# Study of isotope composition in crystals by high resolution spectroscopy of monoisotope impurity

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(Submitted 3 February 1993)
Zh. Eksp. Teor. Fiz. **103**, 2215–2222 (June 1993)

We have found that the frequencies of electronic transitions within the single-isotope $Ho^{3+}$ impurity in $LiYF_4$ crystal depend on the composition of lithium isotopes in the immediate vicinity of $Ho^{3+}$ and that the region includes a different number ($N=4$ or 8) of $Li^+$ sites for different transitions. We investigate the isotope structure for a large number of transitions of different symmetries and show that the $N=4$ or 8 situation is not connected with the transition symmetry. The spectral line at 11235 $cm^{-1}$ is proposed to be used for precise determination of the unknown ratio $^6Li$:$^7Li$ of lithium isotopes in crystals.

## 1. INTRODUCTION

Recently, the isotope structure in the optical spectra of $Ho^{3+}$ in $LiYF_4$ due to the lithium isotopes has been found.[1] It was the first observation of isotope shifts in the electronic optical spectrum of an impurity due to crystalline-matrix isotopes. Holmium is monoisotopic, as are yttrium and fluorine, but lithium has two isotopes, namely, $^7Li$ and $^6Li$.

The $Ho^{3+}$ ion substitutes for the $Y^{3+}$ ion and is situated at the sites of tetragonal symmetry ($S_4$ point group) in the $LiYF_4$ crystal. Its ground state is $\Gamma_{34}$ and for the next one lying 7 $cm^{-1}$ higher is $\Gamma_2$. The calculations show that the energy levels of $Ho^{3+}$ in $LiYF_4$ can be satisfactorily described using the $D_{2d}$ point group of higher symmetry.[2,3] In this group, the symmetry of the ground state is $E$ and that of the next state is $B_1$.

Since the $Ho^{3+}$ ion has practically the same ionic radius as the $Y^{3+}$ ion, it does not distort the lattice. The inhomogeneous broadening of spectral lines in $LiYF_4$ crystals is extremely small (0.008 $cm^{-1}$ for some lines,[1] and the nuclear hyperfine (hf) structure due to the interaction between the electronic core and the holmium nucleus can be observed even without selective excitation technique.[4,5] Each hf component in the spectrum of $Ho^{3+}$ in $LiYF_4$ crystal containing both $^7Li$ and $^6Li$ isotopes is split into equidistant lines with 0.01–0.03 $cm^{-1}$ separation between them (depending on the particular hf multiplet). The relative intensities $I_n$ of these lines are proportional to the probabilities to find $n$ $^6Li$ isotopes (whose relative concentration is $x$) in the $Ho^{3+}$ ion environment, which consists of $N=4$ sites for lithium ions, supposing a random distribution of the $^6Li$ and $^7Li$ isotopes over these sites:

$$I_n = C_N^n x^n (1-x)^{N-n}. \quad (1)$$

This fact has been established by comparing the calculated intensities according to (1) and the measured ones for the crystal with natural isotope abundance ($x=0.0742$) and the crystal enriched with $^6Li$ isotope ($x=0.9$ as was indicated in the certificate). The measurements were performed on a high-resolution Fourier-transform spectrometer (FTS).[1]

Two exceptions were found:[1,6] for the hf multiplets near 5149 $cm^{-1}$ and near 5153 $cm^{-1}$ it was necessary to assume that not only the four nearest neighbors contribute but also the four next nearest ones and so $N=8$. The first of these hf multiplets corresponds to the transition $\Gamma_2 \rightarrow \Gamma_{34}$ ($B_1 \rightarrow E$ in the approximate point group $D_{2d}$), while the second multiplet corresponds to the transition $\Gamma_{34} \rightarrow \Gamma_2$ ($E \rightarrow B_1$). All the other transitions studied exhibit some different symmetry in the $D_{2d}$ group (the crystal field levels in the term $^5I$ were classified in terms of the irreducible representations of the point group $D_{2d}$ by Agladze.[3]).

The present work was performed in order to extend the study of the relative intensities of lines within the isotope structure to other spectral transitions of different symmetry, especially of $B_1 \rightarrow E$ symmetry, and to study in more detail the widths and shapes of lines due to impurity centers with different lithium isotope composition, using the better resolution of the diode laser ($1 \cdot 10^{-4}$ $cm^{-1}$).

## 2. EXPERIMENT

The transmission spectra of $^7Li_{1-x}{}^6Li_xYF_4$ $Ho^{3+}$ single crystals (0.1 at.%) of different thickness with $x=0.0742$ (natural abundance of isotopes), $x=0.005$, and $x=0.9$ were measured at 5.0 K in the region of $^5I_8 \rightarrow {}^5I_7$, $^5I_6$ and $^5I_5$ transitions in the $Ho^{3+}$ ion (frequency regions of 5200 $cm^{-1}$, 8600 $cm^{-1}$, and 11250 $cm^{-1}$). These spectra were obtained using the BOMEM DA3.002 high-resolution Fourier-transform spectrometer at the Institute of Spectroscopy. The spectral resolution $\delta\nu_0$ was up to 0.004 $cm^{-1}$ at 5200 $cm^{-1}$ and 8600 $cm^{-1}$ and $\delta\nu_0=0.03$ $cm^{-1}$ at higher frequencies. The distance between the first zeros of the FTS instrumental function $\sin x/x$ is indicated here as the "resolution." The full width at half maximum

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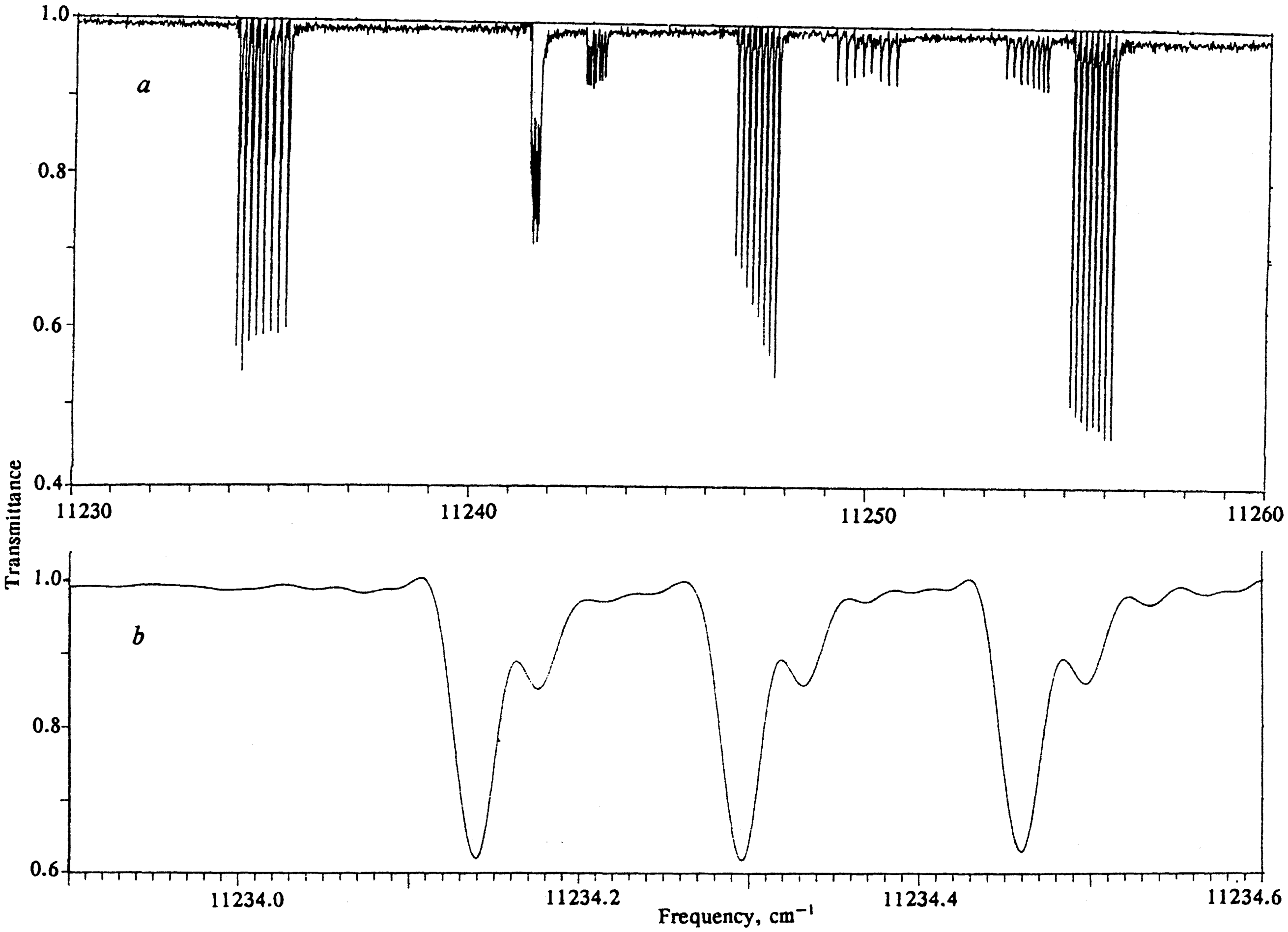

FIG. 1. FTS transmission spectra in the region of the $^5I_8\rightarrow{}^5I_5$ transition in LiYF$_4$-Ho$^{3+}$ (0.1 at.%) with natural abundance of Li isotopes at 5.0 K. E,H⊥ c polarization. (*a*) Broad band spectrum. (*b*) The isotope structure of hf components.

of this instrumental function is $0.6\delta\nu_0$, and the spectral lines separated by a distance smaller than $\delta\nu_0$ are actually resolved. The transmission spectra of the crystal with the natural abundance of lithium isotopes also were measured with a Mitsubishi ML51018 tunable diode laser at LENS in the frequency region of $^5I_8\rightarrow{}^5I_5$ transition at 4.2 K.

The line intensities within the isotope structure were measured as total intensities in the absorption spectrum calculated from the transmission spectrum. An interactive computer program was used for the contour decomposition for superimposed lines.

### 3. EXPERIMENTAL RESULTS

Figure 1(a) shows the broad-band FTS transmission spectrum in the low-frequency part of the $^5I_8\rightarrow{}^5I_5$ transition. The isotope structure of the hf components in the 11235 cm$^{-1}$ hf multiplet is seen in Fig. 1(b). This particular hf multiplet corresponds to the $\Gamma_2\rightarrow\Gamma_{34}$ transition ($B_1\rightarrow E$ in the $D_{2d}$ group) and exhibits the largest interval within the isotope structure ($\approx$0.03 cm$^{-1}$). So it corresponds to a desired symmetry and is also convenient for the studies of linewidths, lineshapes, and relative intensities.

The shape of the spectral lines in the FTS spectrum obtained with resolution 0.03 cm$^{-1}$ clearly shows that this resolution is not sufficient to reproduce the lineshape correctly; the FTS instrumental function $\sin x/x$ is presented in Fig. 1(b).

Figure 2 displays a part of the same multiplet 11235 cm$^{-1}$ which was registered by a tunable diode laser. The lines within each hf component due to Ho$^{3+}$ centers with different number of lithium isotopes nearby are well resolved in this spectrum. They are equidistant within experimental error (connected with instability of the frequency sweep), the intervals between them being $\delta\nu=0.034 \pm 0.003$ cm$^{-1}$. All lines are of the same width $\delta\nu=0.013$ cm$^{-1}$ and their shape are Gaussian. The ratio of their relative intensities is $1:(0.31\pm0.01):(0.035\pm0.005)$, as determined for different hf components and different spectral scans. This ratio agrees well with the theoretical one according to (1) used for $x=0.0742$ provided $N=4$, while it strongly differs from the theoretical ratio for $N=8$ (see Table I). The table gives the measured relative intensities of the lines within the isotope structure of different hf multiplets together with the calculated intensities according to (1) with $N=4$ and $N=8$.

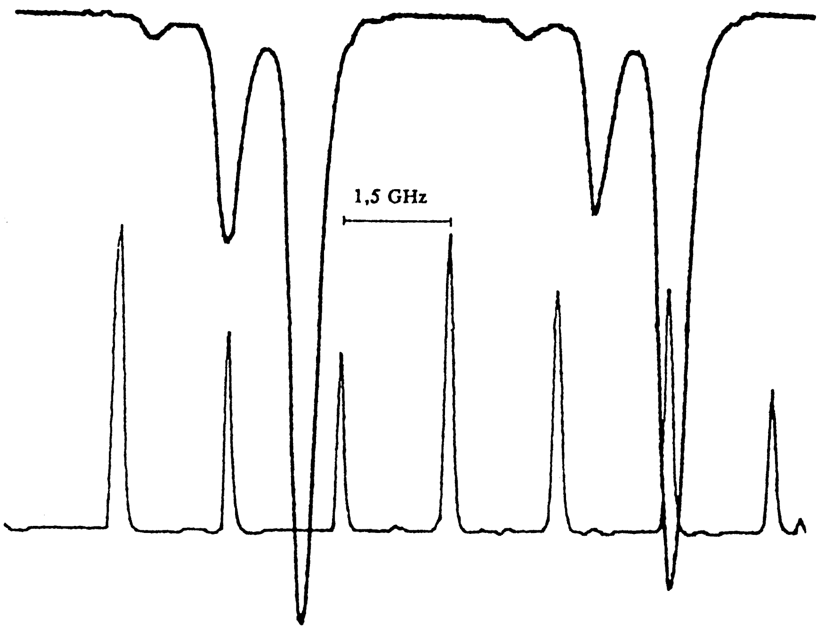

FIG. 2. Diode laser transmission spectrum in the region of the hf multiplet near 11235 cm$^{-1}$ of Ho$^{3+}$ in LiYF$_4$ (natural abundance of Li isotopes). $T$=4.2 K. E,H⊥ c polarization. Interferometric calibration is given in the lower part of the figure.

## 4. DISCUSSION

In LiYF$_4$ the four Li$^+$ ions nearest to the Ho$^{3+}$ ion are located at the corners of a square, the Ho$^{3+}$ ion being in the center of this square. The distance Ho–Li inside this square is 3.66 Å. The Holmium impurity centers with all four identical lithium isotopes give the main spectral line, those with one foreign isotope in any of four positions provide a shifted line whose intensity is proportional to a total number of such centers. The centers with two $^7$Li and two $^6$Li isotopes give one more shifted line. It should be mentioned that there are two different types of such centers: with the identical isotopes located (1) at the neighboring corners and (2) at the ends of diagonals. Their frequencies evidently coincide or almost coincide. One line, not two, is detected, with its intensity proportional to the total number of such centers. The diode–laser study is undistorted by the instrumental function and is of good quality (low noise). Our diode–laser study of nonsuperimposed spectral lines in the 11235 cm$^{-1}$ hf multiplet, which are due to the centers with different isotope composition, showed that the widths and shapes of the lines originating from different centers are the same with great precision. Hence the frequencies of the electronic transition within two different centers with two $^7$Li and two $^6$Li isotopes really coincide with great precision.

There are four next-nearest Li$^+$ ions (located at the corners of a tetrahedron) whose distances from the central Ho$^{3+}$ ion are only slightly greater (3.73 Å). From our spectral data appears that in most cases the lithium isotopes in these positions do not influence the frequencies of

TABLE I. Calculated and measured relative intensities of the lines within the isotope structure in $^6$Li$_x$$^7$Li$_{1-x}$YF$_4$–Ho$^{3+}$. For the measured hf multiplets their positions (in cm$^{-1}$) and symmetries in the $S_4$ and $D_{2d}$ point groups are indicated.

| | | | $x$ = 0.0742 (natural abundance of isotopes) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Calculated | | | | | Measured | | | | |
| | $P_N(n)/P_N(0)$ | | 5149 | 5156 | 5162.8 | 5178 | 5185 | 8673 | 8679 | 11235 |
| | | | $2 \to 34$ | $34 \to 34$ | $34 \to 1$ | $2 \to 34$ | $34 \to 34$ | $34 \to 1$ | $2 \to 34$ | $2 \to 34$ |
| $n$ | $N = 4$ | $N = 8$ | $B_1 \to E$ | $E \to E$ | $E \to A_2$ | $B_1 \to E$ | $E \to E$ | $E \to A_1$ | $B_1 \to E$ | $B_1 \to E$ |
| 0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| 1 | 0.321 | 0.641 | 0.63 | 0.31 | 0.29 | 0.25 | 0.32 | 0.26 | 0.33 | 0.31 |
| 2 | 0.038 | 0.180 | 0.13 | 0.03 | 0.04 | | | | 0.04 | 0.035 |
| 3 | 0.002 | 0.029 | 0.02 | | | | | | | |
| 4 | | 0.002 | 0.004 | | | | | | | |
| | | | $x$ = 0.9 (enrichment with the $^6$Li isotope) | | | | | | | |
| | $P_N(N-n)/P_N(0)$ | | 5149 | 5156 | 5162.8 | 5152 | 5163.3 | 8673 | 8679 | 8688 |
| | | | | | | $34 \to 2$ | $34 \to 2$ | | | $34 \to 2$ |
| $N - n$ | $N = 4$ | $N = 8$ | | | | $E \to B_1$ | $E \to B_2$ | | | $E \to B_1$ |
| 0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| 1 | 0.444 | 0.889 | 0.85 | 0.43 | 0.46 | 0.89 | 0.51 | 0.42 | 0.52 | 0.47 |
| 2 | 0.074 | 0.346 | 0.33 | | 0.08 | 0.37 | 0.10 | | | 0.08 |
| 3 | 0.005 | 0.077 | 0.08 | | | 0.10 | | | | |
| 4 | | 0.011 | 0.01 | | | 0.02 | | | | |

spectral transitions in the $Ho^{3+}$ ion. However, for some hf multiplets, as follows from the relative intensities of the lines within the split hf components, the main spectral line is formed by $Ho^{3+}$ impurity centers with all eight (nearest and next-nearest) identical $Li^+$ isotopes. The first shifted line is formed by centers with one foreign isotope in any of the eight positions and the second shifted line is formed by the centers with two foreign isotopes in any pair of these eight positions and so on.

Our present study shows that the different role of four nearest and four next-nearest lithium neighbours for different transitions is not related to the symmetry of these transitions (see the Table). Of six $Ho^{3+}$ hf multiplets of $B_1 \leftrightarrow E$ symmetry studied in this work only two (5149 $cm^{-1}$ and 5152 $cm^{-1}$ mentioned in the introduction) are sensitive to all eight lithium neighbours, while the other four are sensitive to four of them. The hf multiplets of $E \rightarrow B_2, A_1, A_2, E$ symmetries exhibit sensitivity to only four lithium neighbors. The true cause of this situation remains unclear, and more experimental and theoretical analysis is needed.

Regardless of the nature of the influence of the four nearest and next-nearest neighbors, the relative intensities of lines within the isotope structure can be used to determine the unknown concentration of isotopes. Previously, the spectroscopic method has been proposed to find the ratio $^6Li$:$^7Li$ of the lithium isotopes in $LiYF_4$ crystals.[6] Well-separated isotope components of the particular hf multiplet 11235 $cm^{-1}$ can be a good analytical probe for this problem during operation with a diode laser.

We are grateful to M. A. Petrova and V. J. Egorov from the State Optical Institute for growing the $LiYF_4$ crystals of high quality with different compositions of lithium isotopes. One of the authors (G.N.Z.) appreciates his fruitful stay at LENS.

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