the incident photons 5%, or 1.5×10^{10} photons/sec were absorbed, or assuming an inhomogeneously broadened transition, the fraction of Pr^{3+} that interacts can be determined as $6/10^4$. For a strain-broadened width of 6.5 GHz, one obtains a homogeneous linewidth of 4 MHz. This compares with a calculated width obtained from equations of Fig. 3 of 2 MHz and a laser jitter of 15 MHz. If a nonfocused beam of uniform intensity is used for saturation, substantially better agreement with the laser-jitter figure is expected. This result illustrates quite vividly that the $^1D_2$ (16872) level is not making a significant contribution to the large fluorescence-narrowed linewidth. A number of possible contributors to the linewidth might be considered.

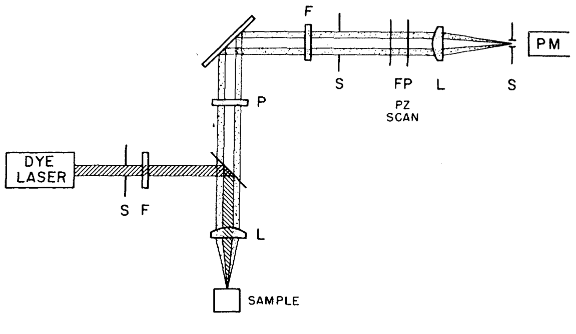

FIG. 4. Schematic diagram of the fluorescence-line-narrowing experiments is shown. A beam of light from a single-frequency dye laser is focused on the sample in a cryostat and the fluorescence, recollimated by the same lens, is analyzed by a piezoelectrically scanned Fabry-Perot interferometer. Interference filters are used to reject dye-laser fluorescence and Pr^{3+} luminescence other than from the transitions of interest.

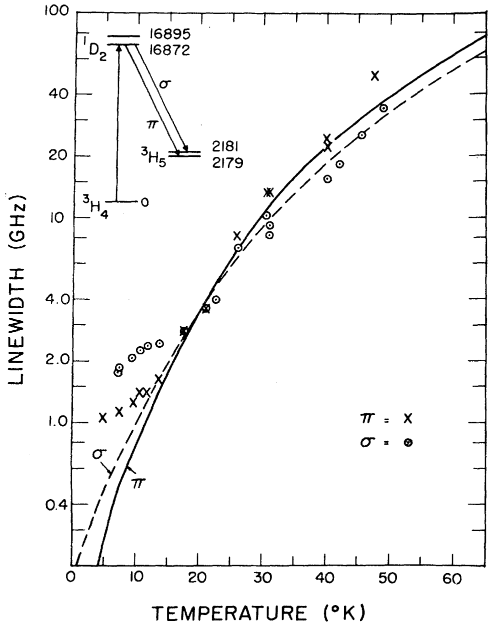

FIG. 6. Fluorescence-narrowed linewidth of 0.05-at.% $Pr^{3+}:LaF_3$ vs temperature is shown. The solid π line was given by:

$$\Delta\nu_\pi = 0.2p(2.0) + 60p(58) + 50p(101) + 2.7p(22) + 8000\,(T/\Theta_D)^7\,\xi_6(\Theta_D/T)\ \mathrm{GHz};$$

the dashed σ line was given by:

$$\Delta\nu_\sigma = 0.2p(2.0) + 90p(58) + 70p(101) + 2.7p(22) + 8000\,(T/\Theta_D)^7\,\xi_6(\Theta_D/T)\ \mathrm{GHz}.$$

The $^{141}Pr^{3+}$nucleus has a nuclear spin of $\frac{5}{2}$ and consequently nonzero magnetic dipole and electric quadrupole moments. If the Pr^{3+} site symmetry is in fact C_{2v},[7] all of the energy levels are nondegenerate and to first order have no magnetic splitting.[12] Therefore the nuclear magnetic interactions (hyperfine and superhyperfine) should be small. The nuclear electric quadrupole interactions are nonzero, and each electronic level could split into 3 levels. The allowed transitions are $\Delta m_I = 0, \pm 2$. These interactions should be 10 MHz or less. If, however, a magnetic field is applied to "bias" the ions to give a first-order magnetic splitting, then the nuclear magnetic interactions should become significant. A preliminary fluorescence-line-narrowing experiment with a 2-kG magnetic field applied parallel to the crystal c axis gives an asymmetric π line with shifts to higher frequency (1 GHz). (See Fig. 7.) These magnetic interactions will be the subject of a forthcoming paper. Lack of knowledge of the crystal field of LaF_3 prevents calculation of the hyperfine interactions. As a result these arguments are only qualitative.

The second contribution considered is that of dipolar broadening. In a system with all nondegenerate levels, the effective magnetic moments of the ions in the absence of a dc magnetic field is zero. Even in the presence of the small[13] dipolar fields of the nuclear magnetic dipoles, the broadening effect should be quite small. The narrow 5925-Å σ absorption line must argue against any such source of spectral broadening in the $^3H_4(0)$ or $^1D_2(16872\ \mathrm{cm}^{-1})$ levels. A fluorescence-line-narrowing measurement of a 1-at.%$Pr^{3+}:LaF_3$ sample yielded homogeneous linewidths of 3.5-GHz π and 5.1-GHz σ at 10 °K. Thus a factor 20 increase in Pr^{3+} concentration yielded a linewidth change by a factor of only 2.7. If the linewidth was due entirely to dipolar broadening, it should be linear in concentration.[14] Conversely, if the 1-at.%-sample linewidth is due only to dipolar broadening, then the 0.05-at.%-sample linewidths due to dipolar broadening should be 175-MHz π and 255-MHz σ.

Brown[15] and Yen[16] have considered broadening of Pr^{3+} transitions due to Nd^{3+} impurities in the host crystal. The 0.05-at.% sample used in these experiments had a Nd^{3+} concentration of 100 ppm, which would yield a $^3H_5$, Pr^{3+} linewidth of 180 MHz.[16]

These three line-broadening mechanisms, in addition to that of phonon-assisted relaxation, contribute a possible total of 200+175+180=555-MHz π, and 380+255+180=815-MHz σ at 4 °K, compared to observed linewidth of 1.0-GHz π and an estimated 1.6-GHz σ. Other contributions to the linewidth must be considered.

Future experiments should include measurements of Pr^{3+} in a crystal field of higher symmetry where the crystal-field parameters are known, so that some quantitative estimates might be made of the hyperfine interactions. It seems clear that some attention must be paid to the presence of rare-earth impurities in the crystals. For study of

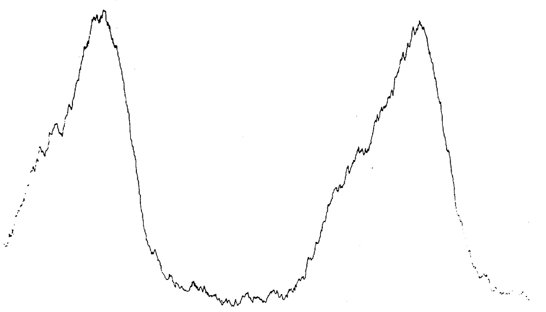

FIG. 7. Effect of a magnetic field on the fluorescence is shown. Increasing frequency is toward the left. A 2.0-kG magnetic field was applied parallel to the crystal c axis.

fluorescence line narrowing to the ground state, an ion with Kramers degeneracy would permit use of magnetic field splitting to examine the luminescence at a wavelength slightly different from the exciting light.[2]

The phonon-induced relaxation of Pr^{3+} in LaF_3 has been considered at low temperature, where it no longer is the dominant factor in the homogenous width of the $^1D_2 \rightarrow {}^3H_5$ transition. Three possible contributions to the observed width were discussed. At temperatures exceeding 15 °K, the linewidths are dominated by phonon-induced relaxation

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