Paramagnetic Resonance of Cr^{3+} in Yttrium Oxide

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The paramagnetic resonance spectrum of Cr^{3+} in single-crystal yttrium oxide has been observed at microwave frequencies from 9 to 71 kMc/sec at temperatures from 4.2° to 300°K. The spectrum is described in terms of the spin Hamiltonian $\mathcal{H} = g\beta H \cdot S + D[S_z^2 - S(S+1)/3]$, where $g = 1.97 \pm 0.01$, $S = \frac{3}{2}$, and $2D = 72.9 \pm 0.2$ kMc/sec at 300°K, and 72.7 ± 0.2 kMc/sec at 77°K and 4.2°K.

THE ground-state splitting of Cr^{3+} has been observed in a newly available single-crystal host lattice, yttrium oxide (Y_2O_3). In this crystal the Cr^{3+} ion has one of the largest zero-field splittings yet reported. We present here the observed paramagnetic resonance spectrum and its interpretation in terms of the crystal structure and the spin Hamiltonian.

Yttrium oxide has been reported[1,2] to be of the cubic Tl_2O_3 structure (Bixbyite) of crystal class T_h. The metal ion sites are coordinated by 6 oxygens, but in two distinctly different symmetries. The oxygens are located at the corners of a hypothetical cube and at the first site, say A, the positions at opposite ends of a body diagonal are vacant, while at site B the oxygen positions at opposite ends of a face diagonal are vacant. The metal ion is located at the center of the cube at site A, but is displaced from this position towards the plane of the four oxygens at site B. The metal ion at site A is at a lower coordination energy than at site B. Experimentally it is found that Cr^{3+} chiefly occupies the A sites.

The six ligating oxygens of complex A, each at a distance d from the metal ion, produce a crystalline field of point group symmetry S_6, and at site B the symmetry is C_2. The next nearest neighbors in each case are twelve metal ions, and in complex A are located at a distance $2d/\sqrt{3}$. A further inequivalence in the metal ion sites occurs in the orientation of the symmetry axes with respect to the crystal system (cubic) axes. The four different orientations of the S_6 symmetry axes are along the normals to the faces of an octahedron with corners located at the faces of the cube of the crystal axes, as shown in Fig. 1. Finally, the C_2 symmetry axes are along the crystal axes and hence in six different directions.

The crystals were grown by an extension of the Verneuil flame fusion method using high purity Y_2O_3 starting powder. Because of the high melting point (2410°C) of Y_2O_3, burn-out losses of Cr_2O_3 are high (e.g., a starting powder concentration of 1% by weight of Cr_2O_3:Y_2O_3 yields a product of concentration 0.04%). The boules tend to fracture along (111) planes, the resulting crystals

being octahedral. Samples for paramagnetic resonance spectroscopy were oriented by x-ray analysis.

The samples were oriented for rotation about the $[0\bar{1}1]$ direction with the magnetic field H perpendicular to the axis of rotation as shown in Fig. 1. Denoting by α the angle between H and the $[100]$ direction, the symmetry axes z_3 and z_4 make equal angles $\theta_3 = \theta_4 = \cos^{-1}$ ($\frac{1}{3}\cos\alpha$) with H, while the axes z_1 and z_2 are at angles $\theta_1 = 54°44' - \alpha$ and $\theta_2 = 125°16' - \alpha$, respectively. Figure 2 presents the magnetic field for resonance as a function of α as observed as 35 kMc/sec and 77°K. The data fit curves obtained from the usual spin Hamiltonian[3]

$$\mathcal{H} = g\beta H \cdot S + D[S_z^2 - S(S+1)/3], \qquad (1)$$

where $S = \frac{3}{2}$, $g = 1.97 \pm 0.01$, and $2D = 72.7 \pm 0.2$ kMc/sec $= 2.42$ cm^{-1}, for the four cases of the magnetic z axis along the S_6 symmetry axes. The theoretical data were obtained from the numerical work of Chang and Siegman[4] on ruby by converting the Hamiltonian used there into
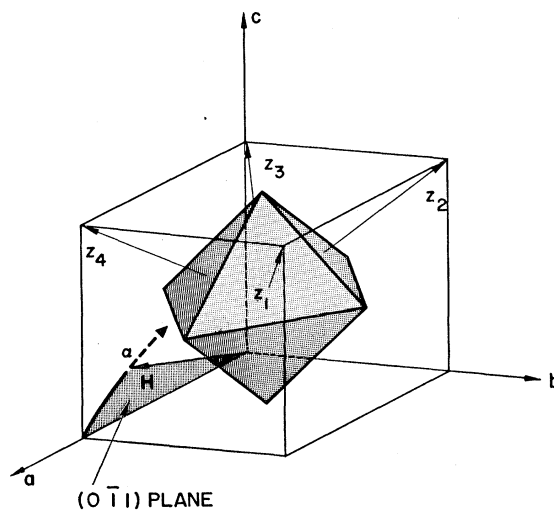

FIG. 1. Orientation of the external magnetic field H with respect to the symmetry axes z_1, z_2, z_3, and z_4 of the S_6 point group complexes. The crystalline axes are a, b, and c.

[1] R. W. C. Wyckoff, *Crystal Structure* (Interscience Publishers, Inc., New York, 1957), Vol. II.
[2] H. H. Landolt and R. Börnstein, *Zahlenwerte und Functionen, Atom-und Molekular-physik* (Springer-Verlag, Berlin, 1955), Vol. 4.
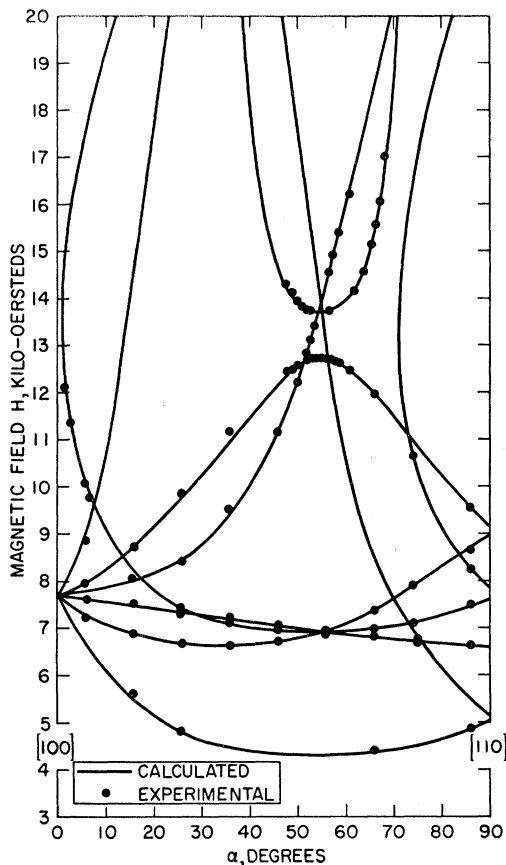[3] B. Bleaney and K. W. H. Stevens, *Reports on Progress in Physics* (The Physical Society, London, 1955), Vol. 16.
[4] W. S. Chang and A. E. Siegman, Stanford Electronics Laboratory Tech. Report No. 156-2, Stanford University, California, and as reproduced by J. Weber, Revs. Modern Phys. **31**, 681 (1959).

FIG. 2. Paramagnetic resonance spectrum of Cr^{3+} in an S_6 symmetry site in Y_2O_3 at 35 kMc/sec. The resonant field H is plotted as a function of α, the angle between H and the crystal [100] direction. H was confined to the $(0\bar{1}1)$ plane. The solid lines represent resonant fields calculated from the spin Hamiltonian given in the text.

urements at 9 kMc/sec on the $\pm\frac{1}{2}$ transition indicate a relaxation time T_1 of the order of 10^{-2} sec at $4.2°K$. Linewidths varied markedly from sample to sample; the narrowest linewidth observed was 30 Mc/sec for the $\pm\frac{1}{2}$ transition at $0°$ orientation. The observed variation in line width may be attributed to a spatial variation of crystalline axes in the sample; a pronounced tendency toward twinning was noted in many samples.

In the crystal sample where the $\pm\frac{1}{2}$ transition was observed to be 30 Mc/sec (10 oe) wide, the weak isotropic line was resolved when the external magnetic field was parallel to the magnetic z axis of the Hamiltonian of Eq. (1). A direct comparison of the g values could then be made. The isotropic line was observed at 45 oe below the $\pm\frac{1}{2}$ transition thus giving a g value of $(1.0035)g_{11}$. A misalignment of the crystal axes with respect to the magnetic field could reduce the separation of these lines but could not cause the isotropic line to appear to have the larger g. It is unlikely that the isotropic line is caused by an impurity: No resonances could be observed in pure Y_2O_3, and of the possible impurities in Cr_2O_3 (mainly the iron-group), none have yet been reported giving the type of resonance observed. Consequently our conjecture that the coordination cube is complete with 8 oxygens at some sites appears reasonable.

The effect on the Cr^{3+} spin Hamiltonian due to a variation in the crystalline field from cubic to axial and rhombic symmetry within the same crystal has been reported for MgO.[5-7] There the perturbation in the crystal field results from vacancies in the next nearest
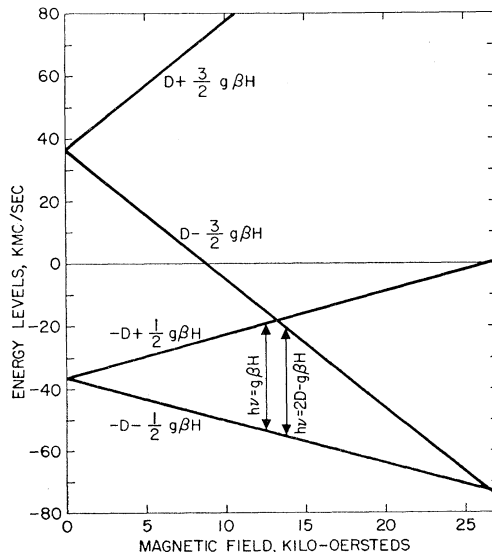
one with the coefficients of Eq. (1). The g value, g_{11}, was found to be 1.97 ± 0.01, independent of temperature; it is assumed that $g_{11}=g_\perp=g$. The zero-field splitting, $2D$, consistently decreased slightly from 72.9 ± 0.2 kMc/sec at room temperature to 72.7 ± 0.2 kMc/sec at $77°K$ and $4.2°K$. Several additional lines of lesser intensity were detected and are taken to be due to impurities and/or chromium at the B sites. A narrow isotropic line with a $g=1.97$ was also observed. This resonance may be accounted for by assuming that a small fraction of the Cr^{3+} sites have all 8 oxygen ions present, giving a crystalline field of cubic symmetry. For clarity, these last mentioned resonances are not shown in Fig. 2.

The values of g_{11} and D were obtained from the transitions indicated in Fig. 3 using a microwave frequency of 35 kMc/sec. As a further check on the magnitude of D, resonances were observed in an unoriented sample at 71 kMc/sec at magnetic fields less than 1000 oe. The positive sign of D was determined from comparison of the integrated intensities of different transitions at room temperature and at $77°K$. Rough cw saturation meas-

FIG. 3. Energy levels of Cr^{3+} in an S_6 symmetry site for the case of the external magnetic field H parallel to the magnetic z axis. The two indicated transitions were used to obtain g_{11} and D.

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[7] J. H. E. Griffiths and J. W. Orton, Proc. Phys. Soc. (London) 73, 948 (1959).

neighbor sites. In MgO the distortion from cubic symmetry produced a variation in the g values of at most a fraction of a percent, while the largest zero-field splitting (11.5 kMc/sec) resulted from a rhombic field. The effect of the distortion in Y_2O_3 as compared to MgO is thus about an order of magnitude larger in the zero-field splitting and of the same order of magnitude in g.

In summary, the intense part of the spectrum observed in Y_2O_3 is accurately described by the spin Hamiltonian of Eq. (1) when the magnetic z axis is along the symmetry axes of the A sites. The remarkably large zero-field splitting of the Kramers' doublets results when the Cr^{3+} enters the lattice substitutionally at the Y^{3+} sites in the crystal field of point group symmetry S_6. The weak isotropic line in the spectrum is notable because of the only slight change in the g value.

Magnetic Resonance in Canted Ferrimagnets*

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The classical theory of the uniform ($k=0$) modes of a four-sublattice, planar canted ferrimagnet is developed. Two of these modes should lie in the microwave range for reasonable values of applied field, anisotropy, and exchange constants: the normal low-frequency mode familiar in collinear ferrimagnets and the mode excited by longitudinal rf fields at a frequency depending on anisotropy and angle of cant. Observation of this latter mode should allow analysis of ferrimagnetic structures and phase changes.

IN his original theory of magnetic structures in ferrospinels, Néel[1] conceived of phases either with parallel aligned groups of spins or with spins in random paramagnetic arrangements. Yafet and Kittel[2] extended and partly corrected this idea by pointing out that triangular spin arrangements become energetically favorable in the molecular field model when the interactions between spins that are all on tetrahedral A or all on octahedral B sites become comparable with the intersite AB interaction. Lotgering[3] formulated this model in some detail.

These concepts have been further extended by Kaplan[4] and, for the case of antiferromagnets, by Yoshimori,[5] to include generalized helical spin arrangements. Our present knowledge of the stability ranges for these various structures in the presence of anisotropy and in noncubic spinels is still far from complete.

On the experimental side Gorter[6] and more recently Lotgering,[3] Prince,[7] and Dwight and Menyuk[8] have invoked canted sublattices to account for the relatively low saturation magnetization observed in various spinels. Wickham and Goodenough,[9] on the other hand, interpreted the same observations in terms of a partly reversed but collinear B sublattice. Presumably their structure would differ from the Néel model by a physical distortion identifying the lattice sites for reversed spins.

The high-field susceptibility measurements of Jacobs[10] on Mn_3O_4 are consistent with a canted lattice structure but in principle depend only on the existence of low effective exchange fields. Neutron-diffraction data[7] for $CuCr_2O_4$ are also consistent with canted lattices, but the evidence has not uniquely determined individual spin alignments.

It is our purpose here to point out that the magnetic resonance spectrum of canted ferrimagnets differs characteristically from that of ferrimagnets with collinear sublattices, and that this difference should permit the detection and analysis of canted structures. Such experiments appear capable of showing definitely the existence of canting and, together with magnetization data, of indicating the spins involved and their relative orientations.

RESONANCE CONDITIONS

Some aspects of the canted lattice resonance problem have been treated previously by Eskowitz and Wangs-

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