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EPR OF SOME RARE EARTH IONS AND Cr^{3+} IN $LiNbO_3$ CRYSTALS

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The EPR spectra of Nd^{3+}, Dy^{3+}, Er^{3+}, and Cr^{3+} impurity ions in lithium metaniobate ($LiNbO_3$) crystals grown by the Czochralski method are investigated experimentally. For all ions in these crystals a single intense spectrum with axial symmetry is observed. The only exception is the Nd^{3+} ion, for which two axially symmetric spectra of equal intensity are observed. The results on measurements of the EPR line widths and the results pertaining to the asymmetric shape of the line corresponding to the $\Delta M = -1/2 \leftrightarrow 1/2$ transition for Cr^{3+} are discussed.

1. INTRODUCTION

CRYSTALS of lithium metaniobate $LiNbO_3$ are of considerable interest from the point of view of utilizing their ferroelectric, acoustic, piezoelectric, and optical properties. Recently, they have been increasingly used in quantum electronics for obtaining harmonics of laser radiation and for laser modulation,[1] and also (with the introduction of certain rare earth ions as an isomorphous impurity) as active laser materials.[2]

Burns et al.[3] briefly described an investigation of the absorption and luminescence spectra of certain trivalent rare earth ions and Cr^{3+} ions introduced into $LiNbO_3$ crystals in the form of the oxides Nd_2O_3, Ho_2O_3, Cr_2O_3, etc. It was established that the rare earth and Cr^{3+} ions rather easily enter the $LiNbO_3$ lattice and many of them yield a strong luminescence; the luminescence line is narrow, about 7 Å at 4.2°K for Nd^{3+}, for example. Evlanova et al.[2] tell of obtaining induced emission with a low threshold in crystals of $LiNbO_3$ activated with Nd^{3+}. At present, there is no information of any kind on detailed investigations of the optical and EPR spectra of rare earth ions in $LiNbO_3$ crystals.

The goal of the present work was an EPR investigation of $LiNbO_3$ containing the trivalent ions of the rare earths Er, Dy, Nd, Pr and of Cr as impurities. Single crystals of $LiNbO_3$ with additions of the impurity ions were prepared by the Czochralski method from a platinum crucible 15 cm^3 in volume. The drawing rate was about 10 mm/h, and the rate of rotation of the seed was 30 rpm. The temperature was stabilized to ±0.2°C. Seeds parallel and perpendicular to the c axis of the crystal were used. The impurity ions were introduced in the form of the oxides directly into the melt. The EPR investigation was carried out with superheterodyne spectrometers in the 3- and 2-cm regions at 4.2 and 77°K. The magnetic field was measured by proton resonance.

2. STRUCTURE OF $LiNbO_3$

Lithium metaniobate crystals belong to the ditrigonal-dipyramidal class of C_{3v}^6—R3c. Its rhombohedral elementary cell has the parameters a = 5.4944 Å and $\alpha = 55°52'$ and contains six formula units; the parameters of the equivalent hexagonal cell are a = 5.1483 Å, c = 13.863 Å.[4] This cell also contains six formula units. The lattice has a single polar axis of third order with three symmetry planes passing through it. In the ferroelectric phase (Curie temperature 1210°C) the spatial structure of the hexagonal unit cell in the direction of the polar c axis consists of six relatively densely packed oxygen layers, with spacing c/6 = 2.310 Å. The layers form distorted octahedral spaces which are alternately occupied by an Nb^{5+} ion, occupied by a Li^+ ion, and unoccupied (see Fig. 1a).

In the paraelectric phase (at temperatures above 1210°C) the Li^+ ions are located in the planes of the oxygen layers, but the Nb^{5+} ions take up a mean position between them. As the temperature is lowered below the Curie point, both ions move along the polar axis, and at room temperature the Nb^{5+} ion is found to be shifted by 0.25 Å from its initial position and the Li^+ ion by 0.45 Å in the same direction (Fig. 1b).[4]

In the octahedron occupied by Nb^{5+} there are two characteristic Nb-O spacings in the ferroelectric phase at 24°C: 1.889 and 2.112 Å; correspondingly, in the Li^+ octahedron the Li-O spacings are 2.068 and 2.238 Å. Keeping in mind that the ionic radii are 1.36 Å for O^{2-}, 0.68 Å for Li^+, and 0.66 Å for Nb^{5+}, it can be seen that the octahedral spaces are practically completely filled by the positive ions and the replacement of them by the significantly larger rare earth ions must lead to distortion of the structure. Based on the crystallographic data, it may be presumed that the EPR spectra of the rare

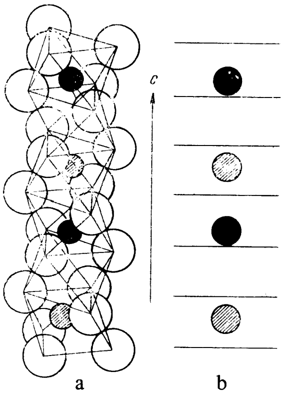

FIG. 1. Structure of lithium metaniobate (along the direction of the polar c axis): a—spatial structure of the hexagonal unit cell, solid circles —Li^+, open circles—O^{2-}, cross-hatched circles—Nb^{5+}; b—arrangement of the Nb^{5+} and Li^+ ions relative to the oxygen layers (the solid horizontal lines) in the $LiNbO_3$ lattice. (From [4].)

earth and chromium ions will possess axial symmetry, with a trigonal distortion arising from the nearest-neighbor oxygens.

3. EXPERIMENTAL RESULTS

$Dy^{3+}(4f^9, {}^6H_{15/2})$. The EPR spectrum of Dy^{3+} in $LiNbO_3$ crystals was observed with a 3-cm spectrometer at 4.2°K at a paramagnetic-ion concentration of about 0.08 atomic %. With the external field H directed parallel to the c axis of the crystal, the observed EPR spectrum consisted of a single intense line with unresolved hfs. The spectrum is interpreted using a spin Hamiltonian of the form

$$\mathcal{H} = g_{\|}\beta H_z\hat{S}_z + g_{\perp}\beta(H_x\hat{S}_x + H_y\hat{S}_y), \qquad (1)$$

where $g_{\|} = 8.7 \pm 0.1$ and $g_{\perp} = 1.3 \pm 0.1$, and one of the axes of the g tensor, namely $g_{\|}$, is in the same direction as the polar c axis of the crystal.

The width and intensity of the EPR line depend strongly on the angle θ between the direction of H and the c axis. The intensity is a maximum and the width a minimum when $H \parallel c$. The width at half height of the absorption line ΔH is 80—100 Oe in this orientation.

$Er^{3+}(4f^{11}, {}^4I_{15/2})$. The EPR spectrum of Er^{3+} in $LiNbO_3$ crystals was observed in a 3-cm spectrometer at 4.2°K and is similar to the EPR spectrum of Dy^{3+}. It is also described by the Hamiltonian (1), with $g_{\|} = 15.4 \pm 0.1$ and $g_{\perp} = 2.1 \pm 0.1$. The width ΔH in this case is 20 Oe.

$Pr^{3+}(4f^2, {}^3H_4)$. The attempt to observe the EPR spectrum of Pr^{3+} in $LiNbO_3$ crystals in the 3-cm and 9.5-mm regions did not yield positive results, although these crystals displayed an intense orange luminescence, indicating the presence of praseodymium ions in the $LiNbO_3$ lattice.

$Nd^{3+}(4f^3, {}^4I_{9/2})$. Paramagnetic resonance of Nd^{3+} ions in $LiNbO_3$ crystals was observed in the 2- and 3-cm region at 4.2°K in samples with an introduced concentration of paramagnetic ions of 0.09, 0.4 and 0.9 at.%. With $H \parallel c$, two wide lines were observed (we call them I and II) of equal intensity and with g factors $g_{\|}^{I} = 1.43 \pm 0.02$ and $g_{\|}^{II} = 1.33 \pm 0.02$. On changing the orientation of the crystal from $H \parallel c$ to $H \perp c$, both lines move toward lower fields and gradually melt into one line with $g_{\perp} = 2.95 \pm 0.05$. The angular dependence of both lines is shown in Fig. 2.

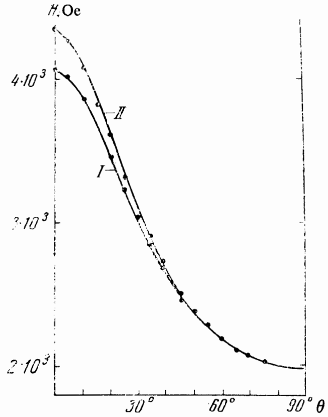

FIG. 2. Angular dependence of the EPR spectra of Nd^{3+} ions; direction of magnetic field H varies from $H \parallel c$ to $H \perp c$ ($\lambda = 3.67$ cm).

The width of the line at half height in the orientation $H \parallel c$ for a paramagnetic-ion concentration of 0.09 at.% was 150 Oe for line I and somewhat greater for line II, thus complicating the investigation of the EPR spectra at intermediate orientations and making it practically impossible to accurately trace out the angular dependence $H(\theta)$ of each line separately. We remark that increasing the concentration of neodymium to 0.9 at.% does not lead to any significant changes in the spectra, except for line broadening.

The effect of single-domainization of the crystals on the EPR spectrum of the Nd^{3+} ions introduced in them was investigated. Single-domain crystals were obtained by annealing them in an electric field of 50 V/cm (minimum air gap). The field was turned on at 1220°C, after which the temperature was taken down to 60°C in the course of 1 hour and the field turned off. The samples were arranged in such a way that the electric field intensity vector was along the c axis. Completeness of single-domainization was checked by etching the surface of the crystals with a mixture of nitric and hydrofluoric acids.

As a result of this process the line width decreased from 150 to 100—110 Oe, i.e., by approximately 30%. For some of the single-domain crystals with an introduced paramagnetic-ion concentration of 0.4 at.%, the line width was about 90 Oe. Measurements of the line width in the orientation $H \parallel c$ carried out at different frequencies showed that the line width changes significantly with the frequency of observation. For example, the width of line II measured at $\nu = 9400$ MHz was 110 Oe, but 160 Oe at $\nu = 13\,300$ MHz.

It was found that in the orientation $H \parallel c$ the quantity $\delta H = H_{II} - H_I$ was almost directly proportional to ν (H_I and H_{II} are the resonance fields of lines I and II in this orientation). Any departure from proportionality can be explained by considering the effect of the overlap of the wings of lines I and II. The frequency dependence of δH has the form:

ν, MHz:	7500	10 000	13 300
δH, Oe	290±20	360±30	460±40

Thus, the EPR data indicate the existence of two different spectra from the Nd^{3+} ions (I and II) that obey the Hamiltonian (1). We remark that the width and intensity of line II vary with orientation of the magnetic field relative to the crystal significantly faster than the same parameters of line I. In investigations at frequencies of the order 7500—8000 MHz it was established that line II breaks up into at least three components as the crystal orientation is changed. Hence, it may be presumed that spectrum II, unlike spectrum I, is made up of several (three or more) magnetically inequivalent ions for which the magnetic axes make a small angle (not greater than 10°) with the c axis.

In a crystal field of trigonal symmetry the lowest state of Nd^{3+} is written in the form

$$a|\pm{}^7/_2\rangle + b|\pm{}^1/_2\rangle + c|\mp{}^5/_2\rangle. \qquad (2)$$

Hence it follows that

$$g_{\|} = \Lambda(7a^2 + b^2 - 5c^2), \quad g_{\perp} = \Lambda(8ac + 5b^2), \qquad (3)$$

where $\Lambda = 8/11$ is the Landé factor for a free Nd^{3+} ion.

Substituting the experimental values for g^I in (3), we obtain the following values for the coefficients in (2):

$$a^2 = 0.38. \quad b^2 = 0.33. \quad c^2 = 0.29.$$

$Cr^{3+}(3d^3, {}^4F_{3/2})$. The EPR spectrum of Cr^{3+} in $LiNbO_3$ was studied in the 2- and 3-cm regions at 77 and 4.2°K. Crystals with paramagnetic-ion concentrations of 0.02, 0.1, and 0.2 at.% were used. A brief report on the EPR of Cr^{3+} in $LiNbO_3$ was presented earlier in[3]. It was established that the spectrum has axial symmetry and is described by the spin Hamiltonian

$$\hat{\mathscr{H}} = g\beta H\hat{S} + D[S_z^2 - {}^1/_3\hat{S}(\hat{S}+1)], \qquad (4)$$

with $g_{\parallel\mathrm{eff}} = 1.97$ and $D = 0.45\ \mathrm{cm}^{-1}$.

At 77°K and with $H \parallel c$ we observed two absorption lines, corresponding to the two transitions $\Delta M = -1/2 \leftrightarrow 1/2$ and $\Delta M = -3/2 \leftrightarrow -1/2$, with the first transition much stronger than the second. We therefore subsequently investigated the width and shape of the line corresponding to the transition $\Delta M = -1/2 \leftrightarrow 1/2$.

At liquid helium temperatures and in the same orientation a line was observed at a field of about 1000 Oe (ν = 9300 MHz), corresponding to the forbidden transition $\Delta M = -3/2 \leftrightarrow 3/2$. The line corresponding to $\Delta M = -1/2 \leftrightarrow 1/2$ is asymmetrical, with a steeper slope on the low-field side, and its width is practically unchanged in going from 77°K to 4.2°K. As the investigation of samples with different Cr^{3+} concentrations showed, the asymmetry of the line becomes more marked as the concentration of paramagnetic ions decreases (see Fig. 3).

Measurements of the line width ΔH as a function of Cr^{3+} concentration gave the following results:

c, at.%	0.2	0.1	0.02
ΔH, Oe:	75	60	53

Single-domainization of $LiNbO_3$ crystals containing Cr^{3+} as an impurity produced a certain narrowing of the line corresponding to $\Delta M = -1/2 \leftrightarrow 1/2$. Thus, for example, the line width for a concentration of 0.1 at.% decreased from 75 to 65 Oe, but the asymmetric line shape persisted.

4. DISCUSSION

The fact of greatest interest coming out of all the EPR spectra considered above is the existence of Nd^{3+} ions in a different crystalline site, whereas for all the other ions studied only a single spectrum of high intensity is observed. At present the available experimental data does not permit giving a well-defined reason for this peculiarity of the Nd^{3+} EPR spectrum, and the question requires further investigation. Since $LiNbO_3$-Nd^{3+} has turned out to be an effective active laxer medium, it is all the more important to have an answer to this question. We remark that the optical spectrum of neodymium in lithium niobate that we have observed also shows the presence of two different optical centers with slightly different Stark splittings.

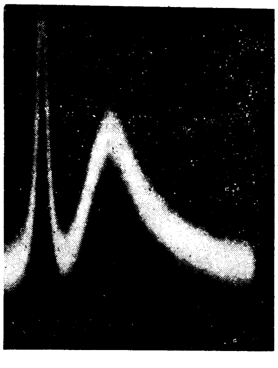

FIG. 3. EPR line corresponding to the transition $\Delta M = -1/2 \leftrightarrow 1/2$ (the sharp line to the left of the Cr^{3+} line is the DPPH line).

It is also difficult to answer the question of which lattice ions (Li^+ or Nb^{5+}) are replaced by the triply charged ions (Li^+ and Nb^{5+} have about the same ionic radius, about the same as that of Cr^{3+} (0.64 Å), but 1.3 times smaller than the radii of the investigated rare earth ions). It is true that if one considers not the formal ratio of the valences of Nb and Li, which is 5 to 1, but the ratio of their effective charges in the $LiNbO_3$ lattice, which is 2 to 1,[4] then it can be assumed that the isomorphous replacement of Nb ions by trivalent impurity ions is more favorable from the point of view of charge compensation.

Because of the large disparity in ionic radii, when the positive ions of the lattice are replaced by rare earth ions random deviations will arise in the magnitude of the crystal field in the vicinity of a paramagnetic ion. It is this, apparently, which is responsible for the large width of the EPR lines. The narrowing of the EPR line as a result of single-domainization of $LiNbO_3$ crystals containing Nd^{3+} or Cr^3 gives a basis for assuming that there is also a certain dispersion in the direction of the c axis associated with multi-domain structure.

We now consider the explanation of the asymmetric character of the shape of the $\Delta M = -1/2 \leftrightarrow 1/2$ line of Cr^{3+}. Such an asymmetry can be explained by assuming the existence of a random distribution in magnitude of an additional rhombic distortion of the axially symmetric crystal field. To take this into account in the spin Hamiltonian (4), one adds one more term of the form

$$e(\hat{S}_x^2 - \hat{S}_y^2),$$

where e is a quantity which varies from 0 to $|e_{\max}|$.

The transition frequency for the $\Delta M = -1/2 \leftrightarrow 1/2$ line observed in the orientation $H \parallel c$ is given by

$$h\nu_{-1/2\leftrightarrow 1/2} \approx g\beta H\left[1 - \frac{3e^2}{D^2 - (g\beta H)^2}\right] \qquad (5)$$

In deriving this expression we have omitted terms of higher order in the parameter e, since we assume that $|e/D| \ll 1$. When $e = 0$, this formula goes over to the expression for the transition frequency in the case of purely axial symmetry. A numerical estimate of the average value $\langle e \rangle$ gives a magnitude of the order of $0.02-0.04\ \mathrm{cm}^{-1}$.

Thus, in the superposition of an additional rhombic field with statistical scattering of the parameter e, the whole EPR line should broaden predominantly (as can be seen from Eq. (5)) on the high-field side. This rhombic distortion also explains the existence of a line corresponding to the forbidden transition $\Delta M = -3/2 \leftrightarrow 3/2$. A possible reason for the rhombic distortion may be a small displacement of the oxygen ions from their positions in the unit cell.

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