Antiferromagnetic Resonance in Cr_2O_3

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The antiferromagnetic resonance spectrum of single-crystal Cr_2O_3 has been mapped within the wavelength region from 12 mm to 2.8 mm and magnetic field intensities from 0 oersteds to 30 000 oersteds. The resonance frequencies were observed in this region in a temperature interval from about 17°C to 35°C, the Néel temperature, T_N. When the [111] crystal axis is perpendicular to the direction of the external magnetic field, the observed resonance locus on a frequency *vs* magnetic field diagram forms a single curve at each temperature; when the two are parallel, the resonance locus forms a curve of two branches, one of which has not previously been observed for this material. These loci are found to be in good agreement with the resonance theory of Nagamiya, and of Keffer and Kittel. Good theoretical agreement is also found for variations of line width with magnetic field strength and for variations in the peak absorption intensity at resonance. The anisotropy energy K which depends upon the temperature, T, as obtained from the data is proportional to $(T_N - T)^{0.87}$ over the observable interval. Assuming that K is proportional to a fixed power of sublattice magnetization at all temperatures and that sublattice magnetization behaves as the appropriate Brillouin function of temperature, we can extrapolate to absolute zero and thus find $K = 800\,000$ ergs/cm^3.

INTRODUCTION

ELECTRONIC magnetic resonance absorption provides a particularly valuable tool for the study of antiferromagnetism due to the usual failure of conventional methods to yield information about anisotropy energy. This is because there is no externally appearing magnetization at any temperature for torque measurements except for the small induced moment which contains the anisotropy constant only in presently unobservable terms of higher order. It is therefore important to apply the resonance method to a wide sampling of antiferromagnetic materials, ranging from those with weak molecular fields and low Néel temperatures to those with strong molecular fields and high Néel temperatures, and possessing a variety of crystal structures and anisotropy symmetries. The principal technical difficulties which beset such a program are that single-crystal samples are necessary in the present state of the art owing to the strong orientation dependence of the resonance, and that for all except materials of low Néel temperature the main part of the resonance spectrum lies at very high frequencies (wavelengths of a few millimeters). The latter difficulty is gradually being removed by new technological developments, but the former remains and severely limits the choice of materials.

Chromium sesquioxide (Cr_2O_3) is antiferromagnetic below the Néel temperature, T_N, of approximately 35°C; above this temperature it is paramagnetic. It has the corundum crystal structure, with rhombohedral symmetry. The unit cell can be taken as a cube stretched along a [111] body diagonal which forms a threefold symmetry axis. The elementary spin orientations have been shown to lie in the direction of the crystal axis,[1] a conclusion verified by neutron diffraction studies[2]; hence one expects any macroscopic single-crystal sample

to be a single domain, unless very severe strains are present.

Resonance absorption of microwave energy by Cr_2O_3 has been reported at a frequency of about 9 kMc/sec by Trounson, Bleil, Wangsness, and Maxwell[3] in powdered samples and at 24 kMc/sec by McGuire, Scott, and Grannis[1] using single-crystal samples. Both of these investigations reported a paramagnetic resonance for temperatures above T_N which either disappeared or was reduced in amplitude and shifted toward lower fields as antiferromagnetic alignment set in below T_N. The former found in one powder sample a shift amounting to 3000 gauss at 116° below T_N while other samples showed only a complete disappearance of resonance in the antiferromagnetic state. Through close observation on single-crystal samples, McGuire[1] found an antiferromagnetic shift of resonance field amounting to 9000 gauss in a 0.5° temperature interval below T_N. The origin of the former shift is not known, but may be connected with the impurities or physical state of the sample. Because of the narrow range of temperatures over which McGuire could observe the antiferromagnetic resonance, it was not possible for him to extrapolate reliably his anisotropy data to absolute zero, nor was it possible for him experimentally to determine the relation between resonance frequency and field.

The present work improves on both these points. Reports of other experimental observations of antiferromagnetic resonance include the following: (a) orthorhombic $CuCl_2 \cdot 2H_2O$, which is antiferromagnetic in the liquid helium temperature range and which has been studied extensively by the Leiden group[4,5]; (b) orthorhombic $CuBr_2 \cdot 2H_2O$, which is similar to the foregoing[6]; (c) $MnBr_2 \cdot 4H_2O$[7]; (d) tetragonal MnF_2, which

[1] McGuire, Scott, and Grannis, Phys. Rev. **102**, 1000 (1956).
[2] Nathans, Riste, Shirane, and Shull, Bull. Am. Phys. Soc. II, **2**, 21 (1957).

[3] Trounson, Bleil, Wangsness, and Maxwell, Phys. Rev. **79**, 542 (1950).
[4] References may be found in Gerritsen, Garber, and Drewes, Physica **22**, 213 (1956) and reference 10.
[5] J. Ubbink, thesis, Leiden, 1953 (unpublished).
[6] M. Date, Phys. Rev. **104**, 623 (1956).
[7] B. Bolger, *Conjerence de Physique des Basses Temperatures, Paris, 1955* (Centre national de la Recherche Scientifique and UNESCO, Paris, 1956), p. 244.

has a much stronger molecular field than the above as evidenced by its Néel temperature of 65°K[8]; (e) rhombohedral Cr$_2$O$_3$, which differs from the above mainly in having a still stronger molecular field.[9] Of these, only (d) and (e) have uniaxial magnetic anisotropy.

THEORY

1. Resonance Equations

The molecular-field theory of antiferromagnetic resonance has been given mainly by Nagamiya, Keffer and Kittel, and Yosida and Ubbink.[10] More general discussions of resonance in multiple sublattice systems, which can be reduced in special cases to the antiferromagnetic problem, have been given by others, especially Wangsness.[11] Since the published theory has been worked out for only cubic and orthorhombic crystalline fields, some justification is needed before it can be applied to Cr$_2$O$_3$ with confidence.

The equation of motion, without damping for the ith sublattice system, is

$$\partial \mathbf{M}_i / \partial t = \gamma \mathbf{M}_i \times \mathbf{H}_i, \tag{1}$$

where $\mathbf{H}_i$ is an effective magnetic-field representation for the orientation-dependent energy of the ith sublattice. It includes the externally applied field $\mathbf{H}_0$, the effective isotropic exchange field $\mathbf{H}_e$, and a term to represent the effect of the anisotropic part of the sublattice energy. The latter especially may have a complicated dependence upon orientation, and results, in general, in nonlinear equations of motion for the magnetization components. To linearize these equations, the above writers have represented the anisotropy energy as arising from an equivalent magnetic field, the anisotropy field $\mathbf{H}_a$ (or a set of anisotropy fields for the orthorhombic case). Two distinct assumptions are involved in the representation of the anisotropy-energy term by a single axially directed magnetic field energy, namely: that the energy of sublattice magnetization will vary with the cosine of its angular displacement from the crystal axis, and that the anisotropy energy is uniaxial. These assumptions, which are basic to the treatment of cubic crystals as done by Keffer and Kittel, can be valid also for crystals of symmetry lower than cubic.

The anisotropy energy in Cr$_2$O$_3$ must have threefold rotational symmetry about the major axis. One might make the simplifying assumption, however, that there is no variation of magnetic energy in the equatorial plane, thus reducing the problem to that of a uniaxial crystal and linearizing the equations of motion. Then the results derived by Nagamiya and by Keffer and

Kittel for "cubic" crystals should be fully applicable. The real justification for this procedure, as with any approximation, must ultimately rest upon its success in matching experimental results. Some empirical evidence that Cr$_2$O$_3$ does behave as a uniaxial crystal is provided by the observation that the antiferromagnetic resonance frequency is sensibly independent of the azimuth angle of an applied magnetic field with respect to the crystalline [111] direction and, more important, by the good agreement, shown below, of the observed spectrum with that predicted from Eq. (1) with the uniaxial assumption. Recent work[8] on the resonance spectrum of MnF$_2$, a tetragonal crystal, suggests that the above assumptions apply also to that material.

If one considers now only the modes of oscillation of the antiferromagnetic system in which the rf and dc magnetic fields are perpendicular, the resonance equation is (in Nagamiya's form)

$$[\alpha_N{}^2 \cos^2\theta + \alpha_N(1 + \alpha_N(3 + 2\alpha_N)/G^2) \sin^2\theta \cos^2\theta]h_\theta{}^4$$
$$- [(1 + \alpha_N{}^2 + 2\alpha_N G^2) \cos^2\theta + (1 - G^2) \sin^2\theta]h_\theta{}^2$$
$$+ (1 - G^2)^2 = 0, \tag{2}$$

where θ is the angle from crystal axis to magnetic-field direction, h_θ is the reduced resonant magnetic field H_θ/H_p, H_p is the field for paramagnetic resonance $(=\omega/\gamma)$, G is $(2\lambda K)^{\frac{1}{2}}/(\omega/\gamma)$, λ is the interlattice exchange coupling constant equal to $1/\chi_\perp$, and K is the anisotropy energy constant. We use Nagamiya's form for the parameter $\alpha(=1 - \chi_{||}/\chi_\perp)$ which we call α_N. This equation always has 4 solutions for h_θ, corresponding to 4 normal modes of oscillation as discussed by Keffer and Kittel.[12] Following their notation we distinguish these modes by the signs and magnitudes of their frequencies $\omega_i(=\gamma H_{pi})$, as follows: ω_1 and ω_4 are positive with $\omega_1 \geq \omega_4$ in a weak external magnetic field; ω_2 and ω_3 are negative with $|\omega_2| \geq |\omega_3|$ in a weak external field. The physically observed resonances we take as representing positive ω and positive H_θ. Thus Eq. (2) has at most 2 interesting solutions. We list below some equations giving special cases of (2) in which α_N can be treated as a fixed number over a useful temperature range. Each is written to cover all positive solutions for which the corresponding normal mode has an oscillating magnetization-component perpendicular to the applied field.

(1) Curie temperature region; $\alpha_N \cong 0$.

$$\theta = 0: \quad \pm H_{||} = \frac{\omega}{\gamma} - \frac{2\lambda K}{(\omega/\gamma)} \quad \text{unless} \quad H_{||}{}^2 > \frac{2\lambda K}{\alpha_N}, \tag{3}$$

$$\theta = \tfrac{1}{2}\pi: \quad H_\perp{}^2 = (\omega/\gamma)^2 - 2\lambda K.$$

(2) Region of absolute zero; $\alpha_N \cong 1$.

$$\theta = 0: \quad \pm H_{||} = (2\lambda K)^{\frac{1}{2}} - (\omega/\gamma) \quad \text{unless} \quad H_{||}{}^2 > 2\lambda K, \tag{4}$$

$$\theta = \tfrac{1}{2}\pi: \quad H_\perp{}^2 = (\omega/\gamma)^2 - 2\lambda K \quad \text{or} \quad (\omega/\gamma)^2 = 2\lambda K.$$

[8] F. M. Johnson and A. H. Nethercot, Phys. Rev. **104**, 847 (1956).

[9] E. S. Dayhoff, Bull. Am. Phys. Soc. II **1**, 283 (1956).

[10] See review article by Nagamiya, Yosida, and Kubo, *Advances in Physics* (Taylor and Francis, Limited, London, 1955), Vol. 4, p. 1.

[11] R. K. Wangsness, Phys. Rev. **93**, 68 (1954).

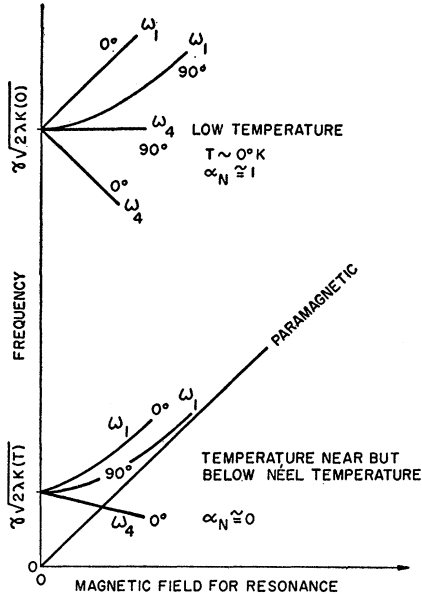[12] F. Keffer and C. Kittel, Phys. Rev. **85**, 329 (1952).

Fig. 1. Typical resonance loci for crystals with single anisotropy constant $K(T)$. See Eqs. (3) and (4). The resonance curves shift vertically when the temperature is changed. Note that the ω_4 branch for $\theta=90°$ does not have an oscillating magnetization normal to the external magnetic field in the $\alpha_N=0$ approximation and is not discussed in this paper.

Nagamiya has also given a first-order correction term in α_N for Eq. (3). The corrected resonant field H_C can be expressed in terms of the uncorrected H_U as

$$\theta=0: \quad H_C=H_U[1-2\alpha_N(1\mp H_U)]^{\frac{1}{2}} \quad (5a)$$

for the ω_1 and ω_4 branches, respectively;

$$\theta=\tfrac{1}{2}\pi: \quad H_C=H_U. \quad (5b)$$

A useful property of the resonant fields for various orientations is the angular invariant,

$$(\sin^2\theta)h_\theta{}^2\pm[(\sin^4\theta)h_\theta{}^4+4(\cos^2\theta)h_\theta{}^2]^{\frac{1}{2}}, \quad (6)$$

which is independent of θ. The positive sign is for the ω_1 branch and the negative sign for ω_4. This invariant (valid near the Curie temperature) enables one to calculate the resonant field for any θ, knowing what it is for some other θ at the same temperature and frequency. It is useful for correcting small errors in orientation. The preceding three sets of expressions are plotted in Figs. 1 and 2.

2. Intensities

The intensity of the absorption at resonance can be compared, in an experimentally useful way, to the intensity of paramagnetic absorption at the same frequency. We may calculate the peak absorption susceptibilities by solving the undamped equations of motion and then adding the damping to the resulting expressions by using complex ω's to avoid infinite

poles. Keffer and Kittel[12] have done this using the absolute-zero approximation. On inserting the required factors of 2 in their expression and for the $\theta=0°$ orientation and linearly polarized microwave field, it becomes

$$\chi_{AF}/\chi_P\cong(2\lambda K)^{\frac{1}{2}}/4H_P, \quad (7)$$

for the ratio of absorption peak height for one antiferromagnetic normal mode to that for the paramagnetic state. Referring both susceptibilities to the same frequency, this expression has the value $\frac{1}{4}$ when the antiferromagnetic resonance occurs at zero external field and approaches zero with $K^{\frac{1}{2}}$ as the Néel temperature is approached. This latter result is in disagreement with our observations near the Néel point. We therefore have calculated the susceptibility from the same equations of motion without approximation for temperature region. The result is:

$$\chi_{AF}(\theta=0)$$
$$=\frac{2K\gamma^2(\omega^2-\omega_1\omega_4)+(1-\alpha_N)H^2\gamma^2(\omega^2+\alpha_N\omega_1\omega_4)/\lambda}{(\omega^2-\omega_1{}^2)(\omega^2-\omega_4{}^2)}, \quad (8)$$

which reduces to Keffer and Kittel's Eq. (11)[12] when the second term is removed by making the low-temperature approximation $(\alpha_N=1)$. We have chosen to use ω_1 and ω_4 in this expression as they are both positive under experimental conditions.

When the Néel-region approximation $(\alpha_N=0)$ is made, the microwave susceptibility without damping becomes

$$\chi_{AF}(\theta=0)=\frac{2K\gamma^2(\omega^2-\omega_1\omega_4)+\omega^2\gamma^2H^2/\lambda}{(\omega^2-\omega_1{}^2)(\omega^2-\omega_4{}^2)}. \quad (9)$$

The first term here is identical to the low-temperature result but the second term causes the peak susceptibility for the ω_1 branch at constant frequency to rise with the resonant field as the Néel point is approached. This behavior will be seen below to be in good qualitative agreement with experiment. The numerical value of the ratio χ_{AF}/χ_P at a fixed frequency goes from $\frac{1}{4}$ at $H=0$ to $\frac{1}{2}$ at $H=H_P$, per mode.

3. Anisotropy

The magnetic anisotropy energy appears in the resonance theories only as a temperature-dependent parameter. Comparison of its temperature dependence with that calculated for various special models can lead to knowledge of the active mechanisms for anisotropy production. Unfortunately, no presently available theories have been worked out specifically for the Cr_2O_3 structure, although some general considerations and specific calculations for other substances can be usefully compared. Li[13] has given a semiempirical discussion of structure deformation in antiferromagnetic

[13] Y.-Y. Li, Phys. Rev. **100**, 627 (1955).

materials and suggests a very high value ($\sim10^8$—10^9 ergs/cm³) for the typical anisotropy energy constant at absolute zero. Keffer[14] has given a detailed discussion of the origin of anisotropy in antiferromagnetic MnF_2, a tetragonal but nearly cubic crystal and obtains values near 10^6 ergs/cm³. The antiferromagnetic crystals FeF_2 and CoF_2 have been discussed by Moriya et al.[15]

It has been shown by Néel and others that there exists a critical value of magnetic field applied parallel to the crystal axis which will cause the sublattice spins to rotate from the axial direction to a direction perpendicular to the crystal axis. This critical field depends upon the anisotropy constant and the susceptibilities through the relation

$$(H_{crit})^2 = 2\lambda K/\alpha_N, \qquad (10)$$

which may, in principle, form the basis of an alternate method for measuring K. Keffer has given the behavior of H_{crit} in MnF_2 based on his theoretical results for K as follows: The critical field rises almost linearly from 10^5 oe at $0.2T_N$ to 1.7×10^5 oe at T_N. We shall see below that this behavior is somewhat different in Cr_2O_3.

EXPERIMENTAL PROCEDURE

4. Experimental Method

A hybrid junction microwave-bridge apparatus was used similar to that described by McGuire et al.[1] One arm of the balanced microwave bridge was terminated in an approximately matched cavity resonator in which the sample was placed and the other arm in a matched load. Absorption was detected through its unbalancing effect on the bridge as indicated by the current flowing in a microwave detector. The cavity resonator was formed by an iris in the wave guide backed up by a movable shorting plunger, except for the 106 kMc/sec data where an aluminum circular cavity with side-hole coupling was used with two adjustable choked plungers forming the end walls. This cavity (0.157-inch diam) could be operated in the $TE011$ mode where the Q factor when loaded by the wave guide, but not the sample, was about 500. In this mode good coupling to the sample could be had by cementing the sample to the center of one of the shorting plungers. The power source was a reflex klystron oscillator (with 1000-cps square-wave repeller modulation) feeding a silicon crystal distorter harmonic generator. For most of our results at 72 kMc/sec the third harmonic of a K-band type $2K33A$ klystron was used; for 106 kMc/sec the third harmonic of an 8.5-mm type QK-288 klystron was used. Our detector was a silicon crystal rectifier arrangement. Both harmonic generator and detector were somewhat similar to designs described by Johnson, Slager, and King.[16] A 40-

[14] F. Keffer, Phys. Rev. **87**, 608 (1952).
[15] Moriya, Motizuki, Kanamori, and Nagamiya, J. Phys. Soc. Japan **11**, 211 (1956).
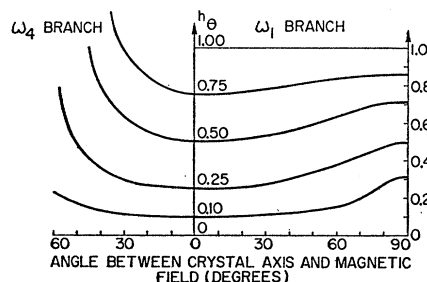[16] Johnson, Slager, and King, Rev. Sci. Instr. **25**, 213 (1954).

FIG. 2. Curves for conversion of resonance fields with change of crystal orientation according to expression (5).

cps pass-band amplifier centered at 1000 cps was used to amplify the output signals. The sensitivity of the setup at 106 kMc/sec was estimated to be such that antiferromagnetic resonance could be detected with a signal-to-noise ratio of 3 at a sample weight of about $\frac{1}{3}$ mg.

All the cavity resonators, except the one for 106 kMc/sec, could be mounted in the gap of an electromagnet in such a manner that the field could be varied slowly up to a maximum of 30 000 oersteds. A linearly proportional signal for recording the field sweep was obtained from a rotating search coil driven by a synchronous motor. The temperature of the cavity resonator was measured with thermocouples and a potentiometer. No special temperature-regulation methods were needed as the temperature-drift rate could be made quite slow. The cavity resonator for 106 kMc/sec was swept in temperature in zero magnetic field.

5. Samples

Almost all of our measurements were made on single crystals grown by E. J. Scott of this laboratory by the flame-fusion method. Some pieces were annealed for 24 hours at 1200°C and cooled at 1 degree per minute. Others which were not annealed showed no significant differences. Pieces from several parts of the boule showed no differences. Most of the samples were prepared by hand grinding a well-formed piece of material to a roughly spherical shape. The powdered grinding debris had the green color characteristic of Cr_2O_3 powder though the original crystal appeared black to the unaided eye except in quite thin chips. Chemical analysis of this type of material has shown a marginally significant deficiency of 0.3% chromium.

A second type of sample was a coarse powder made from very thin plate-like single crystals grown by the vapor deposition method by E. P. Trounson of this laboratory. These crystals were transparent with a slight greenish tint. Unfortunately they were too small to exhibit resonance singly. They were formed into a cake with a binder of "Koloid" cement. For this sample the antiferromagnetic resonance could not be readily resolved, but the Néel temperature, taken as the point of disappearance of the paramagnetic resonance, was
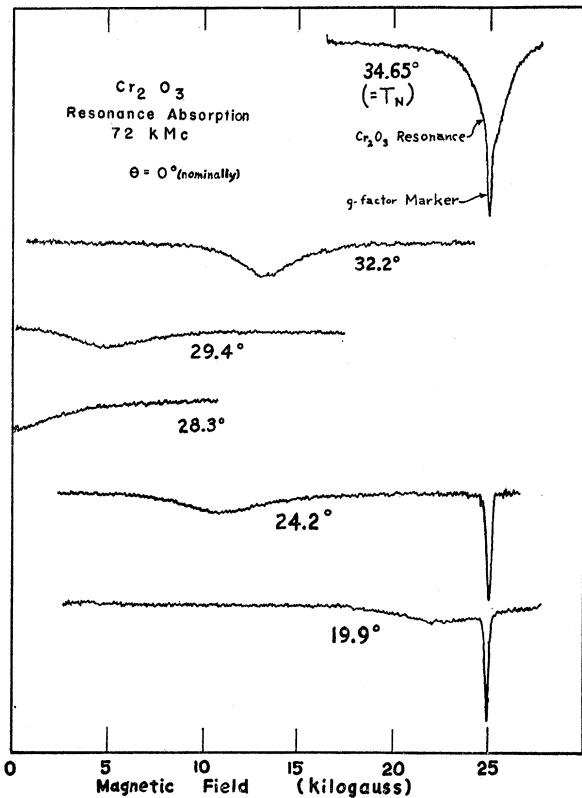
FIG. 3. Sample adsorption curve. Considerably greater signal-to-noise ratio was available through the use of larger crystal samples but broadening would then result.

found to agree with the Néel point of the flame-fusion crystals to within about 0.1°C or 0.03% of the absolute Néel temperature. This suggests that the flame-fusion crystals are quite close to correct stoichiometry since the average number of nearest-neighbor interacting ions (which is proportional to the Néel temperature) is sensibly the same for both methods of preparation, an

unlikely result unless both methods produced good stoichiometry.

EXPERIMENTAL RESULTS AND DISCUSSION

6. Resonance Diagram

Measurements were made of the resonant field as a function of temperature at the following frequencies: 24 kMc/sec ($\theta=65°$), 48 kMc/sec ($\theta=65°$), 48 kMc/sec ($\theta=0°$, 65°, 90°). In addition the temperature for resonance in zero field was found for 106 kMc/sec. Typical absorption curves at various temperatures are shown in Fig. 3. The g-factor marker was a small amount of Mg_6MnO_8, an inorganic powder material with the murdochite structure made by P. L. Edwards of this laboratory ($g=1.99$).

A plot of resonant field against temperature is shown in Fig. 4. These data (taken from our best wide-range run) apply to a frequency of 72 kMc/sec and crystal orientation angles of about 0° and 90° between crystal axis and external field and are qualitatively similar to data obtained at other frequencies and orientations. The temperature range ΔT_0 in which the resonance drops from its paramagnetic field to zero field is found to be about 0.45° at 24 kMc/sec, 2.3° at 48 kMc/sec, 6.7° at 72 kMc/sec, and 16.2° at 106 kMc/sec. Hence fairly closely

$$\Delta T_0 \propto (\text{frequency})^{2.3}. \tag{11}$$

As the temperature is reduced below T_0, where the resonance occurs at zero field, all traces of resonance absorption for $\theta=90°$ disappear.

The theoretical curves shown (Fig. 4) have been calculated with the following assumptions: the quantity, λK, which is discussed more fully in Sec. 8, is proportional to $(\Delta T)^{0.872}$, ($\Delta T = T_N - T$); the orientation angles are exactly 0° and 90°; the first-order resonant-field correction term in α_N, Eq. (5), is included as it amounts to 20% near 20°C and is calculated for $\theta=0°$ exactly. On the whole, this curve fits the experimental points
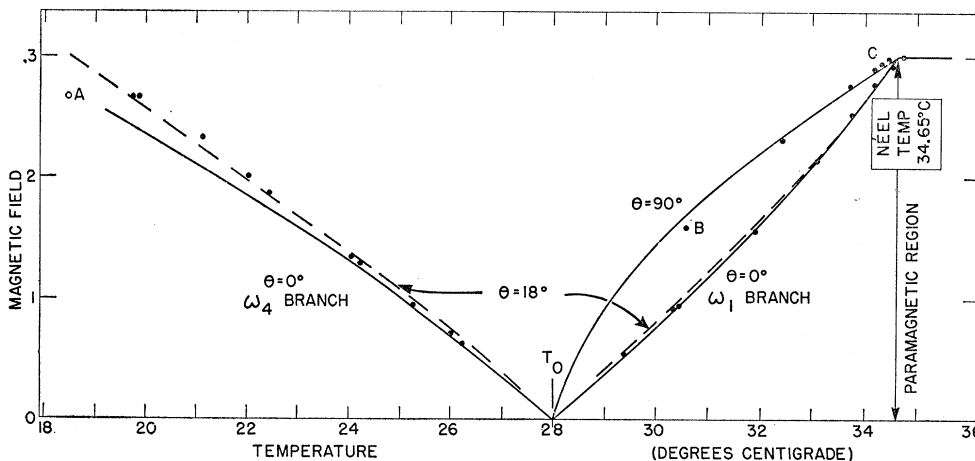

FIG. 4. Resonant field at 72 kMc/sec as function of temperature for two crystal orientations. These data represent our most complete run and are confirmed (except point B) in many other runs. The solid line is theory for $\theta=0°$ and $\lambda K \propto (\Delta T)^{0.87}$ including first-order correction in α_N. An error of about 20° in crystal orientation in this run required fitting the experimental points instead to the dotted line which includes an orientation correction.

fairly well. The most notable difference occurs at the low-temperature end of the available data where the experimental points of the run shown lie at higher fields than the above theory suggests. In this region the results are more sensitive to misorientation shifts than elsewhere and, indeed, an x-ray analysis on the sample of this run does indicate a misorientation by about 20°. To explain the ω_4 data, an actual misorientation of about 18° is needed though this impairs slightly the ω_1 agreement.

The point marked A has been calculated for $\theta = 0°$ resonance at 72 kMc/sec from the value of λK obtained from our zero-field resonance data at 106 kMc/sec. One expects it to lie close to the theoretical curve shown as the zero-field data have been used in determining the anisotropy temperature dependence. The point marked B is believed to be erroneous as it is not confirmed in other runs.

The resonance results are collected into a diagram in Figs. 5 and 6. The scales of ordinate and abscissa in Fig. 6 are chosen to be quadratic for convenience. On such a scale the theoretical resonance line for $\theta = 90°$ is a straight line. The fit of the experimental points to the theoretical lines is reasonably good. In general the points which fit most poorly are also those which are least reliable.

The orientation dependence of the antiferromagnetic resonance is contained implicitly in Figs. 5 and 6. Some simple explicit measurements also were made on crystals which could be rotated in the cavity resonator (and retuned in each position). The agreement with theory again seemed satisfactory. In the K-band results reported by McGuire, an anomaly appeared in which the two orientations revealed to close Néel temperatures separated by about 0.15°C and two values of T_0. This point was checked at 72 kMc/sec in several ways with somewhat erratic results. Our best data, however, shown in Fig. 4 (area labeled C) tend to confirm the existence of this effect, though their accuracy is insufficient to prove definitely its existence. It also appears in Figs. 5 and 6 that the consistency of the zero-field 24 kMc/sec point with the 72 kMc/sec data is aided slightly by using two values for T_0.

7. Line Width

The width of the resonance lines as obtained by sweeping the magnetic field is found to depend apparently upon the temperature and the resonant field. Our measurements of line width are complicated by frequent use of samples large enough to cause broadening by saturation of the cavity resonator-coupling system. On those occasions when small samples were used, a line width of about 1000 oe was obtained near the Néel temperature, in satisfactory agreement with the average width of about 1000 oe obtained by McGuire. The relative variation of line width with magnetic field could be obtained from much of our data and is illustrated in
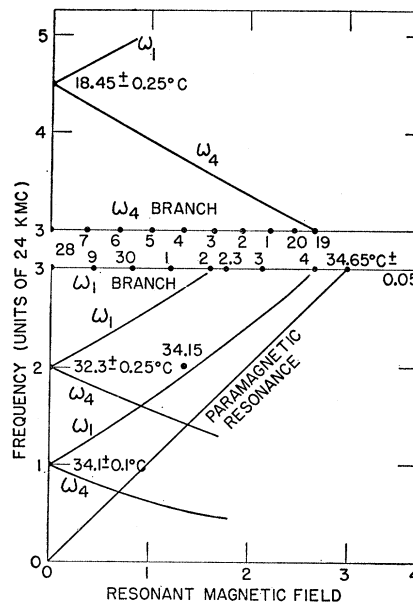

FIG. 5. Resonance diagram for $\theta = 0°$. The solid lines are theoretical resonance loci drawn through the zero-field resonance points. For clarity in labeling the 72 kMc/sec data the axis of ordinates has been expanded at $\omega = 3$. The magnetic-field scale unit is the paramagnetic resonant field for 24 kMc/sec.

Figs. 7(a) and 7(b). This behavior can be understood from the resonance equations through the following first-order calculation: let the normal relaxation time be considered as independent of temperature and of externally applied magnetic field. Then the half-power line width will be a constant $\Delta \omega$ when frequency is swept. When magnetic field is swept instead, the line
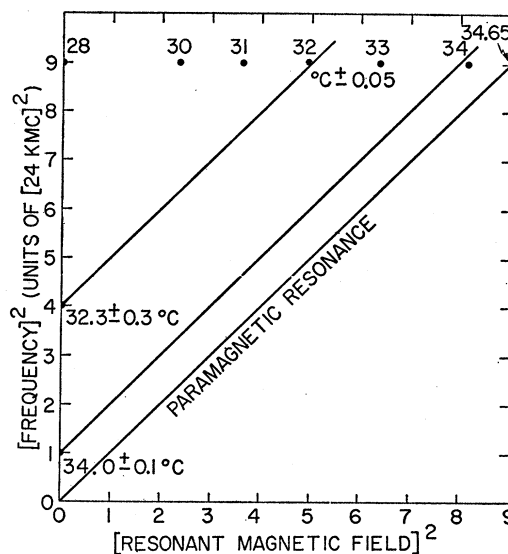

FIG. 6. Resonance diagram for $\theta = 90°$. The solid lines are theoretical resonance loci which are straight lines when plotted on quadratic scales.
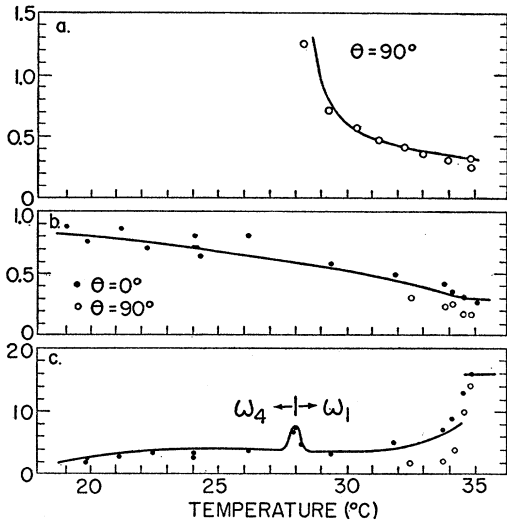
FIG. 7. Variation of line width between half-response points (72 kMc/sec) with resonant magnetic field as the temperature is changed. The solid line shows the theoretical variation [see Eq. (13)] if one assumes that both orientations have the same width at T_N. The ordinate unit is magnetic field reduced to 3 at H_p. In (a) the widths are somewhat greater than for $\theta = 90°$ in (b), probably because of the use of a larger sample. (c) Peak height of recorded resonance (72 kMc/sec) as a function of temperature for $\theta = 0°$ (solid points and $\theta = 90°$ (open circles). The vertical scale is proportional to power absorbed.

width will be to first order

$$\Delta H_\theta = (\partial H_\theta / \partial \omega)_{\text{res}} \Delta \omega. \tag{12}$$

On taking the derivatives from Eq. (3), we obtain the following results.

Region of Curie temperature; $\alpha_N \cong 0$.

$$\begin{aligned} \theta = 0: &\quad \Delta H_{11} = (2 - \gamma H_{11}/\omega)\Delta \omega / \gamma; \\ \theta = \tfrac{1}{2}\pi: &\quad \Delta H_\perp = (\omega / \gamma H_\perp)\Delta \omega / \gamma. \end{aligned} \tag{13}$$

These expressions are plotted as solid lines against temperature in Figs. 7(a) and 7(b) and result in a fairly satisfactory fit of the data, although the fit is materially improved by assuming that $\Delta \omega$ for $\theta = 90°$ is about $\tfrac{2}{3}$ as great as for $\theta = 0°$.

Higher order effects which require computing $\partial H_\theta / \partial \omega$ on the sides of the absorption line will cause the line shape to be unsymmetrical when the magnetic field is swept. This distortion is worst when the resonant magnetic field falls to low values, especially for the $\theta = \pi/2$ orientation. In most cases we have not used data taken by field-sweeping at low resonant fields and therefore will omit the distortion correction formulas, which for present accuracy are not necessary for resonant fields above about $H_p/3$.

8. Anisotropy Constants

The dependence of the product λK upon temperature may be calculated either from the data of resonant field vs temperature taken at one particular frequency

(the higher the better) by the use of the resonance relations (3, 5, 6), or from the zero-field resonance temperatures obtained for each available frequency. The results obtained by these two methods should be identical.

In Fig. 8, values of $2\lambda K$ obtained from Eq. (3) by using observed frequencies for zero-field resonance have been plotted on a log-log scale against ΔT ($= T_N - T$). They are fitted well by the empirical expression $\lambda K \propto (\Delta T)^{0.87}$ [which is equivalent to Eq. (10)]. Also plotted in Fig. 8 are values of $2\lambda K$ derived from our best 72 kMc/sec data with nonzero field. These data have been computed using Eq. (3) including the first-order α_N correction of Eq. (5), and the misalignment correction (6). The fit of the data to the empirical straight line is quite satisfactory.

The quantity $\chi_\perp = \lambda^{-1}$ has been measured by McGuire, Scott, and Grannis[1] and found to be $25.0 \times 10^{-6}/g$ near the Néel temperature with very little variation down to about $77°K$. Hence we have for K, using 5.21 as the density,

$$K = 8300 (\Delta T)^{0.87 \pm 0.03} \text{ ergs/cm}^3. \tag{14}$$

This may be expressed in terms of the sublattice magnetization M by expressing the Brillouin magnetization function for spin $\tfrac{3}{2}$ as a power of ΔT in the vicinity of the Néel point. Thus M is found to be closely proportional to $(\Delta T)^{0.485}$ over the range $0.5° < \Delta T < 20°$. Hence

$$K = \text{const} \times M^{1.80 \pm 0.06}, \tag{15}$$

which may be compared with the expression $K = \text{const} \times M^2$ found in MnF_2.[14,8] The difference in exponent of M suggests that there are significant sources of anisotropy energy in Cr_2O_3 which are not important in MnF_2. It does not seem possible to account for the exponent as an effect of short-range ordering alone using the theory of Oguchi.[17]

The anisotropy constant at absolute zero may be obtained from expression (15) above by extrapolation. For the magnetization M, the Brillouin function should not be approximated. We find

$$K(T = 0°K) = 800\,000 \text{ ergs/cm}^3, \tag{16}$$

and the corresponding resonance frequency is 310 000 Mc/sec. A much larger rough estimate $\sim 10^8$ ergs/g was found by McGuire[1] using K-band data; however, this may be off by several orders of magnitude owing to the difficulties of carrying out a $300°$ extrapolation from a $\tfrac{1}{2}°$ base. For comparison the corresponding K for MnF_2 at absolute zero according to Keffer's result is 5.5×10^6 ergs/cm³, and the resonance frequency is 280 000 Mc/sec.

The critical field of Eq. (10) may now be obtained from our empirical results using (15) for K and the measured values of $\chi_\perp$ and χ_{11}. It is an interesting coincidence that $\alpha_N (= 1 - \chi_{11}/\chi_\perp)$ turns out to be closely expressed by $(\Delta T/310)^{0.78}$, roughly the same exponent

[17] T. Oguchi, Progr. Theoret. Phys. Japan 13, 148 (1955).

as was found for K. Hence the critical-field expression (10) will be only slightly dependent on temperature.

$$(H_0)_{\text{crit}} = 106\ 000\ (\Delta T)^{0.045}\ \text{near}\ T_N$$
$$= 110\ 000\ \text{oe}\ (T = 0^\circ\text{K})$$
$$= 106\ 000\ \text{oe}\ [T = (T_N - 1)^\circ\text{K}] \quad (17)$$
$$= 0\ \text{oe}\ (T = T_N).$$

The sudden drop to zero at the Néel point is the result of the exponent of ΔT being positive though small near T_N. This feature cannot be taken seriously as the susceptibilities are slightly anomalous near T_N.

Extrapolation of α_N down to absolute zero with the above empirical law produces the interesting result that $\chi_\perp$ must rise to about $28 \times 10^{-6}\ \text{g}^{-1}$ from $25 \times 10^{-6}\ \text{g}^{-1}$ below 77°K if $\chi_\parallel$ is to be zero at absolute zero. Measurements by McGuire et al.[1] show what may be the beginning of such a rise at 77°K.

9. Absorption Intensities

The absorption peak height in antiferromagnetic resonance can be given, for most of our data, in the form of a ratio to the paramagnetic-absorption peak height occurring for the same frequency at temperatures slightly above the Néel point which thus serves as an absorption standard. The principal uncertainty entering into these data arises from the partial saturation of the resonator coupling system by the paramagnetic resonance, i.e., the cavity Q was reduced at sample resonance by an amount which was not always small compared to the Q itself. Nevertheless our best results should be accurate enough to make a meaningful comparison with the theoretical microwave susceptibilities.

In Fig. 7(c) is shown the dependence of the observed peak height for antiferromagnetic and paramagnetic resonance on temperature at 72 kMc/sec. Assuming this is proportional to the microwave susceptibility of the sample, we compare it to the solid curve which represents Eq. (9) using the temperature dependence of K found above. The peak at 28°C is due to the overlapping of the ω_1 and ω_4 modes. The similarity of shape between experimental and theoretical curves is good except very near T_N where the experimental curve lacks the theoretical discontinuity. This is probably a manifestation of short-range ordering effects. Our results for the $\theta = 90^\circ$ orientation show more scatter and are not, at present, capable of a good quantitative interpretation, nor should this be expected as our susceptibility Eq. (9) does not apply to this orientation.

CONCLUSION

The two-sublattice theory of antiferromagnetic resonance for uniaxial crystals is seen to describe surpris-
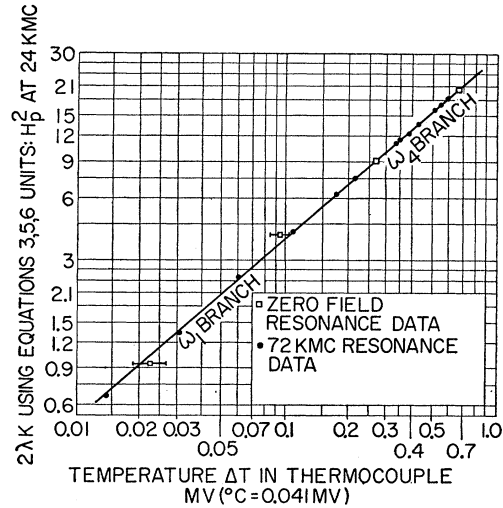

FIG. 8. Dependence of anisotropy constant on temperature. The slope of the solid line best fitting the data is 0.872.

ingly well the resonance phenomena near the Néel temperature in single-crystal Cr₂O₃. Since also a good agreement has been found by Gerritsen et al. for the orthorhombic crystal CuCl₂·2H₂O, and an apparent experimental verification of Keffer's relation of K proportional to M^2 in MnF₂ by Johnson and Nethercot, it seems that the resonance theory is basically adequate though some discrepancies still remain. The dependence of anisotropy energy constant on magnetization in Cr₂O₃, however, must await a more detailed theoretical calculation for evaluation of its significance. At the present time all that can be said is that apparently there are significant contributions to anisotropy energy in Cr₂O₃ of a type not included by Keffer in his work on MnF₂.

Note added in proof.—Equations for the microwave susceptibility and line width in orthorhombic symmetry, which may be reduced to forms similar to ours, have been given by H. J. Gerritsen in his thesis at Leiden. For reasons of brevity we have preferred, in this paper, to avoid detailed comparison of our results with the somewhat more complicated properties of CuCl₂·2H₂O as found at Leiden.