

Observation of paramagnetic resonance on an Fe^{2+} ion in a CaCO_3 lattice

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An absorption line was observed in samples of natural CaCO_3 containing 0.1% Mn^{2+} and $(1 \times 10^{-2} - 3 \times 10^{-2})\%$ iron as impurities. The spectrum of this line can be described by an expression of the type $\hbar\omega = g_{\parallel}\beta H \cos\theta$, where θ is the angle between the C_3 axis of the crystal and the external magnetic field \mathbf{H} , while $g_{\parallel} = 9.85$. At $\theta = 0$ the line was excited at $h_{\parallel}\mathbf{H}$. The measurements were made at 9.62 GHz and temperatures $T = 1.1-4.2$ °K. The observed line is interpreted as a transition within the non-Kramers doublet of the Fe^{2+} ion. By starting with a complete set of functions of the ground state 5D of the Fe^{2+} ion, we calculated the level positions and the value of g_{\parallel} of this ion as functions of the trigonal component Δ of the crystal field. The obtained value of Δ agrees with the results of measurements of the Mössbauer spectrum of an Fe^{2+} ion in a CoCO_3 lattice.

INTRODUCTION

Observation of paramagnetic resonance at the ion of divalent iron in a lattice having axial symmetry entails certain difficulties brought about by the following factors. In a cubic octahedral field, the ground-state level of the Fe^{2+} ion (configuration $3d^6$) splits into a doublet E_g and a lower-lying triplet T_{2g} , the spacing between which is $\sim 10\,000\text{ cm}^{-1}$ (Fig. 1). Allowance for the spin-orbit interaction leads a further splitting of $3 \times 5 = 15$ levels of the orbital triplet with a total spacing on the order of 500 cm^{-1} . The lower level in this case is a triplet, the behavior of which can be described by an effective spin $S' = 1$. An axial field of trigonal or tetragonal symmetry splits the aforementioned triplet into a singlet and a so-called non-Kramers doublet, the spacing between which exceeds 10 cm^{-1} . The relative positions of the doublet and singlet depend on the sign of the axial field.

Thus, at the usual frequencies, the value of the quantum greatly exceeds this spacing, and therefore it is impossible to observe allowed transitions with $\Delta M_S = \pm 1$. Transitions within the doublet, corresponding to $\Delta M_S = \pm 2$, are forbidden. However, if there is a small rhombic distortion due to local defects or stresses, then the probability of a transition with $\Delta M_S = \pm 2$ already differs from zero. The spin Hamiltonian for this case can be written in the form^[1],

$$\hat{\mathcal{H}} = g_{\parallel}\beta H_z \hat{S}_z' + \Delta_x \hat{S}_x' + \Delta_y \hat{S}_y', \quad (1)$$

where $S' = 1/2$ is the effective spin, Δ_x and Δ_y are quantities describing the rhombic distortion, and the g -factor value is $g_{\perp} = 0$. From the form of the Hamiltonian (1) it follows that at $\mathbf{H}_z \parallel \mathbf{h}$, where \mathbf{h} is the magnetic component of the microwave field, transitions within the non-Kramers doublet are possible.

Tinkham^[2] succeeded in observing the weak absorption line on the Fe^{2+} ion, corresponding to the transition $\Delta M_S = \pm 2$ in the tetragonal-symmetry crystal field of the crystal ZnF_2 . The forbidden transition $\Delta M_S = \pm 2$ on the divalent-iron ion was also observed in the cubic crystals MgO ^[3] and CaO ^[4]. Since the spin-lattice interaction of the Fe^{2+} ion is large, it becomes possible to observe acoustic paramagnetic resonance at this ion. This was done by Lewiner and Wigmore in the Al_2O_3 crystal.^[5]

In calcite (space group D_{3d}^6), the iron ion replacing

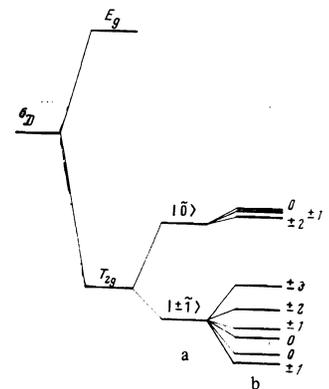


FIG. 1. Diagram of splitting of the ground level of the Fe^{2+} ion in a rhombohedral surrounding: a) trigonal field; b) spin-orbit interaction.

the calcium ion is surrounded by six CO_3^{2-} complexes. This surrounding corresponds to stretching of the cube along the body diagonal (the C_3 axis). The negative sign of the trigonal field can be established by using, for example, the results of Bose et al.^[6] The lower level is then a non-Kramers doublet. An attempt was made earlier^[7] to observe a transition within this doublet of the Fe^{2+} ion in the CaCO_3 lattice. When iron is introduced in the CaCO_3 lattice, some of it goes over into the trivalent state, and the rest into the divalent state. Wakabayashi succeeded in observing only the paramagnetic-resonance spectrum from the trivalent iron.

Interest in this research is due to the fact that studies of the antiferromagnetic-resonance spectrum in CoCO_3 crystals containing 0.1-2% iron have revealed a low-lying additional absorption branch at 45 GHz^[8]. The spectrum of this branch can be described by the expression

$$(\hbar\omega)^2 = g_{\perp}^2 \beta^2 (H_x \cdot H_y)^2 + g_{\parallel}^2 \beta^2 H_z^2, \quad (2)$$

where, assuming an exchange field $H_e = 270\text{ kOe}$, we have $g_{\perp} = 0.13$ and $g_{\parallel} = 6.6$. It was therefore of interest to attempt to observe the EPR spectrum at the Fe^{2+} ion in the diamagnetic crystal CaCO_3 , which is isomorphous to CoCO_3 .

SAMPLES AND MEASUREMENT PROCEDURE

We used in our measurements natural calcite single crystals, which were transparent and had a slight yellow tint. A thorough spectroscopic analysis has shown that the content of the rare-earth ion impurities in both investigated samples was less than $10^{-3}\%$. These

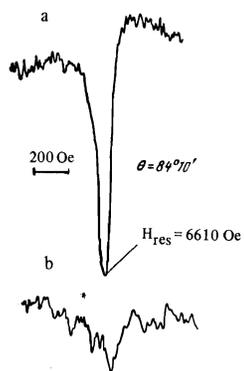


FIG. 2. Absorption line: a) using angular modulation of the external magnetic field, b) using linear modulation.

samples contained about 0.1% of Mn^{2+} and $1 \times 10^{-2} = 3 \times 10^{-2}\%$ iron. An estimate of the content of the trivalent iron, made after measuring the intensity of the paramagnetic-resonance line of the trivalent iron, corresponded to a concentration of the latter amounting to several units of $10^{-3}\%$. All the samples were oriented by x-ray diffraction and their orientation agreed with that obtained from the measurements of the spectrum of the trivalent iron in the same samples.

The measurements were made with an autodyne superheterodyne spectrometer at $\nu = 9.62$ GHz and temperatures from 1.1 to 4.2°K. The heterodyne was an autodyne oscillator loaded by a superconducting resonator, and the circuit registered the frequency change of the working resonator in which the investigated sample was placed. Since the magnetic field was modulated during the measurements at frequency 12 Hz, the automatic recorder registered the second derivative of the absorption curve.

We used a strip resonator, which offers certain advantages. First, it was easy to change the polarization of the microwave field relative to the external magnetic field. Second, owing to the small dimensions of the resonator, the sample/resonator filling factor was increased by one order of magnitude.

The spectrometer had provision for effecting angular modulation of the magnetic field^[9]. In this case the alternating magnetic field was perpendicular to the static field and the line intensity was proportional to the derivative of the position of the resonance line with respect to angle. As a result, the intensity of the anisotropic lines increased strongly, and the intensity of the isotropic lines decreased. This was an important factor in the observation of the line from the divalent iron. Figure 2 shows a line obtained by using angular modulation (top) and by using ordinary linear modulation (lower figure). In addition, in weaker fields there appeared many forbidden lines from the ions Fe^{3+} and Mn^{2+} , and only by using angular modulation were we able to trace the Fe^{2+} line as the orientation of the external magnetic field was varied.

MEASUREMENT RESULTS

We observed strong resolved absorption lines from Mn^{2+} and Fe^{3+} in the paramagnetic-resonance spectra of both investigated samples, and this hindered considerably the search for the desired line. The measurements were therefore carried out in fields from 0 to 2.2 kOe, and from 4.4 kOe to the maximum possible field in the magnet, 10 kOe. In fields from 4.4 to 10 kOe we observed only the Fe^{3+} line investigated by us. The

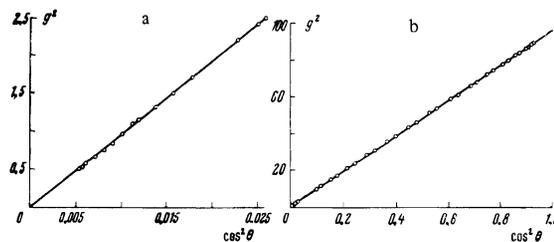


FIG. 3. Obtained plots of $g^2(\cos^2 \theta)$.

directions of the high-frequency magnetic field h and of the electric field e were contained in the plane of rotation of the magnet, with $C_3 \parallel H_Z \parallel h \perp e$. In the measurement of the angular dependence, we varied only the orientation of the external magnetic field H relative to the crystal axis C_3 . The line observable under these conditions was not excited at $H_Z \perp h$. The absorption line investigated by us was investigated at $T = 1.1^\circ K$, where its intensity increased slightly in comparison with $T = 4.2^\circ K$; it decreased to zero at $T \sim 20^\circ K$.

Figure 3 shows plots of the square of the g -factor against $\cos^2 \theta$ for one of the investigated samples (θ is the angle between the external magnetic field and the C_3 axis of the crystal). The observed spectrum of both samples agreed well with the expression

$$(\hbar\omega)^2 = g_{\parallel}^2 \beta^2 H^2 \cos^2 \theta. \quad (3)$$

The values $g_{\parallel} = 9.85 \pm 0.01$ and $g_{\perp} < 0.2$ obtained in this case were the same for both investigated samples.

Since we registered the second derivative of the absorption curve, nothing could be said concerning the line contour. The line width at an external magnetic field $H \parallel C_3$ was 4 Oe for one of the samples and 7 Oe for the other. In a field $H = 10$ kOe, the linewidths were 100 and 150 Oe, respectively. The positions and widths of the lines remained practically unchanged with rising temperature.

DISCUSSION OF RESULTS

The initial calculation of the position of the levels of the Fe^{2+} ion in an axial crystal field was performed in the approximation of Abragam and Pryce^[10]. In this approximation, the orbital triplet T_{2g} can be assigned an effective orbital angular momentum $\tilde{l} = -1$, and the calculation is carried out within the framework of the Hamiltonian

$$\hat{W} = -\Delta(1 - \hat{l}_z^2) + \lambda \hat{l}_z \hat{S}_z, \quad (4)$$

where the first term describes the splitting of the orbital triplet under the influence of the axial component of the crystal field, with a spacing Δ between the doublet $|\pm \tilde{l}\rangle$ and the singlet $|\tilde{0}\rangle$, while the second term describes a spin-orbit interaction with $\lambda = -100$ cm^{-1} . The operator $\hat{l}_z + \hat{S}_z$ commutes with the Hamiltonian (4), so that its eigenvalues $m_z = 0, \pm 1, \pm 2, \pm 3$ can be used to classify the levels. The level scheme for a negative value of Δ is shown in Fig. 1. Knowing the level positions, one can then find the g -factor of the ground state $m_z = \pm 1$ (see, e.g.,^[6]). The dashed line in Fig. 4 shows the variation of g_{\parallel} as a function of the trigonal component of the crystal field Δ . For the maximum value $\Delta = -1000$ cm^{-1} we have $g_{\parallel} = 9.75$. This is less than the value obtained from experiment, where $g_{\parallel} = 9.85$. It was therefore necessary to perform the calculations with allowance for the admixture of the E_g state.

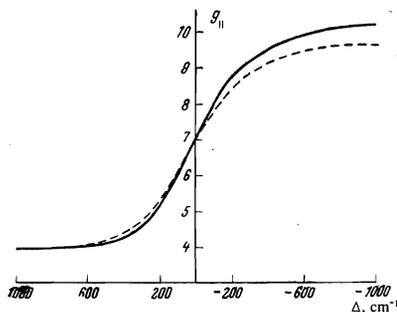


FIG. 4. Calculated values of the g factor g_{\parallel} against the parameter Δ of the trigonal component of the crystal field. The solid curve corresponds to the case $B_4 = 0$ (see the text), and the dashed curve was calculated in the approximation of the method of Abragam and Pryce for the case $B_2^0 = 0$.

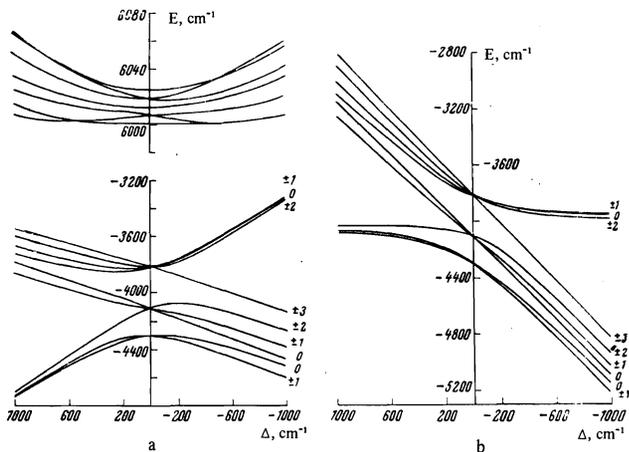


FIG. 5. Level positions of Fe^{2+} ion vs. trigonal component of crystal field: a) for the case $B_4 = 0$; b) for $B_2^0 = 0$.

To this end, we calculated the level positions of the Fe^{2+} ion in the axial field, with allowance for all the 25 states of the ground level of the free ion. The Hamiltonian of the crystal field is given by

$$\hat{V} = B_2^0 \hat{V}_2^0 + B_4^0 \hat{V}_4^0 + B_4^3 \hat{V}_4^3. \quad (5)$$

The forms of the operators \hat{V}_2^0 , \hat{V}_4^0 , and \hat{V}_4^3 can be found in [1]. At $B_4^3 = -20\sqrt{2}B_4^0$ and $B_2^0 = 0$ the operator \hat{V} corresponds to a cubic field. The level splitting of E_g and T_{2g} in the cubic field is $180B_4^0$. The deviation of the coefficients B_2^0 and B_4^3 from the values indicated above corresponds to the presence of an axial component of the crystal field. The connection between Δ and these coefficients for a trigonal field was established from the relations $\Delta = 9B_2^0$, $B_4 = 0$ or $B_2^0 = 0$, $\Delta = 80B_4$, where B_4 is an increment to B_4^3 [1]. The calculation was carried out for both cases, and the parameters were chosen to be the following: $180B_4^0 = 10\,000\text{ cm}^{-1}$, Δ ranging from -1000 cm^{-1} to $+1000\text{ cm}^{-1}$.

We have diagonalized a Hamiltonian of the type

$$\hat{\mathcal{H}} = \hat{V} + \lambda \hat{L}\hat{S} \quad (6)$$

The results of diagonalization of a matrix of 25-th order, carried out with a computer, are shown in Fig. 5. Figure 5a shows the level position as a function of the trigonal component of the crystal field Δ for the case $B_4 = 0$, while Fig. 5b shows the results for the case $B_2^0 = 0$. Figure 6 shows the spacing between the levels of the ground triplet $E_{\pm 1} - E_0$ as a function Δ . As seen from Fig. 6, these distances differ significantly for the

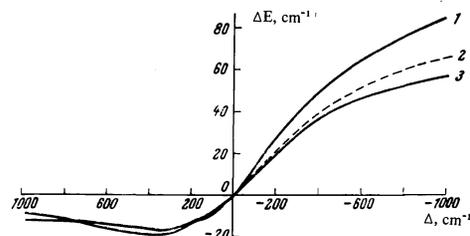


FIG. 6. Spacing $E_0 - E_{\pm 1}$ between levels of ground triplet vs trigonal component Δ of crystal field. Curve 1 was obtained for the case $B_4 = 0$, and curve 3 for $B_2^0 = 0$. Curve 2 was calculated in the approximation of the Abragam and Pryce method.

case $B_4 = 0$ (curve 1) and the case $B_2^0 = 0$ (curve 3). Curve 2 was calculated in the approximation of the method of Abragam and Pryce.

The value of the g factor g_{\parallel} was calculated by substituting in the Hamiltonian (6) a Zeeman term in the form $\beta(\mathbf{L} + 2\mathbf{S})\mathbf{H}$. The results (Fig. 4) show agreement of the g factors calculated by the method of Abragam and Pryce and for the case $B_2^0 = 0$ (dashed curve). The solid curve in Fig. 4 was obtained for the case $B_4 = 0$ and explains the experimental results $g_{\parallel} = 9.85$ at $\Delta = -550\text{ cm}^{-1}$.

The following fact favors the reliability of the value of Δ determined by us. It was established [11] from the temperature dependence of the quadrupole splitting at the Fe^{2+} ion in the CoCO_3 lattice, which is isomorphic to CaCO_3 , that the distance from the ground doublet to the singlet is 50 cm^{-1} . As seen from Fig. 6, this distance corresponds to a trigonal component of the crystal field $\Delta = 430\text{ cm}^{-1}$. At the same time, measurements on the Fe^{2+} ion in the FeCO_3 lattice [12] have shown no dependence of the quadrupole splitting on the temperature, thus indicating an increase in the distance between the ground doublet and the singlet in the FeCO_3 lattice in comparison with CoCO_3 . Therefore the agreement between the values of the parameter Δ , obtained from our measurements and measurements of the Mossbauer spectrum, can be regarded as fully satisfactory.

Measurements of the saturation magnetization of FeCO_3 , carried out by Jacobs [13], yielded a magnetization 6β per Fe^{2+} ion, whereas our measurements give 4.97β . In [13], however, the FeCO_3 samples contained up to 17% impurity, so that one can speak only of qualitative agreement with our results.

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