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HIGH FIELD DATA AND ANISOTROPY FOR Mn₃O₄

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Résument. — Les propriétés magnétiques statiques de monocristaux de Mn₃O₄ ont été mesurées entre 4.2 °K et la température ambiante. En dessous du point de Néel (42 °K), l'axe c est une direction de difficile aimantation \( K_c = -1.60 \times 10^7 \text{ ergs cm}^{-3} \) à 4.2 °K. L'anisotropie persiste dans la phase paramagnétique entre le point de Néel et 100 °K. L'aimantation spontanée extrapolée à 0 °K est 1.84 \( \mu_B \)/mole, suggérant une structure de spin non colinéaire.

D'après nos mesures nous proposons qu'en dessous du point de Néel les spins sont tous dans le plan de base.

Abstract. — The static magnetic properties of single crystals of Mn₃O₄ have been measured from 4.2 °K to room temperature. Below the Néel point (42 °K) the c-axis is a magnetically hard direction \( K_c = -1.60 \times 10^7 \text{ ergs cm}^{-3} \) at 4.2 °K. The anisotropy persists in the paramagnetic phase from the Néel point up to 100 °K. The spontaneous magnetization extrapolated to 0 °K is 1.84 \( \mu_B \)/mole, suggesting a canted spin arrangement. From our static measurements we propose that below the Néel point all spins lie in the basal plane.

Single crystals of Mn₃O₄ (haussmannite), have been grown from a Borax-flux according to [1]. Below 1450 °K the crystal structure is a tetragonally distorted spinel, with \( c/a = 1.16 \) at room temperature. The following description however is given in terms of the chemical bc unit cell where \( c/a = 1.16 \times \sqrt{2} = 1.64 \).

I. Spontaneous magnetization. — From low field measurements (10 kG), Dwight and Menuyk [2] showed the a-axis to be an easy direction of magnetization. We have measured the high field (max 60 kG) a-axis magnetization. The isotherms on figure 1 show an anomalous curvature for temperatures close to the transition point (42 °K), and in fact this point cannot be determined from the spontaneous magnetization obtained by zero-field extrapolation. Figure 2 shows these extrapolations below 40 °K. The 0 °K extrapolation on figure 2 of 1.84 \( \mu_B \)/mole agrees with the result from [2].

![Fig. 1. Magnetization in an a-direction vs. applied field.](image)

![Fig. 2. Zero-field extrapolated a-axis magnetization (= \( M_a \)) and inverse susceptibilities.](image)

II. Anisotropy in (100). Paramagnetic susceptibility. — In a c-direction the magnetization is linear with field over the whole temperature range except between 28 °K and 44 °K, where a slight saturation effect is observed above 40 kG. Below the Néel point the anisotropy energy \( E_c \) referred to this direction can then be written \( E_c = K_c \sin^2 \theta \), where \( \theta \) is the magnetization inclination with c-axis. At 4.2 °K,

\[
K_c = -1.60 \times 10^7 \text{ ergs cm}^{-3}
\]

and \( K_c/M_s = -74 \text{ kG} \).

From the reciprocal susceptibilities shown in figure 2 it follows that the Néel point is determined most accurately from the discontinuity in \( 1/x \) at 42 °K. In the high temperature range our results agree satisfactorily with Rosenbergs data on polycrystalline samples [3], and the paramagnetic anisotropy vanishing at 100 °K has previously been observed by Moruzzi [4].

III. Neutron diffraction. — From previous measurements (Dwight [2], Jacobs [5]) it is assumed that the magnetic structure below the Néel point is a canted arrangement. With raising temperature it follows from molecular field theory that this state must...
be superseded by another ordered state before reaching the disordering temperature. In order to confirm this we have measured the neutron diffraction pattern at 4.2 °K. All magnetic reflections could be indexed according to an orthorhombic doubling in a direction of the chemical unit cell, in agreement with Kaspers result [6]. The most intense pure magnetic reflexion ((001)orthorhombic or (101)orthorhombic) was followed with temperature and it showed a sharp disappearance at 42 °K. At 50 °K we made a new diffraction pattern which neither revealed a magnetic superstructure nor a magnetic contribution to the nuclear peaks compared with room temperature intensities.

IV. Discussion. — The analysis given here is based on the Yafet-Kittel model as treated by Lotgering [7] and extended by Dwight and Menuyk [2] to include magnetocrystalline anisotropy. Their notation is used throughout this discussion. The low spontaneous magnetization at 0 °K has previously been explained from a canted spin configuration: A-site spins are supposed collinear in the basal plane, and B-spins inclined an angle $\psi$ with the A-spins. The resultant of the B-spins is antiparallel with the A-spins. Subdividing the spin system into two A- and B-lattices respectively, the molecular fields may be written

\[
\mathbf{h}_A = -n[a_{21} + b_1 + b_2] \\
\mathbf{h}_B = -n[a_{12} + a_2 + \beta b_1 + \beta b_2],
\]

where $a_1$, $a_2$, $b_1$, and $b_2$ are the respective sublattice magnetizations. $a_1 = |a_2| = |a|$ and $|b_1| = |b_2| = |b|$.

Following [2] we suppose, that the octahedral coordinated B-site Mn$^{3+}$-ions account for the observed c-axis anisotropy energy. Further we suppose, that the magnetocrystalline energy for the B-spins can be written $E_B = K_B \cos^2 \psi$. Then the equilibrium angle $\psi_0$ is given by

\[
\cos \psi_0 = a/b(1 + \kappa) \quad \text{where} \quad \kappa = K_B/nb^2.
\]

If a magnetic field $\mathbf{H}$ is applied in an a-direction, the equilibrium conditions for all individual ions lead to the following total magnetization:

\[
M_a = M_0 + \chi_{res} \cdot H
\]

\[
= 2a \left[ 1 - \frac{1}{\beta + \kappa} \right] + \frac{1}{n(\beta + \kappa)} \cdot H
\]

where $M_0$ is the spontaneous magnetization and $\chi_{res}$ is the residual susceptibility for high fields. For a field applied in the c-direction we obtain

\[
M_c = \chi_{res} \cdot H = \left[ - \frac{(\cos \psi_0 - a/b)^2}{nK \cos 2 \psi_0} + \frac{a/b}{\cos \psi_0} \right] \chi_{res} \cdot H
\]

(2)

In order to discuss the structure at 0 °K we need the paramagnetic asymptotic Curie temperature $T_a$ which is taken from our high temperature data. We find $T_a \approx -640$ °K. The theoretical expression for $T_a$ is

\[
T_a = \frac{3n}{C_A + 2C_B} \left[ \frac{1}{6} C_A^3 + C_A^2 C_B + \frac{4}{3} C_A C_B \right]
\]

where $C_A$ and $C_B$ are the respective sublattice Curie constants. Now at 0 °K we must consider two cases: $\psi_0 = 66.7$ and $\psi_0 = 31.8$ degrees, both angles resulting in $M_a = 1.84 \mu_0$/mole. If $\psi_0 = 66.7$ degrees we find from (1) (neglecting $\kappa$) $\beta = 1.58$ and $n = 42.4$. Inserting these values in the expression for $T_a$, and assuming the spin-only values for the Curie constants, we find $\kappa = 6.4$ and therefore $\beta \approx 1$. Showing that this state is impossible. If $\psi_0 = 31.8$ degrees we find $\beta = 0.73$ and $n = 92$ which yields $\kappa \approx 0$. Considering eq. (2) for $\psi_0$ we find that the last term equals 0.54 $\chi_{res}$, and from figure 2 we see that $\chi_0 \approx 4.8 \chi_{res}$. This means that the first term in (2) must be positive which requires $\kappa$ to be negative. But in that case the B-spins will be in an energy minimum when they lie in the basal plane. Therefore we tentatively propose that all spins lie in the basal plane in contradiction to previous assumptions. However, with our values of $n$ and $\beta$ and any reasonable value of $\kappa$ we at present can give neither a quantitative interpretation of the observed anisotropy in $\chi$ for 42 °K $< T \approx 100$ °K nor of the detailed behaviour of $\chi$ for $T \approx 100$ °K.

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References