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Antiferromagnetism in a Cr_2O_3 Crystal*

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A Cr_2O_3 single crystal was grown by the flame fusion method. It has rhombohedral symmetry and showed an antiferromagnetic Curie temperature (T_c) of 307°K. Below T_c the magnetic susceptibility χ perpendicular to the [111] direction is almost independent of temperature while the value of χ parallel to [111] approaches zero at very low temperatures. According to the Van Vleck theory, this behavior indicates that the spins are aligned along [111]. Above 77°K the parallel susceptibility was found to be proportional to the $\frac{3}{2}$ power of the temperature. Resonance measurements (23 500 Mc/sec) at the Curie temperature showed a shift in the peak of the absorption curve as a function of temperature. This shift was towards lower magnetic fields, and exhibited an anisotropy effect depending on the direction of the magnetic field which is in agreement with theory. From the temperature dependence of the resonance absorption and the Kittel theory of antiferromagnetic resonance, an estimate of the anisotropy constant and its temperature dependence can be made.

I. INTRODUCTION

FROM powder measurements of magnetic susceptibility first made by Honda and Soné,[1] and neutron diffraction by Brockhouse,[2] chromium sesquioxide is known to be antiferromagnetic with a Curie temperature in the region of 305° to 315°K. It has rhombohedral symmetry which can be thought of as a cube stretched along a body diagonal or along a [111] direction. The neutron diffraction results show that there is a single magnetic axis along which the electron spins are aligned; however, this axis was not uniquely determined. Greenwald,[3] from x-ray diffraction measurements of Cr_2O_3, has found nonlinear changes in the lattice parameters with temperature; an expansion in the [111] direction and a contraction perpendicular to it. Knowing that a single magnetic axis exists and using the Li[4] theory of magnetocrystalline deformations, the x-ray study gives evidence that the spin axis is along the [111] direction.

The discovery that electronic magnetic resonance effectively disappeared in an antiferromagnet was first made by Trounson *et al.*[5,6] using Cr_2O_3. There is a very abrupt disappearance of the absorption peak as the temperature of the material is lowered through the Curie point. Since the resonance measurements were made on powder material, detailed information about the resonance transition is difficult to obtain. This paper reports on both the magnetic susceptibility and microwave resonance for a single crystal of Cr_2O_3 and compares the results with existing theory and data on polycrystalline materials.

II. PREPARATION OF SAMPLE

The single crystal was prepared by the Verneuil (flame fusion) technique[7] using a powder obtained by the thermal decomposition of ammonium dichromate.[8] Chemical analysis[9] showed impurities of 0.3% by weight and a chromium content given by the formula $Cr_{1.95}O_3$. Since the oxygen was determined by weight difference a slight error in the chromium content, about 1%, could also lead to the above formula. From outward appearances, as well as from the measurements reported in this paper, the crystal seemed to be in excellent condition. The sample was annealed from 1200°C at approximately one degree per minute.

III. MAGNETIC SUSCEPTIBILITY

The magnetic susceptibility measurements were made by the body-force method[10] using fields up to 10 000 gauss. The direction representing the minimum susceptibility (χ) was identified from the symmetry of the Laue x-ray pattern to be the [111] direction. In Fig. 1 is shown the susceptibility perpendicular ($\chi_\perp$) and parallel ($\chi_{\parallel}$) to [111]. From 77°K to room temperature, $\chi_{\parallel}$ is proportional to $T^{\frac{3}{2}}$ while $\chi_\perp$ is almost temperature independent. There is, however, a very slight increase in $\chi_\perp$ at temperatures near 77°K. In the region of the Curie temperature the two susceptibilities differ by over 1%. At all temperatures, both $\chi_{\parallel}$ and $\chi_\perp$ were independent of the magnetic field. The susceptibility measurement is difficult to make in the direction parallel to [111] because this is an unstable position. Since the specimen is mounted on the end of a long thin quartz fiber loosely coupled to a balance arm, there is a tendency for it to turn in the direction of maximum susceptibility ($\chi_\perp$). Unless considerable care

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* A preliminary report of this work was given at the Baltimore Meeting of the American Physical Society [Phys. Rev. **98**, 1562(A) (1955)].

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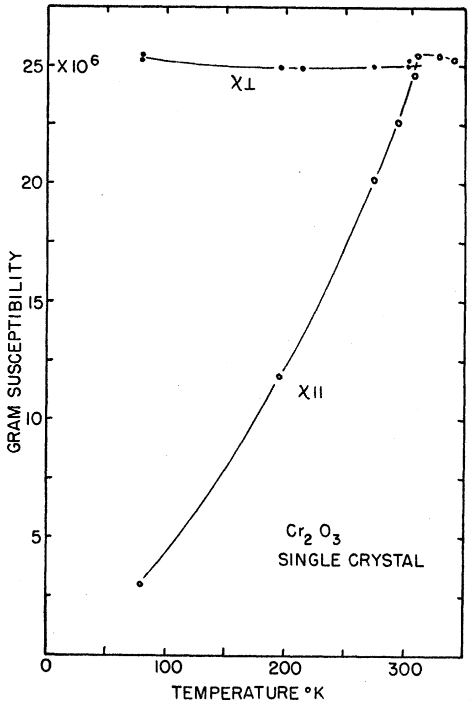

FIG. 1. Temperature-dependent magnetic susceptibility of a Cr_2O_3 single crystal perpendicular ($\chi_\perp$) and parallel ($\chi_\parallel$) to the [111] direction.

is taken this can be misinterpreted as an apparent magnetic field dependence of $\chi_\parallel$.

The theory of antiferromagnetism proposed by Van Vleck[11] predicts that below the Curie temperature the susceptibility of a single crystal should decrease with decreasing temperature in the direction that the electron spins are aligned, while perpendicular to the spin axis the susceptibility is constant. This means that for Cr_2O_3 the spin system is aligned along the [111] direction.

Van Vleck also calculated $\chi_\parallel$ as a function of temperature:

$$\chi_\parallel = C_M \frac{3S_0(S_0+1)^{-1}B'(y^0)}{T-3S_0(S_0+1)^{-1}B'(y^0)\theta}, \qquad (1)$$

where C_M is the molar Curie constant, $y^0 = 2zS|J,S_0|/kT$, S_0 is the spin-only value which for Cr^{+++} is $\frac{3}{2}$, and B' is the derivative of the Brillouin function. The above equation is for a body-centered cubic lattice and is not strictly applicable to the corundum structure of Cr_2O_3, but it gives some idea of the behavior predicted by theory. Using the value $\theta = -360$ and $T_c = 307$°K, Eq. (1) is plotted as the dashed curve in Fig. 2. The curve shown is actually a reduced plot in the sense that the susceptibility from Eq. (1) at the Curie temperature is made to agree with the single-crystal value at T_c and the rest of the curve is proportionately reduced. It is seen from the shapes of the two curves that there is only approximate agreement. Smart[12] has pointed out a similar behavior for MnO.

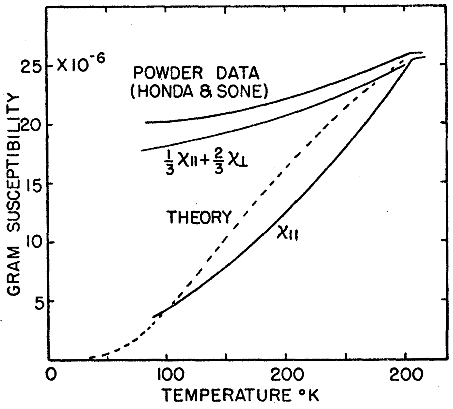

FIG. 2. Various magnetic susceptibility curves for Cr_2O_3.

To compare the powder susceptibility with the single-crystal susceptibilities, the following relation is used:

$$\chi_c = \tfrac{1}{3}\chi_\parallel + \tfrac{2}{3}\chi_\perp. \qquad (2)$$

χ_c is plotted in Fig. 2 in comparison with the experimental data of Honda and Soné.[1] Powder Cr_2O_3 measured by us was also high in comparison with χ_c. The lack of agreement is significant in that it illustrates the difficulty of using powder and $(\chi_\perp - \chi_\parallel)$ measurements on a single crystal to obtain $\chi_\perp$ and $\chi_\parallel$ individually.

Bizette and Tsai[13] have discussed the lack of agreement of susceptibility data between powder and single crystals of MnF_2. They conclude that in measurements of powder susceptibility the larger value of χ is due to reorientation of the small crystallites of the powder in favor of $\chi_\perp$. Thus χ can increase with increasing magnetic field. According to them, if particle motion is prevented by fixing the grains in paraffin, the susceptibility remains field-independent.

Nagamiya[14] has obtained formulas for the dependence of the susceptibility with the applied field which shows that it varies proportionally to the square of the field and inversely as the anisotropy constant. For those compounds such as Cr_2O_3 which show no field dependence of susceptibility, a large anisotropy might therefore be expected.

IV. MICROWAVE RESONANCE ABSORPTION

The microwave study of Cr_2O_3 crystal was made with apparatus described by Maxwell and McGuire[6] using a frequency of 23 500 Mc/sec. At approximately 34°C the resonance disappears as the temperature is lowered. Its disappearance has three important characteristics. The resonance curves become broader and at

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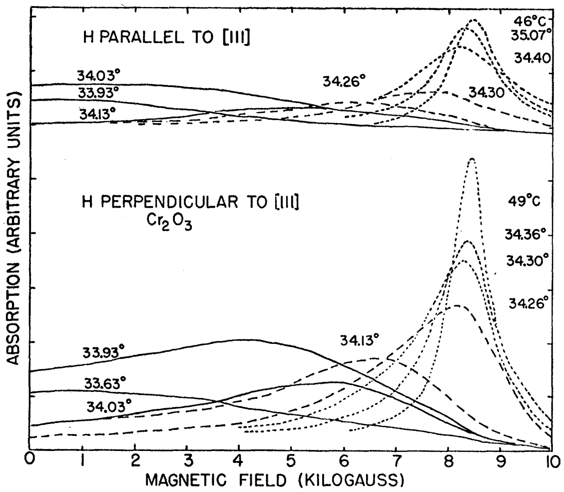

FIG. 3. Microwave resonance absorption at 23 500 Mc/sec with the static field parallel and perpendicular to the [111] directions for a series of temperatures.

the same time shift toward lower magnetic fields as shown in Fig. 3. In addition, there is a temperature difference between equal g values (Fig. 4) depending on whether H is parallel or perpendicular to [111]. In powder measurements the shift in resonance as well as the anisotropy of g were not explicitly observed.[6]

The two sets of absorption curves (Fig. 3) were taken under identical conditions except that the crystal was rotated from [111] parallel to [111] perpendicular to H, the applied static magnetic field. The specimen was located in the center of a full-wave cavity, and the microwave field was perpendicular to H. During a measurement sequence involving a rotation of the crystal, the temperature of the cavity was maintained constant within approximately 0.03°K and the microwave power was also kept constant. This means that the relative amounts of absorption can be compared. We see that the absorption is strongest for H perpendicular to [111]. The nonsymmetry of the absorption as it shifts to lower magnetic fields makes it difficult to estimate half-widths.

The disappearance of the resonance absorption below the Curie temperature was explained by Kittel,[15] who derived the resonance condition:

$$\omega/\gamma = H_0 \pm [H_A(H_A + 2H_E)]^{\frac{1}{2}}, \tag{3}$$

where H_A and H_E are the anisotropy and exchange fields, respectively, and γ is the gyromagnetic ratio. There is an effective field added or substracted from the applied field H_0 which can account for a shift as found above. Although Eq. (3) will be applied to these data measured near the Curie temperature, it must be remembered that (3) was derived for magnetic saturation and a cubic lattice.

If H_A is considerably smaller than H_E, the effective field reduces to

$$H_{\text{eff}} = \pm[2H_AH_E]^{\frac{1}{2}} = \pm[2\lambda K]^{\frac{1}{2}}, \tag{4}$$

where we have made the substitutions $K = H_AM$ and $H_E = \lambda M$, with M the magnetic moment per unit volume for a sublattice, K the anisotropy constant, and λ the molecular field coefficient.

It is known that the ferromagnetic anisotropy constant, K, is strongly dependent on the temperature and is given at low temperature by the relation $K(T)/K(0) \cong (M_T/M_0)^m$, where $m=10$. According to theory[16] the "tenth-power" gradually drops with increasing temperature. The above statements refer to ferromagnetic anisotropy in a cubic crystal.

Near the Curie temperature of an antiferromagnet, we assumed $K(T) = B(T_c - T)^n$; then, from (4),

$$H_{\text{eff}} = (2\lambda B)^{\frac{1}{2}}(T_c - T)^{n/2}. \tag{5}$$

The data shown in Fig. 4 can be used to establish approximate values for n and K using (5). This can only be done, however, if T_c is chosen and for this analysis a value of $T_c = 34.48$°C was taken. Inspection of Fig. 4 indicates that this T_c is below the point where the shift in resonance is first observed. It is perhaps equivalent to neglecting the small tail that is associated with magnetization curves at the Curie temperature due to short-range order. H_{eff} is given by the difference in the resonance fields above and below the Curie temperature. When H_{eff} is plotted with respect to $T_c - T$ on log-log paper, a value of $n = 7/2$ is found. Fields below 200 gauss are neglected. Large values of n in Eq. (5) lead to an estimate that K can easily have values 10^8 to 10^{10} ergs/cc at low temperatures. Large anisotropy energies such as these are in agreement with values Li[3] found necessary to explain deformations in the crystal structure of antiferromagnetics at the Curie temperature.

In the powder sample of Cr_2O_3, no shift in resonance was observed.[6] What is observed, however, is a very pronounced lack of symmetry of the resonance curve toward lower magnetic fields somewhat similar to that shown in Fig. 3. This can be interpreted as a distribution of resonance curves depending on the angle each crystallite of the powder makes with the magnetic field. It is a direct consequence of the anisotropy occurring when

TABLE I. Experimental values of the resonant field combinations expected to equal 1 and 2, respectively, near T_c and 0°K.

T(°C)	For T_c	For 0°K
34.45	1.005	1.98
34.4	1.005	1.97
34.3	1.09	1.98
34.2	1.25	1.99
34.1	1.45	1.95
34.0	1.37	1.62

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H is parallel or perpendicular to [111] as shown in Fig. 4.

It has been pointed out by Wangsness[17] that these resonance data obtained just below the Curie temperature now enable one to make a quantitative test of the detailed predictions of the semiclassical theory of antiferromagnetic resonance. For this purpose it is most convenient to use the formula given by Nagamiya[14] for the resonance field H_0 as a function of frequency and the angle θ made by the constant field with the direction of spin alignment:

$$\begin{aligned}&[\alpha^2\cos^2\theta+\alpha(1+\alpha)\sin^2\theta\cos^2\theta]h^4\\&\quad-[(1+\alpha^2+2\alpha G^2)\cos^2\theta+(1-G^2)\sin^2\theta]h^2\\&\qquad+(1-G^2)^2=0,\end{aligned}$$

where $h=H_0/H_p$, $\alpha=1-(\chi_{\parallel}/\chi_{\perp})$, $G=(2H_AH_E)^{\frac{1}{2}}/H_p$, and $H_p=\omega/\gamma$ is the resonance field in the paramagnetic state. If we let $\theta=0$ and $\pi/2$, we get two equations for $H_{\parallel}$ and $H_{\perp}$, respectively, from which G can be eliminated to give the following relation which involves only experimentally determined quantities:

$$(\alpha H_{\parallel}{}^2+H_{\perp}{}^2)/H_{\parallel}H_p=1+\alpha. \tag{6}$$

Since $H_p>H_{\parallel}$, the above equation is easily seen to predict that $H_{\perp}>H_{\parallel}$ for all values of $\alpha\neq 0$ which agrees with our results. Near the Curie temperature ($\alpha\simeq 0$), we should expect our data to approximately satisfy the relation $H_{\perp}{}^2/H_{\parallel}H_p=1$, and if results were available near 0°K ($\alpha\simeq 1$), they would be connected by the formula $(H_{\parallel}{}^2+H_{\perp}{}^2)/H_{\parallel}H_p=2$. In Table I, we give the experimental values of both of these combinations, although, of course, our data were obtained only near T_c. We see that the results satisfy the relation applicable at T_c quite well, the agreement being extremely good very near to the Curie temperature.[18] Surprisingly enough, they also agree closely with the value predicted for the formula derived for 0°K. In principle, Eq. (6) could be used to determine α from the resonant fields and thus should enable one to study the temperature dependence of the susceptibilities near the Curie temperature where the resonances are observable; in our case, the results obtained for α in this way were not consistent, since small errors in $H_{\parallel}$ and $H_{\perp}$ result in large uncertainties in α.

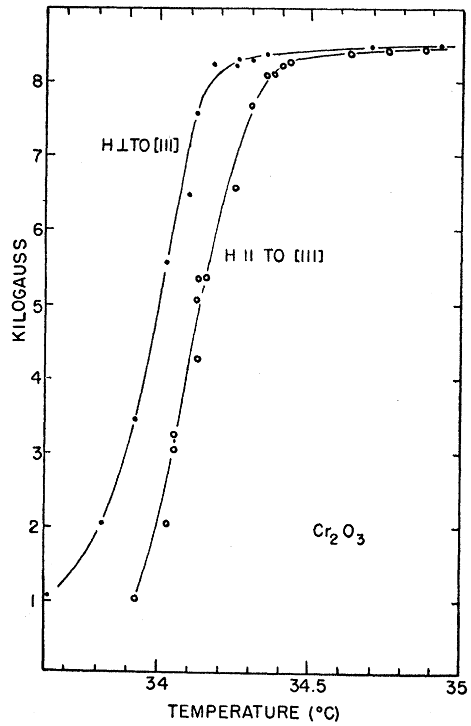

FIG. 4. Temperature dependence at the Curie temperature of the resonant magnetic field both parallel and perpendicular to [111].

Since Cr_2O_3 is not cubic, the agreement of our data with Eq. (6), which was derived for cubic symmetry, seems sufficiently good to show that the semiclassical resonance theory is quite adequate for use even close to the Curie temperature.

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