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INVESTIGATION OF THE LINE WIDTH AND SHAPE IN THE PARAMAGNETIC RESONANCE SPECTRUM OF THE Cr^{+++} *ION IN CORUNDUM SINGLE CRYSTALS*

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The broadening of the fine-structure lines in the paramagnetic resonance spectrum of Cr^{+++} in single crystals of Al_2O_3 has been studied. The width and shape of the lines have been investigated for different electronic transitions and for different concentrations of chromium. The experimental results can be qualitatively interpreted on the basis of an assumption of a broadening mechanism and of a local inhomogeneity in the crystalline electric field. However, quantitative comparison of the experimental data with the theory of dipole broadening of paramagnetic resonance lines does not yield satisfactory agreement.

INTRODUCTION

ACCUMULATION of data on the broadening of electron paramagnetic resonance (e.p.r.) absorption lines is required for the study of internal interactions in a spin-system. The shape and the width of absorption lines enable us to draw conclusions with respect to the nature and the magnitude of these interactions.

In the present work we have studied the width and the shape of e.p.r. absorption lines of a Cr^{+++} ion in the corundum (Al_2O_3) lattice at room temperature. The samples were in the form of single crystals of $Al_2O_3 \cdot Cr_2O_3$ with chromium content from 10^{-5} to 10^{-2} (the concentration was determined as the ratio of the number of paramagnetic chromium ions, which had isomorphically replaced the diamagnetic aluminum ions, to the number of aluminum ions). The broadening of the lines of the "parallel" spectrum was studied (the trigonal symmetry axis of the crystal was parallel to the constant applied magnetic field). This spectrum is described by the spin Hamiltonian

$$\hat{\mathcal{H}} = -\sum_i D_i \hat{S}_{zi}^2 + g_{\parallel}\beta H \sum_i \hat{S}_{zi} + \sum_{i,k} \hat{W}_{ik}, \qquad (1)$$

where the summation indices i and k denote the paramagnetic chromium ions; H is a constant magnetic field; $\hat{S}_{zi}$ is the operator for the component of the spin of the i-th chromium ion in the direction of the constant magnetic field; $2D_i$ is the splitting of the energy levels in the crystalline electric field for the i-th chromium ion; $g_{\parallel}$ is the spectroscopic splitting factor for the "parallel" orientation of the sample; β is the Bohr magneton; $\hat{W}_{ik}$ is the operator for the energy of the spin-spin interaction between the i-th and the k-th chromium ions. The constants of the spin Hamiltonian have been measured in references 1.

The investigations were made at a frequency of ν = 9375 Mcs. The "parallel" e.p.r. spectrum of the ion consists of three lines corresponding to the transitions

$$M_1 = {}^3/_2 \rightarrow {}^1/_2, \qquad M_2 = -{}^1/_2 \rightarrow {}^1/_2, \qquad M_3 = {}^1/_2 \rightarrow {}^3/_2,$$

observed respectively for the following values of the constant magnetic field:

$$H_1 = (2D_i - h\nu)/g_{\parallel}\beta, \qquad H_2 = h\nu/g_{\parallel}\beta,$$
$$H_3 = (2D_i + h\nu)/g_{\parallel}\beta. \qquad (2)$$

Here M_i are the magnetic quantum numbers corresponding to the operator $\hat{S}_z$, $\hbar$ is Planck's constant.

EXPERIMENTAL RESULTS AND QUALITATIVE DISCUSSION

Our experiments show that the width of the e.p.r. absorption lines of the Cr^{+++} ion in corundum does not vary on cooling the samples from 300° to 77°K. Therefore, the spin-lattice interaction does not affect the line width.

We have also found that the anisotropic broadening of absorption lines is negligibly small for all samples, owing to the imperfections in the single crystals investigated. This conclusion follows from the experimental fact that the lines corresponding to the $1/2 \rightarrow 3/2$ and $3/2 \rightarrow 1/2$ transitions have the same width. Had anisotropic broadening taken place, the $1/2 \rightarrow 3/2$ line would be considerably broader than the $\frac{3}{2} \rightarrow \frac{1}{2}$ line, for if the crystal symmetry axis deviates from the parallel orientation by as little as 1° or 2° the shift of the resonance frequency of the $\frac{1}{2} \rightarrow \frac{3}{2}$ transition is comparable with the line width, while it is negligibly small for the $\frac{3}{2} \rightarrow \frac{1}{2}$ transition.

Thus, the broadening of the spectrum lines is apparently due only to the magnetic dipole interactions between the spins (cf. later with respect to the effect of the exchange interactions).

We have measured the concentration dependence of the width, the peak intensity, and the shape of the lines for different electronic transitions. The concentration dependence of the width and the peak intensity is shown for different transitions in Figs. 1 and 2. The width and the shape of the line are the same for the $\frac{3}{2} \rightarrow \frac{1}{2}$ and the $\frac{1}{2} \rightarrow \frac{3}{2}$ transitions, so that in all subsequent discussions the data are given for only one of these two transitions. The measurements were carried out by comparing different samples under identical experimental conditions, so that the relative accuracy of the results is sufficiently high. A comparison of the line shapes for different transitions among themselves and also with the Gaussian

$$G(x) = (\sigma\sqrt{2\pi})^{-1}\exp(-x^2/2\sigma^2)$$

and the Lorentz

$$L(x) = a/\pi(x^2 + a^2)$$

curves was made by using the values of the ratios $I\Delta/S$ and Δ/Δ' which have the characteristic values:

$I\Delta/S = 0{,}936,\quad \Delta/\Delta' = 1{,}175$ for the Gaussian curve,
$I\Delta/S = 0{,}637,\quad \Delta/\Delta' = 1{,}734$ for the Lorentz curve.

Here I is the peak line intensity, Δ the line width at the I/2 level, Δ' the line width taken between points of maximum slope, and S the area of the absorption line.

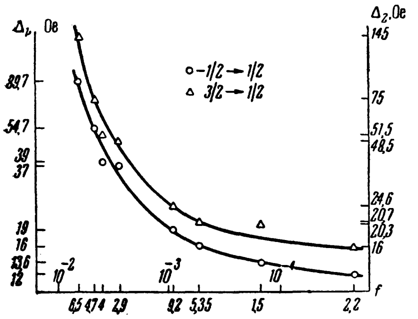

FIG. 1. Dependence of the width of e.p.r. absorption lines of the Cr^{+++} ion in corundum on chromium concentration for two electron transitions in the "parallel" spectrum.

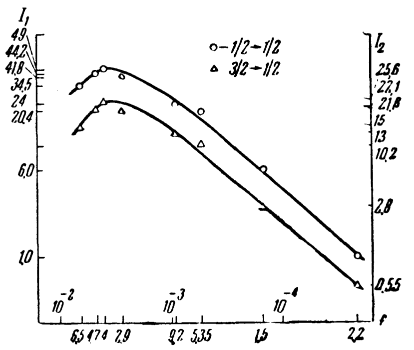

FIG. 2. Dependence of the peak intensity of of e.p.r. absorption lines of the Cr^{+++} ion in corundum on chromium concentration for two electron transitions in the "parallel" spectrum (the peak intensity is expressed in relative units).

The results of the measurements are given in the table. The table also gives the values of the concentration of chromium in the samples investigated determined from the area of the absorption line. The index 1 denotes quantities which refer to the transition $-\frac{1}{2} \rightarrow \frac{1}{2}$, the index 2 denotes the transition $\frac{3}{2} \rightarrow \frac{1}{2}$. From the experimental data exhibited it can be seen that a) the line corresponding to the $\frac{3}{2} \rightarrow \frac{1}{2}$ electronic transition is broader than the line corresponding to the $-\frac{1}{2} \rightarrow \frac{1}{2}$ transition; b) at low concentrations ($\sim 10^{-5}$) the line widths for both transitions tend to constant values; c) the peak intensity for both lines has an absolute maximum within the given range of concentrations; d) the ratios of the widths and the ratios of the peak intensities for lines corresponding to two transitions are approximately constant and begin to increase at the highest of the concentrations investigated; e) the line shape for both transitions at high dilutions is approximately Gaussian and varies little with concentration, changing towards the Lorentz curve only at the maximum concentrations studied; f) the line shapes for the two transitions differ insignificantly (there is a small difference always in the direction of greater similarity to the Lorentz curve for the line shape of the $\frac{3}{2} \rightarrow \frac{1}{2}$ transition compared with the line corresponding to the $-\frac{1}{2} \rightarrow \frac{1}{2}$ transition); g) the chromium concentrations in the corundum, determined from the areas of the absorption lines agree with the results of optical measurements.

We have not succeeded in explaining the observed large difference in the line widths for the two transitions by means of the single mechanism of dipole interactions. As shown by theoretical calculations (cf. below), $\sigma_1 > \sigma_2$ (σ_2 is the second moment of the absorption curve). But from the experimental data it can be seen that the line shapes are approximately the same for both transitions. Therefore, the contribution to the line width from the dipole spin-spin interactions is greater for the $-\frac{1}{2} \rightarrow \frac{1}{2}$ transition, while experimentally it gives a narrower absorption line. The greater line width for the $\frac{3}{2} \rightarrow \frac{1}{2}$ transition can be qualitatively explained by the spatial inhomoge-

Cr concentration in Al_2O_3 (from line areas)	I_1/I_2	Δ_2/Δ_1	$I_1\Delta_1/S_1$	$I_2\Delta_2/S_2$	Δ_1/Δ_1'	Δ_2/Δ_2'
$2.2 \cdot 10^{-5}$	1.85	1.32	0.89	0.87	0.91	0.89
$1.5 \cdot 10^{-4}$	2.13	1.50	0.89	0.85	1.0	1.22
$5.35 \cdot 10^{-4}$	2.0	1.30	1.0	0.86	1.06	1.18
$9.2 \cdot 10^{-4}$	1.84	1.30	0.815	0.77	1.12	1.21
$2.9 \cdot 10^{-3}$	1.93	1.30	0.88	0.80	1.11	1.27
$4 \cdot 10^{-3}$	1.91	1.32	0.79	0.74	1.19	1.23
$4,7 \cdot 10^{-3}$	2.0	1.37	0.85	0.79	1.16	1.31
unknown	2.14	1.43	0.86	0.78	—	—
$6,5 \cdot 10^{-3}$	2.30	1.65	0.81	0.71	1.17	1.46

neity of the electric crystalline field. This inhomogeneity is associated with local distortions of the crystal lattice, which lead to different initial splitting of the spin levels for the Cr^{+++} ions situated at different points of the sample. This effect appears in the spin Hamiltonian as a fluctuation of the constant D and, in accordance with (2), contributes only to the line widths of the $3/2 \rightarrow 1/2$ transition.

Local distortions of the crystalline field can arise for two reasons. Firstly, the isomorphic introduction of chromium into the corundum lattice distorts the lattice somewhat. Secondly, distortions are due to the large mechanical stresses in the corundum crystals containing chromium (single crystals of chromium-containing corundum are grown from a melt at high temperatures). The fact that the ratio of the widths Δ_2/Δ_1 does not vary at first with increasing chromium concentration shows that at low concentrations the introduction of chromium does not add anything to the stresses that are present in the pure Al_2O_3 lattice. An increase in the ratio Δ_2/Δ_1 in samples with higher concentrations shows that the introduction of a large quantity of chromium into the corundum lattice introduces additional local distortions of the crystalline field compared with the pure corundum lattice.

The existence of a residual line width for the $-1/2 \rightarrow 1/2$ transitions at high magnetic dilutions can be explained by magnetic dipole interactions of the Cr^{+++} ions with the Al^{27} nuclei.

Let us consider the dependence of the peak intensity of the lines for the two transitions on the concentration of the solid solution $Al_2O_3 \cdot Cr_2O_3$. The maximum in the peak intensity of the line for the $-1/2 \rightarrow 1/2$ transition observed experimentally in the range of concentrations investigated can be explained in the following manner. For high chromium concentrations (~ 1%) not all the chromium ions are properly situated in the lattice. Some are situated in an entirely different crystalline field. These ions give no contribution to the intensity of the absorption line, but broaden the lines by interacting with the ions which are responsible for the resonance absorption corresponding to the transition being observed. The decrease in I_2 with increasing concentration is relatively more rapid than the decrease in I_1, since the width Δ_2 increases more rapidly than Δ_1, also because of the increase in the inhomogeneity of the crystalline field.

COMPARISON OF EXPERIMENTAL DATA WITH THE THEORY OF DIPOLE BROADENING

We have compared the experimental line width for the $-1/2 \rightarrow 1/2$ transition, for which the dipole contribution must be the principal one, with the theoretical value obtained by using the calculated dipole broadening of the second moment of the absorption curve.

The formulas for the second moment of the absorption curves have been given by Pryce and Stevens[2] for the case when the ion spectrum consists of several lines, while Kittel and Abrahams[3] have taken into account the effect of the concentration of the paramagnetic ions in the solid solution on the dipole broadening. In our case the formula for the second moment has the form

$$\overline{\langle \Delta\nu^2 \rangle} = X/N\,(2S+1),$$

$$\begin{aligned} X = \sum_{i,k} [& |\langle 1,1 | \hat{W}_{ik} | 1,1 \rangle - \langle 2,1 | \hat{W}_{ik} | 2,1 \rangle \\ & - \langle 2,1 | \hat{W}_{ik} | 1,2 \rangle |^2 + | \langle 1,2 | \hat{W}_{ik} | 1,2 \rangle - \langle 2,2 | \hat{W}_{ik} | 2,2 \rangle \\ & + \langle 2,1 | \hat{W}_{ik} | 1,2 \rangle |^2 + | \langle 1,3 | \hat{W}_{ik} | 1,3 \rangle \\ & - \langle 2,3 | \hat{W}_{ik} | 2,3 \rangle |^2 + | \langle 1,3 | \hat{W}_{ik} | 3,1 \rangle - \langle 2,3 | \hat{W}_{ik} | 3,2)|^2 \\ & + | \langle 1,4 | \hat{W}_{ik} | 1,4 \rangle - \langle 2,4 | \hat{W}_{ik} | 2,4 \rangle |^2 \\ & + | \langle 1,4 | \hat{W}_{ik} | 4,1 \rangle - \langle 2,4 | \hat{W}_{ik} | 4,2 \rangle |^2], \end{aligned} \tag{3}$$

with $\nu_{12} \neq \nu_{23} \neq \nu_{34}$ (the superior bar denotes an average). Here N is the number of paramagnetic ions, the spin is $S = 3/2$, the indices $j = 1, 2, 3, 4$ denote the energy levels of the paramagnetic ion, and ν_{12} is the frequency of the transition for which the second moment of the absorption curve is calculated. In our case this is the $-1/2 \rightarrow 1/2$ transition.

On substituting for $\hat{W}_{ik}$ the Hamiltonian for the dipole interaction between the spins

$$\hat{W}_{ik} = g^2 \beta^2 r_{ik}^{-3} [\hat{S}_i\hat{S}_k - 3r_{ik}^{-2} (\hat{S}_i\hat{r}_{ik})(\hat{S}_k\hat{r}_{ik})]$$

and on evaluating the matrix elements in formula (3), we obtain for the line corresponding to the $-1/2 \rightarrow 1/2$ transition

$$h^2 \overline{\langle \Delta\nu^2 \rangle} = f \sum_k \tfrac{81}{8} \varkappa_{ik}^2, \quad \varkappa_{ik} = g_\parallel^2 \beta^2 r_{ik}^{-3} \left[\tfrac{3}{2}\gamma_{ik}^2 - \tfrac{1}{2}\right]; \qquad (4)$$

f is the concentration of the chromium in the corundum, and γ_{ik} is the cosine of the angle between the radius-vector $\mathbf{r}_{ik}$ and the z symmetry axis. We note that for the $3/2 \rightarrow 1/2$ transition

$$h^2 \overline{\langle \Delta\nu^2 \rangle} = f \sum_k \tfrac{69}{8} \varkappa_{ik}^2,$$

which is smaller than the second moment of the absorption curve for the $-1/2 \rightarrow 1/2$ transition (we have made use of this fact in the preceding section). On evaluating the lattice sums we obtain, for $M = -1/2 \rightarrow 1/2$, $\sigma_1 = 3960\sqrt{f}$ oe. For $f = 5 \times 10^{-3}$ we have $\sigma_1 = 280$ oe, while for $f = 2 \times 10^{-5}$ we have $\sigma_1 = 18$ oe. If we take into account the fact that for the Gaussian curve $\Delta/\sigma = 2.35$, for the Lorentz curve cut off at $x = 10a$ the ratio is $\Delta/\sigma = 0.86$, while the observed line shape is intermediate between the Gaussian and the Lorentz curves (being closer to the Gaussian curve), then the calculated line widths exceed the experimental ones by a factor of several fold for all the investigated concentrations.

We have also evaluated the contribution made to the line width by the interaction of the chromium ions with the aluminum nuclei. This contribution turns out to be ~ 4.5 oe (for $\Delta = 2.35\,\sigma$), which is less than the minimum observed width of 12 oe in a sample with $f = 2 \times 10^{-5}$.

CONCLUSION

Thus, analysis of the experimental data on the broadening of absorption lines in the "parallel" e.p.r. spectrum in chromium-containing corundum shows that we can qualitatively explain the experimental data on the basis of the dipole interaction mechanism and of the assumption of local inhomogeneity of the crystalline electric field. However, we have not succeeded in obtaining quantitative agreement between the experimental widths of the transitions with those calculated theoretically by evaluating the second moment of the absorption curve. The experimentally observed values of the line width are smaller by a factor of several fold than those calculated theoretically on the basis of the dipole mechanism. This suggests that the difference might be due to exchange interactions. However, exchange interactions in such highly magnetically-dilute samples of chromium-containing corundum as we have investigated could hardly have any appreciable effect on the absorption line widths.

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