

## Isotope Structure in Optical Spectra of $\text{LiYF}_4:\text{Ho}^{3+}$

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We report the first observation of isotope shifts in optical spectra of an impurity in a solid associated with isotopes in the impurity surrounding. Static and dynamic couplings of impurity electronic states with the crystal lattice are discussed as a possible cause of the observed isotope structure in optical spectra of  $\text{LiYF}_4:\text{Ho}$ .

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To our knowledge, the previously observed isotope shifts in optical spectra of impurity centers in solids always originated from the presence of more than one isotope of the impurity itself. The shift of the  $R_1$  line in ruby discovered by Schawlow<sup>1</sup> is probably the best known example. The frequency of the electronic transition in chromium shifts by  $0.27\text{ cm}^{-1}$  when the main isotope  $^{52}\text{Cr}$  is replaced by  $^{50}\text{Cr}$ . This shift is mainly due to the difference in the frequencies of the local vibrations associated with chromium isotopes in the ground and excited states. In this Letter we present evidence for isotope shifts in optical spectra of  $\text{Ho}^{3+}$  impurity in  $\text{LiYF}_4$  associated with the isotopes  $^7\text{Li}$  and  $^6\text{Li}$  in its neighborhood. Holmium itself has only one stable isotope ( $^{165}\text{Ho}$ ), as does yttrium ( $^{89}\text{Y}$ ) and fluorine ( $^{19}\text{F}$ ).

The  $\text{Ho}^{3+}$  ion substitutes for the  $\text{Y}^{3+}$  ion in the  $\text{LiYF}_4$  crystal and is at sites of tetragonal symmetry (point group  $S_4$ ). Its ground state is  $\Gamma_{34}$ ; the next one, lying  $7\text{ cm}^{-1}$  higher, is  $\Gamma_2$ . Since the  $\text{Ho}^{3+}$  ion has practically the same ionic radius as the  $\text{Y}^{3+}$  ion it does not distort the lattice. Inhomogeneous broadening of spectral lines in  $\text{LiYF}_4:\text{Ho}$  crystals is extremely small, so one can observe very fine effects even without selective-excitation techniques. In particular, nuclear hyperfine structure due to the interaction between the electronic core and the holmium nucleus has been observed and analyzed<sup>2</sup> in optical spectra of  $\text{LiYF}_4:\text{Ho}$  (1 at. %).

To investigate isotope effects three  $\text{LiYF}_4:\text{Ho}$  (0.1 at. %) single crystals with different contents of  $^6\text{Li}$  and  $^7\text{Li}$  isotopes were grown by the Stockbarger method. The  $\text{Li}_2\text{CO}_3$  compound with known lithium isotope composition was taken as a starting material. It was transformed into  $\text{LiF}$  by the "dry" method.<sup>3</sup> The crystals were then grown from the mixture of appropriate fluorides.<sup>3</sup> The absorption spectra in the regions of the  $^5I_8 \rightarrow ^5I_{7,6,5}$  transitions in the  $\text{Ho}^{3+}$  ion were taken at 5.0 K with spectral resolution up to  $0.004\text{ cm}^{-1}$ , employing the high-resolution Fourier-transform spectrometer DA3.002 produced by BOMEM.

Figure 1 shows an example of a spectrum with well

resolved hyperfine structure. The inset demonstrates the splitting of each hf component observed in the spectra of  $\text{LiYF}_4:\text{Ho}$  crystals with both the  $^7\text{Li}$  and  $^6\text{Li}$  isotopes present. This structure within a hf component is equidistant in most cases; separate lines in a split component are as narrow as  $0.008\text{ cm}^{-1}$  in some transitions. Their relative intensities depend upon the lithium isotope composition. Table I lists these intensities for the nonsaturated spectral lines of Fig. 1, and also the calculated ones according to the well known formula

$$P_N(n) = C_N^n x^n (1-x)^{N-n}, \quad (1)$$

where  $P_N(n)$  is the probability to find  $n$   $^6\text{Li}$  isotopes (whose relative concentration is  $x$ ) in the  $\text{Ho}^{3+}$ -ion environment which consists of  $N$  sites for lithium ions. The measured intensities correspond well to the calculated ones provided  $N=4$ . The only exception found is for the line  $5149\text{ cm}^{-1}$  of the transition  $\Gamma_2^{(1)}(^5I_8) \rightarrow \Gamma_{34}^{(1)}(^5I_7)$  where it is necessary to assume that not only four nearest neighbors contribute but also four next-nearest ones and

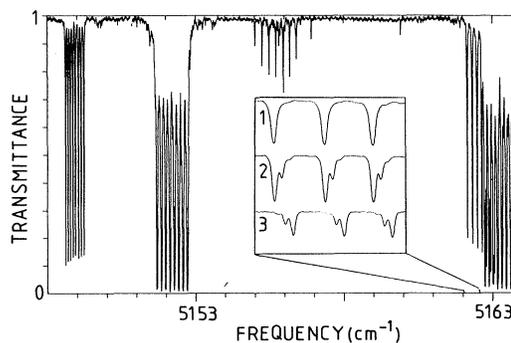


FIG. 1. The low-frequency part of the transition  $^5I_8 \rightarrow ^5I_7$  of  $\text{Ho}^{3+}$  in  $^7\text{LiYF}_4:\text{Ho}$  (0.1 at. %) at 2.0 K. **E, H**  $\perp$  **c** polarization. Spectral resolution  $0.004\text{ cm}^{-1}$ . Inset: The splittings of hf components in the mixed crystals  $^7\text{Li}_{1-x}^6\text{Li}_x\text{YF}_4:\text{Ho}$  (0.1 at. %): (1)  $x=0.005$ , (2)  $x=0.0742$  (natural abundance), (3)  $x=0.9$ .

TABLE I. Measured and calculated relative intensities of the lines in the split hyperfine components and the frequency shifts  $\Delta\nu$  ( $\text{cm}^{-1}$ ) between them in  ${}^7\text{Li}_{1-x}{}^6\text{Li}_x\text{YF}_4:\text{Ho}$ .

| $x=0.0742$ (natural abundance) |          |                                    |                                       |                                    |                          |
|--------------------------------|----------|------------------------------------|---------------------------------------|------------------------------------|--------------------------|
| $n$                            | $P_N(n)$ | $\Gamma_2 \rightarrow \Gamma_{34}$ | $\Gamma_{34} \rightarrow \Gamma_{34}$ | $\Gamma_{34} \rightarrow \Gamma_1$ |                          |
|                                | $N=4$    | $N=8$                              | $5149 \text{ cm}^{-1}$                | $5156 \text{ cm}^{-1}$             | $5162.8 \text{ cm}^{-1}$ |
| 0                              | 0.735    | 0.540                              | 0.56                                  | 0.74                               | 0.75                     |
| 1                              | 0.235    | 0.346                              | 0.35                                  | 0.23                               | 0.22                     |
| 2                              | 0.028    | 0.097                              | 0.072                                 | 0.024                              | 0.03                     |
| 3                              | 0.0015   | 0.016                              | 0.011                                 |                                    |                          |
| 4                              |          | 0.0016                             | 0.002                                 |                                    |                          |
| $\Delta\nu$                    |          |                                    | 0.015                                 | 0.015                              | 0.025                    |

| $x=0.9$     |            |        |                        |                        |                          |
|-------------|------------|--------|------------------------|------------------------|--------------------------|
| $N-n$       | $P_N(N-n)$ |        |                        |                        |                          |
|             | $N=4$      | $N=8$  | $5149 \text{ cm}^{-1}$ | $5156 \text{ cm}^{-1}$ | $5162.8 \text{ cm}^{-1}$ |
| 0           | 0.656      | 0.430  | 0.45                   | 0.70                   | 0.65                     |
| 1           | 0.292      | 0.383  | 0.37                   | 0.30                   | 0.30                     |
| 2           | 0.049      | 0.149  | 0.15                   |                        | 0.05                     |
| 3           | 0.0036     | 0.033  | 0.034                  |                        |                          |
| 4           | 0.0001     | 0.0046 | 0.0049                 |                        |                          |
| $\Delta\nu$ |            |        | 0.015                  | 0.015                  | 0.025                    |

so  $N=8$ . The nearest surroundings of the  $\text{Ho}^{3+}$  ion can be seen in Fig. 2.

The lithium isotopes differ in their masses and nuclear magnetic moments. The difference in magnetic moments cannot account for the observed spectral changes primarily because the interaction with these moments is too small. Estimates show that the corresponding super-hyperfine structure is on the scale of  $10^{-4} \text{ cm}^{-1}$ . Two mechanisms of isotope shifts can arise from the difference in masses: the dependences of (i) the static crystal field and (ii) the electron-vibrational coupling for the  $\text{Ho}^{3+}$  ion upon the isotope composition around it.

(i) Because of the difference in masses of the lithium isotopes the amplitudes of their zero-field vibrations differ and this may lead to different equilibrium positions of the nearest fluorine ions through the anharmonicity of zero-field vibrations.<sup>5</sup> Provided the  ${}^6\text{Li}$  and  ${}^7\text{Li}$  isotopes are distributed randomly over the lattice sites, the long-range electrostatic contribution to the crystal field is practically the same for all  $\text{Ho}^{3+}$  impurities. The exchange contribution, on the contrary, depends critically on the positions of the nearest fluorines (ligands) only, which, in turn, may depend on whether the nearest-neighbor lithium is the  ${}^6\text{Li}$  or  ${}^7\text{Li}$  ion. According to the superposition model of the crystal field<sup>6</sup> the contributions from separate ligands are additive, so it would be easy to explain the observed equidistance in the isotope structure within a hf component.

There exists experimental evidence that the static crystal field for the  $\text{Ho}^{3+}$  ion is indeed sensitive to the lithium isotope. We first note that the possible change in the crystal field for the  $\text{Ho}^{3+}$  ion when introducing one foreign isotope into its surrounding includes a lowering

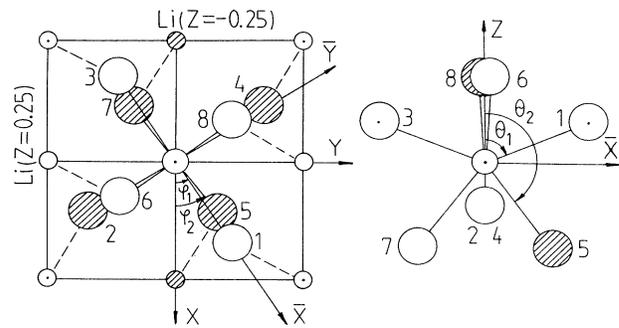


FIG. 2. The projections of the nearest surroundings of the  $\text{Ho}^{3+}$  ion in  $\text{LiYF}_4$  on the  $X$ - $Y$  plane and of the F ligands on the  $X$ - $Z$  plane. The ions lying above the planes are shown as open circles, those below are shaded, while those in the planes have a point in the center. The F ligands 1-4 are at  $R_1=2.246 \text{ \AA}$  and 5-8 are at  $R_2=2.293 \text{ \AA}$  from the  $\text{Ho}^{3+}$  ion (in the center).  $\theta_1=67.08^\circ$ ,  $\theta_2=142.05^\circ$ ,  $\varphi_1=33^\circ$ ,  $\varphi_2=36.98^\circ$ . Each ligand is at  $1.88 \text{ \AA}$  from the nearest  $\text{Li}^+$  ion shown by the dotted line (see Ref. 4).

of the center symmetry. Let us consider a small low-symmetry crystal-field perturbation  $\hat{V}$  acting upon a hf sublevel of the  $\Gamma_{34}$  electronic state. Each hf sublevel is doubly degenerate, the states  $\Gamma_3M$  and  $\Gamma_4M$  having the same energy<sup>2</sup> [ $M$  runs over  $2I+1$  values of possible projections of the nuclear momentum  $K = \frac{7}{2}$ ; see Fig. 3(a)]. It is easy to show that the first-order correction of the perturbation theory shifts all the hf sublevels equally. The second-order correction is  $M$  dependent:

$$\epsilon_2(\Gamma_3M) = \epsilon_2(\Gamma_4M) = \frac{|\langle \Gamma_3 | \hat{V} | \Gamma_4 \rangle|^2}{E(\Gamma_3M) - E(\Gamma_4M)}. \quad (2)$$

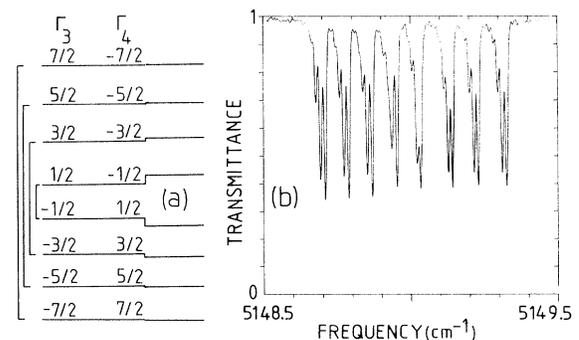


FIG. 3. (a) Transformation of the hyperfine structure of the  $\Gamma_{34}$  level under a low-symmetry perturbation. The energy denominators entering into formula (2) are marked at the left. (b) The transition  $\Gamma_2^{(1)}(5I_8) \rightarrow \Gamma_{34}^{(1)}(5I_7)$  disturbed by a low-symmetry perturbation. The crystal  ${}^7\text{Li}_{0.1}{}^6\text{Li}_{0.9}\text{YF}_4:\text{Ho}$  (0.1 at.%) at 4.0 K. The strongest lines within hf components belong to the main center ( $\text{Ho}^{3+}$  ion with no  ${}^7\text{Li}$  isotopes in the vicinity), and the next strongest, to the center with one  ${}^7\text{Li}$  isotope in the vicinity.

The denominator in this expression is the smallest for the middle hf components with  $M = \pm \frac{1}{2}$ , and as a result the hyperfine components move apart as is shown in Fig. 3(a). The 5149-cm<sup>-1</sup> line in Fig. 3(b) demonstrates an experimentally observed example of such a behavior: The middle interval between hf components is larger for the center with one foreign isotope than for the main center. This difference is 0.01 cm<sup>-1</sup>, and one has to anticipate the same order of magnitude for the shifts of the impurity electronic levels due to the change of crystal-field parameters.

The isotope shifts measured for the hf components with well resolved structure<sup>7</sup> are actually 0.014–0.030 cm<sup>-1</sup> (see, e.g., Table I), the lines of the centers with light isotopes always being at the high-frequency side. Careful measurements of the line positions in the whole crystal-field multiplet for the <sup>7</sup>LiYF<sub>4</sub> and <sup>6</sup>LiYF<sub>4</sub> crystals established shifts of 0.02–0.1 cm<sup>-1</sup>, always to higher frequencies for the crystal with the light isotope relative to the crystal with the heavy one. Since the shifts of crystal-field levels due to the change in crystal-field parameters are expected to have different signs within a given multiplet (we have confirmed that by direct calculations), to account for the result mentioned above it is necessary to assume additional shifts of the centers of gravity of the crystal-field multiplets due to a change in the “free ion” parameters. Such a change might be caused by the dependence of the Ho<sup>3+</sup> effective charge upon the positions of the ligands. We note, however, that in this case the shifts would increase from the <sup>5</sup>I<sub>7</sub> level to the <sup>5</sup>I<sub>5</sub> one.<sup>8</sup> This is not observed.

(ii) Another mechanism which might cause the isotope frequency shifts is the coupling between lattice vibrations and the electrons in the 4f shell of the Ho<sup>3+</sup> ion. Such a coupling appears due to the modulation of the crystal field by lattice vibrations. It gives rise to, in general, temperature-dependent shifts of the electronic levels and hence of the corresponding transitions.<sup>9,10</sup> The temperature-independent “zero-phonon-field” contribution to the energy  $E_i$  of the  $i$ th electronic level (similar to the Lamb shift due to the interaction with zero electromagnetic field) is given by<sup>9</sup>

$$E_i = \frac{1}{2\hbar} \sum_j \sum_{\Gamma\gamma} |\langle j | \hat{V}_{\Gamma\gamma} | i \rangle|^2 \int \frac{|b_{\Gamma\gamma}(\omega)|^2 \rho(\omega) d\omega}{\omega(E_i - E_j - \hbar\omega)}, \quad (3)$$

where  $\hat{V}_{\Gamma\gamma}$  are the electronic irreducible tensor operators which transform in accordance with the  $\gamma$  row of the  $\Gamma$  representation of the impurity-center point group,  $\rho(\omega)$  is the vibrational density of states, and  $b_{\Gamma\gamma}(\omega)$  describes the contribution of the crystal vibration with frequency  $\omega$  to the vibration  $\Gamma\gamma$  of the complex formed by the impurity ion and the ligands.  $b_{\Gamma\gamma}(\omega)$  is proportional to the linear combination of the ligand displacements in a given crystal vibrational mode. The product  $|b_{\Gamma\gamma}(\omega)|^2 \rho(\omega)$  may be called the “effective density of states.” The summation is performed over the electronic states. Principal

value of the integral is supposed. Only the linear term in vibrational coordinates of the electron-vibrational interaction is taken into account in (3).

In an ideally periodic crystal the values of  $b_{\Gamma\gamma}(\omega_s)$ , as well as of the ion displacements in a given vibrational mode  $\omega_s$ , have the order of magnitude  $1/\sqrt{3N}$  ( $N$  being the total number of atoms in a crystal). The introduction of an impurity much lighter than the atoms of a crystal leads to the appearance of a local mode whose frequency lies above the bands of crystal vibrations and whose amplitude is localized at the impurity. But even in the case when the difference in masses is not sufficient for the occurrence of a local vibration, and the frequencies of crystal vibrations practically do not change, the amplitude patterns change dramatically for some vibrations.<sup>10</sup> One may anticipate that the displacements of the <sup>6</sup>Li impurity and its nearest neighbors in a <sup>7</sup>LiYF<sub>4</sub> crystal increase for high-frequency vibrations. As a result, the effective density of states shifts to higher frequencies for the Ho<sup>3+</sup> ion with a <sup>6</sup>Li isotope in its neighborhood. Taking into account the frequency dependence of the vibrational density of states in LiYF<sub>4</sub> crystals<sup>11</sup> [the first peak at  $\omega \approx 100$  cm<sup>-1</sup>, maximum at  $\omega \approx 350$  cm<sup>-1</sup>,  $\rho(\omega) \approx 0$  for  $\omega > 500$  cm<sup>-1</sup>] and the crystal-field splittings [ $\Delta E(^5I_7) = 140$  cm<sup>-1</sup>;  $\Delta E(^5I_6) = 126$  cm<sup>-1</sup>;  $\Delta E(^5I_5) = 93$  cm<sup>-1</sup>], it is easy to show that the energy shift is smaller for such a Ho<sup>3+</sup> ion and the difference  $\delta E - \delta E^{(6)}$  is positive ( $\delta E$  denotes the energy shift for the main center, and  $\delta E^{(6)}$  the shift for the center with one <sup>6</sup>Li isotope present). The frequency shift in the transition between the initial state  $i$  and the final one  $f$  is given by

$$\Omega = (\delta E_f - \delta E_f^{(6)}) - (\delta E_i - \delta E_i^{(6)}). \quad (4)$$

To account for the observed positive values of  $\Omega$  the second term in (4) must be smaller than the first one. The energy shifts in the ground state might be smaller due to either smaller constants of electron-vibrational interaction  $\langle j | \hat{V}_{\Gamma\gamma} | i \rangle$  or smaller integrals in (3). The latter is quite possible in view of the crystal-field level structure of the ground state: There are two groups of levels approximately 230 cm<sup>-1</sup> apart, the whole splittings being 317 cm<sup>-1</sup>—2.5 times more than for the excited states <sup>5</sup>I<sub>7,6,5</sub>. Calculations are necessary to evaluate the effects under consideration quantitatively. We hope these calculations can solve the enigma of the 5149-cm<sup>-1</sup> line with eight ligands taking part in the formation of the structure within its hf components. Simple symmetry considerations do not help here.

In summary, we have observed and characterized the isotope shifts in optical spectra of a monoisotope impurity in a solid associated with isotopes in its neighborhood. The changes both in crystal-field parameters for the rare-earth impurity ion and in the coupling of its electronic states with lattice vibrations when introducing an isotope into the impurity surrounding apparently play a

role in the formation of the isotope structure of the spectral lines. The nature of this isotope structure gives evidence that the exchange interaction with ligands is of principal importance for the spectra formation.

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<sup>5</sup>It is worth mentioning that while the anharmonicity of thermal vibrations leads to the well known phenomenon of thermal expansion, the anharmonicity of zero-field vibrations should lead to a difference in lattice parameters for crystals of different isotope composition.

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<sup>7</sup>High-frequency lines in each crystal-field multiplet are dramatically broadened due to the nonradiative phonon relaxation.

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