MAGNETIC PROPERTIES OF A MONOCLINIC $Na_2Mn_2Si_2O_7$ *SINGLE CRYSTAL*

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The temperature dependence (1.7–300°K) of the magnetic susceptibility of a $Na_2MN_2Si_2O_7$ single crystal with a symmetry described by the $P2_1/c$ group was investigated. The crystal was magnetically isotropic above T = 26°K. The Curie-Weiss law with $\Theta = -91°$ and $C_{mol} = 7$ was obeyed at temperatures between 100 and 300°K. A very broad susceptibility peak was observed at T = 60°K. It was suggested that the peak was due to the appearance of antiferromagnetic ordering within the Mn^{2+} groups. A uniaxial anisotropy of the magnetic susceptibility and a ferromagnetic moment appeared below 26°K. This was an indication of the transition of the substance to the antiferromagnetic state with weak ferromagnetism. The temperature dependence (27–300°K) of the EPR line width was determined.

THE existence and anisotropy of weak ferromagnetism are known to depend strongly on the symmetry of a crystal. Therefore, it is interesting to investigate a typical representative of each crystallographic structure. The monoclinic system has been investigated most thoroughly in this respect. Consequently, it seemed worth while to study in detail the magnetic properties of a monoclinic single crystal of $Na_2Mn_2Si_2O_7$, first synthesized by B. N. Litvin, I. M. Dianova, and L. A. Kachan at the Crystallography Institute of the U.S.S.R. Academy of Sciences.[1][1)]

1. CRYSTAL STRUCTURE

An X-ray structure analysis of samples of $Na_2Mn_2Si_2O_7$, carried out by Astakhova et al.[2], has shown that this compound crystallizes in the monoclinic system with a space group $P2_1/c$.

A unit cell contains four molecules, i.e., eight magnetic atoms. The lattice includes two systems of non-equivalent ions: Mn_I^{2+} and Mn_{II}^{2+}, which differ in the symmetry of their oxygen environments. The Mn_I^{2+} ions are located at the centers of distorted tetrahedra, consisting of O^{2+} ions. The Mn_{II}^{2+} ions are centers of irregular triangular prisms. Identical Mn^{2+} ions form dumb-bells whose centers coincide with inversion centers and have the coordinates (000) and $(0\frac{1}{2}\frac{1}{2})$ (cf. Fig. 1). $Na_2Mn_2Si_2O_7$ single crystals are well faceted and one of the faces coincides with the plane of symmetry of the crystal.

The following properties of these samples were investigated:

1) the magnetic properties in the temperature range 1.5–300°K, in fields up to 17 kOe;

2) the electron paramagnetic resonance at temperatures of 27–300°K.

2. MAGNETIC MEASUREMENTS

The magnetic properties of $Na_2Mn_2Si_2O_7$ single crystals were investigated using a magnetic balance.[3] Two crystals weighing 2.77 and 11.35 mg were used.

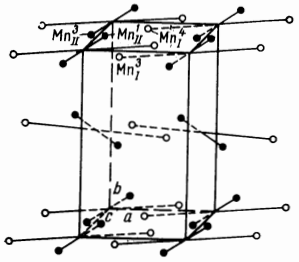

FIG. 1. Positions of Mn^{2+} ions in the crystal lattice of $Na_2Mn_2Si_2O_7$: ○ – Mn_I (x = 0.711a, y = 0.008b, z = 0.138c), ● – Mn_{II} (x = 0.119a, y = 0.082b, z = 0.339c); a = 8.4 Å, b = 13.5 Å, c = 5.69 Å.

The absolute values of their molar parameters differed by 10% and the results quoted are the averages for the two crystals.

No anisotropy of the magnetic properties of this material was observed in the temperature range 300–26°K. Between 300 and 100°K, the magnetic susceptibility obeyed the Curie-Weiss law (Fig. 2):

$$\chi = C/(T + \Theta). \qquad (1)$$

A very broad susceptibility maximum was observed in the region of 60°K. This maximum can be seen most clearly in Fig. 3, which shows the temperature depend-

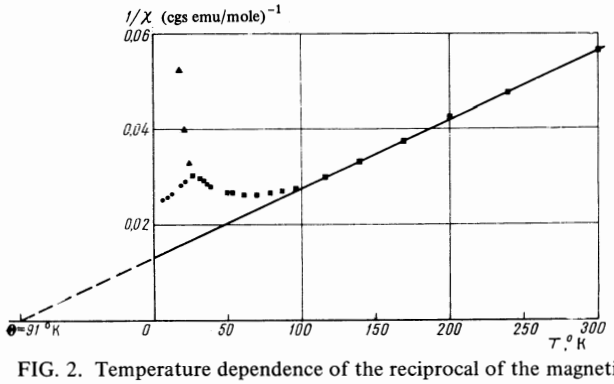

FIG. 2. Temperature dependence of the reciprocal of the magnetic susceptibility: ○ – in the plane of symmetry; ▲ – along the b axis; ■ – isotropic values.

[1)]The authors are grateful to B. N. Litvin, I. M. Dianov, and L. A. Kachan for kindly supplying the $Na_2Mn_2Si_2O_7$ crystals.

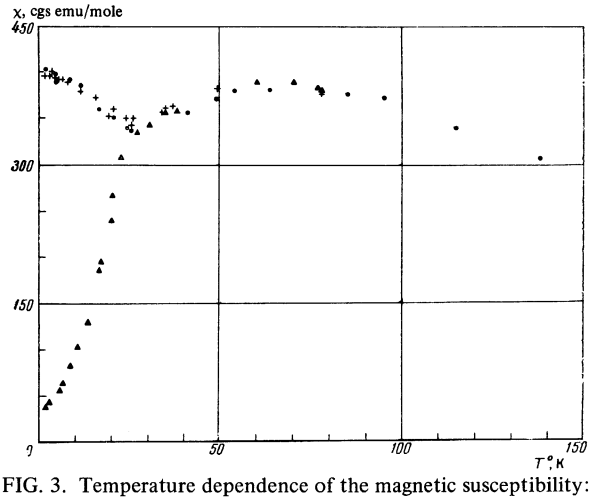

FIG. 3. Temperature dependence of the magnetic susceptibility: +, ● – in the plane of symmetry; ▲ – along the b axis.

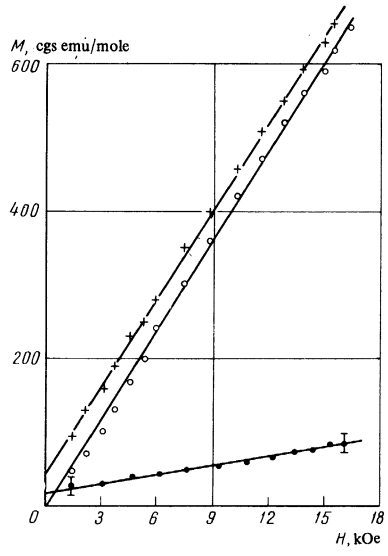

FIG. 4. Dependence of the magnetic moment on the field at T = 4.2°K: + – along c* direction; ○ – along a*; ● – along b axis.

ence of the susceptibility. It follows from the same figure that a uniaxial magnetic anisotropy appeared at T ≈ 26°K. The susceptibility χ_b along a binary axis decreased when the temperature was lowered. The susceptibility was isotropic (to within 5%) in the plane of symmetry and increased somewhat (by ≈ 15%) when T → 0. Below 26°K, a weak ferromagnetic moment appeared along one of the directions in the plane of symmetry (we shall denote this direction by c*).[2)] This can be seen in Fig. 4, which gives the field dependence of the magnetic moment along three directions at T = 4.2°K. The dependence m(H) along c* was described satisfactorily by the formula

$$m_{c^*} = \sigma_{c^*} + \chi_{c^*} H. \qquad (2)$$

Figure 5 shows the temperature dependence of σ_{c^*}, obtained from curves of the type of Eq. (2), recorded at various temperatures. The value of the residual ferromagnetic moment at T = 0°K was 38 cgs emu/mole.

A study of the dependence of the magnetic moment on the external field, applied along the b axis, showed that a small ferromagnetic moment appeared along this direction (Fig. 4). However, because the total moment along the b axis was very small and our sample was in unstable equilibrium, the accuracy of the measurements was very low. Therefore, it was not possible to conclude definitely that a ferromagnetic moment was indeed observed along the b axis.

In addition to these investigations, we also measured the magnetic moment anisotropy in various planes of a crystal at T = 20.4°K. These measurements were carried out by T. A. Shalnikova and by N. M. Kreĭnes in the laboratory of Dr. J. Kaczér at the Physics Institute of the Czechoslovak Academy of Sciences.[3)] The results obtained confirmed the presence of a ferromagnetic moment in the plane of symmetry of the crystal.

3. PARAMAGNETIC RESONANCE

The paramagnetic resonance was investigated at a frequency of 10 kMc in the temperature range 27–300°K using a magnetic spectrometer with low-frequency modulation of the magnetic field. A two-coordinate electronic potentiometer was used to record the derivative of the absorption curve in the magnetic field. A sample was placed in a resonator in such a way that it could be rotated with respect to the mutually perpendicular high-frequency and static magnetic fields.

The position of the EPR line did not vary with temperature at all in the whole investigated temperature range. A weak anisotropy of the g-factor, representing 1.5% of its average value of 2, was observed. The EPR line width, ΔH, was fairly strongly anisotropic and this anisotropy varied with temperature. Figure 6 shows the temperature dependence of the extremal values of ΔH.

The largest value of ΔH was observed along the symmetry axis: this quantity passed through a minimum at ≈ 60°K and increased strongly when the temperature was reduced further. Above 60°K, the symmetry plane included two directions with minimal and maximal values of ΔH, differing approximately by a factor of 2. When 60°K was approached, the difference between these values tended to zero and changed its sign at T ≈ 60°K. At the same time, the directions themselves changed in the plane (by an angle of ≈ 20°). When temperature was reduced further, these lines broadened rapidly. At 27°K, there was no absorption signal.

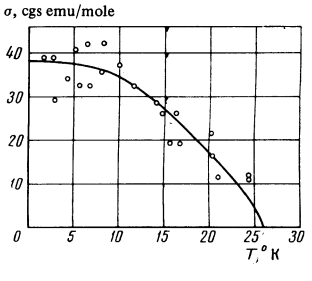

FIG. 5. Temperature dependence of the spontaneous magnetic moment.

[2)]The orientations of the directions a* and c* with respect to the crystallographic axes a and c were not known.

[3)]The authors thank Prof. J. Kaczér and T. A. Shal'nikova for making available the experimental facilities and for their direct help in the experiments.

4. MAGNETIC SYMMETRY

Following Dzyaloshinskiĭ[4] we shall determine the possible types of magnetic ordering permissible for the $P2_1/c$ space group, to which the investigated compound $Na_2Mn_2Si_2O_7$ belongs. However, we shall consider only the case when a unit cell contains four equivalent magnetic ions. The case of eight magnetic ions, forming two non-equivalent systems, such as observed in $Na_2Mn_2Si_2O_7$, will not be considered because of the laborious calculations required.

We shall consider the case when a transition to the antiferromagnetic state takes place without any change in the unit cell. Then, we can consider only[4] the $\widetilde{P}2_1/c$, which differs from $P2_1/c$, because in the former all translations by a full period are identity transformations. The generating symmetry elements in the $\widetilde{P}2_1/c$ group are: an inversion I, a twofold screw axis 2_1 $(0, y, \frac{1}{4})$, $(0, y, \frac{3}{4})$, $(\frac{1}{2}, y, \frac{1}{4})$, $(\frac{1}{2}, y, \frac{3}{2})$, and a glide plane c $[x, \frac{1}{4}, z]$, $[x, \frac{3}{4}, z]$ (cf. Fig. 7). The magnetic ions $s_1(x, y, z)$, $s_2(\bar{x}, \bar{y}, \bar{z})$, and $s_3(x, \frac{1}{2} - y, \frac{1}{2} + z)$, $s_4(\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z)$ are grouped in dumb-bell pairs, whose centers coincide with the positions of the inversion centers.

We shall introduce the vectors $\mathbf{m}, \mathbf{l}_1, \mathbf{l}_2, \mathbf{l}_3$, defined by the equations

$$\begin{aligned} \mathbf{m} &= \mathbf{s}_1 + \mathbf{s}_2 + \mathbf{s}_3 + \mathbf{s}_4, \quad & \mathbf{l}_1 &= \mathbf{s}_1 + \mathbf{s}_2 - \mathbf{s}_3 - \mathbf{s}_4, \\ \mathbf{l}_2 &= \mathbf{s}_1 - \mathbf{s}_2 - \mathbf{s}_3 + \mathbf{s}_4, \quad & \mathbf{l}_3 &= \mathbf{s}_1 - \mathbf{s}_2 + \mathbf{s}_3 - \mathbf{s}_4. \end{aligned} \tag{3}$$

Expanding the representation of the $\widetilde{P}2_1/c$ group—formed by twelve quantities of the type given in Eq. (3)—in terms of irreducible representations, we can show that this space group allows the following types of magnetic ordering

$$\begin{aligned} &\text{AWF}_y\text{: } l_{1x}, l_{1z}, m_y; \quad && \text{A}_1\text{: } l_{2x}, l_{2z}, l_{3y}; \\ &\text{AWF}_{x,z}\text{: } l_{1y}, m_x, m_z; \quad && \text{A}_2\text{: } l_{2y}, l_{3x}, l_{3z}. \end{aligned} \tag{4}$$

Thus, we can have either a pure antiferromagnetic state or an antiferromagnetic state with weak ferromagnetism (AWF) (A). The weakly ferromagnetic state is obtained for the ordering represented by $\mathbf{l}$, i.e., when the magnetic moments in the dumb-bells are parallel.

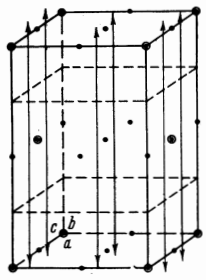

FIG. 7. Positions of symmetry elements of the space group $P2_1/c$: ● – inversion center I, O – positions of centers of Mn^{2+} dumb-bells; glide planes are shown dashed and arrows are used to indicate twofold screw axes 2_1.

5. DISCUSSION OF RESULTS

A. The appearance of a uniaxial anisotropy of the magnetic susceptibility below 26°K and the simultaneous appearance of a weak ferromagnetic moment indicate that a single crystal of $Na_2MN_2Si_2O_7$ undergoes, at $T_N = 26°K$, a transition to the antiferromagnetic state with weak ferromagnetism. The temperature dependence of $\chi_b = \chi_{\parallel}$ below T_N indicates that the directions of the sublattice magnetizations are close to a binary symmetry axis b. The relatively high value of the susceptibility $\chi_{\parallel}$ at $T = 1.7°K$ may be due to an inaccurate orientation of a sample (within $\approx 5°$).

A weak ferromagnetic moment appears in the plane of symmetry of the crystal. Its value is very low. It represents only 0.07% of the nominal value. The effective Dzyaloshinskiĭ field, $H_D = \sigma/\chi_{\perp}$, is ≈ 1 kOe.

Comparing the experimental data with the results obtained in Sec. 4, we shall try to determine the type of magnetic ordering established in the crystal. We must mention that such a comparison is valid only if both systems of non-equivalent ions in the crystal are ordered in an identical manner. It follows from Eq. (4) that the ferromagnetic moment can appear only when the ordering is of the $\mathbf{l}_1$ type. Since the experimental

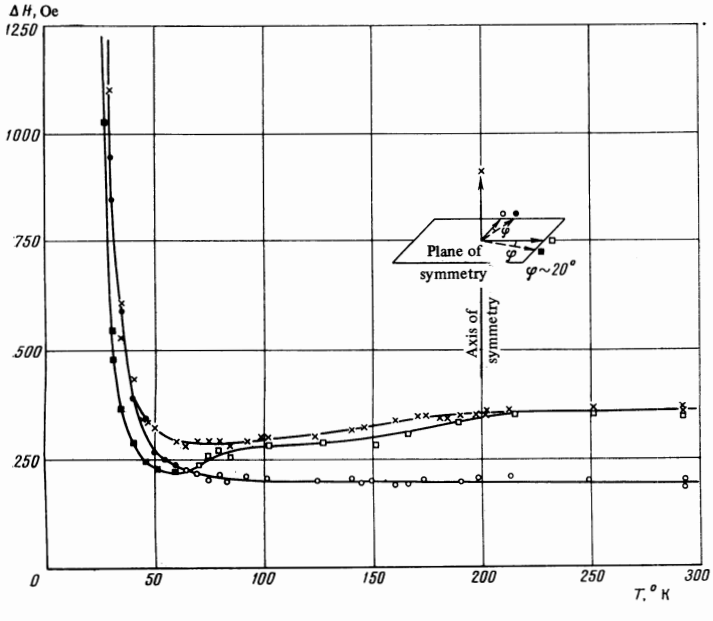

FIG. 6. Temperature dependence of the EPR line width ΔH.

data show clearly that the ferromagnetic moment lies in the plane of symmetry and that the antiferromagnetic vector is directed along the y axis, it follows unambigously that the $AWF_{x,z}$ type of ordering applies here. It corresponds to a magnetic symmetry group (I, 2_1R, cR).

B. The presence of a broad susceptibility maximum and the fall of the susceptibility at low temperatures in the paramagnetic region were reported first for copper acetate.[5] This effect has been explained by Bleaney and Bowers [6] in terms of the presence of a strong antiferromagnetic interaction between pairs of closely spaced Cu^{2+} ions, whose spins form a triplet state. Low-symmetry crystals may have groups of closely spaced magnetic ions such that the exchange interaction between them within a group is much stronger than that between groups. Consequently, magnetic ordering may be established within each group although the crystal as a whole may still be magnetically disordered. The temperature dependence of the susceptibility of such a system is described by the formula (cf. Fig. 6),

$$\chi = \frac{Ng^2\beta^2 S(S+1)}{3kT}\frac{1}{A+Be^{-J/kT}} + D, \qquad (5)$$

where S is the total spin of a group; J is the exchange integral within the group; A, B, and D are constants.

At high temperatures, the susceptibility obeys the Curie law. When the temperature is lowered, the susceptibility departs from this law, which is equivalent to a decrease in the Curie constant C; then, having passed through a maximum, the susceptibility decreases. At absolute zero, the crystal is diamagnetic. The temperature of the susceptibility maximum, T_1, is a measure of the intensity of the exchange interaction within a group.

The behavior of the susceptibility of a $Na_2Mn_2Si_2O_7$ single crystal in the temperature range 27–300°K is in qualitative agreement with the proposed explanation. First of all, the experimentally determined value of the constant C in the Curie-Weiss law is in fact 15% lower than the theoretical value calculated assuming one type of Mn^{2+} ions with $s = 5/2$. Secondly, when the temperature is lowered the susceptibility passes through a maximum and then decreases. The observed anomalies can be explained by the appearance of order within groups. This conclusion is supported also by an analysis of the crystal structure of the compound. It has been found that the $Na_2Mn_2Si_2O_7$ lattice includes groups consisting of four Mn^{2+} ions (Mn^3_I, Mn^4_I, Mn^1_{II}, Mn^3_{II}) and the distances between these ions are ≈3.5 Å. All the remaining Mn^{2+} ions are separated by distances greater than 5 Å. Thus, a direct exchange interaction within a group may be considerably stronger than that between groups.

Since the spins of Mn^3_I and Mn^4_I, as well as of Mn^3_{II}, Mn^1_{II}, are mutually parallel in the antiferromagnetic state, we may assume that these spins are reoriented in the same way when order is established within a group. Consequently, the spins of these pairs are antiparallel. The resultant weak ferromagnetic moment of a crystal should be equal to the difference between the moments of each of the systems of manganese ions considered separately. This can explain the low value of the experimentally observed ferromagnetic moment.

The ordering within groups may be responsible also for the anomalous temperature dependence of the EPR line width. The observed anisotropy of the line width, which is found even at room temperature, is evidently due to the different intensities of the dipole-dipole interaction along different directions within a group. However, at present we cannot suggest any working hypothesis to explain these anomalies.

Summarizing our discussion, we can say that two successive stages are observed in the investigated compound: first, a partial ordering within groups, governed by the exchange integral J_1, and then a complete ordering of the magnetic system governed by J_2.

The values of these integrals determine, respectively, the temperature of the susceptibility maximum (T_1) and the temperature at which anisotropy appears (T_N). Since the appearance of a short-range order is observed in many antiferromagnets but a broad susceptibility maximum is a rare phenomenon, it follows that T_N is usually greater than T_1. However, there are cases when $T_N < T_1$. This has been observed most clearly for $CuF_2 \cdot 2H_2O$,[7] for which the difference $T_1 - T_N$ is 12°. In our case, $T_1 - T_N \approx 30°$.

In conclusion, the authors express their deep gratitude to A. S. Borovik-Romanov for a detailed discussion of the experimental results and for his constant interest in this investigation.

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