ELECTRON PARAMAGNETIC RESONANCE AND SPIN-LATTICE RELAXATION OF Co²⁺ IN CORUNDUM

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The electron paramagnetic resonance of Co²⁺ in corundum has been observed and the spin-Hamiltonian constants for the two nonequivalent ion systems have been measured. The temperature dependence of the spin-lattice relaxation time has been studied. It was found that at liquid helium temperatures Co²⁺ has an anomalously large relaxation time. Effects were observed which are associated with spin-spin cross relaxation between hyperfine structure components.

It is important to investigate the electron paramagnetic resonance (EPR) of iron-group ions in corundum for both theoretical and practical reasons. For example, the working material in most paramagnetic amplifiers is corundum containing an admixture of chromium or iron ions.¹-³ An important part in the future development of paramagnetic amplifiers may be played by corundum containing two paramagnetic ions, one of which serves as the working material for the amplifier while the other shortens the spin-lattice relaxation time of the first ion. In one investigation cerium ions were used to modify the relaxation time of gadolinium ions in lanthanum ethyl sulfate.

In the present work the EPR spectrum of Co²⁺ in corundum was studied, the spectrum was interpreted theoretically and the spin-lattice relaxation time was investigated.

1. The ground state of the free Co²⁺ ion is ⁴F of the 3d⁷ configuration. The other term of the same symmetry, ⁴P, is located 14 000 cm⁻¹ above the ground level. In the corundum single crystal the Co²⁺ ion levels undergo Stark splitting induced by the electric field of neighboring ions. The crystalline electric field is generated by an octahedron of O²⁻ ions and is of cubic symmetry with a small admixture of trigonal symmetry.

The behavior of Co²⁺ energy levels in crystalline fields of different symmetries has been investigated in references 5 and 6. In a cubic field the lowest level, which possesses sevenfold orbital degeneracy, is split into a singlet and two triplets, with the triplets lying below the singlet. The trigonal field further splits a triplet into a singlet and a doublet (neglecting the spin-orbit interaction). The singlet can lie either above or below the doublet, depending on the specific form of the crystalline field. Each orbital level possesses fourfold spin degeneracy. When spin-orbit coupling is taken into account the trigonal field splits the lower triplet into six Kramers doublets. Abragam and Pryce⁷ have shown that the orbital moment ℓ' = 1 can be assigned to the lower orbital triplet and that the behavior of the energy levels in the trigonal field with spin-orbit coupling can be described by the fine-structure Hamiltonian

\[ W = \Delta (1 - \hat{I}_z^2) - \alpha \hat{I}_z \hat{S}_z - \alpha' \hat{I}_z (\hat{I}_x \hat{S}_x + \hat{I}_y \hat{S}_y), \]  

where \( \Delta \) is the splitting of the lower triplet by the trigonal field, \( \lambda \) is the spin–orbit coupling constant (\( \lambda = -180 \text{ cm}^{-1} \)), \( \alpha \) and \( \alpha' \) are factors depending on the admixture of higher states belonging to the ⁴F and ⁴P terms in the wave functions of the lower triplet. When these admixtures are omitted we have \( \alpha = \alpha' = 3/2 \).⁶ The z axis of the rectangular system is a trigonal crystal axis. \( \alpha \) and \( \alpha' \) can be calculated only if the complete scheme of level splitting by the crystalline field is known.

The fine-structure levels can be classified by means of the quantum number \( m = \ell_z + S_z \). In the representation where \( \hat{I}_z \) and \( \hat{S}_z \) are diagonal it is easy to write the secular determinant of the Hamiltonian (1), which undergoes triple splitting corresponding to \( m = \pm \frac{1}{2}, \pm \frac{3}{2}, \pm \frac{5}{2} \). The solution of the secular equation gives three Kramers doublets belonging to \( m = \pm \frac{1}{2} \), two doublets for \( m = \pm \frac{3}{2} \), and one doublet for \( m = \pm \frac{5}{2} \). The lowest energy level is a doublet with \( m = \pm \frac{1}{2} \); its wave functions are superpositions of the wave functions for the states with \( m = \pm \frac{1}{2} \);
\[ |1/2\rangle = a | -1; 0 \rangle + b | 0 \rangle ; | 1/2\rangle + c | 1 \rangle , \]

\[ | -1/2\rangle = a | 1 \rangle + b | 0 \rangle - c | -1 \rangle , \]

(2)

with the coefficients \( a, b, c \) depending on \( \alpha, \alpha', \Delta \). When the wave functions of the lowest doublet are known we can calculate the spectroscopic splitting factors \( g_L \) and \( \Delta g \) of the level. Vice versa, when the \( g \) factors are known, \( \Delta, \alpha, \alpha' \), can be calculated.

The hyperfine splitting constants can be represented as the sums of three terms:

\[ A = A_L + A_{Sd} + A_{Sa} \]
\[ B = B_L + B_{Sd} + B_{Sa} \]

(3)

Here \( A_L \) and \( B_L \) depend on electron orbital motion, \( A_{Sd} \) and \( B_{Sd} \) result from the d-electron admixture of configurations containing unpaired s electrons. The first and second terms in (3) can be represented as follows:

\[ A_L = P g_{L1}, B_L = P g_{L2}, A_{Sd} = -(k/2) P g_{Sd}, B_{Sd} = -(k/2) P g_{Sd} \]

(4)

Here \( P \) are the orbital and spin parts of the \( g \) factors; \( P = 2y\beta_n\gamma^{-3} \), where \( \gamma \) is the nuclear gyromagnetic ratio, \( \beta \) is the Bohr magneton, \( \beta_n \) is the nuclear magneton and \( k \) characterizes the admixture of configurations containing unpaired s electrons.

The terms \( A_{Sd} \) and \( B_{Sd} \) make only a small contribution and may be neglected in approximate calculations.

2. We have reported our observation of the EPR of \( \text{Co}^{2+} \) in corundum at 4.2°K in an earlier paper. The spectrum consists of two strong lines, each having eight hyperfine components (corresponding to the nuclear spin \( I = 1/2 \) of \( \text{Co}^{59} \)), and a few weak lines which also exhibit the characteristic hyperfine structure of cobalt.

All lines become stronger with decreasing temperature. They therefore belong to transitions between levels of the lowest Kramers doublet and are not associated with excited states.

The strong lines can be interpreted by means of the spin Hamiltonian with effective spin

\[ S' = 1/2; \]

\[ \hat{H} = g_1 \beta H_x \hat{S}_x + g_2 \beta (H_y \hat{S}_y + H_z \hat{S}_z) + A \hat{L} \hat{S} + B \left( \hat{I}_x \hat{S}_x + \hat{I}_y \hat{S}_y \right), \]

(5)

where \( \hat{S}_x, \hat{S}_y, \hat{S}_z \) are projections of the spin, \( \hat{I}_x, \hat{I}_y, \hat{I}_z \) are projections of the nuclear spin, and \( H_x, H_y, H_z \) are the external magnetic field components. Measurements of the EPR spectrum at 9000 and 38 000 Mcs yielded the following values of the constants in the Hamiltonian:

- Line I: \( g_1 = 2.292 \pm 0.001, \quad g_2 = 4.947 \pm 0.003, \quad A = 3.24 \pm 0.01, \quad B = 9.72 \pm 0.05 \)
- Line II: \( g_1 = 2.808 \pm 0.003, \quad g_2 = 4.855 \pm 0.005, \quad A = 2.08 \pm 0.09, \quad B = 15.10 \pm 0.11 \)

A and \( B \) are given in units of \( 10^{-3} \text{ cm}^{-1} \).

Line I of \( \text{Co}^{2+} \) in corundum was also measured at 9100 Mcs and \( T = 1.6^\circ \text{K} \) by Geusic, whose hyperfine constants are in good agreement with our values, although there is a small but appreciable difference of the \( g \) factor.

The hyperfine splitting of both cobalt lines is greater for perpendicular than for parallel orientation. Therefore the parallel orientation is accompanied by strong second-order effects which destroy the equal separation of hyperfine components for line I and even cause partial overlapping of the components at one end of the spectrum of line II (Fig. 1).

As the crystal departs from parallel orientation a slight splitting of each hyperfine component appears, which disappears for both \( \theta = 0^\circ \) and \( \theta > 30^\circ \).

Lines I and II evidently belong to different nonequivalent ion systems. The existence of two \( \text{Co}^{2+} \) ion systems in corundum may be accounted for as follows. The lattice contains two kinds of octahedral cavities in which the cobalt ion may be located. One system of cavities in the normal lattice is occupied by aluminum ions, while the second system is not entirely occupied and there is one unoccupied site for every two occupied cavities. Aluminum is included in the corundum lattice as the trivalent ion \( \text{Al}^{3+} \) while the cobalt ion is divalent. Charge neutralization therefore requires the replacement of two \( \text{Al}^{3+} \) ions by three \( \text{Co}^{2+} \) ions, two of which occupy the \( \text{Al}^{3+} \) sites while one fills an unoccupied octahedral cavity. The separation of cobalt ion centers from the centers of the nearest oxygen ions is identical for both ion systems, so that the cubically symmetric field should be approximately the same for both systems. However, the trigonal field may differ considerably, since in the trigonal axis direction a \( \text{Co}^{2+} \) ion has one \( \text{Al}^{3+} \) ion as its nearest neighbor, while in the second case there are two \( \text{Al}^{3+} \) ions (Fig. 2). The measured ratio of integrated intensities for lines I and II in the case of parallel orientation was 2.3:1, in good agreement with the expected value of 2:1. The weaker cobalt lines in corundum probably result from ions having anomalous crystalline environments resulting from other cobalt ions, dislocations, etc.

Using the values obtained for \( g_{||} \) and \( g_{\perp} \), we calculated \( \alpha, \alpha', \Delta \), the constants of the Hamil-
FIG. 1. Traces of the derivative of the EPR lines of Co\textsuperscript{2+} in corundum for parallel orientation at 4.2°K. a—line II, b—line I. The magnetic field increases from left to right.

FIG. 2. Positions of two nonequivalent Co\textsuperscript{2+} ions in the corundum lattice.

3. At room temperature Co\textsuperscript{2+} has a very short spin-lattice relaxation time $\tau_1$, which hinders the observation of EPR lines. This difficulty is associated with the closeness of the lower orbital levels, which have separations of a few hundred cm\textsuperscript{-1}. The short relaxation time $\tau_1$ hinders detection of EPR even at the temperature of liquid nitrogen.

$\tau_1$ was measured at liquid helium temperatures for the saturated 9500 Mcs resonance line, using corundum single crystals containing $10^{-2}$% cobalt. The absolute accuracy of $\tau_1$ in the saturation technique was ±50%, although the relative error was considerably smaller. For line I in parallel orientation at 4.2°K we obtained $\tau_1 \approx 1$ sec and the temperature law $\tau_1 \sim T^{-1}$ in the range 1.8—4.2°K. Relaxation above 4.2°K was investigated during the heating of the cavity resonator from liquid helium temperature to liquid nitrogen temperature. In the range 4.2—22°K the relaxation time drops off sharply from 1 sec at 4.2°K to $3 \times 10^{-8}$ sec at 22°K.

In the range 22—50°K we were able to calculate $\tau_1$ from the broadening of the EPR line as a result of spin-lattice relaxation. Below 22°K the magnetic field width of a single hyperfine component of line I at half maximum is 7.5 oe. The line begins to broaden with heating up to 22°. At 31° the width is 15 oe; with further heating the hyperfine components begin to overlap. At 50°K the line is ~200 oe wide with no trace of hyperfine structure. The temperature dependence of $\tau_1$ in the interval 22—50° fits the formula $\tau_1 \sim T^{-n}$ with $n = 5 \pm 0.5$. Figure 3 shows the overall temperature dependence of $\tau_1$.

A few additional remarks are needed regarding the use of the saturation technique for measuring $\tau_1$. This procedure does not determine $\tau_1$ but rather the product $\tau_1 \tau_2$, where $\tau_2$ is the spin-spin relaxation time. $\tau_2$ can be calculated from the line width $\Delta \nu$ when the latter is associated with homogeneous broadening, i.e., when it is induced.
These ions are weakly coupled to the lattice and contribute the anomalous relaxation time of cobalt at liquid helium temperatures compared with room temperatures. At such a low concentration the dipole–dipole interaction makes an extremely small contribution to the total line width, which in this case is determined mainly by spin interaction with the nuclear magnetic moments of the diamagnetic environment and by crystal imperfections. An analysis showed that at liquid helium temperatures the line shape is Gaussian with somewhat broadened wings and that it is not affected by saturation. The hypothesis that homogeneous broadening determines the line widths is thus confirmed. For small concentrations of paramagnetic ions the interactions that cause homogeneous broadening result in a Lorentz line shape. The concept of cross relaxation enables us to conclude that even in the case of inhomogeneous broadening the line is saturated identically over its entire contour and that the saturation factor in \(1 + y^2 H_l^2 \tau_1 \tau_2\) requires replacement of \(\tau_2\) by \(\tau_2^*\), which is determined from the observed line width. We performed this substitution.

We also note that cobalt exhibits a spin–spin cross interaction between different hyperfine components. This was first noted by Townes et al. for copper ions, and when one component is saturated leads to partial saturation of the other components. This effect distorts the measurements obtained by the saturation technique and results in lowered values of \(\tau_1\).

The results presented here for the spin–lattice relaxation time of \(\text{Co}^{3+}\) exhibit an anomalously long relaxation time of this ion at liquid helium temperatures compared with \(\text{Cr}^{3+}\) and \(\text{Fe}^{3+}\). These ions are weakly coupled to the lattice and spin–lattice relaxation does not impede the observation of EPR lines even at room temperature, while at liquid helium temperatures \(\tau_1\) is of the order \(10^{-14} - 10^{-12}\) sec. We might attempt to attribute the anomalous relaxation time of cobalt to low thermal conductivity of the corundum lattice containing cobalt, i.e., we may assume that the true spin–lattice relaxation time is short but that the rate of energy removal from the spin system is limited by the process of energy transfer from lattice phonons to the helium bath. This hypothesis is refuted as follows. When one hyperfine component of line I was saturated at frequency \(\nu_1\) we were able to observe the behavior of another hyperfine component at frequency \(\nu_2\), both components being observed in the same external magnetic field. In this case an emission line was obtained at \(\nu_2\) instead of an absorption line, i.e., a negative spin temperature was attained. In the presence of strong ion–lattice coupling a negative temperature cannot exist between levels, since the lattice temperature is always positive because of the absence of an upper limit to the phonon energy spectrum. The cause of the anomalous relaxation of \(\text{Co}^{2+}\) in corundum must therefore be sought in the nature of the ion itself. We note that in experiments using parallel fields Van den Broek et al. also observed anomalously large values of \(\tau_1\) in certain cobalt salts at liquid helium temperatures.

The relationship \(\tau_1 \sim T^{-1}\) at liquid helium temperatures may be associated with the relaxation mechanism resulting from direct emission and absorption of single phonons. The steep drop of the relaxation time in the range 4.2–22° is still unexplained. The relationship between \(\tau_1\) and \(T\) at higher temperatures may be represented as the superposition of direct processes and combination scattering of phonons, resulting in a strong temperature dependence \(\tau_1 \sim T^{-1}\). We note that the temperature dependence of line II relaxation in parallel orientation practically coincides with that for line I (Fig. 3). Since lines I and II originate in ions having different schemes of the lowest orbital levels, the relaxation anomalies cannot be accounted for by specific features of a level scheme (for example, the existence of an excited level \(\sim 10\) cm\(^{-1}\) directly above the lowest level). The observed angular dependence of the relaxation time for line I at 4.2° and 2° showed that, within experimental error, \(\tau_1\) is independent of crystal orientation in an external magnetic field.

4. EPR of \(\text{Co}^{2+}\) results in several properties associated with spin–spin cross interactions between different components. As already mentioned, when a component at frequency \(\nu_1\) is saturated an emission line can be obtained for a neighboring component at frequency \(\nu_2\). When \(\nu_1 > \nu_2\) this effect is observed for components...
lying on the stronger magnetic-field edge of the line. When \( \nu_2 > \nu_1 \) the effect is observed for components on the other edge of the line. This effect can be utilized in a paramagnetic amplifier with working frequency above that of the auxiliary radiation.

The cross relaxation processes of cobalt in corundum are now being investigated in greater detail.

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10 E. S. Rudnitskaya, Tr. Ин-та кристаллографии (Trans. Crystallographic Inst.) 8, 13 (1953).

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