ELECTRON PARAMAGNETIC RESONANCE OF Co^{2+} IONS IN CORUNDUM

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EPR investigations of Co^{2+} in corundum have been carried out and afford a check on existing theories of the EPR of this ion. The frequency dependence of the $g_\perp$ factor has been investigated up to 71 Gc/sec. The $g_\perp$ factors are found to be independent of frequency within the limits of experimental error. The temperature dependence of the spin-lattice relaxation time of Co^{2+} ions in corundum was also studied. At temperatures of 10 to 25°K the dependence has the form $\tau_1 \sim \exp(\delta/kT)$, where δ is the distance to the nearest excited Kramers doublet. The values $\delta_I = 110\ cm^{-1}$ and $\delta_{II} = 185\ cm^{-1}$ are obtained for the two nonequivalent systems of Co^{2+} ions in Al_2O_3. The theoretical values of δ calculated according to the Abragam–Pryce theory are in agreement with the experimental values derived from the relaxation measurements.

1. INTRODUCTION

IN a previous paper [1] the EPR (electron paramagnetic resonance) spectrum and spin-lattice relaxation of Co^{2+} ions in corundum (Al_2O_3) were investigated.

In the Al_2O_3 lattice, cobalt ions form two nonequivalent systems, which have a common axis of trigonal symmetry, but differ in their spin-Hamiltonian constants:

system I:

$$g_\parallel = 2.292 \pm 0.001, \qquad g_\perp = 4.947 \pm 0.003,$$
$$A = (3.24 \pm 0.01)\cdot 10^{-3}\,cm^{-1}, \quad B = (9.72 \pm 0.05)\cdot 10^{-3}\,cm^{-1};$$

system II:

$$g_\parallel = 2.808 \pm 0.003, \qquad g_\perp = 4.855 \pm 0.005,$$
$$A = (2.08 \pm 0.09)\cdot 10^{-3}\,cm^{-1}, \quad B = (15.1 \pm 0.11)\cdot 10^{-3}\,cm^{-1}.$$

The results of a theoretical interpretation of the EPR spectrum of cobalt in corundum, based on the theory of Abragam and Pryce, [2] were also presented in [1]. In that theory it is assumed that the cobalt ion is situated in a crystalline field of predominantly cubic symmetry and that the trigonal component of the crystalline field and the spin-orbit coupling have the same order of magnitude.

The temperature dependence of the spin-lattice relaxation time τ_1 was studied for the Co^{2+} ions of system I in the intervals 1.8 to 5 and 20 to 50°K, where it was found that τ_1 becomes 10^7 times shorter as the temperature increases from 5 to 20°K. An explanation for such an anomalously rapid change in τ_1 was not given.

Al'tshuler and Zaripov [3] have made an attempt to clarify the spectrum and observed spin-lattice relaxation of the Co^{2+} ion in corundum under the assumption that the crystalline field of trigonal symmetry in the corundum crystal acting on the Co^{2+} ions is much stronger than the spin-orbit coupling. Under such assumptions, the lower levels of a Co^{2+} ion turn out to be two spin doublets similar to those of Cr^{3+} ions. The calculation of the initial splitting 2D of these doublets performed by Al'tshuler and Zaripov [3] on the basis of the experimental values for the g factors yielded the result $2D = 24\ cm^{-1}$. The authors also explained the anomalous spin-lattice relaxation by taking into account the large initial splitting of the spin doublets in the combination scattering processes and assuming that first order processes between the levels of the lower Kramers doublet give a small probability for a relaxation transition.

The interpretation of the spectrum presented in the paper referred to pertains to system-I ions. An attempt to extend it to system-II ions encounters difficulties, since the factor $g_\parallel = 2.808$ differs greatly from the free spin value $g = 2$, indicating a significant spin-orbit interaction.

The aim of the present work was the experimental test of the various theories of the EPR of Co^{2+} ions. The g factors were measured at frequencies of 37 and 71 Gc/sec, and the temperature dependence of τ_1 in the interval 4.2 to 25°K for the two

groups of Co^{2+} lines was investigated in detail.

2. MEASUREMENT OF THE g FACTORS AT DIFFERENT FREQUENCIES

It follows from the theoretical interpretation of Al'tshuler and Zaripov [3] that the constant $g_\perp$ for system I of nonequivalent Co^{2+} ions in corundum should depend on the frequency of observation. In fact, it is easy to show from the Hamiltonian presented in [3] that

$$g_\perp^{exp} = g_\perp [2 - \tfrac{3}{2}(g_\perp \beta H/2D)^2]. \quad (1)$$

Here $g_\perp$ is one-half the value of $g_\perp^{exp}$ measured at very low frequency, i.e., when $(g_\perp \beta H/2D)^2$ is negligibly small (β is the Bohr magneton). An estimate shows that for $2D = 24\ cm^{-1}$ the shift in g factor approaches 0.2%, if one makes measurements at about 70 Gc/sec.

We have measured $g_\perp$ for both systems of ions at 37 and 71 Gc/sec. In doing this, special attention was given to the accuracy of the measurement of the generator frequency and the magnetic field strength. The frequency was measured with a quartz-calibrated heterodyne wave meter. The magnetic field was measured by proton resonance; a correction was introduced to take into account the difference in field between the location of the sample and the place where the field was measured.

The measurements were carried out in liquid helium at temperatures greater than 4.2°K (~ 10°K). For this the plunger in the cavity to which the sample of corundum was affixed was warmed by means of a special electric heater. The temperature rise eliminated saturation effects and permitted the use of a spectrometer with scope presentation. It was established that heating to a temperature of ~ 10°K did not change the position of the EPR line at all.

The results of the measurements are presented in the table. The values of $g_\perp$ for 9 Gc/sec were taken from previous work. [1] It is seen that all the measurements give practically the same result for system II. For system I the values of $g_\perp$ for 37 and 71 Gc/sec are the same within experimental error, but differ somewhat for 9 Gc/sec. It follows from Eq. (1) that they should differ noticeably (~ 0.15%) from the value of $g_\perp$ for 37 and 71 Gc/sec.

ν, Gc/sec	$g_\perp^{exp}$	
	System I	System II
9	4.947±0.003	4.855±0.005
37	4.936±0.003	4.850±0.005
71	4.938±0.003	4.850±0.005

The experiment at the lowest of the three frequencies gave somewhat higher results for both systems of ions. Possibly, this is due to the fact that at this frequency the magnitude of the hyperfine structure (total splitting ~ 290 Oe for system I and 470 Oe for system II) becomes comparable with the mean values of the magnetic field (~ 1300 Oe), which reduces the accuracy of this experiment even when second order effects are taken into account.

These experiments give a basis for the assertion that the decrease in $g_\perp$ with increasing frequency, expected from theory, [3] does not occur, i.e., that the distance to the excited state exceeds $24\ cm^{-1}$.

3. TEMPERATURE DEPENDENCE OF THE SPIN-LATTICE RELAXATION TIME OF Co^{2+} IONS IN CORUNDUM

A detailed investigation of the function $\tau_1(T)$ was carried out with an X-band spectrometer using the continuous saturation method. The resonant cavity of the superheterodyne spectrometer could be heated to any desired temperature in the interval from 2 to 60°K. [4]

The dependence $\tau_1(T)$ was studied in much greater detail for system I. In this case the pulse method for measuring relaxation time was used to improve the results. At temperatures greater than 20°K, the spin-lattice relaxation time τ_1 was computed from the line broadening.

All experiments were performed with the trigonal axis of the crystal parallel to the external magnetic field. The results are shown in Figs. 1a and 1b.

For the system of nonequivalent ions I, the function $\tau_1(T)$ in the interval 9 to 30°K is well described by the law $\tau_1 = 1.6 \times 10^{-11} \exp(\delta_I/kT)$ sec (the linear part of the graph in Fig. 1a). At temperatures less than 4.2°K, τ_1 is inversely proportional to T. For system II, the relation $\tau_1 = 10^{-12} \exp(\delta_{II}/kT)$ sec is valid for temperatures 14—26°K; at the lowest temperatures τ_1 is again inversely proportional to T. The quantities δ_I and δ_{II} have the values

$$\delta_I = 110 \pm 15\ cm^{-1}, \quad \delta_{II} = 185 \pm 20\ cm^{-1}.$$

The exponential dependence of τ_1 on T can be interpreted by means of a relaxation mechanism that takes place through an excited state, such as that proposed by Orbach et al [5] for cerium magnesium nitrate.

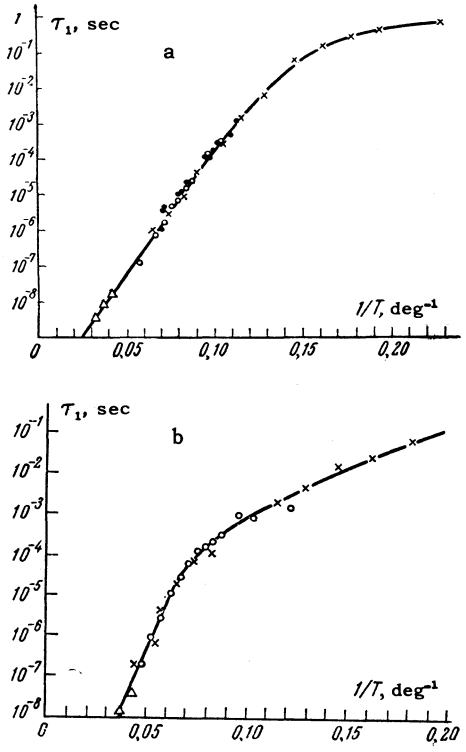

FIG. 1. Dependence of the spin-lattice relaxation time of Co^{2+} ions in corundum on the reciprocal temperature: a, for group I ions; b, for group II ions. Open circles and crosses represent measurements by the saturation method (two series of experiments); triangles, by the broadening method; solid circles, by the pulse method.

Let the scheme of the lower energy levels of a paramagnetic ion have the following form: a Kramers doublet below and a singlet above, at a distance δ (Fig. 2). Now if the probability of a direct relaxation transition between levels 1 and 2 is much less than the probabilities of transitions between levels 1—3 and 3—2, then it will be possible to establish a two-step process in which a particle originally in level 2 gets into level 3 and only then falls into level 1.

The probability for such a relaxation process under the conditions $\delta \gg kT$, $\delta \gg h\nu$ is proportional to $\exp(-\delta/kT)$.[5] This dependence is easily obtained from the following qualitative estimates:

$$w_{13} \sim [e^{\delta/kT} - 1]^{-1}, \qquad w_{32} \sim e^{\delta/kT}/[e^{\delta/kT} - 1].$$

For $\delta/kT \gg 1$, we will have $w_{13} \sim \exp(-\delta/kT)$, $w_{32} \sim 1$, and the relaxation via the excited level appears as the "bottleneck" of a two-step process, the probability of which w_{13} (or w_{23}) $\sim \exp(-\delta/kT)$. These considerations are not altered if a Kramers doublet serves as the upper level.

In the case of Co^{2+} ions in corundum, the lowest level is a Kramers doublet and direct spin-lattice

FIG. 2

relaxation between the components of this doublet has low probability. From our experiments it is seen that $w_{12} \sim 1$ sec^{-1} at 4.2°K. Hence, with an increase in temperature relaxation begins to proceed via an excited state that is located 110 cm^{-1} higher than the ground level for group I ions and 185 cm^{-1} for group II. This process will determine the relaxation up to 30°K, when observation of the EPR lines ceases to be possible because of their extreme width.

We note that the experimental dependence $\tau_1(T)$ differs from the theoretical one presented by Al'tshuler and Zaripov.[3]

4. COMPARISON OF EXPERIMENT AND THEORY

We shall compare the magnitudes of δ found from the relaxation experiments with the values calculated from the g factors on the basis of the Abragam-Pryce theory.[1,6] With the assumption that the spin-orbit interaction and the effect of the trigonal field are of the same order, the energies of the six lowest Kramers doublets have been calculated for the two systems of ions[6] (energy in cm^{-1}):

System I:	—1030	—860	—270	60	210	400
System II:	—790	—540	—250	160	260	400

These values were obtained, using $\lambda = -180$ cm^{-1}, for the spin-orbit coupling constant and $\Delta_I = -760$ cm^{-1}, $\Delta_{II} = -400$ cm^{-1} for the trigonal field parameters. The value for λ was taken equal to the value for the free ion. We obtain for the separations δ that we need (δ is the difference in energy between the two lowest Kramers doublets) the values $\delta_I = 170$ cm^{-1} and $\delta_{II} = 250$ cm^{-1}.

It is known that in dense crystals like corundum, magnesium oxide, etc., the covalent bond of the d electrons of the paramagnetic ion with the electrons of the surrounding oxygen ions plays an important role. If this is taken into account in a rough way, by decreasing the value of λ by 30%, then as calculations show, the values Δ_I and Δ_{II}, as well as all the energy levels are likewise decreased by 30%.

Setting $\lambda' = 0.7\lambda = 126$ cm^{-1}, we find that the corrected values $\delta'_I = 120$ cm^{-1} and $\delta'_{II} = 175$ cm^{-1} agree with the experimental data to within the limits of experimental error. We see that the values of the g factors and spin-lattice relaxation times of Co^{2+} ions in the Al_2O_3 lattice can be explained

in the frame of the usual assumptions about the character of the crystalline field.

The values of δ determined from the relaxation experiments can be used for the concretization of more rigorous calculations that take covalent coupling into account.[7]

We note that the mechanism of "two-step" relaxation ought to play an important role also in other iron group ions that have half-integral spin and closely spaced lower energy levels.

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