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FINE STRUCTURE OF ELECTRON PARAMAGNETIC RESONANCE OF THE Fe^{3+} IONS IN THE Al_2O_3 LATTICE

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THE electron paramagnetic resonance spectrum of Fe^{3+} ions, introduced isomorphically into the Al_2O_3 lattice to an iron concentration of 10^{-3} , has been investigated at room temperature at three frequencies in the range from 2.5×10^{10} to 4×10^{10} cps and for magnetic fields up to 16.2 kilo-oersteds. It was found that the Fe^{3+} ions form two nonequivalent systems each of which gives a spectrum of five resonance lines. When the external magnetic field is applied parallel or perpendicular to the crystal axis, both spectra overlap. This indicates that the crystal axis fields lie in the same direction for both ion systems. The nonequivalence is due to the difference in the directions of the cubic field axes. For orientations far from the "parallel" and "perpendicular" ones, the lines of each system broaden and a weak splitting into two components is observed. This indicates that each nonequivalent ion system consists of two subsystems with somewhat differently directed cubic crystal field axes.

In order to interpret the spectrum observed, we used a Hamiltonian of the form¹

$$\hat{H} = g\beta(H_z\hat{S}_z + H_x\hat{S}_x + H_y\hat{S}_y) + \frac{1}{6}a[\hat{S}_x^4 + \hat{S}_y^4 + \hat{S}_z^4 - \frac{1}{5}S(S+1)(3S^2 + 3S - 1)] \\ + D\left[\hat{S}_z^2 - \frac{1}{3}S(S+1)\right] + \frac{1}{180}F[35\hat{S}_z^4 - 30S(S+1)\hat{S}_z^2 + 25\hat{S}_z^2 - 6S(S+1) + 3S^2(S+1)^2],$$

where g is the spectroscopic splitting factor, β is the Bohr magneton, S is the electron spin and is equal to $5/2$ for Fe^{3+} , \hat{S} is the spin operator, H is the magnetic field strength, a is the cubic lattice constant, and D and F are the second and fourth degree trigonal field constants. The $\xi\eta\zeta$ coordinate system is constructed of the cubic crystal field axes, and the Z axis lies along the direction of the trigonal axis which is also the (111) axis of the $\xi\eta\zeta$ coordinate system.

The formulas for the fields of the observed lines given by Bleaney and Trenam¹ (which are valid for strong fields when $g\beta H \gg a, D,$ and F) are inapplicable because of the relatively high value of D . Therefore the energy levels were evaluated by perturbation theory, to second order in the case of the "parallel" orientation, and to first order in the case of the "perpendicular" orientation. The unperturbed Hamiltonian was taken as

$$\hat{H}_0 = g\beta(H_z\hat{S}_z + H_x\hat{S}_x + H_y\hat{S}_y) + D\left[\hat{S}_z^2 - \frac{1}{3}S(S+1)\right].$$

For the "parallel" orientation the formulas for the $\Delta M = \pm 1$ transitions are

$$M = \pm \frac{5}{2} \leftrightarrow \pm \frac{3}{2} : H_{1,5} = H_0 \pm \left\{ 4D - \frac{4}{3}(a-F) \right\} - \frac{20}{27} \frac{a^2}{H_{1,5} \mp 2D},$$

$$M = \pm \frac{3}{2} \leftrightarrow \pm \frac{1}{2} : H_{2,4} = H_0 \pm \left\{ 2D + \frac{5}{3}(a-F) \right\} + \frac{20}{27} \frac{a^2}{H_{2,4} \pm 3D},$$

$$M = + \frac{1}{2} \leftrightarrow - \frac{1}{2} : H_3 = H_0 - \frac{20}{27} a^2 \left(\frac{1}{H_3 + 2D} + \frac{1}{H_3 - 2D} \right),$$

where M is the electron spin magnetic quantum number, $H_0 = h\nu/g\beta$ (ν is the frequency of the radiation field, and h is the Planck's constant), and D , a , and F are expressed in oersteds and are obtained from the corresponding constants in the expression for the Hamiltonian by dividing by $g\beta$. These formulas give good agreement with the experimental data for the following values of the constants:

$$g = 2.003 \pm 0.001, |D| = (1801 \pm 3) \text{ Oe}, |a-F| = (357 \pm 2) \text{ Oe}, |a| = (280 \pm 20) \text{ Oe}.$$

The calculated spectrum for the "perpendicular" orientation also gives good agreement between the theoretical and experimental data at the lowest of the frequencies used.

We also investigated the spectrum of a sample enriched in the isotope Fe^{57} . No line of the allowed hyperfine structure was observed, which verifies the hypothesis¹ that the nuclear magnetic moment of this iron isotope is small.

¹B. Bleaney and R. S. Trenam, Proc. Roy. Soc. (London) 223, 1 (1954).

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THE PROBLEM OF PIEZOMAGNETISM

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IN the recent literature one encounters assertions that piezomagnetic bodies in general cannot exist in nature. This conclusion has been based on the invariance of the equations of mechanics with respect to a change of the sign of time when a simultaneous change is made in the signs of all magnetic fields and spins; from this the inference has been directly drawn that in the expression for the thermodynamic potential of an arbitrary substance, there can be no terms linear in the magnetic field.¹ In actuality, however, such an argument is valid only for paramagnetic bodies, whose magnetic symmetry group contains the transformation (we denote it by R) consisting of a change of sign of the magnetic field and the spin. In substances possessing, for instance, the magnetic structure of antiferromagnetics, the magnetic symmetry group does not contain the element R by itself; this element enters only in combination with other symmetry elements, or else is not present at all. Consequently such substances, in general, are capable of possessing piezomagnetic properties.^{2,3} In this note several substances are pointed out that actually occur in nature and that should, on the basis of magnetic symmetry considerations be piezomagnetic.

We consider, for example, the antiferromagnetic crystals $\alpha\text{-Fe}_2\text{O}_3$ and FeCO_3 . As has been shown,⁴ they have the same magnetic symmetry class, composed of the following elements:

$$2C_3, 3U_2, I, 2S_6, 3\sigma_d.$$

(This refers to that one of the two antiferromagnetic phases of $\alpha\text{-Fe}_2\text{O}_3$ that exists below 250°K). Here the symbols for symmetry elements are the same as in Ref. 4; a rectangular coordinate system is chosen with the x axis along one of the twofold axes. It is easy to verify that such symmetry permits the presence, in the expression for the thermodynamic potential Φ , of two combinations linear in the components of the stress tensor σ_{ik} and of the magnetic field H :