VOLUME 69, NUMBER 3 PHYSICAL REVIEW LETTERS 20 JULY 1992

Inhomogeneous Broadening by Nuclear Spin Fields: A New Limit for Optical Transitions in Solids

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(Received 30 March 1992)

Using a low-strain, isotopically pure crystal of $YLiF_4$, we have measured extremely narrow inhomogeneous linewidths (as low as 40 MHz) for the optical transitions of Er^{3+} impurities. Inhomogeneous broadening due to strains and other defects is so low that a new mechanism limits the inhomogeneous linewidth: local magnetic fields due to fluorine nuclear spins. These ultranarrow lines enabled us to make the first direct measurement of the isotope shifts of *f-f* transitions in a solid, and we find for the isotopes ^{164}Er, ^{166}Er, ^{168}Er, and ^{170}Er a shift of 76 ± 2 MHz/unit mass on the $^4I_{15/2}(1) \rightarrow {}^4F_{9/2}(1)$ transition. We show that this is consistent with a mechanism of coupling to zero-point vibrations.

PACS numbers: 78.50.Ec

At low temperatures optical transitions in solids are often inhomogeneously broadened. This broadening is ascribed to strains and defects such as vacancies and dislocations produced in the crystallization process, or to the presence of impurities, often the absorbing centers themselves. At doping levels of ~100 ppm these inhomogeneous linewidths are typically 1-30 GHz, depending on the host material and crystal quality. It was recently reported [1] that a doublet structure on the *f-f* absorption lines of Ho^{3+} in $YLiF_4$ has its origin in the statistical distribution of near neighbors of ^6Li and ^7Li ions in $YLiF_4$. We have observed similar structure with splittings of 1.4 GHz and linewidths of 600 MHz in crystals of $YLiF_4$ with natural abundances of lithium isotopes and doped with 100 ppm Er^{3+} ions. The implication of this large lattice-induced isotope shift is that a distribution of isotopes in more distant neighbor positions can lead to significant inhomogeneous broadening.

Using a low-strain, isotopically pure (99.9% ^7Li) crystal of $YLiF_4$ containing naturally occurring levels of Er^{3+} impurities (~1 ppm) we have observed extremely narrow linewidths of 40-160 MHz for the $^4I_{15/2}(1) \rightarrow {}^4F_{9/2}(1)$ transition at 15302.4 cm^{-1}, and the absence of a host-induced doublet structure due to lithium isotopes. A comparison of the observed optical linewidths with computer simulations of the contributions to the linewidths resulting from the magnetic dipole-dipole interactions between the magnetic moments of the ^{19}F nuclear spins and the Er^{3+} magnetic moment reveals, for the first time, that the superhyperfine interaction can be directly observed in the inhomogeneous optical line shape of a material. In other words, the strain broadening is so low that magnetic interactions provide a new limit on the inhomogeneous broadening. Under these conditions we were able, for the first time, to directly resolve the isotope shifts of an *f-f* transition in a solid, in this case those of the major naturally occurring even-mass isotopes ^{164}Er (1.6%), ^{166}Er (33.4%), ^{168}Er (27.1%), and ^{170}Er (14.9%), and the complex hyperfine splitting pattern of ^{167}Er (22.9%). The temperature dependence of the line position is used to attribute the isotope-shift mechanism to a differential coupling to zero-point vibrations of the lattice.

The undoped crystal of $YLiF_4$ was grown by the Czochralski technique. In order to avoid any contamination of the melt by a seed, we grew the crystal on a Pt wire. The starting materials were ^7LiOH (Oak Ridge) and Y_2O_3, 99.999% (Research Chemicals). Lithium hydroxide was converted to lithium fluoride by hydrofluorination with gaseous hydrogen fluoride, and purified by zone refining in a hydrogen-fluoride atmosphere. Lithium fluoride (53 mol%) and yttrium oxide (47 mol%) were mixed together, hydrofluorinated, reacted, and premelted in an HF atmosphere.

The line shapes and positions of transitions between the $^4I_{15/2}$ ground state and the lowest crystal-field component of the $^4F_{9/2}$ state were measured in the temperature range between 1.6 and 50 K. The transitions were also studied as a function of magnetic field in the range 0 to 6 kG directed along the crystal *c* axis. The spectra were obtained in excitation by scanning a single-frequency tunable dye laser (1 MHz linewidth) across the inhomogeneous line profiles while monitoring the fluorescence to the higher-lying components of the $^4I_{15/2}$ state at longer wavelengths than the laser. Low laser intensities (~10 mW/cm^2) were used to clearly avoid line-shape distortion or heating.

The structure in the optical spectra shown in Fig. 1 for the laser polarized parallel (π) and perpendicular (σ) to the *c* axis has two contributions: isotope shifts and hyperfine interaction. The relative absorption strengths of the three major lines are approximately in the ratio of the abundances of the three major even-mass Er isotopes, with a separation of 76 MHz/unit mass. The multiple

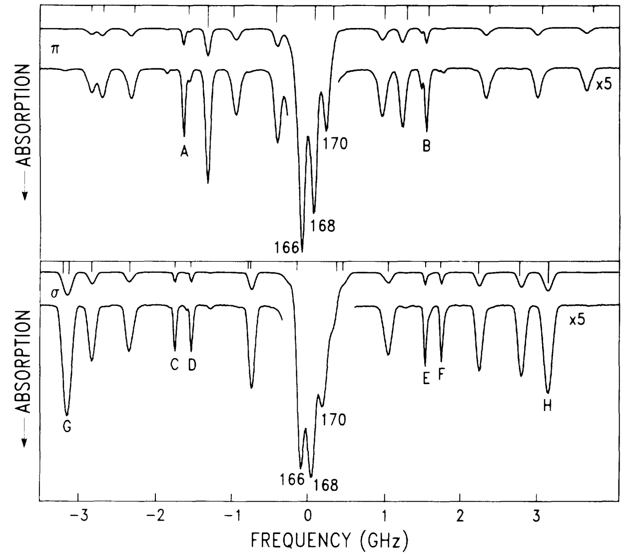

FIG. 1. Polarized excitation spectra of the $^4I_{15/2}(1) \rightarrow {}^4F_{9/2}(1)$ transition of Er^{3+}:Y^{7}LiF$_4$ at 15 302.4 cm^{-1} showing resolved isotope shifts (^{166}Er, ^{168}Er, ^{170}Er) in the main line and the weaker, resolved hyperfine structure of ^{167}Er^{3+}. Calculated positions and intensities normalized to the even-isotope lines are shown by the sticks. The amplified trace of the ^{167}Er hyperfine lines shows in the π spectrum narrow singlet transitions (A,B), with line shifts of only 0.23 MHz at 1 G and 5.5 MHz at 5 G (quadratic in field), and in the σ spectrum narrow weakly magnetic doublet transitions with linear splittings of 0.44 MHz/G (C,D,E,F) and broad more strongly magnetic doublets (e.g., H) with a linear splitting of 17.9 MHz/G. Hyperfine parameters (in MHz) for ^{167}Er are as follows: ground state, $A=-325.8$, $B=840$, $P=0$; excited state, $A'=-1280$, $B'=50$, $P'=48$.

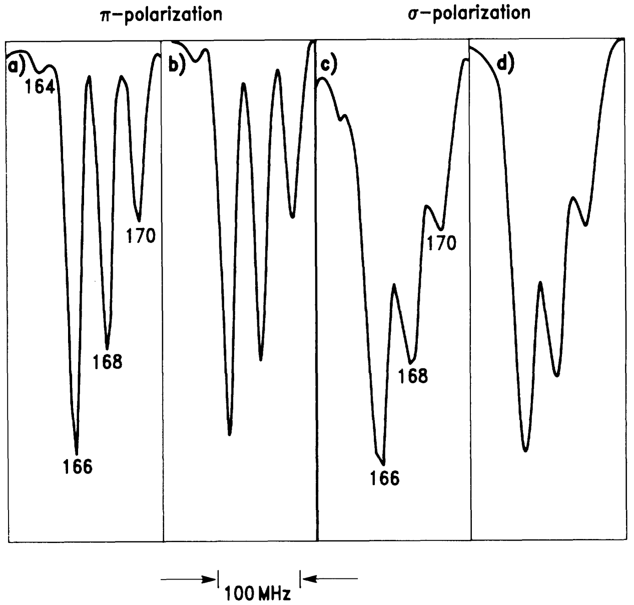

FIG. 2. Fit to the isotope shifts of the π [(a) experiment, (b) fit] and σ [(c) experiment, (d) fit] $^4I_{15/2}(1) \rightarrow {}^4F_{9/2}(1)$ absorption at 74 G using natural abundances of the erbium isotopes and the following parameters. For the π spectrum $\Gamma_{\text{inhom}}=75$ MHz; isotope shift, 76 MHz/unit mass. For the σ spectrum $\Gamma_{\text{inhom}}=120$ MHz; isotope shift, 76 MHz/unit mass. Note the appearance of ^{164}Er in the π spectrum.

weaker lines are due to transitions between the components of the ground- and excited-state Kramers doublets of ^{167}Er (nuclear spin $I=7/2$), split into a complex pattern by the hyperfine interaction. Some of these hyperfine lines occur at nearly the same frequencies as those of the even isotopes and this may explain the small deviations at zero field of the intensities from those predicted on the basis of the natural abundances. The application of a small magnetic field can remove these accidental degeneracies, giving better agreement between the intensities and the isotope abundances. It also separates the Zeeman components, which exhibit an unresolved splitting in the local field of the fluorine ions, thereby producing narrower inhomogeneous linewidths which enable the observation of ^{164}Er in the π spectrum. This is shown in Fig. 2 where two Zeeman transitions (one each in π and σ) in a magnetic field of 74 G are compared with a spectrum for the even isotopes assuming a superposition of single lines for each isotope, weighted by their natural abundance. A best fit obtained by varying the isotope shift and the Gaussian linewidth of each component (same for each isotope in a given polarization) is shown in Fig. 2 where the four major even isotope contributions follow the expected natural abundance ratios. The fit yields an isotope shift of 76 ± 2 MHz/unit mass and inhomogeneous linewidths of 75 ± 3 and 120 ± 5 MHz for the π and σ spectra, respectively. For comparison, an isotope shift of 180 MHz/unit mass was reported for LaCl$_3$:Nd^{3+} [2]. It was inferred from the shift in transition frequency (unresolved splitting) of several samples doped with different enrichments of Nd isotopes.

The mechanism for the isotope shift was examined by comparing its magnitude with the temperature dependence of the line shift as was done in ruby by Imbusch *et al.* [3], who showed that the interaction of Cr^{3+} ions with the zero-point vibrations of the lattice dominated the isotope shift. We find a similar result for Er^{3+}:YLiF$_4$. This role for the zero-point vibrations was previously indicated [2] for LaCl$_3$:Nd^{3+}. The observed temperature dependence of the line position for the transition to $^4F_{9/2}(1)$ is shown in Fig. 3 and it is described by $\Delta\nu(T) \equiv \nu(T) - \nu(0) = DT^4$, where $\nu(0)$ is the zero-temperature transition frequency, and $\nu(T)$ is the transition frequency at the temperature T. We find $D=-3.5\times10^{-4}$ MHz/K^4.

In the model of Imbusch *et al.* [3] the ratio of the zero-temperature isotope shift to the thermal shift is proportional to the ratio of rms displacements due to zero-point vibrations to that of the thermally activated vibrations. For an impurity in a host lattice the predicted isotope shift per unit mass is approximately

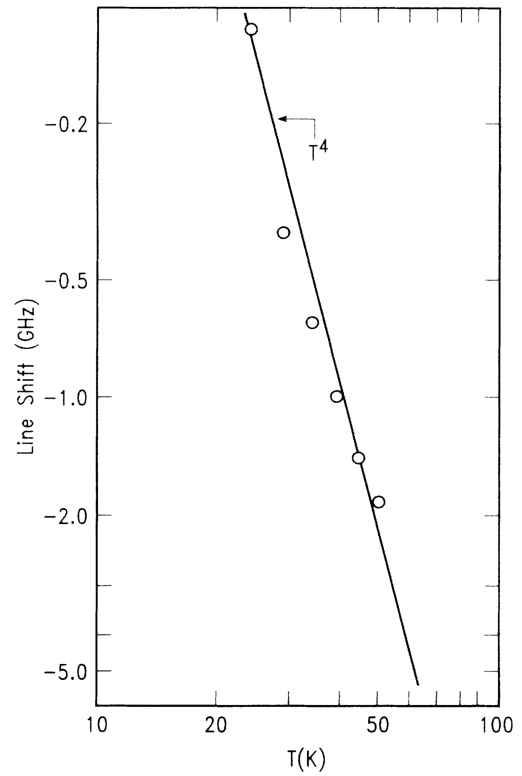

FIG. 3. Temperature dependence of the position $[\Delta=\bar{\nu}(T)-\nu(0)]$ of the 15302.4-cm^{-1} line.

$$\delta(\Delta\nu(0)) \cong -\frac{\Delta\nu(0)}{2m'}\left[\frac{(m/m')^{1/2}}{1+(m/m')^{1/2}}\right], \qquad (1)$$

where $\Delta\nu(0)$ is the shift of the optical transition frequency due to zero-point vibrations, m is the average host-lattice mass ($m=29$ for YLiF$_4$), and m' is the impurity mass ($m'=168$ for Er). Using the Debye theory we obtain $\Delta\nu(0)$ from the thermal shift, $\Delta\nu(T)$, as

$$\frac{\Delta\nu(0)}{\Delta\nu(T)}=\frac{15}{8\pi^4}\left[\frac{T_D}{T}\right]^4, \qquad (2)$$

where T_D is the Debye temperature for YLiF$_4$. Since the specific heat has not been measured for YLiF$_4$, we use an estimate of the Debye temperature, $T_D=279$ K, based on the measured elastic constants [4]. The predicted result for the isotope shift is 36 MHz/unit mass which is in reasonable agreement with the observed result of 76 MHz/unit mass considering the simplicity of the model and the uncertainty in the Debye temperature. A value of $T_D=336$ K brings experiment and theory into complete agreement. Further confirmation of the phonon mechanism for the isotope shift comes from measurements on the ${}^4I_{15/2}(1)\rightarrow{}^4I_{9/2}(1)$ transition at 12361.1 cm^{-1}, where we measure an isotope shift of 26 MHz/unit mass and calculate from the thermal line shift a value of 16 MHz/unit mass. Again the calculated value is low by about a factor of 2 and agreement with experiment is obtained with $T_D=315$ K.

The remaining weaker lines were confirmed as resulting from the optical hyperfine structure for ^{167}Er, by fitting their energies and intensities using the spin Hamiltonian

$$\mathcal{H}=g_\parallel\beta H_zS_z+g_\perp\beta(H_xS_x+H_yS_y)+AI_zS_z$$
$$+B(I_xS_x+I_yS_y)+P[I_z^2-\tfrac{1}{3}I(I+1)] \qquad (3)$$

and the known ground-state hyperfine parameters [5] for Er^{3+} in YLiF$_4$. We then varied the excited-state parameters to give the best fit shown by the sticks under the spectra of Fig. 1. The heights of the sticks indicate the calculated intensities relative to the even-isotope intensities and include the degeneracies of the transitions at zero field. The heights should be compared with the integrated area in the observed lines since their widths are not equal. The coupling of the half-odd-integer electron and nuclear spins results, for S_4 site symmetry, in both nonmagnetic singlets and magnetic doublet levels. Spectra obtained in a small magnetic field confirm the predicted degeneracies. The fit is excellent. Note that some of the ^{167}Er hyperfine lines underlie the even-isotope transitions.

The evidence for the contribution of the superhyperfine interactions to the inhomogeneous line shape is based on the difference in the linewidths of the π and σ spectra of the even isotopes, and the linewidths observed for the hyperfine components of ^{167}Er. For all magnetic fields, the linewidths of the σ spectrum for the even isotopes exceed those of the π spectrum by 40–50 MHz. We show below that this is just what is predicted based on the interactions of the Er^{3+} magnetic moments in the ground and excited states with the random distribution of the F nuclear spins.

In these very dilute samples ($\cong 1$ ppm), we can estimate from previous measurements of T_2 in 200-ppm samples as a function of magnetic field and temperature [6] that even at zero field $\Gamma_{\text{hom}}<1$ MHz. Therefore this contribution is negligible and the lines are inhomogeneously broadened. Since we studied transitions between the Zeeman sublevels of a pair of crystal field levels (ground and excited state), we consider the contribution to the linewidth from strains and crystal defects to be a constant for all transitions, independent of magnetic field and polarization.

The frequency shift due to the magnetic dipole-dipole superhyperfine interaction between the Er^{3+} electron spin moment and the surrounding F nuclear moments is obtained from H_{loc}, the local field acting at the Er^{3+} site and is given by

$$\Delta\nu=\pm\tfrac{1}{2}(g\pm g')\beta H_{\text{loc}} \qquad (4)$$

for the four Zeeman transitions where $g=3.14$, the ground-state g value, $g'=9.61$, the excited-state g value, and β is the Bohr magneton. The contribution to the optical line shape due to the magnetic dipole-dipole interaction is obtained by calculating H_{loc} for a large number

(2000) of random distributions of orientations of F nuclear spins located on the $YLiF_4$ lattice. The calculation was performed by including the 3600 nearest F spins. The resulting contribution to the line shape is found from a histogram of the resulting values of $\Delta\nu$.

The calculation of H_{loc} requires a knowledge of the fields at each of the F nuclei, H_F, since that will determine the direction of the F magnetic moment. H_F consists of the sum of the external field H_0 and the local field produced by the Er^{3+} magnetic moment, H'_F (H'_F can be as large as 2 kG on the F nearest the Er^{3+}). The situation is simplest for large fields where $H_0 \gg H'_F$. Under this condition, the F nuclear spins and the Er^{3+} electron spins are all quantized along the H_0 direction (c axis here). $\Delta\nu$ is then determined solely by the c-axis component of H_{loc} according to Eq. (4). A computer simulation of the magnetic dipole-dipole line shape gives a Gaussian of 30 MHz width for the π spectrum and 60 MHz for the σ spectrum. The σ spectrum is broader because the line splits with the sum of ground- and excited-state g values, whereas for the π spectrum it is the difference. Note that the linewidths in the zero-field spectra of Fig. 1 are broader than those of the separated Zeeman components in Fig. 2 because at zero field there is an additional unresolved splitting of the two Zeeman levels in the local field of the fluorine spins. For intermediate fields such that $H_{loc} < H_0 < H'_F$ the Er^{3+} spins are still quantized along the c axis but the F spins have an axis which is different for each spin depending on the direction of H'_F. While the distant spins are quantized along the c axis, F nuclei near the Er^{3+} may have very different spin directions. A correct calculation would require an evaluation of H'_F at each F nucleus. We have not performed such a simulation, but one would not expect this to alter the calculated linewidths by more than $\pm 20\%$ (< 10 MHz). Finally for low fields such that $H_0 < H_{loc}$ the Er^{3+} moments are no longer quantized along the c axis and the anisotropy of the g tensor must be considered in calculating the difference in excited- and ground-state magnetic moments along the local field direction. In addition, for very low fields, the two π (σ) transitions, while split, are not resolved, so that a calculation of the observed linewidth must consider the sum of two slightly separated transitions even for $H_0 = 0$.

From the excellent fit of the 74-G spectra (Fig. 2), inhomogeneous linewidths of 75 MHz (π) and 120 MHz (σ) were obtained. These linewidths are the sum of the strain and magnetic dipole-dipole contributions. Since the latter are 30 MHz (π) and 60 MHz (σ), we conclude that a strain broadening of ~50 MHz contributes to the optical linewidth of these Er^{3+} transitions.

For very low fields, some of the hyperfine lines of ^{167}Er exhibit even narrower linewidths as shown in Fig. 1 for an amplified $H_0 = 0$ spectrum. The hyperfine calculations show that lines labeled A and B in the π spectrum are the only observable singlet-singlet transitions and their energies are insensitive to the c-axis component of the local magnetic field [$\Delta\nu(5\ G) = 5.5$ MHz]. In addition, the transitions labeled C, D, E, and F in the σ spectrum, while they are doublets, each have shifts of ~4 and ~6 MHz resulting in splittings of only 2.2 MHz at 5 G. These sensitivities to the magnetic field are more than an order of magnitude less than those of all the other hyperfine transitions. It is just these lines which have the smallest widths, with those of A and B being only 40 MHz. Therefore these linewidths represent the upper limit on the strain broadening which is 40 MHz, in agreement with the even-isotope line-shape fits. Conversely, line H in the σ spectrum, the broadest doublet, is also the doublet with the largest calculated low-field splittings (89 MHz at 5 G), further confirming the role of the random local fields due to the superhyperfine interaction in determining the inhomogeneous linewidths.

It is now possible to make some general statements about the limits on the inhomogeneous broadening of Er^{3+} in $YLiF_4$. For Er^{3+} concentrations $> 0.1\%$, the inhomogeneous broadening (> 1 GHz) is dominated by the strain fields caused by the presence of other Er^{3+} ions. For concentrations $< 0.1\%$ it is the random distribution of ^6Li (7.24% abundance) and ^7Li (92.58% abundance) isotopes in the lattice which limits the inhomogeneous width ($\simeq 600$ MHz) for materials of natural isotopic abundance. However, in isotopically pure Y^7LiF_4 the strain broadening is 40 MHz and the limit on the inhomogeneous linewidth comes mostly from superhyperfine interactions (up to 120 MHz depending on the magnetic character of the levels) with a constant strain determined width of ~50 MHz. This has enabled us to precisely determine the small isotope shift of a f-f transition.

Certainly there must be other materials with comparable or even narrower inhomogeneous linewidths. These are likely to be found only in cases of ultralow dopant concentration and in isotopically pure samples.

We acknowledge the support of the National Science Foundation Grants No. DMR-90-15466 (R.S.M.) and No. DMR 90-22933 (A.C.).

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