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THE POLYCRYSTALLINE EPR SPECTRUM OF FE^{+3} IONS IN MAGNESIUM OXIDE

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The paramagnetic resonance spectrum of reagent grade MgO shows an anisotropic line near $g = 2.00$. The purpose of this paper is to establish that this line is the powder spectrum of the transition $M_S = +\frac{1}{2} \longleftrightarrow -\frac{1}{2}$ for Fe^{+3} ions in a cubic field. While the contributions for Zeeman splitting factors and nuclear hyperfine interactions have been investigated,[1] the effect of a cubic field on the powder spectrum of S-state ions has not been previously reported. In addition to identifying the Fe^{+3} spectrum, it was of interest to see if the cubic-field-splitting parameter was greater in powders than in larger single crystals, since Walsh[2] has shown that this parameter is a function of hydrostatic pressure or lattice spacing.

In MgO, which has the NaCl structure, Fe^{+3} ions are found to occur almost entirely in a pure cubic field.[3] The spin Hamiltonian of the $^6S_{5/2}$ state in a cubic field has the form[3]

$$\mathcal{H}_s = g\beta H\cdot S + \frac{1}{6}a\left[S_x^4 + S_y^4 + S_z^4 - \frac{1}{5}S(S+1)(3S^2 + 3S - 1)\right] \qquad (1)$$

In the case of $g\beta H \gg |a|$ the positions of the fine-structure lines are given by the formula[4,5]

$$H_r = H_0 + \frac{10}{3}\Phi(7 - 25\Phi)\frac{a'^2}{H_0} + \cdots, \qquad (2)$$

for the transition $M_S = +\frac{1}{2} \longleftrightarrow -\frac{1}{2}$. In Eq. (2) $\Phi = \alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2$, where α_1, α_2, and α_3 are the direction cosines of the static magnetic field with respect to the cubic axes, H_0 is defined by $h\nu = g\beta H_0$, and a' is the cubic-field-splitting parameter, equal to $a/g\beta$. Low has reported for Fe^{+3} in MgO single crystals a value of $g = 2.0037$ and an a of $+0.0205\ cm^{-1}$ (which is equivalent to an a' of 220 gauss) at 290° K. Power series expressions similar to Eq. (2) show that for the transitions $M_s = \pm 3/2 \longleftrightarrow \pm 1/2$ and $\pm 5/2 \longleftrightarrow \pm 3/2$ the spectrum would be too broad to detect in powders of low iron content.

A theoretical polycrystalline spectrum was calculated using Eq. (2) and the parameters reported by Low.

The number of spins having for their environment cubic field axes at an orientation with respect to the applied magnetic field between θ and $\theta + d\theta$ and φ and $\varphi + d\varphi$ is given by

$$dN = \frac{No}{4\pi} \sin \varphi \, d\theta \, d\varphi \tag{3}$$

To obtain $\frac{dN}{dH}$ as a function of H, the differential element dN was set equal to a small constant, ΔN. The value of φ was varied from 0 to $\pi/2$ in small increments of $\Delta\varphi$ and, at each value of φ, $\Delta\theta$ was calculated from Eq. (3). The $\Delta\theta$'s (which varied with φ) and the $\Delta\varphi$'s lead to a set of φ and θ values which corresponded to all orientations of the cubic axes with respect to the magnetic field. Furthermore, for each value of φ and θ (averaged over the increment of solid angle) the value of H_r is given by Eq. (2) since $\Phi = f(\theta, \varphi)$.

The line shape for a single orientation was approximated by an isosceles triangle with a height equal to that of a Lorentzian curve and sides tangent to the curve. The line width at maximum slope is then about equal to $1/3\ \delta$, where δ is 1/2 of the base of the triangle. In addition, the line width which we measured in single crystals is a function of orientation, as described in Fig. 1. As a crude approximation ΔH or δ was initially assumed to vary linearly with H. This was later improved upon by letting δ actually change in the manner described by the curve in Fig. 1. In practice δ was treated as a function of Φ and was not double valued. Since the number of spins contributing to each Lorentzian curve is a constant, it was necessary to adjust the height of the triangle so the area would remain constant.

Finally, for each H_r calculated from Eq. (2) a line simulated by a triangle was constructed. When the range of H's was covered, the contributions from all triangles at each H were summed to give the final curve or dN/dH as a function of H. All of these calculations were carried out with the aid of a digital computer.

Fig. 2(a) shows the actual experimental derivative curve of the anisotropic line as well as the spectrum of cubic Cr^{+3} with hyperfine lines from Cr^{53}. It was necessary to extrapolate the iron line in regions where the Cr^{+3} line dominated. Results of the calculations and an integrated form of the experimental curve are shown in Fig. 2(b).

The calculated curve is in good agreement with the experimental curve; every inflection is accurately described. One may therefore conclude that the anisotropic spectrum observed is from Fe^{+3} ions in a cubic field. It is interesting to note that the linear approximation for the variation of line width gave the salient features of the experimental curve. In fact, a constant line width was used with satisfactory results.

If the line width was reduced below a certain limit, another inflection occurred in the absorption curve, as shown in Fig. 2(c). This seems to be an important extension of these calculations since the additional inflection would cause another peak in the derivative curve. It is possible that in other powders of cubic material such a spectrum might be observed.

The cubic-field-splitting parameter could be obtained by fitting calculated curves to the experimental curve. Surface forces should appreciably increase the internal pressure of small crystals which are 500 to 1000 Å on a side. An estimated internal pressure of 500 kg/cm^2 would lead to an increase in a of about 0.5 percent. A value of $a = 0.0205\ cm^{-1}$, the value reported for single crystals,[6] seems to fit the powder as well; however, the accuracy of this method is not sufficient to detect changes smaller than ±5 percent. One cannot, therefore, detect increases in a of 0.5 percent by this technique.

FOOTNOTES

1. For a literature survey see, for example, J. A. Weil and H. G. Hecht, J. Chem. Phys., 38, 281 (1963).
2. W. M. Walsh, Phys. Rev. Letters, 4, 507 (1960).
3. J. H. E. Griffiths and J. W. Orton, Phys. Soc. (London) 73, 948 (1959).
4. R. de L. Kronig and C. J. Bouwkamp, Physica, 6, 290 (1939).
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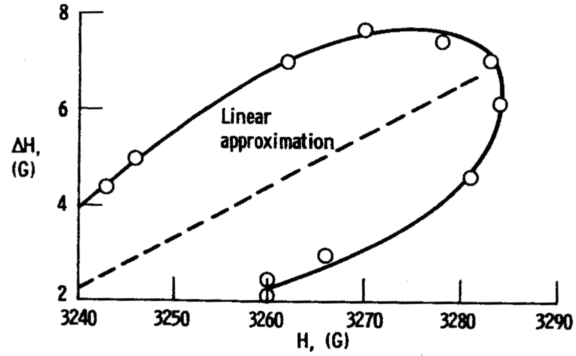

Fig. 1 - ΔH versus H for Fe^{+3} ions in an MgO single crystal.

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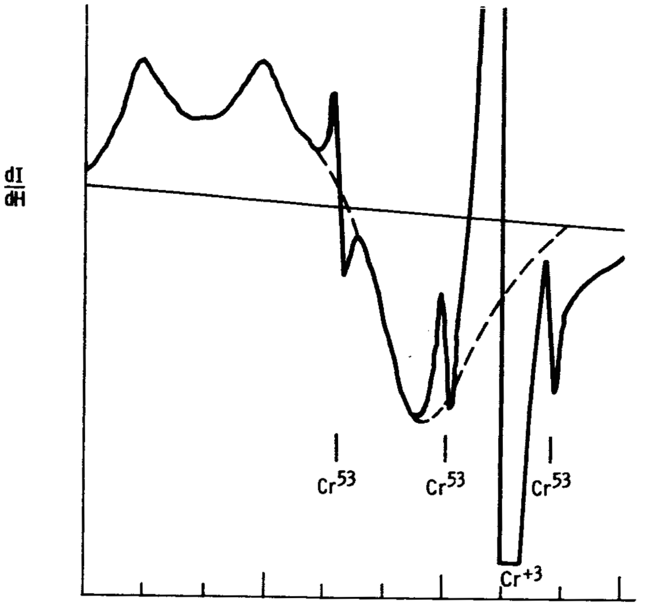
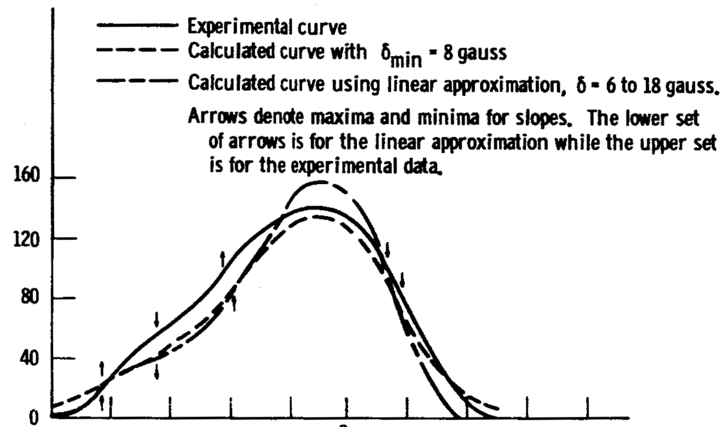
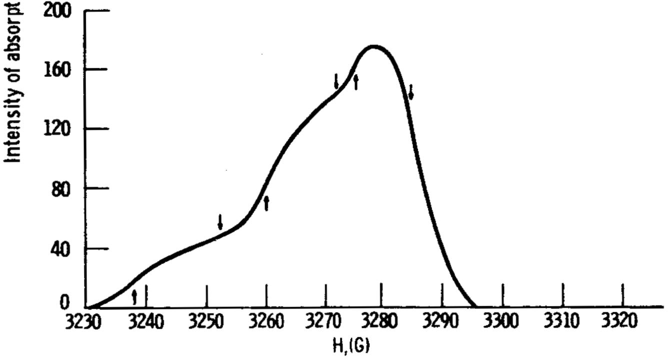


(a) Derivative spectrum of reagent grade MgO powder at ν = 9145 Mc/sec.



(b) EPR absorption curve for Fe^{+3} ions in MgO. a = 220 gauss.



(c) EPR absorption curve for S-state ion. a = 220 gauss; δ_{min} = 4 gauss.

Fig. 2 - Experimental and theoretical curves for the EPR spectrum of F_e^{+3} in polycrystalline MgO.

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