EPR OF Nd$^3$ IONS IN FLUORITE

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The cubic EPR spectrum of the Nd$^{3+}$ ion in CaF$_2$ is investigated. The value of the parameter $X$ which defines the wave functions of the $T_3$ quadruplet is $-0.5$. The presence of rhombic and trigonal distortions in the cubic potential explains a number of features of the spectrum such as the shape of the lines, their broadening with decrease of the high frequency quantum, and the absence of transitions between the levels of various Kramers doublets. The EPR spectra and spin-lattice relaxation of Nd$^{3+}$ ions involved in the complex Nd$^{3+}$-TR$^{3+}$ centers in CaF$_2$ crystals are investigated. It is found that the symmetry of the crystal field in which the Nd$^{3+}$ ion is located in Nd$^{3+}$-La$^{3+}$ and Nd$^{3+}$-Pr$^{3+}$ pairs differs from the field symmetry in the similar Nd$^{3+}$-Nd$^{3+}$ pair.

1. EPR OF Nd$^{3+}$ IONS IN THE CUBIC FIELD OF A CaF$_2$ CRYSTAL

The problem of the wave functions and energy levels (within the multiplets having $L \neq 0$ and $J > 5/2$) of rare earth ions in a crystalline field of cubic symmetry was investigated by Lea, Leask, and Wolf. These authors calculated the dependence of the wave functions and relative splittings, and determined the dependence of the ground state upon the parameter $X$, which characterizes the ratio of the fourth to the sixth degree terms in the expansion of the crystalline field potential in spherical harmonics. According to them, the ground state of Nd$^{3+}$ in a field of cubic symmetry is a $T_3$ quadruplet. Figure 1 shows the $X$-dependence of the G-factors that characterize the splitting of the levels in the $T_3$ quadruplet, in a magnetic field directed along a [001] crystalline axis. The G-factors were calculated from the wave functions of Ref. [2]. The continuous and dashed lines of Fig. 1 denote level splittings, the transitions between which are, respectively, allowed ($\Delta m_J = \pm 1$) or forbidden.

Vinçow and Low reported that they observed in heat-treated crystals of CaF$_2$ with a magnetic field along a [001] axis the following lines of Nd$^{3+}$, which are related to $T_3$: one with $G = 2.26 \pm 0.02$, and another, of smaller intensity, with $G = 1.1 \pm 0.05$. They deduced that terms of sixth order in the expansion of the potential could be neglected ($X = -1$), which is not in accordance with results obtained for other rare earth ions. In particular, it has been shown that $X = -0.55$ for Pr$^{3+}$, which is isoelectronic with Nd$^{3+}$. At the same time, Ranon, citing Ref. [2], uses $X = -0.61$. As is seen in Fig. 1, for this value of the parameter there exist in fact splittings between the levels, corresponding to the transitions observed in Ref. [3]. But the most intense transition, at $G = 2.26$, ought to be forbidden.

In the present work, the spectrum of Nd$^{3+}$ ions in a cubic field was detected in crystals grown by the Stockbarger method in a fluorinating atmosphere. The most intense spectrum was in crystals with Na impurity, which clearly is related to the decrease in the number of interstitial F$^-$ ions. In some crystals the spectrum was not seen at all.

The measurements were made at a frequency of about 38 GHz and a temperature of 4.2°K. The lines had unusual shapes (see Fig. 2), and broadened upon passage to lower frequencies. The spectrum could not be detected in the 3-cm range of frequencies. Two lines

![Fig. 1. G-factor values, characterizing the level splitting in the $T_3$ quadruplet in a magnetic field ($H || 001$). Curve 1 corresponds to the difference of the energy eigenstates $| +3/2 \rangle$ and $| -3/2 \rangle$, 2 to $| 1/2 \rangle$ and $| -1/2 \rangle$, 3 to $| +1/2 \rangle$ and $| +3/2 \rangle$, 4 to $| 1/2 \rangle$ and $| -1/2 \rangle$. The horizontal lines are the observed values of the G-factors.](image-url)
were observed with the magnetic field along \( [001] \); one with a G-factor of 3.18 ± 0.04, having a sharp fall-off on the high-field side (Fig. 2a), and the other with \( G = 1.78 ± 0.02 \), having the shape represented in Fig. 2b. As is seen from Fig. 1, in which the horizontal lines correspond to the experimental values of G, the most appropriate value of the parameter X is \(-0.5\), and the allowed transitions 1 and 2 are observed. For \( X = -0.5 \), transition 3 with \( G \approx 2.4 \) is also allowed, but, as will be seen below, the transition is not observed because of its large breadth, induced by random splittings of the quadruplets into two doublets as a result of the distortion of the cubic symmetry of the crystalline field. The eigenstates of the basic quadruplet and the corresponding energy levels \( W_i \) in a magnetic field can be written as (6 J
\[ J = (J + 1) / 2 \]), where \( J = g \mu_B H / \hbar \) and \( f = 1.42 \). The angular dependence of the energy levels, the corrections from the rhombic and trigonal distortions of one sign predominate, and that the maximum of the distribution function is unsymmetrical. The asymmetry is due to the fact that distortions of one sign predominate, and that the maximum of the distribution function occurs at nonvanishing distortions.

\[ W = \gamma g \mu_B H / \hbar + \gamma f \mu_B H / \hbar, \]

where \( \gamma = g + \gamma f, \delta = f(g + \gamma f), \) and \( \gamma, \delta, \alpha, \) and \( \alpha \) are the direction cosines.

In Figs. 3 and 4 the angular dependence of the resonance transitions, both experimental and calculated from Eq. (2), are depicted as functions of the orientation of the magnetic field in the (001) and (110) planes.

The unusual line shapes, the absence of the transition at \( G \approx 2.4 \) (for \( H \parallel [001] \)), and the broadening of the lines with decrease in frequency can be explained if one assumes that random distortions of the cubic potential of the lattice are induced by the displacements of the neighboring \( F^- \) ions. The cause of the displacements of these ions can be the relatively large ionic radius of \( Nd^{+2} \). Since one or two \( F^- \) ions will most likely be displaced, the distortion must have rhombic or trigonal character. Considering only the most important terms,\(^{11}\) one can compare, respectively, the following Hamiltonians for such distortions:

\[ V_{tr} = A_1(S^2J^2 - 3J(J + 4) + 3J^2J_3^2), \]

\[ V_{rh} = A_3(3J^2J - J(J + 4) + 3J_3^2J_3^2). \]

(3)

The values of the constants \( A_1 \) and \( A_2 \), which characterize the magnitude of the distortion, change from one cell with a \( Nd^{+2} \) ion to another. The operators (3) and (4) have the following nonvanishing matrix elements between quadruplet states:

\[ \langle \chi_{\alpha}, \beta | J_{\alpha, \beta} \rangle = \frac{-1}{2} (\delta_{\alpha, \beta} - \delta_{\alpha, \beta} - \delta_{\alpha, \beta} + \delta_{\alpha, \beta}). \]

(5)

In first order perturbation theory, the distortion of the crystalline field leads to the splitting of the \( \Gamma_8 \) quadruplet into two doublets. The magnitude of the splitting is

\[ \Delta E = (V_{tr} + V_{rh}) \Delta \omega, \]

(6)

In second order perturbation theory, we find that for a magnetic field directed along a \( [001] \) axis, the corrections to the energy levels \( W_i \) are

\[ \delta E_i = \frac{V_{tr}^2}{2g \mu_B H} + \frac{V_{rh}^2}{2g \mu_B H}, \]

(7)

From (7) it follows that for the levels \( W_1 \) and \( W_4 \) of the quadruplet, the transition between which is observed at a field corresponding to \( G = 3.18 \), both types of distortion of the crystalline field produce an increase in the splitting \( \Delta E_1 = \Delta E_4 \), and consequently the absorption line must have a small slope on the low-field side, as is indeed observed (see Fig. 2a). For the \( W_2 \) and \( W_3 \) levels, the corrections from the rhombic and trigonal distortions have different signs, and lead, respectively, to converging and diverging of the levels. Thus the line at \( G = 1.78 \) will have small slopes on both sides (see Fig. 2b): on the high-field side owing to the distortion of rhombic character, and on the low-field side owing to the trigonal distortion. The fact that the line has two peaks can be explained by assuming that the distortion of the crystalline field distribution function is unsymmetrical. The asymmetry is due to the fact that distortions of one sign predominate, and that the maximum of the distribution function occurs at nonvanishing distortions.

\[ ^{11} \]For the \( Dy^{+3} \) ion, the ground states of which are also \( \Gamma_8 \) in the cubic field of a \( CaF_2 \) crystal, but whose ionic radius is smaller than that of \( Nd^{+2} \), the effects enumerated above are not observed \([7]\).
tions. The relatively large ionic radius of Nd\textsuperscript{3+} is the cause for the distortion which produces such a distribution function.

With decrease in magnetic field, the magnitude of the corrections (7) increases, which explains the line broadening with decrease of the radio-frequency quantum.

From the shape of the line at $G = 1.78$, it is possible to estimate the values of the matrix elements in Eqs. (7) separately for the distortions of rhombic and trigonal character. Considering that at the frequency of about 38 GHz the line width at half-intensity is about 150 Oe, one can obtain

$$|V_{n_{\perp}}^{n_{\parallel}}| \approx 0.05 \text{ cm}^{-1}, \quad |V_{n_{\perp}}^{n_{\perp}}| \approx 0.1 \text{ cm}^{-1}.$$  \hspace{1cm} (8)

The initial splitting $\Delta E$, Eq. (6), has the same order of magnitude, and thus the transition near $G = 2.4$ is not observed due to its very large width ($\sim 1000$ Oe).

2. EPR INVESTIGATION OF Nd\textsuperscript{3+}-TR\textsuperscript{3+} CENTERS IN FLUORITE

In (11) it was shown that the Nd\textsuperscript{3+} ion can form complex centers with any other rare earth ion (TR\textsuperscript{3+}) in a crystal of CaF\textsubscript{2}. In such centers the Nd\textsuperscript{3+} and TR\textsuperscript{3+} ions are located in adjacent cells, in which they replace the Ca\textsuperscript{2+} ions. For the same ions, the formation of several types of complex centers is possible, differing in the method of compensation of the excess positive charge. Fairly strong shifts of the Stark components in the absorption spectrum of the Nd\textsuperscript{3+} ions were observed (9) which can hardly be explained only by a change in the radius of the neighboring ion upon replacement of one rare earth ion by another. Most likely, there occurs a displacement of the F\textsuperscript{−} ions which enter into the immediate surroundings of both the Nd\textsuperscript{3+} ion and the neighboring TR\textsuperscript{3+} ion. An EPR investigation of the complex centers is thus of interest, since it can yield directly the symmetry of the immediate surroundings of the paramagnetic ions.

In the present work, an investigation of the EPR spectra of Nd\textsuperscript{3+} ions appearing in complex centers was made. The investigation was carried out at frequencies of 9.14 and 38 GHz at a temperature of 4.2°K, on the same crystals as in (9). In the crystals, an impurity of one of the following trivalent ions existed along with the neodymium impurity: La\textsuperscript{3+}, Ce\textsuperscript{3+}, Pr\textsuperscript{3+}, Sm\textsuperscript{3+}, Tb\textsuperscript{3+}, Dy\textsuperscript{3+}, Ho\textsuperscript{3+}, Er\textsuperscript{3+}, Tm\textsuperscript{3+}, Lu\textsuperscript{3+}, and Y\textsuperscript{3+}. In spite of the fact that in (9) the formation of complex centers of Nd\textsuperscript{3+} with all these ions was detected, new EPR spectra of Nd\textsuperscript{3+} ions, corresponding to Nd\textsuperscript{3+-TR\textsuperscript{3+}} pairs, were observed only for the first four ions of the above series. We remark that in all crystals, spectra of Nd\textsuperscript{3+} ions occurring in crystalline fields of tetragonal and rhombic symmetry were observed. In some crystals the above-described spectrum of Nd\textsuperscript{3+} in cubic surroundings was observed. Furthermore, the following previously studied (see (10)) spectra of ions of the additional impurities were observed: Ce\textsuperscript{3+}-tetragonal spectrum; Tb\textsuperscript{3+}-tetragonal spectrum; Dy\textsuperscript{3+}-tetragonal spectrum; Er\textsuperscript{3+}, cubic, tetragonal, and trigonal spectra.

We shall discuss in more detail the EPR spectra of Nd\textsuperscript{3+} ions, since it is natural to assume that Nd\textsuperscript{3+}-TR\textsuperscript{3+} pair centers are analogous to Nd\textsuperscript{3+-Nd\textsuperscript{3+}} centers in their manner of formation. It was shown in (11) and (12) that the spectrum of rhombic symmetry belongs to Nd\textsuperscript{3+} ions located in neighboring cells. Six inequivalent positions of the pairs are observed. The orthogonal symmetry axes of the EPR spectrum coincide with the crystalline directions [110], [001], and [110]. For pairs arranged along [110], these directions are designated in (11) as the $x$, $y$, and $z$ axes, respectively. The principal values of the $g$-tensor are $g_x \approx 2.03$, $g_y \approx 3.43$, $g_z \approx 2.13$.

According to the results of Voron'ko, Kaninškit, and Osiko (12) optical spectra of three types of centers are observed in crystals of CaF\textsubscript{2} with Nd\textsuperscript{3+} impurity: L, M, and N (we note that the introduction of the additional impurities, (9) while in no way influencing the spectral character of the L centers, leads to a splitting of the lines belonging to the M and N centers; thus the M and N centers are complex centers). Comparison of the distances to the excited levels, determined from optical (12) and relaxation (by EPR methods) (11) measurements, permits one to infer that the tetragonal EPR spectrum corresponds to the L center. Regarding the M and N centers, the accuracy of the relaxation measurements is insufficient, because of the proximity of the energy of the first excited levels of the Nd\textsuperscript{3+} ions in these centers, to establish that the rhombic EPR spectrum of the ion pairs is associated with one of the centers. However, taking into account the change in the optical and EPR spectra upon $\gamma$-irradiation of the crystals, it is possible to infer that the rhombic EPR spectrum corresponds to the M center. On the one hand, it is established in (13) that upon $\gamma$-irradiation approximately one-half of the M centers is destroyed but that the number of N centers is unchanged, while on the other hand it is demonstrated in (14) that the intensity of the rhombic spectrum of the Nd\textsuperscript{3+} ion pairs decreases by one-half upon $\gamma$-irradiation.
CaF$_2$: (Nd$^{3+}$ + La$^{3+}$). A rhombic EPR spectrum of Nd$^{3+}$ ions was detected and investigated in crystals with impurities of Nd$^{3+}$ and La$^{3+}$ ions. The spectrum is characterized by a g-tensor with the principal values:

$$g_x = 1.50 \pm 0.02; \quad g_y = 3.53 \pm 0.05; \quad g_z = 2.13 \pm 0.04.$$  

(9)

The $z$-axis coincides with the crystalline [110] direction, and the $x$- and $y$-axes are displaced in the (110) plane by an angle of $(\pm 20 \pm 1)^\circ$ from the [110] and [001] directions, respectively. Twelve inequivalent ions are observed.

CaF$_2$: (Nd$^{3+}$ + Pr$^{3+}$). A spectrum of ions was detected in crystals with impurities of Nd$^{3+}$ and Pr$^{3+}$ ions, quite similar to the spectrum detected in crystals with La$^{3+}$ impurity. The principal values of the g-tensor for this spectrum are

$$g_x = 1.54 \pm 0.05; \quad g_y = 3.5 \pm 0.05; \quad g_z = 2.05 \pm 0.05.$$  

(10)

The angle through which the $x$- and $y$-axes are displaced from the [110] and [001] directions are $(\pm 20 \pm 1)^\circ$. In spite of the fact that the spectra (9) and (10) are very similar, they are not one and the same spectrum (compare $g_2$ in (9) and (10)).

In crystals with an additional impurity of Ce$^{3+}$ or Sm$^{3+}$ ions, the investigation of the spectra is complicated by the spin-spin interactions, in the complex centers, of these ions with the Nd$^{3+}$ ion: The angular dependence of the EPR lines does not follow the relation

$$g^l = g_2^l + g_3^l m^2 + g_4^l n^2,$$

where $l$, $m$, and $n$ are the direction cosines; furthermore, the intensities of the lines decrease as a result of their splitting. Therefore, although lines with behavior characteristic of spectral pairs were detected in the EPR spectra, a detailed investigation for the case of Ce$^{3+}$ and Sm$^{3+}$ ions was not possible. We remark that for Nd$^{3+}$-Sm$^{3+}$ pairs, a shift in the $x$- and $y$-axes in the (110) plane also occurs.

The rhombic spectrum of Nd$^{3+}$ ions corresponds to the M center, as already stated above. Since the axes of the g-tensor characterizing the rhombic spectrum of the Nd$^{3+}$-Nd$^{3+}$ pairs do not coincide with the axes of the g-tensors which characterize the EPR spectra of the Nd$^{3+}$-Pr$^{3+}$ and Nd$^{3+}$-La$^{3+}$ pairs, one can then naturally assume that in these cases spectra of the Nd$^{3+}$ ions in pairs corresponding to the N center are observed. In order to clarify this question, a measurement and comparison of the temperature dependence of the spin-lattice relaxation times were carried out, in a region where the relaxation is governed by two-phonon processes, for the Nd$^{3+}$-Nd$^{3+}$ pair (M center) and the Nd$^{3+}$-Pr$^{3+}$ pairs. Of particular interest is a comparison of the relaxation of the M center with the relaxation of the Nd$^{3+}$-Pr$^{3+}$ pairs. According to (9), when the additional impurity is the Pr$^{3+}$ ion, the radius of which is the closest to the ionic radius of Nd$^{3+}$, the line splitting in the M and N centers is practically nonobservable. Thus the energy levels and eigenstates of the Nd$^{3+}$ ion when a Pr$^{3+}$ ion is located in an adjacent cell, are the same as in the case of Nd$^{3+}$ ions pairs in the respective M and N centers. Consequently, the temperature dependences of the relaxation times must be identical, if the Nd$^{3+}$-Nd$^{3+}$ and Nd$^{3+}$-La$^{3+}$ pairs are similar in the manner of compensation of excess charge.

The dependence of $T_1$ of the Nd$^{3+}$ ions in theNd$^{3+}$-Nd$^{3+}$, Nd$^{3+}$-Pr$^{3+}$ and Nd$^{3+}$-La$^{3+}$ pairs, is shown in Fig. 5 on a log-log plot for temperatures less than 4.5 K. The relaxation time measurements were made by the pulse method. For the temperature range shown in Fig. 5, the relaxation time is essentially determined by the two-phonon processes of combination scattering (the Raman process, $T_1 \propto T^0$). As follows from the figure, the relaxation times of the neodymium ions in different pairs are very close to one another over the entire range, which argues for an identical method of formation of the pairs. A confirmation of this deduction is the fact that the intensity of the new EPR spectra is decreased upon $\gamma$-irradiation, just as it is for the spectra of the Nd$^{3+}$ ion pairs.

Thus, from the relaxation measurements, it follows that the observed EPR spectra belong to the neodymium ions in the Nd$^{3+}$-TR$^{3+}$ pairs, which arise from the replacement of one of the Nd$^{3+}$ ions in an M center by a rare earth ion of the additional impurity. Nevertheless, the symmetry of the Nd$^{3+}$-TR$^{3+}$ centers differs from the symmetry of the M centers through a difference in direction of the g-tensor axes. The change in the symmetry of the crystalline field at the site of the Nd$^{3+}$ ion originates, possibly, as a result of a shift of one of the two F$^-$ ions found in the immediate surroundings both of the Nd$^{3+}$ ion and its neighboring rare earth ion. The displacement of the F$^-$ ions can be caused by the differences in the ionic radii of Nd$^{3+}$ and TR$^{3+}$. The shift, observed in (14), in the g-tensor axes of the rhombic spectrum of an isolated Nd$^{3+}$ ion, which originates from the rhombic spectrum of the Nd$^{3+}$ ion pairs (M center) upon $\gamma$-irradiation, can be explained similarly. In this case, with a valence change of one of the Nd$^{3+}$ ion pairs as a result of the capture of a slow electron, an increase in its ionic radius results, which leads to the displacement of the F$^-$ ion and to the change in the symmetry of the field at the site of the neighboring Nd$^{3+}$ ion. The explanation of this shift given in (14) is incorrect.
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