High-Field Antiferromagnetic Resonance in Cr_2O_3

SIMON FONER*
Lincoln Laboratory,† Massachusetts Institute of Technology, Lexington, Massachusetts
and
National Magnet Laboratory,‡ Massachusetts Institute of Technology, Cambridge, Massachusetts
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Antiferromagnetic resonance (AFMR) experiments in single-crystal Cr_2O_3 are summarized with specific emphasis on the high-field resonance mode. Most of the experiments involve pulsed magnetic fields and millimeter wavelength radiation. A brief description of the experimental techniques is included. The experimental results include AFMR as a function of temperature (from 4.2°K to the Néel temperature), frequency (36 to 135 kMc/sec), magnetic field, and angle between the magnetic field and the c axis. Results of the spin-flop resonance mode are also presented as a function of temperature, field, frequency, and angle. Magnetic measurements at the spin-flop field and low-field static susceptibility measurement both parallel and perpendicular to the c axis are also given as a function of temperature. Normalized plots of the AFMR based on the molecular field approximation are presented as a function of angle and field and compared with experiment. The AFMR experiments agreed with the molecular field results when the static susceptibility data were included in the calculations. The characteristic quantity $(2\,H_EH_A)^{1/2}$, where H_E is the exchange field and H_A is the anisotropy field, is 60 ± 3 kG from 4.2 to 235°K. The unusual temperature independence of $(2\,H_EH_A)^{1/2}$ is partly accounted for by the crystalline field contribution to H_A which is only 700 G at 4.2°K. Assuming only dipolar and crystalline field contributions to H_A the crystalline field portion at low temperatures is 1000 G. This corresponds to an axial D contribution which is 1/9 that of Cr^{3+} in Al_2O_3 and of the opposite sign. More recent optical and related data which confirm this result are discussed and some possible mechanisms of the unusual temperature dependence are indicated. A nonzero value of the parallel static susceptibility at low fields is also observed and briefly discussed.

I. INTRODUCTION

THE exchange field in a simple uniaxial antiferromagnet can be estimated from dc susceptibility measurements on single crystals with known magnetic ions, but the anisotropy field of such an antiferromagnet is difficult to determine by the usual low-field static susceptibility measurements. The dc susceptibility is small because the antiparallel sublattice magnetic moments almost balance in low applied magnetic fields, so that the change of free energy in the antiferromagnet is small. The anisotropy is exhibited as a second-order term in the dc susceptibility and generally is not observable except under rather special circumstances. However, the anisotropy field stabilizes the antiparallel spin system in an antiferromagnet and, therefore, plays a major role in the static and dynamic response of the magnetic sublattices. Because the magnetic sublattices are also strongly coupled to each other by the exchange field, one expects that the ac susceptibility—electron spin resonance—should be useful for studying both of these internal fields acting on the magnetic sublattices. Kittel,[1] Keffer and Kittel,[2] Nagamiya,[3] and others[4] have treated the dynamic response of antiferromagnetically coupled sublattices with the molecular field approximation, and showed that the antiferromagnetic resonance (AFMR) is quite sensitive to the anisotropy energy. For antiferromagnets with large exchange and anisotropy fields, the natural (zero-field) AFMR frequencies extend into the millimeter or submillimeter wavelength region—a frequency range which is not easily accessible with conventional microwave techniques. Because the AFMR is sensitive to the anisotropy energy, which, in turn, may be strongly dependent on temperature and may be difficult to estimate, an extremely wide range of frequencies are required to follow the resonance. The use of high-magnetic fields to tune the AFMR to a convenient fixed frequency has some advantages here. Since an effective frequency range of about 2×10^6 Mc/sec can be covered with pulsed magnetic fields, AFMR studies in a wide range of antiferromagnetic materials are feasible. In this paper, the high-field AFMR in simple uniaxial antiferromagnets is considered, and the results of such experiments with single-crystal Cr_2O_3 are discussed.

AFMR in the microwave frequency range has been studied in several systems with low exchange fields, and most extensively in orthorhombic $CuCl_2\cdot2H_2O$.[5] The latter system has been investigated with electron spin resonance both in the paramagnetic and antiferromagnetic state, and with nuclear magnetic resonance and static magnetic susceptibility measurements in these regions. The antiferromagnetic resonances for this system showed good agreement with calculations

* Present address: National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts.

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[1] C. Kittel, Phys. Rev. **82**, 565 (1951).

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

[3] T. Nagamiya, Progr. Theoret. Phys. (Kyoto) **6**, 350 (1951).

[4] T. Nagamiya, K. Yosida, and R. Kubo, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1955), Vol. 4, p. 1, present a comprehensive review of antiferromagnetism.

[5] Numerous publications on AFMR of $CuCl_2\cdot2H_2O$ have appeared since the communication of C. J. Gorter and J. Haantjes, Physica **18**, 285 (1952). These are given in the references of H. J. Gerritsen and M. Garber, *ibid.* **23**, 481 (1956). Studies of nuclear magnetic resonance in this system are given by G. E. G. Hardeman, N. J. Poulis, W. van der Lugt, and W. P. A. Haas *ibid.* **23**, 907 (1957) where further references are presented.

employing molecular field approximations. Only limited observations of antiferromagnetic resonance in uniaxial systems have been made, often because the internal fields dictated that very high frequencies or magnetic fields would be necessary for the experiments. Portis and Teaney[6] have recently shown that under special circumstances, microwave Faraday rotation can be used to study AFMR far from resonance. Johnson and Nethercot[7] studied AFMR in uniaxial antiferromagnetic MnF_2, near the Néel temperature T_N with frequencies as high as 213 kMc/sec, Foner[8] extended the measurements to 4.2°K with pulsed magnetic fields and 36 and 70 kMc/sec, and subsequently Johnson and Nethercot[9] extended their high-frequency results to low temperatures with high precision. The anisotropy field for MnF_2 agreed (within a few percent) with that estimated earlier by Keffer[10] both in magnitude and temperature dependence. In this case, Keffer assumed that dipolar interactions gave the major contribution to the anisotropy field, and this was borne out by experiment. Oguchi[11] calculated the temperature dependence of the anisotropy field by a spin-wave method showing that deviations from the molecular field approximation were expected. Such a deviation was evident in the pulsed field data, but much more accurate results were obtained by Johnson and Nethercot[9] in agreement with Oguchi's predictions. In recent years, AFMR has been observed in an increasing variety of antiferromagnets.

High-field AFMR investigations in Cr_2O_3 were attractive for several reasons. The high Néel temperature ($T_N=308$°K) and correspondingly large exchange field permitted experiments to be made over a wide range of field and temperature. The uniaxial crystal structure and simple two sublattice spin arrangement minimized the number of unknown parameters. The large exchange field and very small anisotropy energy also permitted further simplifications of the analysis. The high mechanical strength, chemical stability, and availability of single crystals also made these experiments feasible. Finally, the limited information concerning the anisotropy energy suggested use of the pulse-field techniques already available to us.

The earliest studies of AFMR in polycrystalline Cr_2O_3 were initiated by Trounson, Bleil, Wangsness, and Maxwell,[12] and single-crystal experiments were continued by McGuire, Scott, and Grannis,[13] and Dayhoff[14] at increasingly higher frequencies which permitted AFMR measurements to be made with successively larger excursions from T_N. With time, the estimates of the anisotropy field decreased until preliminary high-field results were extended to 4.2°K.[15] The final anisotropy field was then about 1/1000 of earliest estimates and showed an unusual temperature dependence. More detailed results reported since then[16] corroborated the initial data. The zero-field resonance was predicted to occur at about 2-mm wavelengths at low temperatures.

In this paper, the antiferromagnetic resonance of Cr_2O_3 is discussed with particular emphasis on the high magnetic field experiments. First, the results of the molecular field theory for a uniaxial antiferromagnet are summarized, and normalized curves obtained by numerical methods are presented for the antiferromagnetic resonance versus angle, frequency, and applied field. From these results, some limitations of the high-field technique are indicated. The experimental techniques are then described, and experimental results as a function of field, orientation, temperature, and frequency are summarized. In addition to the usual AFMR, the experimental observations of the resonance above the critical field (spin-flop magnetic resonance SFMR) and magnetic moment measurements of the spin-flop phenomenon are also discussed. The experimental results thus span the range from dc to 135 kMc/sec. Only limited linewidth data versus temperature is presented. Single-crystal susceptibility data, necessary for corrections of the high-field data, are also included. Some results with the mixed single-crystal system $(Cr_2O_3)_{1-x}\cdot(Al_2O_3)_x$ are also mentioned here because they show that large changes of the crystalline field contributions to the anisotropy can be produced with small changes of composition.

II. THE MOLECULAR FIELD THEORY

The molecular field theory of antiferromagnetic resonance[1-3] has been employed successfully to describe many of the general features of antiferromangetic resonance. The magnetic system is divided into i sublattices and these sublattices are treated as macroscopic magnetic systems coupled by average effective fields. The equation of motion for the ith sublattice is given by

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

where $\gamma=ge/2mc$, the gyromagnetic ratio, and g is the spectroscopic splitting factor, $\mathbf{M}_i$ is the magnetization of the ith sublattice, and $\mathbf{H}_i$ is an effective magnetic field acting on $\mathbf{M}_i$. The contributions to $\mathbf{H}_i$ include an

[6] A. M. Portis and D. Teaney, Phys. Rev. **116**, 838 (1959).
[7] F. M. Johnson and A. H. Nethercot, Phys. Rev. **104**, 847 (1956).
[8] S. Foner, Phys. Rev. **107**, 683 (1957).
[9] F. M. Johnson and A. H. Nethercot, Phys. Rev. **114**, 705 (1959).
[10] F. Keffer, Phys. Rev. **87**, 608 (1952).
[11] T. Oguchi, Phys. Rev. **111**, 1063 (1958).
[12] E. P. Trounson, D. F. Bleil, R. K. Wangsness, and L. R. Maxwell, Phys. Rev. **79**, 542 (1950).
[13] T. R. McGuire, E. J. Scott, and F. H. Grannis, Phys. Rev. **102**, 1000 (1956).
[14] E. S. Dayhoff, Phys. Rev. **107**, 84 (1957).
[15] S. Foner, in *Proceedings of the Fifth International Conference on Low-Temperature Physics and Chemistry* (University of Wisconsin Press, Madison, Wisconsin, 1958), p. 576.
[16] A summary of the AFMR in Cr_2O_3 at 36 and 70 kMc/sec was given in (a) Bull. Am. Phys. Soc. **3**, 193 (1958), and briefly in (b) J. Phys. Rad. **20**, 336 (1959). Further results which included 135-kMc/sec AFMR in Cr_2O_3, and some AFMR experiments in mixed crystals of $(Cr_2O_3)_{1-x}$ $(Al_2O_3)_x$ for x up to 0.1 were presented in (c) Bull. Am. Phys. Soc. **4**, 142 (1959).

externally applied field $\mathbf{H}_0$, an effective isotropic exchange field $\mathbf{H}_E{}^i$ acting between the sublattices, an effective anisotropy field $\mathbf{H}_A$ acting on each sublattice, and an applied rf field $\mathbf{H}$ which is assumed to be small. If we assume two equal and opposite sublattices which are oriented by positive uniaxial anisotropy along the symmetry axis and neglect higher order terms of Eq. (1), then for H_0 parallel to preferred spin direction and $H_0<[2H_EH_A/(1-\alpha)]^{1/2}=H_c$ the resonance condition is

$$\begin{aligned}\omega/\gamma&=[2H_EH_A+(\alpha H_0/2)^2]^{1/2}\pm H_0(1-\tfrac{1}{2}\alpha)\\&=[2\lambda K+(\alpha H_0/2)^2]^{1/2}\pm H_0(1-\tfrac{1}{2}\alpha),\end{aligned}\tag{2}$$

where $\alpha=\chi_{\parallel}/\chi_{\perp}$ the ratio of parallel to perpendicular susceptibility, and we have assumed $H_A\ll H_E$, and $H_0\ll H_E$. Since $H_E=\lambda M$ and $H_A=K/M$ where K is the anisotropy energy, $2H_EH_A=2\lambda K$. The terms in Eq. (2) then involve measured quantities, and do not explicitly involve M. The only unknown quantity, K, may then be determined as a function of temperature from Eq. (2). In the ideal uniaxial antiferromagnet we expect that $\chi_{\parallel}=0$ at $T=0$, but actually this is rarely observed. Although the molecular field model is not expected to hold near T_N, the inclusion of experimental quantities $\chi_{\parallel}$ and $\chi_{\perp}$ may partially compensate for this shortcoming.

When H_0 is greater than H_c, the spin system "flops" so that H_0 is then almost perpendicular to the spins if $H_0\ll H_E$. A resonance then occurs when

$$H_0=[2H_EH_A+(\omega/\gamma)^2]^{1/2}.\tag{3}$$

The normal modes have been described earlier.[2,4] Two degenerate modes occur at $\omega/\gamma=(2H_EH_A)^{1/2}$ when $H_0=0$. For $H_0\neq 0$, but $H_0<H_c$, which is the high-field case, the coupled spin system precesses in a sense opposite to that of paramagnetic resonance for $\omega/\gamma<(2H_EH_A)^{1/2}$, and it precesses in the same sense as paramagnetic resonance for $\omega/\gamma>(2H_EH_A)^{1/2}$. For the spin-flop mode, $H_0>H_c$, the small induced moment along H_0 precesses in the same sense as the paramagnetic resonance.

With a sufficiently high-frequency tunable source one can observe resonance at $H_0=0$ and thus avoid the need for experimental values of α. Such a source was not available. Pulsed magnetic fields and additional measurements of α vs T were therefore used to examine the temperature dependence of $2\lambda K$. Only the mode corresponding to the negative sign in Eq. (3) was observed except when the temperature was close to T_N. Use of at least two frequencies for the high-field resonances permitted the dependence of Eq. (2) to be examined over a wide range of temperature and field, and also confirmed that AFMR was being observed. It is seen that a measure of α is required before the high-field resonance data can be interpreted even at low temperatures because its contribution to the H_0 terms in Eq. (2) are large unless $\alpha=0$. On the other hand, the high-field data is insensitive to the exact value of g when $(\omega/\gamma)^2\ll 2\lambda K$ and, of course, completely independent of g for the "zero-frequency" dc spin-flop susceptibility measurements. For large ω, accurate values of g are required in order to evaluate $2\lambda K$.

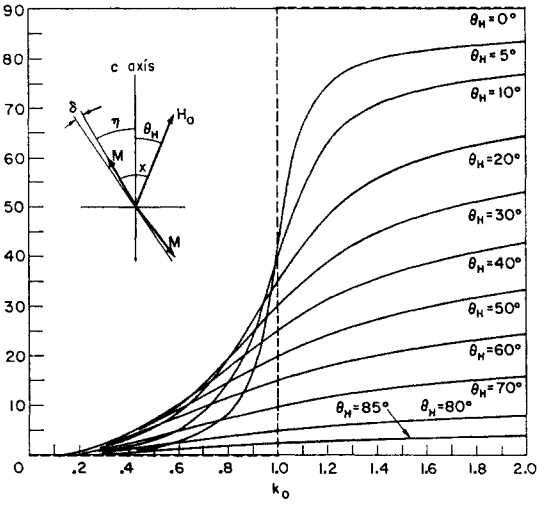

FIG. 1. Angular dependence of an uniaxial antiferromagnet as a function of normalized field $k_0=H_0/(2\lambda K)^{1/2}$ for constant values of θ_H. The angles are defined in the insert. In Figs. 1, 2, and 3 it is assumed that $\delta\simeq 0$ and $\alpha=\chi_{\parallel}/\chi_{\perp}\simeq 0$.

In practice high-field AFMR experiments with small ω/γ are limited by sensitivity considerations, but primarily such measurements are limited by the narrow angle over which the resonance can be observed. This problem will be discussed further when the angular dependence of the AFMR is considered. Small ω/γ experiments also require large values of H_0 at high temperatures because α then approaches 1. Because the available pulsed magnetic fields are much higher than the highest dc magnetic fields yet produced, such a limitation is expected to be of secondary importance.

The general angular dependence of the AFMR calculated by Yosida[17] and simplified for the uniaxial case is given by

$$\begin{aligned}&(\omega/\gamma)^4-(\omega/\gamma)^2\{H^2(\alpha_N{}^2\cos^2\psi+1)\\&\quad+2\lambda K[1+\cos^2(\psi-\theta_H)-2\sin^2(\psi-\theta_H)]\}\\&\quad-H^2\{2\lambda K[\alpha_N\cos^2\psi\cos 2(\psi-\theta_H)\\&\quad+\alpha_N\cos\psi\sin\theta_H\sin(\psi-\theta_H)\\&\quad+\sin\psi\cos\theta_H\sin(\psi-\theta_H)+(\alpha_N\cos^2\psi-\sin^2\psi)]\}\\&\quad+2\lambda K\cos 2(\psi-\theta_H)\cos^2(\psi-\theta_H)+H^4\alpha^2\cos^2\psi=0,\end{aligned}\tag{4}$$

where $\alpha_N=1-\alpha$, and the angles are identified in the insert of Fig. 1. It was not possible to express this result in a simple form. Numerical calculations were carried out in collaboration with H. J. Zeiger. For simplicity, $\alpha=0$ (i.e., $\alpha_N=1$) was assumed and Eq. (4) was transformed under the assumption $\delta=0$, i.e., $\eta=\theta_H-\psi$, where the angles x and η are shown in the insert of Fig. 1. The results agreed with an independent calculation made

[17] K. Yosida, Progr. Theoret. Phys. (Kyoto) 7, 425 (1952).

by Zeiger. The roots of the resonance equation are given by

$$\cos 2\eta = [-B \pm (B^2 - 4AC)^{1/2}]/2A, \quad (5)$$

where

$A = 1$,

$B = \frac{1}{2}[k_0^2(1 - 4\cos^2 x) - 3\nu^2 + 1]$,

$C = \{k_0^4 \cos^2 x + k_0^2[\frac{1}{2} - \cos^2 x - \nu^2(1 + \cos^2 x)] + \nu^4 - \frac{1}{2}\nu^2 - \frac{1}{2}\}$;

$k_0 = H_0/(2\lambda K)^{1/2}$ and $\nu = \omega/\gamma/(2\lambda K)^{1/2}$

subject to the static equilibrium condition

$$\sin 2\eta = -k_0^2 \sin 2x, \quad (6)$$

where $H_0 \ll H_E$, and $H_A^2 \ll (2H_E H_A)$ is assumed. Corresponding results for $\alpha \neq 0$ are given by A_1, B_1, and C_1, respectively, where

$$A_1 = 1 - (\alpha/4), \quad (7)$$

$$B_1 = \tfrac{1}{2}\{1 - 3\nu^2 + k_0^2[1 - (4 - 3\alpha)\cos^2 x]\},$$

$$C_1 = k_0^4(1-\alpha)^2 \cos^2 x + k_0^2\{\tfrac{1}{2} - (1 - \tfrac{1}{2}\alpha)\cos^2 x - \nu^2[(1 + (1-\alpha)^2 \cos^2 x)]\} + \nu^4 - \nu^2 - \tfrac{1}{2} + \tfrac{1}{4}\alpha.$$

The equation corresponding to (6) is

$$\sin 2\eta = -\frac{k_0^2(1-\alpha)\sin 2x}{(1 + a\cos 2\eta)} \simeq -k_0^2(1-\alpha)\sin 2x, \quad (8)$$

where the term $a\cos 2\eta = (K/2M^2\lambda)\cos 2\eta$ is set equal to zero. The plus sign in (5) corresponds to the usual AFMR and the minus sign corresponds to that of the spin-flop mode. Solutions for a wide range of k_0 and ν were initiated with graphical methods and were finally carried out by trial and error procedure with a computer. The results are tabulated here in normalized form. In the text θ_H is replaced by θ when convenient.

The approximations $H_0 \ll H_E$, and $H_A \ll (2\lambda K)^{1/2}$ assumed for the angular dependence are reasonable for MnF_2 and much better for Cr_2O_3. The molecular fields for these two antiferromagnets are tabulated in Table I.

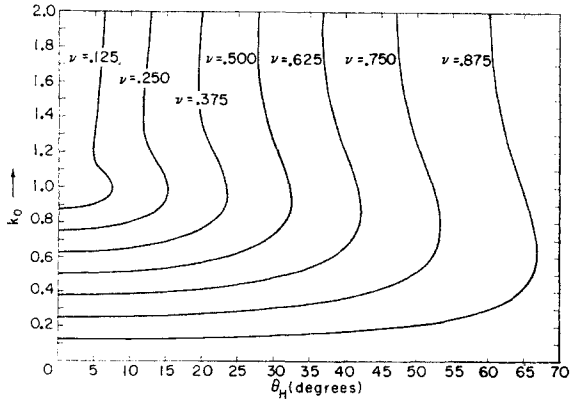

FIG. 2. Angular dependence of usual AFMR as a function of k_0 for constant values of $\nu = (\omega/\gamma)/(2\lambda K)^{1/2}$.

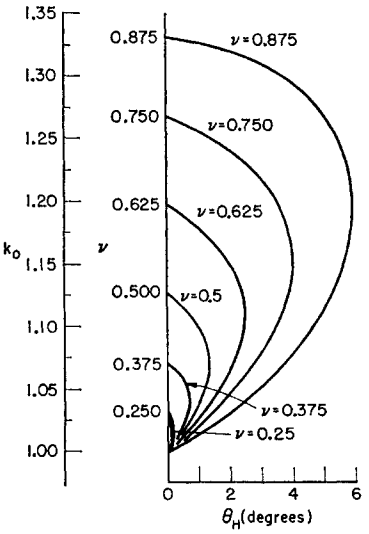

FIG. 3. Angular dependence of spin-flop resonance mode (SFMR) as a function of k_0 for constant values of ν.

TABLE I. Comparison of MnF_2 and Cr_2O_3 molecular fields.

	MnF_2	Cr_2O_3
T_N (°K)	68	308
H_E (G)	5.6×10^5	2.45×10^6
H_A (G)	7.8×10^3	7.0×10^2
H_c (G)	93×10^3	59×10^3
ΔH (G)	≤ 250	≤ 1100
$\delta_0[H_0 = (2\lambda K)^{1/2}]$	9.4°	1.5°
M_0 (G/sublattice)	590	286
λ	9.7×10^2	8.5×10^3
K (ergs/cc)	4.6×10^6	2.0×10^5

For Cr_2O_3, we see that δ_0, the value of δ for $H \perp M$ is very small even when $H_0 = (2\lambda K)^{1/2}$. The large value of H_E and small value of H_A for Cr_2O_3 permit such small correction terms to be neglected ($H_A < 10^{-3}H_E$ and even when $H_0 \simeq H_c$, $H_0 < 0.03H_E$).

Two resonance modes, classified by their characteristics at $\theta = 0$, are obtained. The normalized usual high-field resonance $[H_0^2 < (2H_E H_A)/(1-\alpha)$ at $\theta = 0]$ is shown in Fig. 2. One resonance is expected at small θ, two resonances are predicted for larger θ, and no resonance is predicted for $\theta > \theta_m$. The normalized spin-flop resonance $[H_0^2 > (2H_E H_A)/(1-\alpha)$ at $\theta = 0]$ is shown in Fig. 3. Both Figs. 2 and 3 are calculated for $\alpha = 0$. The orientation of M versus H_0 is shown in Fig. 1 for constant values of θ_H and $\delta = 0$. Some of the data of Figs. 2 and 3 are replotted in Figs. 4 and 5 and limited values of $\alpha \neq 0$ are included for comparison. Figure 4 compares the maximum angle through which resonance should be observed for the usual high-field resonance given by θ_m, and for the spin-flop mode given by θ_m'. In Fig. 5 the normalized field for the point at $\theta = \theta_m$ is given by k_{0m}; for the point at $\theta = \theta_m'$ the normalized field is given by k_{0m}'; and the maximum spin-flop resonance field at $\theta = 0$ is given by k_0^1.

The usual AFMR can be observed at lower fields and over wider ranges of θ when larger values of ν are

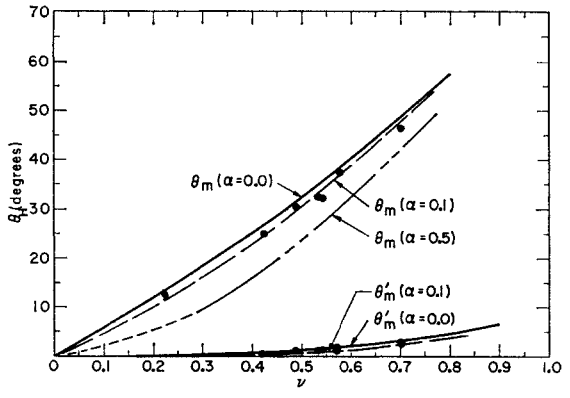

FIG. 4. Maximum values of θ vs ν for the usual AFMR and the primed SFMR. The solid curves for $\alpha=0$ are obtained directly from Figs. 2 and 3, and the dashed curves for $\alpha=0.1$ and $\alpha=0.5$ are obtained from similar numerical calculations. A number of experimental results are also shown.

employed.[18] There is an excluded region centered at $\theta=0$ which also becomes larger as ν increases. Finally, the general shape and gross features of the usual AFMR are not strongly dependent on α.

The spin-flop resonance is restricted to an extremely small region of θ even at large values of ν. This presents some experimental difficulties as well as computational problems. The smoothed curves in Fig. 3 represent calculations with a resolution of about 0.25 degree for θ. The dependence on α is small, but the field at which the spins flop is shifted to $k_0>1$. Many of the qualitative features of this resonance are similar to the ferromagnetic resonance discussed by Smit and Belgers[19] for a highly anisotropic crystal. The angular dependence of the spin system is very sensitive to θ and H particularly near k_0 (e.g., compare the $\theta=0°$ to $\theta=10°$ cases). In order to observe this spin-flop mode, H must be very close to $\theta=0$ (for reasonably low ν) so that the curvature of the energy surface is reduced sufficiently.

If H_0 is aligned within two degrees of the c axis of the crystal, the normal AFMR can be observed for $\nu\approx0.03$. For $\omega/\gamma=25$ kG (70-kMc/sec radiation), AFMR for crystals with $(2\lambda K)^{1/2}$ up to 850 kG should be observable for sufficiently narrow linewidth systems. This corresponds to about 80 μ radiation for $g=2$; far infrared spectroscopy appears to be a more practical way of examining antiferromagnets at shorter wavelengths. The general conclusion is that the normal AFMR for most uniaxial antiferromagnets is well within the range of the pulsed fields now available.[20] The above conclusions do not apply to observations of the spin-flop mode. The orientation limitation for this mode is about 10 times as stringent here as for the normal AFMR mode. If H_0 is aligned within two degrees of the uniaxial anisotropy axis, the "spin-flop" mode should be observed for $\nu>0.6$, and for any detailed study of this resonance $\nu>1$ is desirable. In general, both *high frequencies* and *high fields* are necessary for such measurements.

[18] The reversal for k_0 greater than 1.2 and small ν may not be energetically favorable and should not be seriously considered unless neglected contributions of H_A and H_E are included.

[19] J. Smit and H. G. Belgers, Philips Res. Rept. **10**, 113 (1955).

[20] Similar conclusions were reached for paramagnets with large axial crystalline field contributions [cf. S. Foner and W. Low, Phys. Rev. **120**, 1585 (1960)].

III. EXPERIMENTAL TECHNIQUES

The pulsed fields were produced by an oscillatory discharge of a high voltage capacitor bank (2000 μF charged to a maximum of 3000 V) through suitably designed beryllium-copper coils.[21] The relatively high voltage and low capacitance permitted efficient operation of the pulsed field coils at room temperature. The fields were calibrated at fixed points by observing paramagnetic resonance of MnF_2 at 35 and 70 kMc/sec as a function of time. Absolute calibration of field versus time was obtained from the integrated output voltage of a previously calibrated pickup coil which was accurately positioned in the pulsed field coil. Both values agreed within better than 5%. The relative accuracy of the pulsed-field measurements could be held to better than 1% under favorable circumstances. Since the coils did not deform or deteriorate, the fields were reproducible to at least 1% for a fixed charging voltage. Heating effects were negligible for the pulse repetition rates employed.

The millimeter wave resonance experiments were performed with extremely simple waveguide systems. The samples, thin circular disks of Cr_2O_3 oriented with the c axis perpendicular to the disk, were mounted on a thin, shorting end wall of a long, thin-walled, silvered, stainless-steel waveguide. Resonant absorption was observed as a change in radiation reflected from the end-wall assembly during the field pulse. The relatively high frequencies and the correspondingly large filling factors

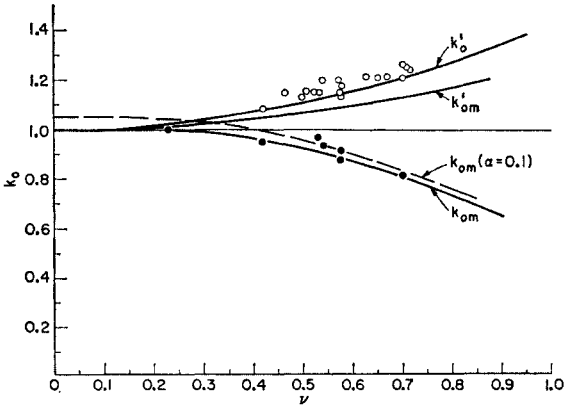

FIG. 5. Maximum values of k_0 vs ν for AFMR and SFMR. Experimental values for the AFMR and SFMR are shown by the closed circles and open circles, respectively.

[21] S. Foner and H. H. Kolm, Rev. Sci. Instr. **27**, 547 (1956); **28**, 799 (1957).

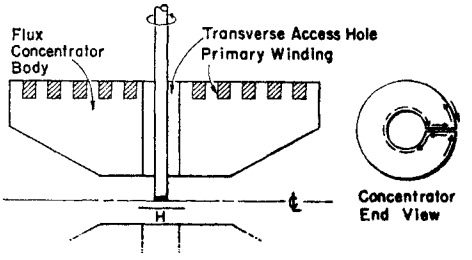

FIG. 6. Cross-section view of transverse access flux-concentrator magnet used for some of the angular dependence experiments. The side view on the left shows the waveguide inserted in the transverse access hole. The magnet is basically a pulse transformer which has an insulated primary winding imbedded in the outer surface of a massive conducting body which acts as an eddy current shield and shapes the magnetic field. The end view at the right shows the slot which permits the field to be generated in the central region. The arrows indicate the primary current excitation and the resulting induced surface currents in the main body of the magnet (for further discussion see reference 22).

permitted measurements without resonant cavity techniques.

The time interval between resonances was compared with the field calibration curves to obtain the corresponding values of pulsed fields. High resolution at high field was attained with observations near the field maximum where the field changed slowly with time. Changes of resonance field of as small as 200 G could be observed at 100 kG (for narrow resonance lines) by adjusting the field peak amplitude to correspond closely to the resonance value.

When low-temperature measurements are made, the available fields are reduced considerably if the Dewar flask is inserted into the pulsed-field solenoid. With the present capacitor bank, fields of as much as 550 kG with the 4-mm system, and 350 kG with the 8-mm system were available when a single glass Dewar was employed. The experiments presented here employed a large 1-in.-i.d. coil, which provided a maximum of 180 kG, uniform over a large volume, and which permitted a double glass Dewar assembly to be inserted with an 8-mm waveguide system. The 3/8-in. i.d. of the inside Dewar also accommodated an 8-mm waveguide assembly with an attached worm gear drive capable of accurately rotating the sample in a plane which contained the applied field vector.

A limited number of AFMR experiments were made with dc magnetic fields. One experiment used the MIT magnet facility and a Bitter solenoid. The other experiments were carried out at 77°K in a 12-in. Varian magnet. With a 5/16-in. air gap between tapered Permandur poles, a maximum field of 37.5 kG could be reached. A single-walled flask, made of a foamed plastic upper reservoir and a small circular nylon cylindrical tail section (0.015-in. wall thickness) permitted 4-mm waveguide or cavity assemblies to be operated in the 5/16-in. air gap at 77°K. Angular data were taken with this arrangement by rotating the magnet in the horizontal plane, perpendicular to the waveguide axis.

Temperature at the sample was measured with a calibrated copper-Constantan thermocouple attached to the end wall of the waveguide assembly. Differential measurements with respect to 4.2°K were made below 77°K. In this way relative changes of less than 1°K could be measured even though the absolute accuracy is estimated to be within 2°K. Above 77°K, both relative and absolute accuracy were within 1°K.

Measurements with fixed crystallographic orientations were made with the waveguide filled with He gas and sealed in order to exclude any liquified gases from the waveguide. If the liquified gases were allowed in the waveguide, the variable reflection coefficient caused by gas bubbles evolved during the field pulse produced a background noise much larger than the AFMR absorption.

One set of continuous rotation experiments was carried out with Cr_2O_3 with an axial pulsed field. Because the rotation waveguide assembly, composed of a plastic worm and drive gear system attached to the Cr_2O_3 disk, did not permit exclusion of liquified gas from the waveguide when the inner Dewar was filled, these measurements were made above 77°K with only the outer Dewar filled with liquid N. The ambient temperature at the sample was close to 100°K, but since the values of α and H_c were not strongly dependent on temperature, the results were satisfactory. The waveguide could be sealed when the sample was rigidly mounted at the end wall, but then the angular orientation could not be maintained or predicted to better than about 2°. A limited number of experiments with this rigid mounting arrangement were also performed.

A second set of continuous rotation experiments was made with a flux-concentrator magnet[22] which had a transverse access hole. The sample was contained in a sealed waveguide and accurate angular orientation was maintained by rotating the entire millimeter wavelength assembly about an axis perpendicular to the applied field as illustrated in Fig. 6. This arrangement was used

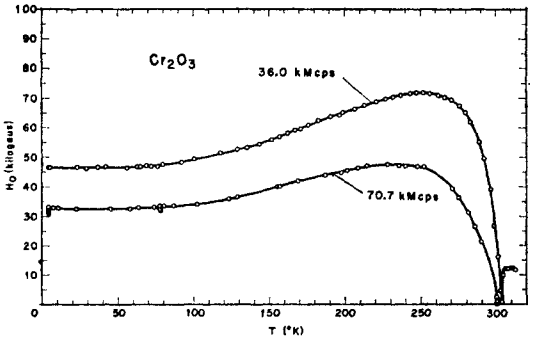

FIG. 7. Temperature dependence of AFMR in Cr_2O_3 at 36.0 and 70.7 kMc/sec for H_0 parallel to the c axis.

[22] B. Howland and S. Foner, in *High Magnetic Fields*, edited by H. H. Kolm, B. Lax, F. Bitter, and R. Mills (Massachusetts Institute of Technology Press, Cambridge, Massachusetts, 1962), p. 289.

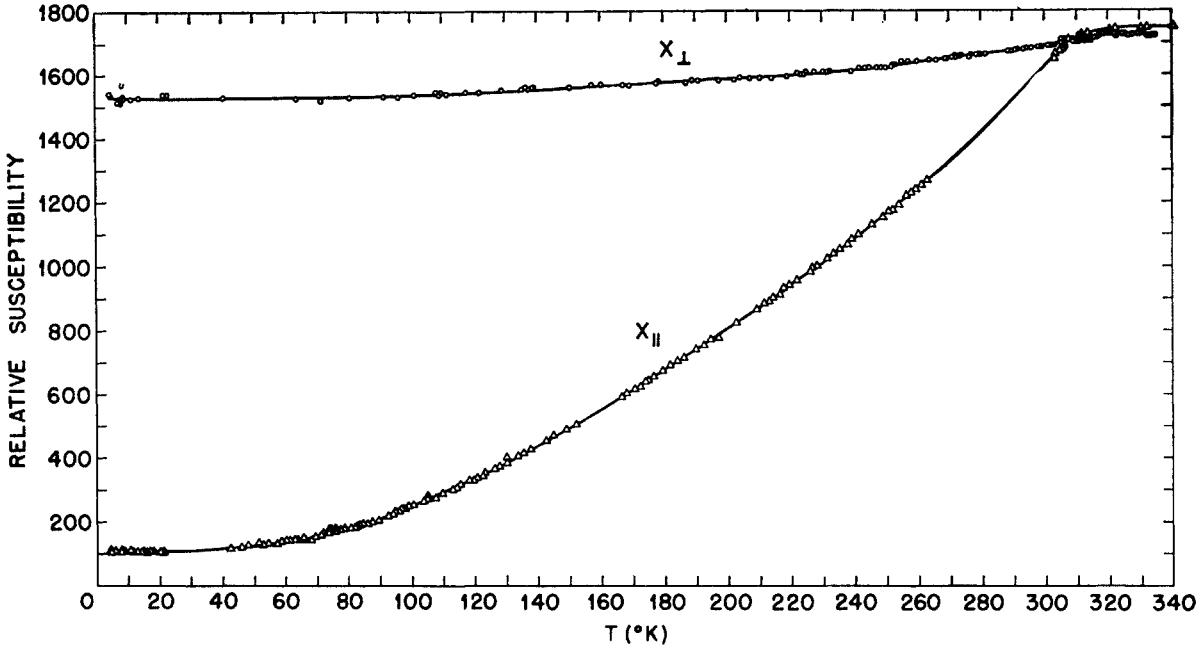

FIG. 8. Temperature dependence of the static susceptibility parallel and perpendicular to the c axis ($\chi_\parallel$ and $\chi_\perp$) or Cr_2O_3. The value of $\chi_\perp$ is $22.4\times10^{-6}\pm0.4$ emu/g at 4.2°K.

for frequencies from 70 to 116 kMc/sec for observation of the usual AFMR and the spin-flop mode.[23]

Samples were ground from Cr_2O_3 single crystals grown by the flame-fusion technique. These were initially obtained from E. S. Dayhoff and grown by E. J. Scott of the U. S. Naval Ordnance Laboratory. Larger single crystals grown at Rutgers University[24] were also used. Most recent measurements used crystals supplied by the Linde Air Products Company, Speedway Laboratory, Speedway, Indiana. Both AFMR and spectroscopic analysis[25] showed that the samples were of comparable purity.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. H_0 Parallel to c Axis $[H_0<H_c]$

Most of the high-field AFMR data for Cr_2O_3 were obtained when H_0 less than H_c was applied along the c axis. The values of resonance field, H_0, from 4.2°K to T_N, are plotted in Fig. 7 for both 36.0- and 70.7-kMc/sec radiation. The general shape of these curves reflects the contributions of α to the high-field terms in Eq. (2).

The present data were analyzed assuming that g was constant below T_N, and the values of α were calculated from single-crystal static susceptibility data. The susceptibility was measured in a uniform magnetic field over a wide range of temperature with a vibrating-sample magnetometer.[26] Relative susceptibilities for the parallel and perpendicular direction are shown in Fig. 8 as a function of temperature. The value of $\chi_\parallel$ does not go to zero as T approaches zero, and $\chi_\perp$ decreases slightly with decreasing T.

The calculated value of $(2\lambda K)^{1/2}$ vs T is plotted in Fig. 9. The high-field resonance data of Fig. 7 have been normalized at one temperature, 4.2°K, by requiring $(2\lambda K)^{1/2}$ be identical for the 36.0- and 70.7-kMc/sec data. The remainder of the data was then calculated by substitutions for α, ω/γ, and H_0 in Eq. (4). Both sets of data are in excellent agreement, but deviate considerably from the normalized associated Brillouin function

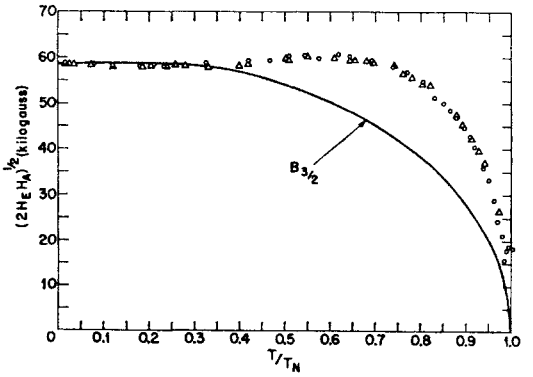

FIG. 9. Calculated values of $(2\lambda K)^{1/2}$ vs temperature derived from Figs. 7 and 8. The triangles and circles correspond to 70.7 and 36.0 kMc/sec, respectively, and the solid line is the associated Brillouin function for $S=3/2$.

[23] S. Foner, Bull. Am. Phys. Soc. 7, 200 (1962).
[24] These crystals were grown at the Rutgers University, Department of Ceramics, under a contract with Lincoln Laboratory.
[25] We are indebted to Dr. E. B. Owens, of Lincoln Laboratory for spectroscopic analyses of these materials.
[26] S. Foner, Rev. Sci. Instr. 27, 548 (1956); 30, 548 (1959).

which is also shown. Of particular interest is the extremely wide range over which $(2\lambda K)^{1/2}$ is almost independent of T. A very slight maximum of $(2\lambda K)^{1/2}$ vs T is also present.

Three dc field experiments with H_0 parallel to the c axis were made at 77°K. One AFMR measurement was performed at the MIT high-field facility at 35.7 kMc/sec. The value of $H_0=47.6\pm0.8$ kG was observed at this frequency for Cr_2O_3. The dc field was calibrated with paramagnetic MnF_2 at the same frequency and the value of H_0 was calculated with the assumption that the magnetic field varied linearly with solenoid current. Subsequent tests showed that this estimate was good to within about 1%. The second dc field experiment was made at 70.0 kMc/sec with a Varian magnet. The value of H_0 for this case was 32.6 ± 0.7 kG. Experiments were made at 135 kMc/sec[16] with direct second harmonic output of a DX-151 klystron kindly furnished by G. S. Heller and J. J. Stickler. H_0 occurred at 10.7 ± 0.2 kG and the linewidth was about 900 G at 77°K. The results were in complete accord with the lower frequency data.[27] Both of these resonances agree closely with the pulsed-field results.

B. g Value

Attempts to measure the g value of Cr_2O_3 in the antiferromagnetic state were made with pulsed-magnetic fields by varying the frequency of the 8-mm klystron for a fixed crystallographic orientation. The precision of these experiments was limited by the small tuning range of the source. The value of $g_{\text{eff}}=1.90\pm0.1$ was measured at 77°K. Comparison of the dc field data at 35.7 and 135 kMc/sec leads to a more accurate $g_{\text{eff}}=1.92\pm0.03$ at 77°K. Here g_{eff} is determined from $\Delta\omega/\Delta H_0$ where

$$g_{\text{eff}}\simeq g\left[[\alpha^2H_0/4(2\lambda K)^{1/2}]\pm\left(1-\frac{\alpha}{2}\right)\right]\simeq g\left(1-\frac{\alpha}{2}\right) \quad (9)$$

reflects the contribution of α. A value of $g=1.97\pm0.03$ at 77°K is obtained when the measured value of α is included in Eq. (9). This result, when compared with Maxwell and McGuire's[28] much earlier value of $g\simeq1.97$ for polycrystalline Cr_2O_3 in the paramagnetic state, Dayhoff's[13] results at T_N, and our present data just above T_N (Fig. 7) indicate that the g value is insensitive to the state of order in Cr_2O_3. In order to determine g accurately the magnetic susceptibility of the antiferromagnet at a given temperature must be known for H_0 parallel to the c axis. It is apparent in the literature that g_{eff} is often reported rather than g. This may account for some differences in reported g values, because g_{eff} depends on α which in turn can depend on many factors including the exact composition of the material studied.

The resonance equations for $H_0\perp c$, consistent with our previous assumptions, is given by

$$\omega=\gamma(2\lambda K+H_0^2)^{1/2}. \quad (10)$$

The dependence on α is not present here, but we note that ω will be rather insensitive to H_0 for $H_0^2\ll2\lambda K$. A second difficulty is that the condition $\omega/\gamma\geq(2\lambda K)^{1/2}$ must be satisfied for resonance which generally rules out this mode in the present discussion.

C. Linewidth

Estimates of linewidth for AFMR in Cr_2O_3 were also made with H_0 parallel to the c axis. The accuracy of this measurement, derived from resonance when the pulsed field was tuned so that the peak of the pulsed field was approximately at H_0, was about 10 to 20%. It was found that the linewidth, ΔH, was less than or equal to 900 G, and was independent of temperature[16] from 4.2 to 200°K. This result is surprising when compared with ΔH of $CuCl_2\cdot2H_2O$ or MnF_2 which both showed ΔH decreasing rapidly with decreasing temperature. Measurements with dc fields and over a wide range of frequencies agreed with the pulsed-field results. More recent measurements[29] with substitutional alloys of $(Cr_2O_3)_{1-x}\cdot(Al_2O_3)_x$ also showed essentially temperature-independent ΔH values which were between 850 to 2000 G.

Several effects[29] influence linewidth measurements at high fields. The field-dependent correction for contributions of $\alpha(T)$ is not large, and can be calculated to first order if we assume that the linewidth is independent of H_0 and that H_0 is along the easy axis. Since these measurements are made at constant frequency rather than at constant field, to first order the linewidth ΔH_0 measured at resonance is given by $\Delta H_0=(\partial H_0/\partial\omega)\Delta\omega_T$, where $\Delta\omega_T$ is the true linewidth at a given temperature. The general result, subject to the condition $H_0<H_c$, is given by

$$\Delta H_0=\mp\frac{\Delta\omega_T}{\gamma}\left(\frac{\omega/\gamma\pm H_0(1-\frac{1}{2}\alpha)}{(\omega/\gamma\pm H_0)(1-\alpha)+\alpha\omega/2\gamma}\right), \quad (11)$$

where the upper sets of signs correspond to the high-field case, i.e., the plus sign in Eq. (2), and the lower sets of signs correspond to the low-field case. When α is small and $H_0\gg(\omega/\gamma)$, the apparent linewidth is multiplied by $\simeq(1+\frac{1}{2}\alpha)$. Thus, this effect is expected to be small at low temperatures, but can superimpose an apparent temperature-dependent linewidth in some

[27] Results reported by Heller at that time [G. S. Heller, in *Microwave Research Institute Symposia Series* (Polytechnic Press of Polytechnic Institute of Brooklyn, Brooklyn, New York, 1960), Vol. IX, p. 73.] showed a complex resonance line for Cr_2O_3 at 77°K with H_0 parallel to the c axis similar to subsidiary resonances reported by Johnson and Methercot (reference 9) for thick samples. More recent data of Heller *et al.* [G. S. Heller, J. J. Stickler, and J. B. Thaxter, Suppl. J. Appl. Phys. **32**, 307 (1961)] are within 2% of our results when the measured values of α are used to calculate the temperature dependence of $(2\lambda K)^{1/2}$.

[28] L. R. Maxwell and T. R. McGuire, Rev. Mod. Phys. **25**, 279 (1953).

[29] S. Foner, Suppl. J. Appl. Phys. **32**, 63 (1961).

instances. The largest correction would be a factor of 2 when $\alpha \simeq 1$ and $H_0 \ll (\omega/\gamma)$ as indicated by Dayhoff.[13]

The angular variation of the AFMR can lead to an apparent broadening of the resonance line. The results are not easily described in a closed form. Qualitative features can be obtained from the normalized curves in Figs. 2 and 3. Corrections are particularly difficult to apply for the spin-flop mode, but not quite as severe for the usual resonance mode. The angular dependence, in general, shows that this effect is minimized as ν is increased. On the other hand, by using relatively low frequencies for AFMR, propagation effects such as those observed by Johnson and Nethercot[8] can be minimized because then a reasonable sample thickness can still be made small compared to the wavelength of the radiation in the sample. Linewidth artifacts produced by demagnetizing effects at high fields would be negligible for Cr_2O_3 (i.e., less than 2 G). Generally circular disks with the cylinder axis parallel to the c axis were used to further reduce this effect.[30]

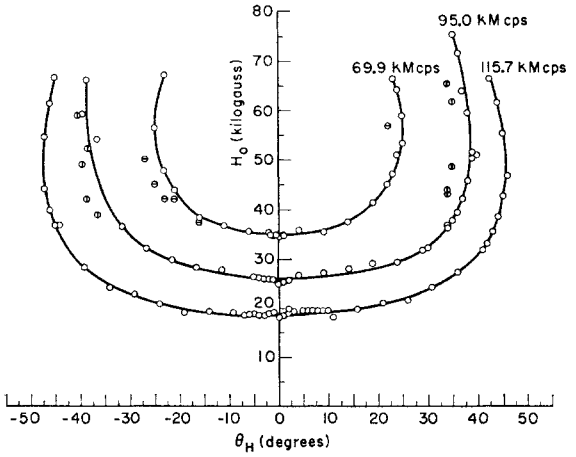

FIG. 11. Angular dependence of AFMR at 77°K. The points with horizontal and vertical bars correspond to additional low-intensity resonances observed at 69.9 kMc/sec and 95.0 kMc/sec, respectively.

D. Angular Dependence of AFMR

1. Usual AFMR Mode

The angular dependence of AFMR in Cr_2O_3 at 37 kMc/sec and about 100°K is shown in Fig. 10. The circular disk of Cr_2O_3 was rotated by a gear drive assembly, and in order to minimize errors in angular position due to backlash, runs were made with continuous sample rotation in the same direction during a given run. The results of several runs are superimposed. Rotations as small as 0.25 deg could be made. The c axis was oriented to within 2 deg of H_0 and the final position of $\theta=0$ was determined from the symmetry of the data after the results were plotted. The maximum angle $\theta_m=12.5°\pm0.5°$ is plotted in Figs. 4 and 5 for comparison with the calculations. No spin-flop resonance was observed in the region of $\theta_H=0$, probably because the c axis was not contained in the plane of rotation. The second resonance was detected at $H_0 > (2\lambda K)^{1/2}$ for 12.5 deg $>\theta>$ 7 deg.

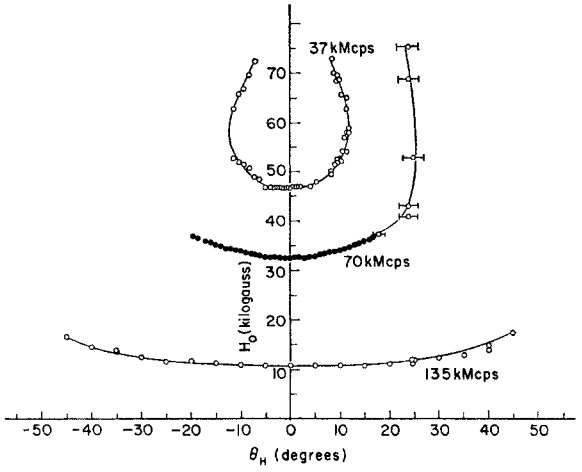

FIG. 10. Angular dependence of AFMR. The 37-kMc/sec data were taken at about 100°K with pulsed fields; the 70-kMc/sec data were taken at 77°K with an electromagnet (solid circles) and pulsed field (open circles); and the 135-kMc/sec data were taken at 77°K with an electromagnet.

The general shape of the data agrees qualitatively with the calculated AFMR curves shown in Fig. 2. At large angles the AFMR linewidth increased, reaching a maximum value at θ_m.

A small nylon Dewar was employed for dc field measurements with 70.0 kMc/sec radiation at 77°K. The results, indicated by the circles in Fig. 10, were obtained by rotating a Varian magnet about the waveguide axis. Pulsed-field measurements were made at a few fixed angles in order to examine the angular dependence above the range of the dc magnet. In this case the orientation error was about 2°. Two sets of points at about 23.5° were taken by simply rotating the 4-mm waveguide section in the pulsed field coil by 180° about the vertical axis. This relatively small orientation change (approximately 2 to 3°) shows the large change in H_0 expected for small changes of θ in this region. The value of $\theta_m=25°\pm2°$ and k_0 are also plotted in Figs. 4 and 5 for comparison. More limited angular data at 135 kMc/sec are also shown in Fig. 10.

Additional angular AFMR data are shown in Figs. 11 and 12. These were obtained by rotating a 4-mm waveguide assembly in the transverse access flux-concentrator magnet (cf. Fig. 6). A cylindrical rod of Cr_2O_3 was mounted with the c axis perpendicular to H_{rf} and

[30] Demagnetizing effects have been considered by Keffer and Kittel (reference 2). Calculations for MnF_2 show that effects of about 20 G could be introduced by demagnetizing terms at high fields (here $\lambda \approx 10^3$ and $\Delta H \approx 200$ G at 4.2°K). Occasionally a splitting of the high-field AFMR has been resolved in MnF_2 at 4.2°K; in each case the disk-shaped sample was fractured. D. H. Douglass and M. W. P. Strandberg, Physica **27**, 1 (1961) have discussed extremely large demagnetizing effects in $MnCl_2$.

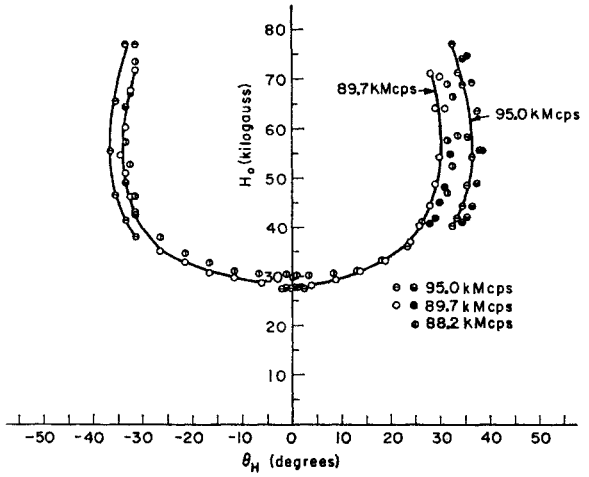

FIG. 12. Angular dependence of AFMR at 77°K. The points which are half-solid or solid correspond to low-intensity resonances. The high-intensity resonance data of Figs. 11 and 12 are plotted in Figs. 4 and 5.

in the plane of H_0, so that as θ was varied, the angle between H_{rf} and H_0 also changed. Occasionally some low-intensity, high-field resonances were also observed at large θ; these are also shown in Figs. 11 and 12. In order to indicate the relation of these resonances to the more intense lines, the relative angular displacement between the low-intensity resonances and the intense lines (which are centered about $\theta=0$) has been preserved. One possible source of this resonance could be the presence of a small crystallite which is displaced by about 2° with respect to the main crystal. The results of the main resonance are also plotted in Figs. 4 and 5.

2. *Spin-Flop Mode*

In Sec. II, it was shown that in order to observe the spin-flop resonance, H_0 must be accurately oriented along the c axis. Since orientation to better than one degree was required, a straightforward experiment was not feasible. Evidence of this mode at 36 kMc/sec was obtained by carefully aligning the sample, but by using large area samples or thick end walls, so that H_0 was not uniform.[8,16] Part of the sample was then properly oriented with respect to H_0 and showed a resonance absorption. No detailed information could be extracted from the data because the exact alignment was not known. The spread of this resonance could be examined more readily for 70.7-kMc/sec radiation, but even then the resonance is difficult to observe. This is illustrated in Fig. 13, which shows more recent data[23] taken with the transverse flux-concentrator arrangement. The composite curves in Fig. 13 show that the spin-flop mode is restricted to less than 0.5° if we assume that the c axis is, in fact, accurately oriented in the plane of H_0. The slight apparent dispersion of the resonance absorption was introduced in order to allow some resolution of the broad absorption, e.g., the spin-flop (c_1-c_2) spin-flop resonance, H_0 must be accurately oriented at $+1.0^0$. The resolution of the spin-flop mode increases rapidly with modest increases in ν above 0.5 (cf. Figs. 3 and 4). At 116 kMc/sec the resonances could be well resolved. The results of two sets of data, compared in Fig. 14, indicate the reproducibility of such measurements. The low-field resonances at a given angle were of much lower intensity than the corresponding high-field resonance. The characteristic parameters, θ_m' and k_0' are plotted in Figs. 4 and 5 for several of these experiments. Higher values of ν are essential for detailed studies of this resonance mode.

Although there is no explicit α dependence in Eq. (3), there are some indirect, but important consequences of $\alpha(T)$. Because the spins do not rotate to the perpendicular orientation (for $\theta_H=0$) until $H=H_c$, the minimum field for spin-flop resonance increases as α increases. The lowest intersection in Fig. 3 is thus raised, and therefore, the minimum value of k_0' must be greater than $k_{0m}(\alpha)$ in Fig. 5. The condition for spin-flop resonance to be observed is then

$$\omega/\gamma \gtrsim \alpha^{1/2} H_c. \tag{12}$$

For 70 kMc/sec and 77°K the total spread of possible resonances for Cr_2O_3 was within the resonance linewidth (close examination of the $\theta_H=0.0$ trace shows a slight structure of the high-field resonance which may be attributed to this cause or to a misoriented crystal-

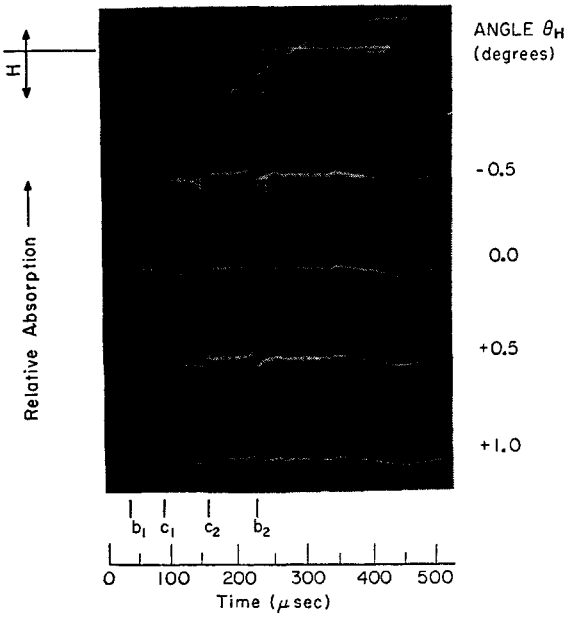

FIG. 13. Spin-flop resonance at 77°K in Cr_2O_3. The top curve shows H_0 vs time corresponding to the lower traces of relative absorption at 69.9 kMc/sec vs time. The low-field AFMR data (b_1,b_2) is plotted in Fig. 11. The SFMR resonances (c_1,c_2) at high field are plotted in Fig. 5. Note the limited range of θ_H for the SFMR mode. The reproducibility of the pulsed field is indicated by part of the AFMR line which happens to occur near the peak value of the second half-cycle (at 450 μsec) of the pulsed field.

lite). The temperature dependence of the spin-flop mode for 95.1 and 116.9 kMc/sec is plotted in Fig. 15. The maximum value of $\alpha^{1/2}H_c$ is indicated where α is based on the magnetic susceptibility data and H_c is taken directly from independent spin-flop measurements[31] obtained by an induction method. The vertical arrows indicate the temperature at which the spin-flop resonance intensity has dropped to a barely detectable level. The results are with two linewidths of the criterion given in Eq. (12).

3. *Spin Flop at $\omega=0$*

When $\omega=0$, the resonance equation (2) reduces to the simple form $H_0=H_c$ for H_0 parallel to the c axis. At this field the spins flop to a position which is perpendicular to H_0. The angular variation of the spin system is indicated in Fig. 1 for the case $\delta_0=0$. Although H_c is much less than H_E for Cr_2O_3, a small magnetic moment change is produced when the spins flop to their perpendicular orientation, and with a suitable experimental arrangement, this magnetic moment change can be detected. Jacobs[32] has examined the spin flop in MnF_2 by measuring the magnetization of this material as a function of H in a pulsed field. In order to improve on sensitivity, we have examined[31] dM/dH or dM/dt versus t. In this way, nonlinear variations of M versus H (or t) could be observed when they were superimposed on much larger linear variations. The change in magnetization, ΔM at $H=H_c$, is given by

$$\Delta M=[2K(1-\alpha)/\lambda]^{1/2}. \tag{13}$$

Despite the general decrease in ΔM as T increased, the spin flop could be observed in Cr_2O_3 up to $T=0.95\ T_N$. Examination of the data showed that the spin-flop transition occurred for a field change of less than 1 kG

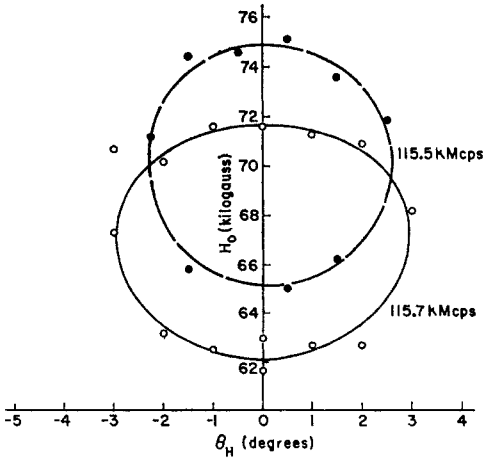

FIG. 14. Angular dependence of SFMR at 77°K for 115.5 and 115.7 kMc/sec. The open circles correspond to the 115.7-kMc/sec data.

[31] S. Foner and S. L. Hou, Suppl. J. Appl. Phys. **33**, 1289 (1962).
[32] I. S. Jacobs, Suppl. J. Appl. Phys. **32**, 61 (1961).

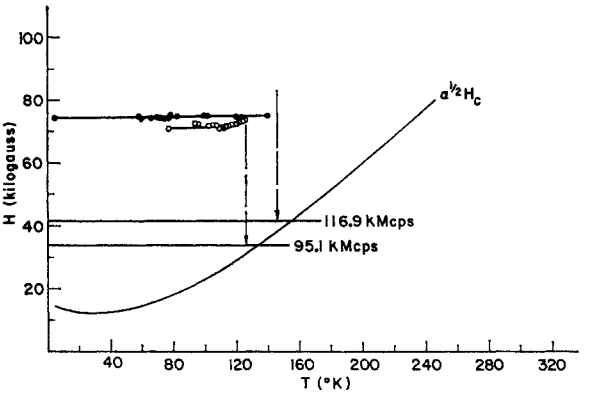

FIG. 15. Temperature dependence of SFMR. The open and solid circles correspond to H_0 for 95.1 and 116.9 kMc/sec, respectively. The horizontal solid lines indicate the values of $H=\omega/\gamma$ for the two frequencies and the curve $\alpha^{1/2}H$ defines the maximum expected temperature for SFMR. The dashed vertical lines show the temperature at which the SFMR intensities have dropped to a very small value.

which corresponded to $\theta<2$ deg. The characteristic curves in Fig. 1 illustrate the necessity of very careful orientation for these measurements.

The values of H_c were measured from 4.2°K to $0.95T_N$ in Cr_2O_3 with the pulsed-field technique, and values of $(2\lambda K)^{1/2}$ vs T were calculated with the independently measured values of α. When these calculated values of $(2\lambda K)^{1/2}$ were superimposed on those of the AFMR data, detailed agreement was observed over the entire range investigated.[33] Although no adjustment of parameters or normalization was used for the spin-flop results, all the points were within 3% of the AFMR data (which is within the experimental error). The values of $(2\lambda K)^{1/2}$ vs T again showed a slight rise in the range of 120 to 250°K as was observed in the earlier AFMR experiments. No evidence for a ferromagnetic contribution to χ_{11} could be detected.[34] If we assume that saturation of any ferromagnetic component would occur within 1 kG, analysis of the data shows that such a contribution would be less than 10% of the measured value of χ_{11} at low temperatures.

[33] The values of H_c were the average value of H_c for H increasing above H_c then returning to a value of H below H_c. I. S. Jacobs and S. Shtrikman (private communication) have suggested that possibly spin-flop hysteresis could be detected. The small value of H_A in Cr_2O_3 indicates that such an effect would be small compared to our experimental error.

[34] The inductive method is directly applicable to spin-flop measurements in materials which also contain ferromagnetic impurities as a second phase. If the ferromagnetic phase saturates at low field it can be readily observed because dH/dt is then a maximum. This effect has been observed in the temperature dependence of the spin-flop in an $MnTiO_3$ single crystal which had a small amount ($\approx 5\%$) of ferromagnetic impurity. This particular single crystal was grown by Thomas Reed of Lincoln Laboratory. Examples of spin-flop data for Cr_2O_3 are shown by S. Foner, in *High Magnetic Fields*, edited by H. H. Kolm, B. Lax, F. Bitter, and R. Mills (Massachusetts Institute of Technology Press, Cambridge, Massachusetts, 1962), p. 495. The spin-flop data for $MnTiO_3$ agree with the AFMR results of J. J. Stickler and G. S. Heller, Suppl. J. Appl. Phys. **33**, 1302 (1962).

E. Molecular Field Approximation

1 AFMR

The early AFMR experiment of McGuire *et al.*[12] and Dayhoff[13] near T_N both seemed in accord with the dependence expected from the molecular field model, yet the values of anisotropy energy deduced from their data differed by orders of magnitude. Dayhoff's value is certainly closer to our value, but still about four times too large.

The results presented in the present paper permit a more detailed check of the molecular field approximation over a wide range of temperature, field, frequency, and angle. All of the data are self-consistent with the molecular field results when we include the measured values of magnetic susceptibility. In particular, the values of θ_m and θ_m' are in good agreement with the numerical calculations as shown in Fig. 4. These quantities do not depend strongly on α, thus it would be difficult to see any disagreement unless it was quite large. Both the normal and spin-flop AFMR results appear to fit the $\alpha=0.1$ (the measured value of α is 0.10 at 77°K) more closely than the $\alpha=0.0$ curves. Although θ_m and θ_m' were convenient parameters as far as numerical results were concerned, and the values of θ_H can be measured accurately, the values of k_0, k_{0m} are at best only broadly defined (see Figs. 2 and 3). This is partly reflected in the tabulated data for k_{0m} and k_0' shown in Fig. 5. Although the experimental data tend slightly above the calculated curve for k_0' it is generally within the experimental error. It is possible that anisotropic exchange could also lead to this result, but higher frequency data, or static susceptibility data well above H_c are required to examine this possibility in further detail. The data in Figs. 10, 11, and 12 follow the general features of the usual AFMR and the results in Fig. 14 show the general features of the spin-flop mode.

Figures 11 and 12 also show a number of low-intensity resonances. The angular dependence of these low-intensity resonances is similar to the high-intensity lines, but they are consistently displaced by about 2 deg with respect to the high-intensity resonances. These subsidiary resonances could be caused by a small crystallite of Cr_2O_3 which is slightly misoriented with respect to the main crystal.[35] X-ray analysis has not been attempted because the particular crystal was too small. Less likely sources of this low-intensity line include canted spin arrangements and multidomain structures.

The spin-flop data at $\omega=0$ also are in good agreement with the high-frequency results. The high-frequency data used low-field static susceptibility data to determine λK as a function of temperature from the AFMR equations. The $\omega=0$ spin-flop data show that there is no appreciable field dependence of α, λ, or K. The close agreement at high temperatures is particularly significant since here α is close to unity so that H_c is much greater than $(2\lambda K)^{1/2}$ and quite sensitive to α, whereas the high-frequency resonance field H_0 is small at high temperatures so that the α correction is less important.

2. Static Susceptibility

Earlier static susceptibility data for single crystal Cr_2O_3 from 77 to 340°K were presented by McGuire *et al.*[12] and compared to powder data of Honda and Soné.[36] Their results showed an almost temperature independent $\chi_\perp$ and a $\chi_\parallel$ which only qualitatively followed the molecular field calculations. The present results in Fig. 8 are in close agreement with McGuire *et al.* in absolute magnitude, but they are more detailed particularly below T_N. The value of $\chi_\perp$ is 22.4×10^{-6} ±0.4 emu/g at 4.2°K. There is a definite decrease in $\chi_\perp$ as the temperature is decreased, and $\chi_\parallel$ approaches a nonzero value at low temperatures. Measurements of several single crystals showed that $\chi_\parallel$ was not zero at low temperatures although the values of α varied slightly from sample to sample. At 4.2°K, values of α from 0.05 to 0.08 have been measured.

It is not surprising that $\chi_\parallel$ is not zero at low temperatures, and our experiments with various single-crystal antiferromagnets have rarely shown a value of $\chi_\parallel$ approaching zero at low temperatures.[37] One source of an appreciable $\chi_\parallel$ at low temperatures may be caused by imperfections. A vacancy in sublattice 1 leads to a net moment in the direction of sublattice 2 approximately equal to the saturation moment of the missing ion. Because the parallel susceptibility measures the difference between $\mathbf{M}_1$ and $\mathbf{M}_2$ we expect a relatively large contribution from this vacancy. However, if we assume a random distribution of vacancies in both sublattices, the net unbalanced moment would still be zero. The large local moment of a vacancy may be an important contributor to magnetic annealing effects recently observed in magnetoelectric experiments (references 41 and 46 below). A vacancy leads to a local misalignment of the neighboring spins, and this effect may extend over a large range. The applied field can then exert a torque on the misaligned spins of both sublattices so that a nonzero parallel susceptibility is obtained at low temperatures. In addition to metal ion vacancies, oxygen vacancies can occur. Changes in valence and charge compensation may also occur.[38] A second source of a nonzero parallel susceptibility was discussed by Orbach[39] based on Dzyaloshinsky's[40] treatment of antiferro-

[35] Independent evidence for presence of slightly misoriented crystals has been obtained by K. A. Wickersheim and C. V. Stager in similar crystals (private communications).

[36] K. Honda and T. Soné, Sci. Repts. Tohoku Imperial Univ. **3**, 223 (1914).

[37] One notable exception seems to be MnF_2. Some of these results were briefly indicated in the case of reference 16(b). More detailed results will be presented elsewhere.

[38] Some models for mixed valence compounds are discussed by P. G. de Gennes, Phys. Rev. **118**, 141 (1960).

[39] R. Orbach, Phys. Rev. **115**, 1189 (1959).

[40] I. Dzyaloshinsky, J. Phys. Chem. Solids **4**, 241 (1958).

magnets with noncolinear magnetocrystalline anisotropy fields. Magnetoelectric experiments of Astrov[41] seem to indicate that no canting exists in Cr_2O_3, but the data are not conclusive. Experiments now in progress at NML with high magnetic fields may clarify this problem.

The shape of the $(2\lambda K)^{1/2}$ versus temperature curve is not expected to fit the $B_{3/2}$ curve except under special conditions. For Cr_2O_3, the temperature dependence of K results in an unusually temperature-independent $(2\lambda K)^{1/2}$ curve. At the lowest temperatures one expects spin-wave contributions to $(2\lambda K)^{1/2}$ to become important, but the various other contributions to susceptibility indicate that detailed analysis of the present data may not be warranted.

The general conclusions are that the molecular field approximation for AFMR is quite good when measured susceptibility data is used for Cr_2O_3 and that experiments of much higher precision are required in order to detect any small deviations. *Note added in proof.* AFMR data, in general, have shown surprisingly good agreement with the molecular field approximation results even in the region near Tn (see, for example, reference 13). There are good reasons for this. The molecular field approximation is not applied exactly to the AFMR—usually independent static susceptibility measurements are also used (and these data generally do not agree with predictions of the molecular field theory). J. Kanamori and M. Tachiki, [J. Phys. Soc. Japan Suppl. B1, **17**, 61 (1962); *ibid.*, **17**, 1384 (1962)], have shown that the Nagamiya-Keffer-Kittel theory of AMFR is exact *in any statistical approximation* if one introduces the phenomenological quantities p_{II}, $\chi_\perp$, and K.

F. Crystalline Field Contributions to Anisotropy

The anisotropy energy for MnF_2 was calculated quite closely[9] by assuming the major contribution was due to dipolar interactions. Because the Mn^{2+} ion is in a ^6S state it was expected that crystalline field effects would be small, and the experiments have demonstrated this fact. Except at lowest temperatures where spin waves are important, H_A varied approximately as the modified Brillouin function for $S=5/2$. We conclude, therefore, that if only dipolar interactions are present, it should be possible to calculate K quite accurately for an antiferromagnet. The Cr^{3+} ion cannot be treated as simply because it is in a ^4F state; in addition to dipolar contributions, a trigonal crystalline field contribution must be included. We shall show that this latter contribution is quite difficult to predict from the electron paramagnetic resonance (EPR) experiments of Cr^{3+} in Al_2O_3 which is isomorphous with Cr_2O_3.

Tachiki and Nagamiya[42] have reviewed possible sources of anisotropy in Cr_2O_3 based on the earlier data of Dayhoff[13] near T_N. They calculated the dipolar contribution to the anisotropy assuming that $g=1.97$ and that the u parameter was that of αFe_2O_3 and αAl_2O_3 ($u=0.105$), which has been confirmed by Newnham.[43] The contributions of anisotropic exchange were estimated to be small compared to the crystalline field contribution. The latter contribution could not be calculated, and even near T_N a value of the fine structure coupling constant D smaller than that for Cr^{3+} in Al_2O_3 was required[44] to fit Dayhoff's results. The molecular field calculations gave

$$K_{\text{dipolar}}=-NCB_s^2(Z), \quad \text{where} \quad C=-0.059 \text{ cm}^{-1} \text{ per ion}, \tag{14}$$

and

$$K_{\text{fine structure}}=-ND\times[S(S+1)-\tfrac{3}{2}SB_s(Z)\coth(Z/2S)], \tag{15}$$

where $Z=g\mu_\beta SH/kT$, $B_s(Z)$ is the Brillouin function, and N is the number of ions/cm^3.

If we assume that the dipolar contributions are accurately given above, then the value of D can be determined from the low-temperature AFMR data. The anisotropy energy is then $+0.034$ cm^{-1}/ion; about 1/9 that of ruby (Cr^{3+} in Al_2O_3) and of opposite sign. In order to compare the temperature dependence of the anisotropy energy with the molecular field approximation, the values of K_{dipolar} and K_{fs} are plotted in Fig. 16. The difference between K_{dipolar} and K_{fs}, K, is plotted in Fig. 17 as a function of temperature. The low-temperature value of the dipolar contribution K_D^1 or K_D^2 is obtained from the calculation of Tachiki and Nagamiya.[42] The temperature dependence of K_D^1 is then calculated from Eq. (14). The temperature de-

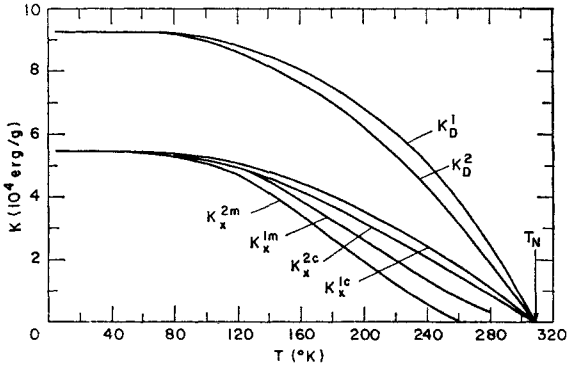

FIG. 16. Anisotropy energy of Cr_2O_3 calculated from the AFMR results. Dipolar contribution is given by K_D^1, and crystalline field contribution is given by K_x^{1c} (sign opposite to that of K_D^1) calculated using only AFMR data at 4.2°K. The curve of K_x^{1m} is then deduced from the measured temperature dependence of the AFMR. The corresponding quantities K_D^2, K_x^{2c}, and K_x^{2m} are obtained in a similar way, but a temperature-dependent exchange constant is included.

[41] D. N. Astrov, Soviet Phys.—JETP **13**, 729 (1961).
[42] M. Tachiki and T. Nagamiya, J. Phys. Soc. Japan **13**, 452 (1958).
[43] R. Newnham (private communications).
[44] J. E. Geusic, Phys. Rev. **102**, 1252 (1956).

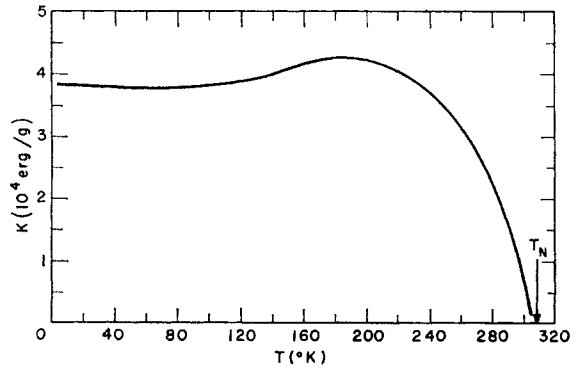

FIG. 17. Anisotropy energy of Cr_2O_3 vs temperature calculated from AFMR and static susceptibility data.

pendence of the calculated trigonal crystalline field contribution K_x^{1c} is then obtained with Eq. (15) when the low-temperature value of K_x^{1c} is determined from the experimental value of $(2\lambda K)^{1/2}$. Here, the measured low-temperature value of λ is used, and the quantity K is assumed to have only two contributions given by

$$K=K_D+K_x. \tag{16}$$

The K_x^{1c} curve thus presents the result of molecular field calculations, where λ is assumed to be independent of temperature. The corresponding measured value of the crystalline field contribution, given by K_x^{1m}, is determined by assuming Eq. (16) and subtracting K_D^1 from the experimentally determined value of K obtained $(2\lambda K)^{1/2}$ of Fig. 9. A corresponding set of curves, given by the superscript 2, was calculated by including the temperature dependence of $\chi_\perp$ of Fig. 8 in Eqs. (14) and (15) where we assumed that the change in $\chi_\perp$ reflects a change in the exchange constant, λ. The results of these calculations show that inclusion of a temperature-dependent λ leads to a somewhat poorer agreement of the data with the molecular field calculations. Because K_D and K_x are of opposite sign, and almost equal in magnitude, the experimental results are quite sensitive to small variations of these quantities. The trigonal crystalline field term thus leads to the small anisotropy field in Cr_2O_3. For only K_{dipolar}, $(2\lambda K)^{1/2}$ would be 136 kG[42] instead of the observed value of 59 kG. That K_{fs} cannot be inferred from the dilute Cr^{3+} in Al_2O_3 data is also demonstrated.

There are several sources which can lead to the almost temperature-independent value of $(2\lambda K)^{1/2}$. First we expect that the molecular field approximation of K will not apply near T_N. It has been observed from nuclear magnetic resonance (NMR) experiments[45] in MnF_2 that the sublattice magnetization drops less rapidly than $B_{5/2}$. A similar behavior of $B_{3/2}$ for Cr_2O_3 would lead to better agreement of K_x^m with K_x^c. Experimental determinations of $M(T)$ by NMR or possibly by the magnetoelectric effects [41,46] would be helpful in evaluating this contribution. In addition to $M(T)$ effects, there may be an appreciable change of D with temperature. Greenwald[47] has measured the distortion which takes place in Cr_2O_3 in the region of T_N and below. There is a small $(\Delta c/c=4\times10^{-4})$ expansion along the c direction within 30 deg of T_N, and a large $(\Delta a/a=4\times10^{-3})$ contraction along the a direction from T_N to 95°K. The value of c/a increases by about 0.5% as the temperature is reduced from T_N to 95°K, whereas c/a is about 0.5% less for Al_2O_3 than it is for Cr_2O_3.

If the trigonal contribution to D is sensitive to small lattice parameter changes, experiments with the isomorphous mixed crystals of Cr_2O_3 and Al_2O_3 should show a marked variation with concentration. Such AFMR experiments showed a very rapidly varying K_x as a function of Al^{3+} concentration. As the concentration of Al^{3+} in $(Cr_2O_3)_{1-x}\cdot(Al_2O_3)_x$ was increased to $x=0.2$, the value of $(2\lambda K)^{1/2}$ at 4.2°K increased to over 80 kG although λ decreased for these mixed crystals.[29,48] Linear extrapolation of K_x in these alloys to ruby (Al_2O_3 with less than 1% Cr^{3+}) gave a value of D which was within a factor of two of that determined by paramagnetic resonance. If D is as sensitive to lattice parameters as it appears to be, the dependence of the AFMR on pressure should be marked. In order to examine this problem further, AFMR experiments with applied uniaxial stresses are in progress.

Sensitivity of the trigonal contribution of the anisotropy of the Cr_2O_3 system to lattice parameter also leads to a natural explanation of the temperature independent linewidth. Lattice defects, lineage, and inhomogeneous strain effects can lead to an appreciably broadened AFMR line because the local AFMR resonance field is modulated by the varying anisotropy energy. We then have $\Delta H=[(2\lambda K)^{1/2}\times(1+\Delta K/2K)]$ which shows that the line width includes a large multiplying factor of $(2\lambda K)^{1/2}$. A temperature-independent linewidth of 1 kG could thus be produced by a 3% spread in K. Since $(2\lambda K)^{1/2}$ is almost independent of temperature we expect that the linewidth would also be independent of temperature. The linewidth then would be expected to vary depending on the crystal perfection.

Tachiki[49] has suggested that the temperature independence of $(2\lambda K)^{1/2}$ may be caused by changes in K_d due to variations in the average position of the Cr^{3+} in the corundum lattice if the anharmonic term in the potential for the Cr^{3+} ion is sufficiently large. A similar mechanism[49] is suggested for the change in sign of anisotropy for αFe_2O_3.

The absolute magnitude and sign of K_d have not yet been discussed. Since it is not expected that a detailed calculation of the crystalline-field contribution to the anisotropy will be available in the near future, the experimental measurements have been pursued in order to evaluate this contribution in the concentrated spin

[45] V. Jaccarino and R. G. Shulman, Phys. Rev. **107**, 1196 (1957).
[46] A recent review is given by G. T. Rado and V. J. Folen, Suppl. J. Appl. Phys. **33**, 1126 (1962).
[47] S. Greenwald, Nature **177**, 286 (1956).
[48] S. Foner, J. Phys. Soc. Japan, Suppl. B1, **17**, 424 (1962).
[49] M. Tachiki (private communication).

system. Recently, several optical measurements have been completed which support the interpretation of our earlier AFMR results. McClure[50] has examined the optical properties of Cr_2O_3 and from his data he concluded that D for Cr_2O_3 is opposite in sign to that in ruby. He was not able to reconcile this result with a point charge calculation unless he assumed that the Cr^{2+} ion was displaced by about 0.1 Å from the position which would be occupied by an Al^{3+} ion in ruby. The larger ionic radius of Cr^{3+} (0.63 Å) versus that of Al^{3+} (0.51 Å) suggests that this approach is reasonable. A similar conclusion was reached by Geschwind and Remeika[51] although they suggest that a point-charge calculation is still not expected to give a reliable result. These authors also point out that a 5% change in the position of an Al^{3+} ion would change the sign of the field gradient at the site.[52] Wickersheim[53] has examined the optical properties of Cr_2O_3 below T_N and by choosing a particular level scheme for transitions between the ground state and the R_1, R_2 excited states, he has been able to measure the sign of D (which turns out opposite to that of ruby). The magnitude of D at 4.2°K is about 1/2 of the AFMR result if we assume that the optical splitting is proportional to the ground-state splitting. Unfortunately, the optical lines broaden at temperatures above 77°K, so that it is difficult to follow the variation of D at high temperatures. There thus now appears to be general agreement of several experiments that the trigonal component of the crystalline field can be very sensitive to the position of the metal ions, and that the parameter D for Cr_2O_3 is small and of opposite sign to that of Cr^{3+} in Al_2O_3.

V. SUMMARY

The AFMR in Cr_2O_3 follows the general dependence predicted by the molecular field approximation as a function of temperature, frequency, field, and angle if independent measurement of λ, the exchange constant, and α, the ratio of parallel to perpendicular suceptibility, derived from static magnetic susceptibility measurements, are included. The data include frequencies from dc to 135 kMc/sec and temperatures from 4.2 to 310°K. The quantity $(2\lambda K)^{1/2}$ is almost independent of temperature up to 260°K. The value of K is smaller than that expected from only dipolar contributions, and if this is caused by a compensating trigonal crystalline field contributions, we conclude that the trigonal contribution is about 1/9 and of opposite sign to that of ruby. Various recent optical experiments confirm this observation. The almost constant value of $(2\lambda K)^{1/2}$ and the magnitude of the trigonal contribution to K appear to be caused by sensitivity of K to lattice parameter.

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[50] D. S. McClure, J. Chem. Phys. **36**, 2757 (1962); H. A. Weakleim and D. S. McClure, Suppl. J. Appl. Phys. **33**, 347 (1962).

[51] S. Geschwind and P. J. Remeika, Suppl. J. Appl. Phys. **33**, 390 (1962).

[52] Reference 51 notes that NMR data to be published by N. Laurence, E. C. McIrvine, and J. Lambe also shows evidence for displacement of metal ions in corundum.

[53] K. A. Wickersheim (private communication, to be published in Eighth Conference on Magnetism and Magnetic Materials, Pittsburgh, Pennsylvania, November 1962). Calculations by J. O. Artman and J. C. Murphy [J. Chem. Phys., (to be published) and private communications] are also in accord with our results.

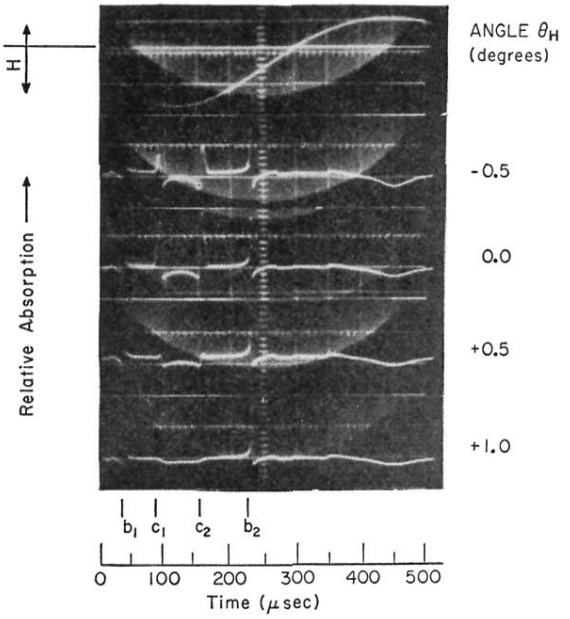

FIG. 13. Spin-flop resonance at 77°K in Cr_2O_3. The top curve shows H_0 vs time corresponding to the lower traces of relative absorption at 69.9 kMc/sec vs time. The low-field AFMR data (b_1,b_2) is plotted in Fig. 11. The SFMR resonances (c_1,c_2) at high field are plotted in Fig. 5. Note the limited range of θ_H for the SFMR mode. The reproducibility of the pulsed field is indicated by part of the AFMR line which happens to occur near the peak value of the second half-cycle (at 450 μsec) of the pulsed field.