INVESTIGATION OF WEAK FERROMAGNETISM IN THE $MnCO_3$ *SINGLE CRYSTAL*

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The magnetic properties of a very pure natural $MnCO_3$ single crystal have been studied in the temperature range from 1.3 to 300°K. In accord with the predictions of the theory,[7] it has been found that the ferromagnetic moment σ is observed only in the basal plane. Along the triple axis, the crystal is paramagnetic. The temperature dependence of σ, $\chi_\perp$, and $\chi_\parallel$ has been investigated in detail through the entire region of existence of antiferromagnetic ordering. It is shown that, in agreement with the theory of second-order phase transitions, $\sigma/\chi_\perp \sim \sqrt{T_N - T}$ near the transition point.

At low temperatures, σ is proportional to T_2 in a broad range from 1.5 to 23°K ($0.7\,T_N$). The dispersion law and the temperature dependences of the thermodynamic quantities for antiferromagnets with magnetic structure of the $MnCO_3$ type have been obtained by the spin-wave theory method. In this case the spontaneous magnetization vector is perpendicular to the crystal axis. As a result, the gap associated with the anisotropy field is missing from the energy spectrum. The theoretical formulas obtained are in qualitative agreement with the experimental results. The possible causes of the large quantitative discrepancy between the values of the coefficients that determine the temperature dependence of σ and $\chi_\perp$ are discussed.

1. INTRODUCTION

THE problem of weak ferromagnetism in antiferromagnets has been attracting considerable attention recently. This phenomenon was observed first experimentally in hematite (α-Fe_2O_3) by Smith[1] as early as in 1916, long before the discovery of antiferromagnetism. The magnetic properties of hematite single crystals have been investigated later in detail by Neel and Pauthenet,[2] while Shull, Strauser, and Wollan[3] proved via neutron diffraction that this compound is antiferromagnetic. The strong dependence of the ferromagnetic properties hematite on the method of preparation of the specimen[4] has led most investigators[2,3,5] to believe that this phenomenon is due to impurities and to lattice defects. Carbonate salts of the elements of the iron group have the same crystallographic structure as hematite. The presence of weak ferromagnetism in $MnCO_3$ and $CoCO_3$ was observed by the author and Orlova.[6] It was shown that the observed weak ferromagnetism was independent of the chemical production of the compounds, and the hypothesis was advanced that it was due to the spins not being completely parallel during the antiferromagnetic ordering. Dzyaloshinskiĭ[7] has shown that antiferromagnetic ordering with incompletely parallel spins is a necessary consequence of the symmetry of the magnetic structure, both in the case of $MnCO_3$ or $CoCO_3$ and in the case of hematite. His detailed thermodynamic investigation of the magnetic properties of such substances led to many interesting conclusions regarding the anisotropy and temperature dependence of the ferromagnetic moment and the paramagnetic susceptibility. To test experimentally the theoretical conclusions, we undertook the investigation of the magnetic properties of single-crystal $MnCO_3$, the results of which are reported in this paper.

Another feature of antiferromagnets with magnetic structure of the $MnCO_3$ type is that the vector of spontaneous magnetization in them does not have one fixed direction, but may rotate almost freely in the basal plane of the crystal. Calculations, given in the first part of this paper, show that one of the branches of the energy spectrum of the spin waves has practically no gaps. As a result, starting already with temperatures less than 1°K, the spontaneous magnetization, the susceptibility, and the specific heat should obey simple power laws. An important advantage of such objects for experimental verification of the theory of spin waves has caused us to make a detailed study of the temperature dependence of the spontaneous magnetization and susceptibility of $MnCO_3$ at low temperatures. The results of these meas-

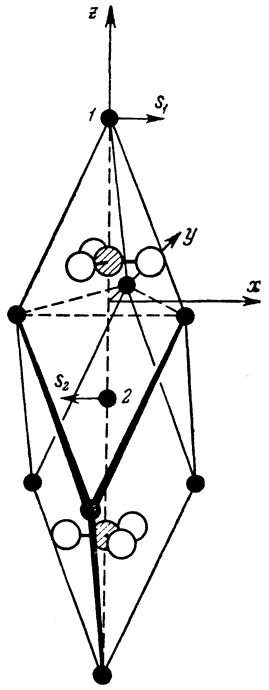

FIG. 1. Structure of $MnCo_3$. Black circles – Mn, white ones – O, crosshatched – C.

urements are reported and compared with the conclusions of the spin-wave theory in the second part of this paper.

2. THEORY

1. $MnCO_3$ has a rhombohedral structure.[8] Its elementary cell (see Fig. 1) contains two metallic ions, 1 and 2. We denote their mean spins as $\mathbf{s}_1$ and $\mathbf{s}_2$. We introduce the molar quantities $\mathbf{M}_1 = N\mathbf{s}_1/2$ and $\mathbf{M}_2 = N\mathbf{s}_2/2$, and their linear combinations $\boldsymbol{l} = \mathbf{M}_1 - \mathbf{M}_2$ and $\mathbf{m} = \mathbf{M}_1 + \mathbf{M}_2$. In the future we shall use a coordinate system in which the z axis is aligned with the trigonal axis, the x axis with one of the binary axes, and the y axis lies in the symmetry plane.

It was shown by Dzyaloshinskiĭ[7] that if the elementary cell does not change in such a structure during antiferromagnetic transition, three types of ordering are possible in the absence of a magnetic field:

I. The antiferromagnetic vector $\boldsymbol{l}$ coincides with the z axis and there is no ferromagnetic moment $\mathbf{m}$.

II. The antiferromagnetic vector $\boldsymbol{l}$ is directed, in the first approximation, along the y axis; there is a weak ferromagnetic moment $\mathbf{m}$ directed along the x axis. In the second approximation the vector $\boldsymbol{l}$ has a small component along the z axis.

III. The antiferromagnetic vector $\boldsymbol{l}$ is directed along the x axis; there exists a weak ferromagnetic moment $\mathbf{m}$, direct in first approximation along the y axis, with a small component along the z axis in the second approximation.

As follows from our earlier paper[6] and also from the results of this investigation, the order-disorder transformation realized in the case of $MnCO_3$ is of type II or III. In what follows we refer indeed to these two types of order-disorder. Dzyaloshinskiĭ has shown that if a sufficiently strong magnetic field $\mathbf{H}$ is applied* the following situation occurs. If the field is applied in the basal plane, the vectors $\boldsymbol{l}$ and $\mathbf{m}$ rotate so that $\mathbf{m}$ is always parallel to $\mathbf{H}$ and $\boldsymbol{l}$ is perpendicular to $\mathbf{H}$. If $\mathbf{H}$ is directed along the z axis, then in the first approximation the antiferromagnetic vector $\boldsymbol{l}$ and the ferromagnetic moment always remain in the basal plane. A more detailed analysis of this case, as will be shown below, disclosed that the application of a field along the z axis may lead to rotation of the vector $\boldsymbol{l}$ in the basal plane.

2. To derive the temperature dependence of the magnetic properties near the transition point, we write down the thermodynamic potential† proposed by Dzyaloshinskiĭ, with allowance for terms up to fourth order in $\boldsymbol{l}$ and $\mathbf{m}$. Without loss of generality we can confine ourselves to an examination of the case when the magnetic field is perpendicular to the y axis.

$$\tilde{\Phi} = \frac{A}{2} l^2 + \frac{B}{2} m^2 + \frac{b}{2} m_z^2 - \beta m_x l + \frac{C}{4} l^4 + \frac{D}{2} l^2 m^2 + \frac{d}{2} l^2 m_z^2 - \mathbf{m}\cdot\mathbf{H}. \quad (1)$$

Minimizing this potential and putting, as usual, $A = \lambda'(T - T_N)$, we obtain

$$l \approx \sqrt{\lambda (T_N - T)}, \quad \lambda = \lambda'/C, \quad (2)$$

and for the magnetic moment in the basal plane

$$m_x = \frac{\beta \sqrt{\lambda (T_N - T)}}{B + D\lambda (T_N - T)} + \frac{H_x}{B + D\lambda (T_N - T)} = \sigma + \chi_\perp H_\perp \text{ for } T < T_N. \quad (3a)$$

In virtue of the isotropy of the magnetic properties in the basal plane, established in reference 7, this formula holds for any direction of the magnetic field in this plane. We have for the magnetic susceptibility along the trigonal axis

$$m_z = H_z/[B + b + (D + d)\lambda (T_N - T)] = \chi_\parallel H_\parallel \text{ for } T < T_N. \quad (3b)$$

*A sufficiently strong field is considered here one in which the magnetic energy $\mathbf{m}\cdot\mathbf{H}$ is much greater than the anisotropy energy in the basal plane. As will be seen from our experimental results, this condition is satisfied when H exceeds 2000 oersteds.

†The symbols we use here for several coefficients differ from those in reference 7. Attention should be called to the fact that similar letters are used for different coefficients in expansions (2) and (3) of reference 7: In Eq. (2) these are constants, and in (3) these are temperature-dependent quantities.

Above the transition point $l = 0$, and therefore

$$m_\perp = H_\perp / B = \chi_\perp H_\perp \text{ and } m_z = H_z/(B+b) = \chi_\parallel H_\parallel \text{ for } T > T_N. \quad (4)$$

Equations (3) and (4) describe the temperature dependence of the quantities measured in this investigation near the transition temperature.

3. The results of our measurement of the magnetic properties of $MnCO_3$ along the z axis (cf. below) display an anomaly, and a more detailed analysis of the behavior of m_z in fields commensurate with the anisotropy field was deemed advisable to explain this anomaly. For this purpose, we must consider the thermodynamic potential with inclusion of the terms that describe the anisotropy in the basal plane [Eq. (6) of reference 7]. To simplify the derivation we neglect in all further calculations the anisotropy of the susceptibility ($b = 0$) and the deviation of the antiferromagnetic vector from the basal plane ($\theta = \pi/2$). Then

$$\tilde{\Phi} = \frac{B}{2} m^2 + q(m_y \cos\varphi - m_x \sin\varphi) + \frac{D}{2}(m_x \cos\varphi + m_y \sin\varphi)^2 + e\cos 6\varphi + f m_z \cos 3\varphi - m_z H_z, \quad (5)$$

where φ is the angle between the direction of the antiferromagnetic vector and the x axis, and the previous remarks apply to the expansion coefficients. Minimizing (5) relative to m for a specified value of φ, we get

$$m_x = (q/B)\sin\varphi; \quad m_y = -(q/B)\cos\varphi; \quad m_z = H_z/B - (f/B)\cos 3\varphi. \quad (6)$$

Inserting (6) into (5) we find the dependence of $\tilde{\Phi}$ on φ and H_z:

$$\tilde{\Phi} = -q^2/2B - H_z^2/2B - e + 2(e - f^2/4B)\cos^2 3\varphi + (f H_z/B)\cos 3\varphi. \quad (7)$$

Differentiating this expression with respect to φ, we obtain two equations for the equilibrium value of the angle φ:

$$\sin 3\varphi = 0, \quad (e - f^2/4B)\cos 3\varphi = f H_z/4B. \quad (8)$$

Which of these conditions corresponds to the minimum of (7) depends on the sign of the coefficient* $e' = (e - f^2/4B)$.

If $e' < 0$, Φ has a minimum for all field intensities when $\sin 3\varphi = 0$. Thus, if a type III (see above) order-disorder is established in the absence of a field, it is retained at all values of H_z and

$$m_z = H_z/B + |f|/B. \quad (9a)$$

If $e' > 0$, the minimum of $\tilde{\Phi}$ at $H = 0$ occurs when $\cos 3\varphi = 0$. A type II order-disorder is established here. When the field H_z is applied, the angle φ begins to change such as to retain Eq. (8) in force. The rotation of the antiferromagnetic vector in the basal plane will continue until the field reaches a value $H_{cr} = 4e'B/|f|$. Here $\tilde{\Phi}_{II} = \tilde{\Phi}_{III}$ and the crystal will be in state III as the field is further increased. Thus, the magnetic moment in this case will change in the field in accordance with the following law

$$m_z = (1 + f^2/4Be')H_z/B \text{ for } H \ll 4e'B/|f|, \quad m_z = H_z/B + |f|/B \text{ for } H \gg 4e'B/|f|. \quad (9b)$$

It must be noted that the ferromagnetic moment $\sigma_z = |f|/B$ should be much less than the moment σ in the basal plane, considered above.

4. To obtain the theoretical temperature dependence of $m_\perp$ and $m_\parallel$ at temperatures close to absolute zero, we must resort to the theory of spin waves. The spin-wave theory for antiferromagnets was developed by several authors.[9-12] A very simple mathematical formalism for the theory of spin waves was developed by Kaganov and Tsukernik *[13] on the basis of a phenomenological examination of an antiferromagnet with two sublattices, characterized by magnetic moments specified as functions of the coordinates and of the time.†

All the theoretical investigations performed to date have considered uniaxial antiferromagnets, in which the direction of the spontaneous magnetization of the sublattices coincides with the principal axis of the crystal. In the case of $MnCO_3$ the spontaneous magnetization is perpendicular to the axis and this, as will be shown below, leads to a substantial modification of the spectrum of the spin waves.

We have used the calculation procedure proposed by Kaganov and Tsukernik to find the spectrum of antiferromagnets with magnetic structure of the $MnCO_3$ type. In accordance with the type of the thermodynamic potential (1) the Hamiltonian must be written in this case as follows:

*In the equilibrium state, the last term in (7) is always negative, since, regardless of the sign of f,

$$f\cos 3\varphi \leq 0. \quad (8a)$$

*An analogous investigation was carried out independently by Turov and Irkhin.[14]

†Dzyaloshinskii (private communication) points out that in the case of antiferromagnets such an approach is strictly phenomenological and involves a model in which the absolute value of the sublattice spontaneous-magnetization vector is independent of the applied field at absolute zero. This model is used in the determination of the ground state of the antiferromagnet.

$$\mathcal{H} = \int dv \left\{ \alpha \mathbf{M}_1 \cdot \mathbf{M}_2 + \frac{a+b}{2}(M_{1z}^2 + M_{2z}^2) + (b-a) M_{1z} M_{2z} + 2\beta (M_{1x} M_{2y} - M_{2x} M_{1y}) - (\mathbf{M}_1 + \mathbf{M}_2)\mathbf{H} + \frac{\rho}{2}\left(\frac{\partial M_{1i}}{\partial x_k}\right)^2 + \rho_{12}\frac{\partial M_{1i}}{\partial x_k}\frac{\partial M_{2i}}{\partial x_k} + \frac{\rho}{2}\left(\frac{\partial M_{2i}}{\partial x_k}\right)^2 \right\}, \quad (10)$$

where $\mathbf{M_1(r, t)}$ and $\mathbf{M_2(r, t)}$ are the magnetic moments of each of the sublattices. We disregard here terms connected with the anisotropy in the basal plane, since (as follows from the results cited later) this anisotropy is very small and is overcome when a field of several hundreds oersteds is applied.

If the external field $\mathbf{H_0}$ is applied in the basal plane (to be specific, we assume it to be directed along x axis) then in the ground state (T = 0°K)

$$M_{1x}^0 = M_{2x}^0 = \beta M_0/\alpha + H_0/2\alpha;$$
$$M_{1y}^0 = -M_{2y}^0 \approx M_0; \quad M_{1z} = M_{2z} = 0, \quad (11)$$

where M_0 is the absolute spontaneous magnetization of each of the sublattices at T = 0°K. The excited states are characterized by the vectors

$$\mathbf{M}_1 = \mathbf{M}_1^0 + \boldsymbol{\mu}_1, \quad \mathbf{M}_2 = \mathbf{M}_2^0 + \boldsymbol{\mu}_2, \quad (12)$$

where $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ are considered proportional to $\exp\{-i(\omega t + \boldsymbol{\kappa}\cdot\mathbf{r})\}$. Using the equation of motion of magnetic moments and the equations of magnetostatics, we obtain, after suitable simplification, the following system of equations for $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$:

$$\begin{aligned}
&i\omega(\mu_{1x} + \mu_{2x}) - \gamma M_0 \{a + (\rho - \rho_{12})\varkappa^2\}(\mu_{1z} - \mu_{2z}) = 0,\\
&i\omega(\mu_{1y} + \mu_{2y}) + (\gamma H_x + 2\beta\gamma M_0)(\mu_{1z} + \mu_{2z}) = 0,\\
&\gamma M_0 (\rho - \rho_{12})\varkappa^2 (\mu_{1x} - \mu_{2x}) - \gamma H_x (\mu_{1y} + \mu_{2y}) + i\omega(\mu_{1z} + \mu_{2z}) = 0,\\
&i\omega(\mu_{1x} - \mu_{2x}) - 2\alpha\gamma M_0 (\mu_{1z} + \mu_{2z}) = 0, \quad \mu_{1y} - \mu_{2y} = 0,\\
&2\alpha\gamma M_0 (\mu_{1x} + \mu_{2x}) - 2\beta\gamma M_0 (\mu_{1y} - \mu_{2y}) + i\omega(\mu_{1z} - \mu_{2z}) = 0,
\end{aligned} \quad (13)$$

where γ is the gyromagnetic ratio.

From this we obtain directly the energy spectrum

$$\varepsilon_1 = [(\mu H_A)^2 + (\mu H_E)^2 (\varkappa d)^2]^{1/2},$$
$$\varepsilon_2 = [(\mu H_E)^2 (\varkappa d)^2 + (\mu H_x)^2 + \mu^2 H_x 2\beta M_0]^{1/2};$$
$$H_A = M_0\sqrt{2\alpha a};$$
$$H_E = M_0\sqrt{2\alpha(\rho - \rho_{12})}/d; \quad \mu = \gamma\hbar, \quad (14)$$

where d is the lattice constant.

A substantial difference between this spectrum and the spectra of uniaxial antiferromagnets with spontaneous magnetization, previously considered, with spontaneous magnetization directed along the axis, is the presence of two branches. In one branch, as in the ordinary case, there is an energy gap caused by the anisotropic field, while the other branch has no such gap and is purely phonon in the absence of a magnetic field.*

If the magnetic field is directed along the z axis, the ground state is characterized by the following values of the moments:

$$M_{1x}^0 = M_{2x}^0 = \beta M_0/\alpha; \quad M_{1y}^0 = -M_{2y}^0 \approx M_0;$$
$$M_{1z}^0 = M_{2z}^0 = H_z/2(\alpha + b). \quad (15)$$

The spin-wave spectrum again has two branches:

$$\varepsilon_1 = [(\mu H_A)^2 + (\mu H_E)^2 (\varkappa d)^2 + (\mu H_z)^2]^{1/2}; \quad \varepsilon_2 = \mu H_E \varkappa d. \quad (16)$$

Knowing the laws of dispersion (14) and (16) we can determine the thermodynamic potential Ω of the spin-wave gaps and use the latter to determine the thermodynamic quantities that characterize the magnetic properties and the specific heat of the spin waves.

If the magnetic field is in the basal plane of the crystal, we obtain from (14)

$$m_{\text{sp.w}} = -(\mu/12 d^3 H_E)(kT/\mu H_E)^2 (\beta M_0 + H). \quad (17)$$

Allowing for the magnetic moment of the ground state, (11), we get

$$\sigma = \sigma_0\{1 - \gamma_1 (T/T_N)^2\},$$
$$\chi_\perp = \chi_{\perp 0}\{1 - 2\gamma_1 (T/T_N)^2\}, \quad (18)$$

where

$$\sigma_0 = 2\beta M_0/\alpha; \quad \chi_{\perp 0} = 1/\alpha;$$
$$\gamma_1 = (\mu/12 d^3 \chi_{\perp 0} H_E)(kT_N/\mu H_E)^2.$$

If the magnetic field is directed along the diagonal axis, the expression for this branch of the spectrum, which depends on the external field, coincides with the corresponding expression for the perpendicular field, cited by Kaganov and Tsukernik.[13] The formulas for $\chi_{\parallel}$ in our case will therefore coincide with the formulas for $\chi_\perp$ in reference 13, i.e., at very low temperatures ($kT \ll \mu H_A$) we have

$$\chi_\parallel = 1/(\alpha + b) - Qe^{-\mu H_A/kT},$$

and for higher temperatures ($\mu H_A \ll kT \ll \mu H_E$) the expression for $\chi_{\parallel}$ coincides with equation (18) for $\chi_\perp$.

The two branches of the energy spectrum will correspond to two terms in the magnetic specific heat

$$c_{\text{magn}} = c_1 + c_2, \quad (19)$$

and the second term is

$$c_2 = (2\pi^2 k/15 d^3)(kT/\mu H_E)^3 = (8\pi^2 k^2 \chi_{\perp 0}\gamma_1 T_N/5\mu^2)(T/T_N)^3, \quad (20)$$

*Allowance for the anisotropy in the basal plane would obviously lead to a gap in this branch, too, although its value, in accordance with the foregoing estimates, does not exceed 0.01°K.

while the first term c_1, as in the ordinary case, has an exponential temperature dependence at low temperatures ($kT \ll \mu H_A$) and is equal to c_2 at higher temperatures.

To conclude this analysis of the application of spin-wave theory to antiferromagnets with $MnCO_3$-like magnetic structure we wish to emphasize that this case is the most convenient from the point of view of comparing theory with experiment, since the power laws obtained above are much easier to verify experimentally than the exponential laws obtained for the case when the spontaneous magnetization is parallel to the anisotropy axis. On the other hand, the condition $\mu H_A \ll kT \ll \mu H_E$ necessary for power laws to be obtained in the latter case, may be impossible to satisfy in general for many substances.

3. EXPERIMENT AND RESULTS

To investigate the anisotropy of magnetic properties of $MnCO_3$ we used a natural crystal of rhodochrosite (from a deposit in the valley of the Aura river in the Pyrenees). We obtained the rhodochrosite from the minerological museum of the U.S.S.R. Academy of Sciences.* From the crystals obtained we chose some of the better ones, fully transparent and having no irregularities that could be seen with the microscope, and with good formation. One of the crystals, 3.8 mg in weight, was used for the magnetic investigations, and two others were used for spectral impurity analysis.† It was established that both crystals alike contain approximately 0.1 — 1% calcium and magnesium and approximately 0.01% silicon.

Magnetic measurements were carried out with apparatus analogous to that previously described.[15] To increase the accuracy of the measurement, the magnetic balance was improved considerably — an automatic photocompensation scheme was produced to increase considerably the stability of the readings, the voltage of the motor-generator supply to the magnet was stabilized, and automatic temperature control was introduced. As a result, the accuracy of the relative measurements of the magnetic moment was ±0.5%. Temperatures were measured by helium vapor pressure from 1.3 to 4°K, with a carbon resistance thermometer from

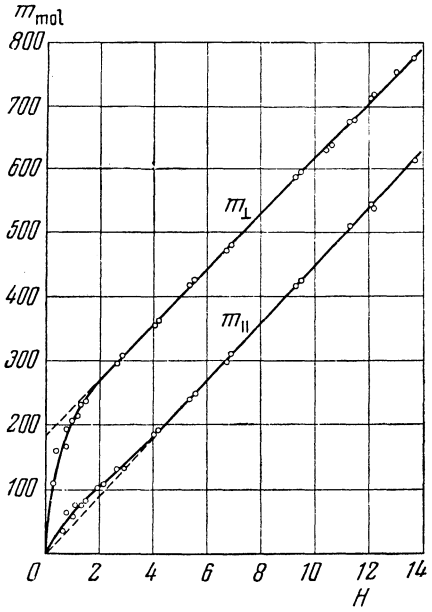

FIG. 2. Dependence of the molar magnetic moment m on the field intensity H at T = 4.2°K. $m_\parallel$ – field along the z axis, $m_\perp$ – field along the y axis (m is in CGS magnetic units and H is in kilo-oersteds).

4 to 20°K, and with a copper resistance thermometer,[17] calibrated against a standard platinum thermometer,[18] from 20 to 300°K.

The accuracy of the temperature measurement in the vicinity of T_N (approximately 30°K) was ±0.02°. In the region most difficult to measure (near 10°K) the accuracy was approximately ±0.1°.

Owing to the good formation, it was not difficult to orient the crystal suitably on the goniometer, after which BF glue was used to secure to it the suspension rod. The accuracy of the crystal orientation was 2 or 3 degrees.

The main investigations were carried out with the specimen so suspended that the suspension vertical line coincided with one of the binary axes of the crystal (the x axis in our notation), while the y and z axes were in a horizontal plane. The magnetic field was rotated in this plane.

Figure 2 shows the results of the measurement of the magnetic moment (all the quantities in this paper are per mole), as a function of the applied field, at T = 4.2°K. The upper curve is obtained when the field is applied along the y axis. As is seen from the diagram, the dependence of the magnetic moment on this field, for H > 2000 oe, can be represented by the following formula

$$m_\perp(H, T) = \sigma(T) + \chi_\perp(T) H_\perp. \qquad (21)$$

Along the trigonal axis (lower curve) in strong fields (H > 4000 oe) the magnetic moment changes linearly with field, like in ordinary paramagnets:

*The author takes this opportunity to thank Prof. G. P. Barsanov and N. A. Kruglov, who graciously helped select very pure rhodochrosite crystals.

†The spectral analysis of the specimens was performed at the Institute of Geochemistry and Analytical Chemistry of the Academy of Sciences of the U. S. S. R. by M. M. Farafonov, to whom the author expresses deep gratitude.

$$m_{\parallel} = \chi_{\parallel} H_{\parallel} \qquad (22)$$

In weak fields one observes an anomalous variation of the magnetic moment with the field. This anomaly is seen at all temperatures below the Neel temperature (T_N = 32.4°K), as shown in Fig. 3

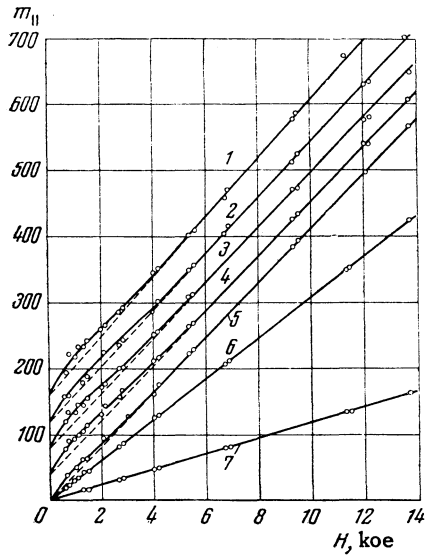

FIG. 3. Dependence of the molar magnetic moment $m_{\parallel}$ on the field intensity at the following temperatures: 1) 4.2°K, 2) 20.3; 3) 29.7 4) 30.8; 5) 31.2; 6) 78.4; 7) 295°K. Curve 4 is shifted along the ordinate axis by Δm = 40 CGS magnetic units. Curve 3 is shifted by 80 units, curve 2 by 120 units, and curve 1 by 160 units.

where the results of an investigation of this anomaly are given for five temperatures. It must be noted that the readings of the balance, in measurement along the z axis at weak fields, are quite unstable and the reproducibility of the results is several times worse than in other measurements. We can therefore describe the observed anomaly only qualitatively.

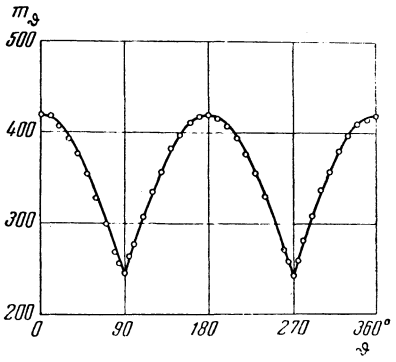

FIG. 4. Angular dependence of the moment in the yz plane at H = 5.37 kilo-oersteds (ϑ is the angle between the direction of the magnetic field and the y axis).

Figure 4 shows the dependence of the magnetic moment m on the angle ϑ between the direction of the magnetic field and the y axis at T = 4.2°K and at a constant value of the field. The experimental results are represented by the dots. The solid curve is the function $m_{min} + a|\cos\vartheta|$, where

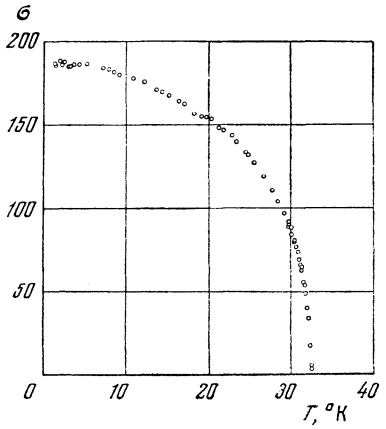

FIG. 5. Temperature dependence of the spontaneous ferromagnetic moment σ (σ is given in CGS magnetic units per mole).

the coefficient $a = m_{max} - m_{min}$ is selected to fit the experimental data.

Our measurements for the case when the trigonal axis coincides with the direction of the suspension have shown that, within the limit of experimental error, the values of m are the same in all directions lying in the basal plane, for all values of the magnetic field.

Curves analogous to those given in Fig. 2 were obtained by us for 50 temperatures, ranging from 1.3 to 32.3°K. These curves were used to obtain graphically the values of $\sigma(T)$, $\chi_{\perp}(T)$, and $\chi_{\parallel}(T)$. In determining σ by extrapolation to H = 0, the accuracy of the results obtained is naturally lower. We estimate the error in the values of σ to be ±2 CGS magnetic units, amounting to approximately 1% of σ_0. The error in the values of $\chi_{\perp}$ and $\chi_{\parallel}$ amounts to approximately ±0.3%. The temperature dependence $\sigma(T)$ is shown in Fig. 5. We see that when $T \to 0$ we get $\sigma(T) \to 188$ CGS magnetic units. The spontaneous moment σ vanishes at T_N = 32.43°K. Figure 6 shows the values of $\chi_{\perp}(T)$ and $\chi_{\parallel}(T)$, while above 32.43°K $MnCO_3$ becomes paramagnetic, and consequently χ is the ordinary paramagnetic susceptibility for these temperatures.

As can be seen from Fig. 6, the susceptibility of $MnCO_3$ is isotropic above 34°K, within the limits of accuracy of our measurements. Our measurements have shown that in the temperature range from 70 to 300°K the paramagnetic susceptibility obeys the Curie-Weiss law

$$\chi = C/(T - \Theta), \qquad (23)$$

with C = 4.46 and $\Theta = -64.5$°K. The dotted Curve 1 of Fig. 6 corresponds to an extrapolation of the Curie-Weiss law (23) to the transition-temperature region. Within the very narrow vicinity of T_N, the susceptibility $\chi_{\perp}$ has small sharp maximum, and at lower temperatures $\chi_{\parallel}$ and $\chi_{\perp}$ are almost parallel to each other, with $\chi_{\perp}$ being 3% less than $\chi_{\parallel}$.

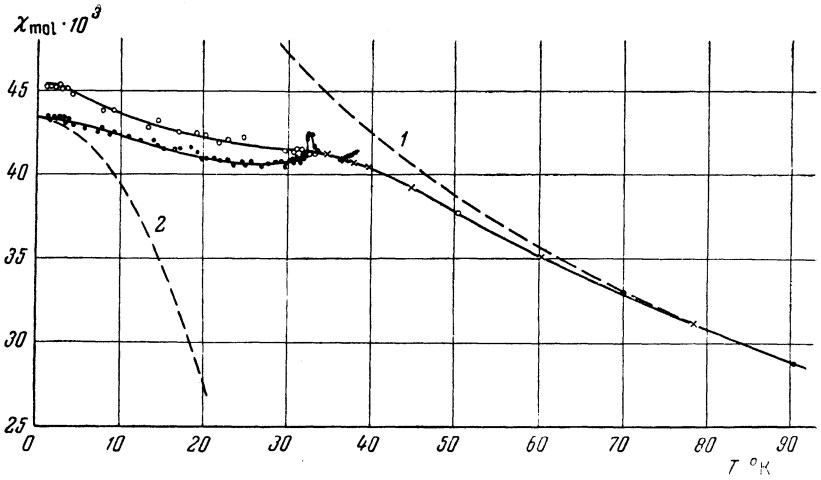

FIG. 6. Temperature dependence of the magnetic susceptibility of $MnCO_3$ in the paramagnetic and antiparamagnetic states. o – $\chi_{\parallel}$; • – $\chi_{\perp}$, × – coinciding values $\chi_{\parallel} = \chi_{\perp}$; Curve 1 – extrapolation of the Curie-Weiss law. Curve 2 – is based on the spin-wave theoretical formula (18) (χ is in CGS magnetic units).

Only two papers devoted to a study of magnetic properties of $MnCO_3$ at low temperatures are known at present. Bizette and Tsai[19] also investigated a natural single crystal $MnCO_3$. They give no analysis of the m(H) curves, and restrict themselves to indicating that at low temperatures $\chi_{\perp}$ depends on the field intensity. We have calculated, using our data for σ and $\chi_{\perp}$, the values of $\chi'_{\perp} = \chi_{\perp} + \sigma/H$ for those values of the field intensity H, given in reference 19. Figure 7 shows

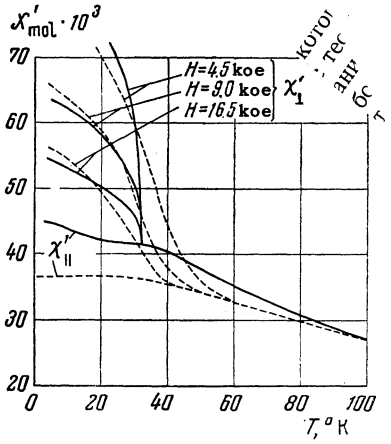

FIG. 7. Comparison of our data of the molar susceptibility of various values of the field (solid curves) with the data of Bizette and Tsai[19] (dotted curves).

the comparison of our values of χ' with those of Bizette and Tsai. We see that the data for the paramagnetic region agreed satisfactorily, but below that the discrepancey becomes noticeable — our values of $\chi_{\parallel}$ are approximately 15% higher than the values of $\chi_{\parallel}$ given in reference 19. Only very rough qualitative agreement is observed for $\chi'_{\perp}$. The quantitative discrepancies in $\chi'_{\perp}$ reach 20 or 30%. Our data characterize a very sharp transition temperature, $T_N = 32.4°K$, below which $\chi'_{\perp}$ begins to depend on the field. In reference 19 this temperature is rather smeared in the region between 40 and 60°K. At low temperatures the discrepancy in the data on $\chi'_{\perp}$ decreases. We believe that these discrepancies are due to the fact that the crystal used by Bizette and Tsai was not sufficiently pure, leading to a considerable smearing of the transition point. This assumption is also confirmed by the fact that Bizette and Tsai investigated large crystals (weighing up to 0.5 grams). Naturally, it was quite difficult to select sufficiently pure crystals of this size.

As already indicated, the author and Orlova[6] were the first to observe a dependence of type (21) for $MnCO_3$. The measurements reported in that reference pertain to polycrystalline chemically-pure specimens. The values we obtained for the moments at different values of H and T agree, within the limit of experimental error, with the data of the present paper. The small discrepancy in the transition temperature (approximately 1°K) is obviously due to the insufficient accuracy of calibration of the thermocouple in the earlier work. The fields employed in reference 6 were not strong enough (reaching 2500 oe) to produce sufficient saturation of the magnetic moment. Consequently, there is a considerable error (approximately 40 — 50%) in the resultant extrapolated values of the ferromagnetic moment σ. In the present work we carried out the measurements at fields five or six times the saturation value. This guarantees sufficiently accurate extrapolation in the determination of the ferromagnetic moment.

4. DISCUSSION OF THE RESULTS

1. From the result of our measurements of the magnetic properties of $MnCO_3$ in the high-temperature region we can determine the value of the g-factor. The value g = 2.04 obtained and its isotropy are in good agreement with the theory that the Mn^{++} ion is in the S state. The large negative value of Θ in (23) indicates the presence of an antiferromagnetic interaction.

2. Below $T_N = 32.43°K$ the substance goes

into antiferromagnetic state that has weak ferromagnetism.* In accordance with the model proposed by us earlier,[6] and in accordance with the Dzyaloshinskiĭ thermodynamic theory, our experiments show that the ferromagnetic vector is always in the basal plane. This is confirmed by agreement between the experimentally established relationships (21) and (22) and the theoretical formulas (3), and is seen particularly clearly on the rotation diagram (figure 4). Were the ferromagnetic vector inclined to the basal plane, we would obtain a curve represented not by $|\cos\vartheta|$, but by a curve with a gentler maximum at $\vartheta = n\pi$ and with a steeper descent at $\vartheta = \pi/2 + n\pi$.

3. The results of our measurements on $m_\perp$ at weak fields ($H < 2000$ oe) shows that, in the case of weak ferromagnetism, domains that become remagnetized at fields of 2 — 2.5 kilo-oersteds are formed in antiferromagnets. The hysteresis of this process is very small. On the other hand, comparison of our results on the anisotropy in the basal plane (which at all fields is less than the accuracy of our measurements) with the theoretical curves (Fig. 5 of reference 7) shows that the effective anisotropy field in the basal plane is at any rate less than 100 oe. Anderson et al.[20] investigated the ferromagnetic resonance in hematite. In this case the value of the anisotropy field in the basal plane was found to be 60 oe.

The foregoing anomalous behavior of $m_\parallel$ in a weak field may be due to the rotation of the direction of spontaneous magnetization of the sublattices in the basal plane, considered in the first part of this paper. True, the experimental data (see Figs. 2 and 3) do not agree with (9a) and (9b). It must be borne in mind, however, that in these experiments the angle φ can assume, in the process of rotation, values corresponding to non-equilibrium states. This violates condition (8) which was assumed in the derivation of (9). The instability in the readings of the balance, noted previously, may also be due to this departure from equilibrium. In any case, the observed anomaly is evidence in favor of assuming that the crystal $MnCO_3$ is in state II when $H = 0$, as does occur in the case of hematite.[3]

4. It is interesting to compare the temperature dependences of σ, $\chi_\perp$, and $\chi_\parallel$, obtained by us, with the theory. We first consider the temperature region close to the transition point. A comparison of the experimental results on the isotropy of below T_N with Eq. (4) leads to $b = 0$. To reconcile (3) with the experimental curves for $\chi_\parallel$ and $\chi_\perp$ (Fig. 6), we must put $D = -d$ and $D > 0$, so that

$$\chi_\parallel = 1/B,$$
$$\chi_\perp = 1/(B + Dl^2). \qquad (3')$$

The experimentally-observed anisotropy below T_N is due to the term $Dl^2(m_x^2 + m_y^2)/2$ in the expression for the thermodynamic potential (1).

Of greatest interest is the temperature dependence of the spontaneous magnetization of the antiferromagnet near the transition point. Using the previously-adopted symbols, the spontaneous magnetization of each of the sublattices is $M \approx l/2$, and, according to (3a) and (2)

$$2M = l = \sigma/\beta\chi_\perp. \qquad (24)$$

It is thus possible to determine, from the temperature dependences of σ and $\chi_\perp$ measured by us, the temperature dependence of the magnetization of the sublattices. If it is assumed that the coefficients β in the expression for the thermodynamic potential (1) and the Hamiltonian (10) are of the same magnitude,* and in accordance with Eq. (11) we get

$$M/M_0 = (\sigma/\sigma_0)\chi_\perp^0/\chi_\perp. \qquad (25)$$

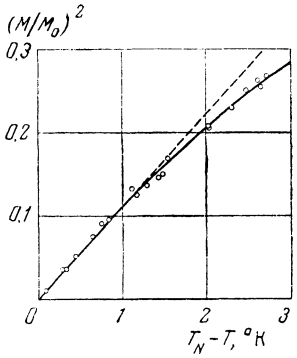

FIG. 8. Temperature dependence of the square of the relative spontaneous magnetization of the sublattices near the transition temperature.

Figure 8 shows the dependence of the quantity $(M/M_0)^2$, calculated from the experimental values of σ and $\chi_\perp$, on the temperature difference $T_N - T$. We see that near 1.5° ($\Delta T/T_N \sim 5\%$) the experimental points fit the straight line

$$(M/M_0)^2 = \xi(1 - T/T_N), \qquad (26)$$

where $\xi = 3.6$. Deviations from this law begin when M/M_0 reaches 40%. It is known that molecular-field theory leads to an equation similar to (26) with $c = 3$.[21] Experiments made on ferromagnetic metals have led to values greater than 3,

*Magnetic measurements alone can only permit us to assume, with high probability, the establishment of antiferromagnetic order-disorder transitions. To obtain a rigorous experimental proof of this fact neutron-diffraction investigations must also be performed.

*Such an assumption is tantamount to adopting the molecular-field model.

namely c = 5 to 7 for nickel (references 22 and 23 respectively) and c = 7 for iron.[24] Measurements made on ferrites yield values of ξ from 0.1 to 0.7. Thus the simple model of the molecular field describes the behavior of the spontaneous magnetization of antiferromagnets more accurately than that of metallic ferromagnets and ferrites. This conclusion is in agreement with the theoretical work of Vonsovskiĭ and Vlasov[26] for ferromagnets and of Neel[27] for ferrites. Prior to this investigation, only one paper was published on a study of the temperature dependence of M near T_N (for $CuCl_2 \cdot 2H_2O$).[28] The curve obtained there is much steeper than ours, and shows no quadratic region. It is possible that this is due to the chain structure of the antiferromagnetic order-disorder in $CuCl_2 \cdot 2H_2O$.[29]

If we assume further that the sublattice magnetization at T = 0°K has the nominal value, i.e., $M_0 = (1/2)\, N\mu_B gS = 14.1 \times 10^3$ CGS magnetic units per mole, then $\sigma_0/2M_0 = 0.0067$, i.e., the ferromagnetic moment amounts to 0.67% of the nominal magnetization. We then obtain, from (11), $\beta = 0.15$. According to the data of Neel and Pauthenet,[2] $\beta = 0.7$ for α-Fe_2O_3. Using Eqs. (2) and (26) and the value of M_0, we get $\lambda = 89 \times 10^6$. The value of $\chi_{\parallel}$ obtained from (3b) yields B = 24.2. The temperature variation of $\chi_{\perp}$ makes it possible to estimate, using Eq. (3a), the coefficient $D = 2 \times 10^{-9}$. The foregoing representation of the molecular-field theory model were used by us only to estimate the coefficients of the thermodynamic potential (1). A qualitative thermodynamic derivation of the validity of Eq. (2) near T_N is confirmed by our experiments independently of these assumed models.

5. Let us turn now to compare our results with Eqs. (18) of the spin-wave theory, derived in the first section of this paper. As follows from these formulas, σ and $\chi_{\perp}$ should diminish with temperature, following a quadratic law. Figure 9 shows the temperature dependence we have obtained for σ/σ_0. Of the three curves shown in the diagram, the first corresponds to linear temperature scale along the abscissa, the second to a quadratic scale, and the third to a cubic. It is seen from the diagram that the experimental points fit the straight line well only in the case of a quadratic temperature scale. This proves at the same time that Eq. (18) fits correctly the temperature dependence of the spontaneous ferromagnetic moment in $MnCO_3$, in the temperature region down to $0.7\, T_N$. This corresponds to a 25% reduction in the spontaneous moment. We find from these experimental data that the coefficient η in Eq. (18) has a value of 0.48. An important factor for the verification of the spin-wave theory is that in our derived equations the same coefficient η determines both the temperature dependence of the spontaneous magnetization and the susceptibility $\chi_{\perp}$. However, as can be seen from Fig. 6, the experimental points for $\chi_{\perp}$ exhibit a much lesser temperature dependence than predicted by (18) with the aforementioned value $\eta = 0.48$ (curve 2). An equally weak dependence is displayed also by the parallel susceptibility $\chi_{\parallel}$. The accuracy of our experiments is insufficient to derive an expression for this weak decrease in $\chi_{\parallel}$ and $\chi_{\perp}$.

The discrepancy we observed in the coefficients of the thermal dependence of σ and $\chi_{\perp}$ is obviously proof of the shortcomings of the spin-wave theory used to derive (18). We have already noted that the principal shortcoming of the theory is that in the assumed model application of an external field at T = 0°K does not change the magnitude of the lattice-magnetization vectors, but merely rotates them. If we forego this model, the Hamiltonian of (10) must be written in the form of an expansion in the terms of the small quantities μ_i.

As already indicated above, antiferromagnets with a magnetic structure of $MnCO_3$ are the most suitable objects for verifying the spin-wave theory. In other crystals, owing to the presence of the large gap in the spin-wave spectrum ($> 0.1\, T_N$), all the thermodynamic quantities should have an exponential temperature dependence at low temperatures, a dependence difficult to verify experimentally. Measurements of the temperature dependence of the magnetic susceptibility of MnF_2,[30] $NiSO_4$,[31] and $CuSO_4$[32] in the region above $(0.2 - 0.4)\, T_N$, confirm that the T^2 law holds, as called for by the spin-wave theory. However, what fails to make this deduction convincing is that the temperature range in which the T^2 law

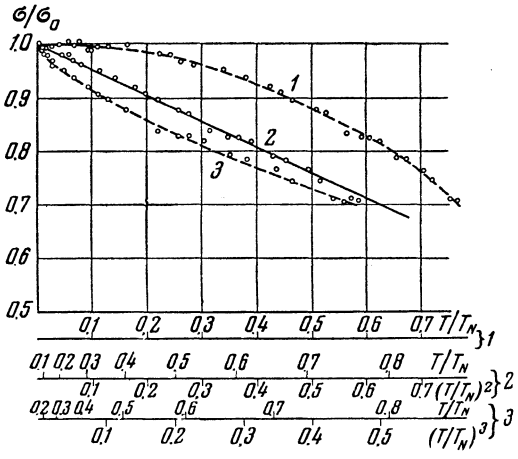

FIG. 9. Dependence of the relative ferromagnetic moment σ/σ_0 on the relative temperature T/T_N. 1) linear temperature scale along the abscissa, 2) quadratic scale, 3) cubic scale.

holds may, generally speaking, lie above the limits of applicability of the theory. On the other hand, more accurate measurements of the temperature dependence of the sublattice magnetization, performed by the nuclear-resonance method, give contradictory results. Poulis and Hardeman[28] have found in the case of $CuCl_2 \cdot 2H_2O$ that $M - M_0 \sim T^4$ in the range $(0.3 - 0.7)\,T_N$. Jaccarino and Shulman have found that $M - M_0 \sim T^{3.5}$ for MnF_2[33] in the region $(0.02 - 0.3)\,T_N$, and $M - M_0 \sim T^5$ for CoF_2[34] in the region $(0.03 - 0.5)\,T_N$. We believe that these results apply to temperatures in the transition region between the exponential and power laws.

For a more complete experimental verification of the spin-wave theory it would be important to obtain data on the specific heat of $MnCO_3$. We used Eq. (20) to estimate the value of the magnetic specific heat $MnCO_3$, using the previously mentioned value $\eta = 0.48$, and found for the magnetic specific heat

$$c_2 = 460\,(T/67)^3 \text{ cal/deg-mole} = 1.9 \cdot 10^{10}\,(T/67)^3 \text{ erg/deg-mole.}$$

For convenience in comparing the magnetic specific heat with the lattice specific heat we write here the formulas with the same numerical coefficients as in the Debye law, choosing suitable values of Θ_D. These formulas show that the magnetic specific heat will be the same as that of a lattice with $\Theta_D = 67°K$. According to Anderson[35] who measured the specific heat of $MnCO_3$ from 50 to 300°K, $\Theta_D = 220°$. This value, obtained from experimental data at relatively high temperatures, may be grossly in error. In any case, one might think that at helium temperatures the magnetic specific heat should exceed the lattice specific heat by 5 or 10 times.

CONCLUSION

The principal results of this paper can be formulated as follows:

1. It has been shown experimentally that the weak ferromagnetism of $MnCO_3$, previously observed by the author jointly with Orlova[6] has an anisotropy which is predicted by the theory proposed by Dzyaloshinskiĭ. At any direction of applied magnetic field, the ferromagnetic vector σ always remains in the basal plane of the crystal.

2. The magnetic properties of the $MnCO_3$ crystal at $T < T_N$ are isotropic in the basal plane, within the limits of experimental accuracy. This means that the effective anisotropy field in the basal plane does not exceed 100 oe.

3. An anomaly has been observed in the dependence of the magnetic moment on the field ($H < 2500$ oe), when the field is directed along the trigonal axis. This anomaly may be due to rotation of the antiferromagnetic vector $\boldsymbol{l}$ in the basal plane, due to the field applied along the trigonal axis. Such a rotation was justified theoretically as a consequency of reference 7.

4. It has been shown that near T_N the spontaneous magnetization of the sublattices, M, in $MnCO_3$ in accordance with the thermodynamic theory, obeys the following law

$$(M/M_0)^2 = \xi\,(1 - T/T_N).$$

The value $\xi = 3.6$ agrees satisfactorily with $\xi = 3$, predicted by the molecular-field theory.

5. From an analysis of the experimental curves of the temperature dependence of σ, $\chi_{\parallel}$, and $\chi_{\perp}$, we estimated the coefficients in the expansion for the thermodynamic potential.

6. It has been established that in the $1.3 - 23°K$ range the spontaneous ferromagnetic moment decreases and follows a quadratic law.

7. The spin-wave theory was used to calculate the dispersion of an antiferromagnetic with a magnetic structure of $MnCO_3$ and to show that in this case two branches of the structure were obtained, one of which has practically no gap.

8. With the aid of the dispersion law obtained, formulas were derived for the temperature dependence of σ, $\chi_{\perp}$, $\chi_{\parallel}$, and c_{magn}. These formulas show that σ and $\chi_{\perp}$ should diminish as the second power, with $\chi_{\perp}$ decreasing twice as fast as σ. The experimental results, to the contrary, show very small decrease in $\chi_{\perp}$ as compared with σ. This is evidence of the incompleteness of the existing spin-wave theory.

In conclusion the author expresses deep gratitude to Academician P. L. Kapitza for continuous interest in this work. The author is very grateful to I. E. Dzyaloshinskiĭ for useful discussions and to V. I. Kolokol'nikov for help with the performance of the experiment.

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