NEUTRON DIFFRACTION STUDY ON MANGANESE TELLURIDE

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Résumé. — L'étude en diffraction neutronique du tellurure de manganèse, a été faite sur une poudre. L'échantillon soigneusement analysé par rayons X à haute température a été prouvé être exempt de traces de MnO et de $MnTe_2$ qui peuvent contaminer l'échantillon. L'étude a montré que la structure magnétique de MnTe consistait en plans c, ferromagnétiques couplés antiferromagnétiquement suivant l'axe c. La direction des spins est dans le plan c. Le facteur de forme magnétique des ions Mn dans MnTe a été trouvé très proche des valeurs expérimentales déjà données par Corliss *et al.* La valeur la plus probable du nombre quantique de spin d'après les résultats de la diffraction est 4,6/2 et, d'après les mesures de susceptibilité magnétique 5,05/2. Ceci implique que l'ion manganèse dans MnTe a 5 électrons non appariés.

Abstract. — A neutron diffraction study of manganese telluride has been made using powder specimen. The specimen has been carefully checked by high temperature X-ray analysis and has been proved to be free from MnO and $MnTe_2$ which are apt to contaminate the specimen. This investigation has shown that the magnetic structure of MnTe consists of ferromagnetic sheets in c-planes which are coupled antiferromagnetically along the c-axis. The d irection of spins lies within the ferromagnetic sheet. The magnetic form factor of Mn ions in MnTe has been found to be very close to the experimental values obtained by Corliss and others. The most probable value of the spin quantum number is obtained by neutron diffraction data as 4.6/2 and by the measurement of the magnetic susceptibility as 5.05/2. It implies that the maganese ion in MnTe has five unpaired electrons.

1. **Introduction.** — Manganese telluride crystallizes in the well-known nickel arsenide structure with hexagonal symmetry (D^4_{6h}). Typical antiferromagnetic susceptibility has been observed firstly by Squire [1] and later by many investigators. The observed Néel point lies between 37 °C and 50 °C and the spin magnetic moment ranges from 5.10 to 6.08 indicating $S = 4/2$ or $5/2$ which may be ascribed to four or five unpaired electrons in a manganese ion. The spin orientation has been predicted to be antiparallel between adjacent (001) planes by Greenwald [7] from the temperature dependence of the lattice parameter and to lie in (001) plane by Hirakawa [8] from the measurement of magnetic anisotropy. Recently, Komatsubara, Murakami and Hirahara [6] have made a detailed study of magnetic anisotropy on a single crystal specimen and have compared the experimental results with three kinds of spin structure models proposed by Hirone and Adachi [9] on the basis of the molecular field theory. They have concluded that the spin arrangement is the simplest one in which spins of manganese ions couple ferromagnetically in the same c-plane and antiferromagnetically in the adjacent c-planes. However a powder neutron diffraction study by Doroshenko, Klyushin, Loshmanov and Goman'kov [10] has shown that their results cannot be interpreted in terms of this model. They observed an enhancement of the (002) reflection with the development of the magnetic order and its disappearance in the paramagnetic region. Since the nickel-arsenide structure, like manganese telluride, should show a nuclear (002) reflection, it should be necessary to assume not only a complex magnetic structure but also a crystal structure other than nickel-arsenide.

As manganese telluride is easily contaminated by manganese oxide, manganese ditelluride and metallic tellurium [11], the main purpose of the present paper is to determine the magnetic structure by measuring the neutron diffraction pattern for carefully prepared samples and to compare our results with those obtained by the Russian scientists and with the conclusion drawn from the anisotropy measurement.

According to the previous magnetic measurements [2-6] each manganese ion in manganese telluride should be di or tri-valent with five or four unpaired electrons. The crystalline field at the position of metal ions induced by six metalloids is nearly cubic since c_0/a_0 is very close to 1.63 in MnTe. The conductivity of the compound is rather semiconductive than ionic, therefore it is of interest to examine how the covalent bonding in the cubic environment affects the distribution of unpaired electrons. The second purpose of the present work is to obtain this information from the measured magnetic form factor.

In this paper, the method and the results of

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the neutron diffraction are described in Section 5 and 6 and subsidiary properties such as the crystal structure and the magnetic susceptibility in Section 3 and 4. Pure samples are made by the method described in Section 2.

2. **Sample preparation.** — Electrolytic 99,9 % manganese and 99,99 % tellurium were respectively purchased from Kanto Chemical Co, and Chiyoda and Co. The materials were ground into powder, mixed in the stoichiometric composition, and doubly sealed in quartz tubes evacuated at 10^{-5} mmHg. The mixture was heated up to 750 °C with a rate of 40 °C/hr, kept at the temperature for 2 days and then cooled down to room temperature at the same rate. The temperature treatment was determined by the reason that MnTe becomes more stable than $MnTe_2$ above 700 °C and that it will react with the quartz capsule above 900 °C.

Since electrical and magnetic properties of MnTe are much influenced by a small contamination of MnTe [11] it is essential to obtain pure MnTe. In order to diminish the residual $MnTe_2$ which inevitably appears in the course of the reaction, the substance was ground again and two or three cycles of the heat-treatment were repeated until any traces of $MnTe_2$, free manganese and free tellurium had disappeared in the X-ray diffraction patterns which were obtained by the usual G-M counter method using Cu-$K\alpha$ radiation. The specimens were confirmed to be a single phase of homogeneous nickel-arsenide structure with lattice parameters of $a_0 = 4.15$ Å, $c_0 = 6.71$ Å at room temperature, in very close agreement with values reported by Furberg ($a_0 = 4.146$ Å, $c_0 = 6.709$ Å) [12].

3. **Crystal structures at high temperatures.** — Electrical resistivity of MnTe at high temperatures has been investigated in vacuum (10^{-2} mmHg) by Uchida, Kondoh, and Fukuoka [3] with samples sintered at 725 °C. They found a M-shaped variation as a function of the temperature with two maxima at 50 °C and 200 °C, and one minimum at about 130 °C. Although the first peak has been interpreted as arising from an antiferromagnetic transformation with a Néel temperature at 50 °C, the second maximum has been considered as an evidence of a crystallographic phase transformation starting at 130 °C.

For the neutron diffraction analysis of the magnetic structure, the existence of the crystallographic transition makes the experiments difficult, because the difference pattern of the paramagnetic and antiferromagnetic phases would include not only contributions from the ordering of the magnetic moments, but also from the crystallographic phase transformation. In order to isolate the magnetic contribution from the observed difference pattern it should be necessary to have a complete knowledge of the crystallographic structures above and below the transformation temperature.

For this aim MnTe has been investigated by X-rays at several temperatures. The sample is maintained at a pressure of 10^{-2} mmHg in a small vacuum furnace. Although only extremely sharp peaks of MnTe were found at room temperature, characteristic peaks of $MnTe_2$ were observed at 250 °C with an order of magnitude comparable to those of MnTe. The diffraction pattern taken at 720 °C again shows no observable peaks of $MnTe_2$. In order to confirm these results, the intensities of some representative peaks of MnTe and $MnTe_2$ were carefully measured by raising the temperature continuously. The intensities of lines showing MnTe structure decrease from about 130 °C and rise again at about 650 °C, while those of $MnTe_2$ begin to appear from about 130 °C showing a flat maximum at about 250 °C, and decrease again, vanishing at 700 °C. The crystallographic transformation seems to be an $\alpha \rightarrow \beta \rightarrow \alpha$ type transition with MnTe structure at room and higher temperatures and with $MnTe_2$ structure at the intermediate temperatures. One of the interesting features of the observed phase transformation is that the $MnTe_2$ structure is not stable above 700 °C. Although the annealing temperature for the synthesis of the specimen was chosen as 750 °C only regarding the reaction kinetics first, it turned out that this temperature was slightly above the stable region of $MnTe_2$.

On the other hand, similar experiments made in higher vacuum of 10^{-4} mmHg *have not revealed such a transformation* and only the reflections from single phase NiAs structure have been observed in the whole temperature range under investigation. Therefore, it should be concluded that the crystallographic transition proposed by Uchida et al. is a fictitious one only observed in low vacuum. This crystallographic behavior at high temperatures is easier to understand as a chemical reaction rather than a phase transformation. Since reflections from MnO have been observed in X-ray patterns taken at high temperatures and in low vacuum as well as those from $MnTe_2$, the first transformation is considered to be an oxidation reaction expressed as

$$2MnTe + (1/2)O_2 \rightarrow MnO + MnTe_2.$$

The second transformation is a decomposition process

$$2MnTe_2 \rightarrow Te_2 + 2MnTe.$$

in which tellurium evaporates because of its extremely high vapor pressure. In fact a deposit of metallic tellurium has been observed inside the furnace.

Since Uchida and others have made their experiments under low vacuum, the M-shaped temperature dependence of the resistivity should be also well explained by the fictitious transition. The intrinsic resistivity of MnTe has been found to decrease exponentially with increasing temperature and to be approximately 0.5 ohm-cm at room temperature [5]. Below the Néel temperature, increasing development of the magnetic order diminishes electrical resistivity and, therefore, a resistivity maximum appears near the Néel point as schematically shown in figure 1 by

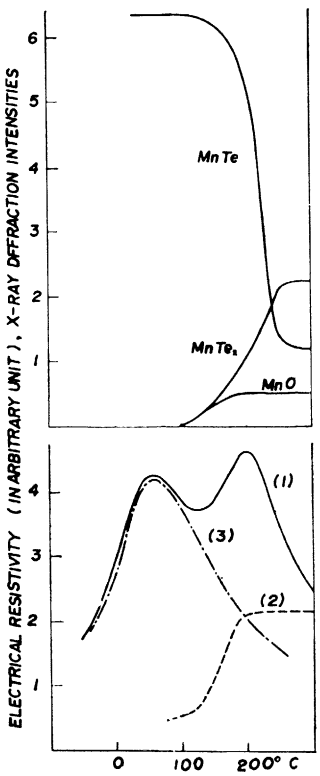

FIG. 1. — Change of the electrical resistivity and the X ray patterns for the samples in low vacuum.
Upper figure shows the relative intensities of the characteristic reflections of MnTe, $MnTe_2$ and MnO. The lower figure shows the temperature dependence of the electrical resistivity. The solid curve (1) shows the experimental results, dotted curve (2) the estimated contribution from the oxidation, and the curve (3) the intrinsic behavior of the electrical resistivity with magnetic transformation. Curve (1) is composed by adding curve (2) and (3).

Curve 3. Curve 2 shows the additional increase of the resistivity corresponding to the oxidation process. This excess restivity is assumed to be proportional to the amount of MnO which is determined by X-ray analysis as shown in the upper part of the figure. The M-shaped temperature dependence of the resistivity shown in figure 1. Curve 1, is explained by combining Curves 2 and 3.

4. **Magnetic measurement.** — The number of the unpaired electrons on Mn ion can be calculated from the magnetic susceptibility which depends on temperature through the equation :

$$\chi_{mol} = \frac{N\mu^2}{3k(T - T_p)} = \frac{NP_{eff}^2}{3k(T - T_p)} \mu_B^2, \qquad (1)$$

where χ_{mol} is the magnetic molar susceptibility, N the Avogadro number, k the Boltzmann constant, T the absolute temperature, T_p the paramagnetic Curie Point, μ the magnetic moment of the manganese ion, μ_B the Bohr magneton, and P_{eff} the effective number of Bohr magnetons.

TABLE 1

CURIE- WEISS CONSTANT C, EFFECTIVE BOHR MAGNETON P_{eff} AND SPIN QUANTUM NUMBER S OF MnTe CALCULATED FROM THE MAGNETIC SUSCEPTIBILITIES

C	P_{eff}	S	SOURCE
4.59	6.08	5.16/2	Serres [2]
3.24	5.11	4.19/2	Uchida et al. [3]
4.46	6.00	5.08/2	Banewicz et al. [4]
	5.60	4.70/2	Hirahara et al. [22]
4.43	5.97	5.05/2	Present Authors

In Table I are listed values of P_{eff} and the spin quantum number S defined by:

$$P_{eff} = 2\sqrt{S(S+1)}, \qquad (2)$$

under the assumption that the orbital moment is completely quenched. According to the preceeding section, MnTe is easily oxidized producing MnO and $MnTe_2$. The variety of the spin quantum number listed in Table I should be attributed to the difficulty of the sample preparation.

In the present study, the susceptibility has been measured between 293 °K and 983 °K with the specimen material sealed in a small quartz capsule evacuated at 10^{-5} mmHg by means of an automatic magnetic balance with a differential transformer as a detector [13]. This is an improvement of the balance originally developed by Hirone and others using capacity plates as a detector [14].

The antiferromagnetic Néel point has been found at 50 °C. The reciprocal susceptibility is shown in figure 2 as a function of absolute temperature after making the diamagnetic correction for the closed shell :

$$\chi_{dia} = 60 \times 10^{-6} \text{ emu/mol.}$$

Applying Curie-Weiss law to the results obtained between 603 °K and 983 °K, the paramagnetic Curie temperature T_p and P_{eff} are calculated to be — 692 °K and 5.97 $\pm$ 0,03 μ_B respectively. Since the value of S calculated from eq. (2) is 5.05/2,

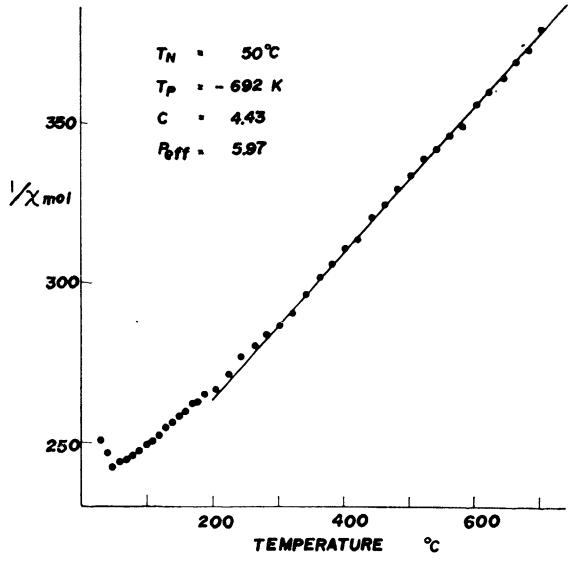

FIG. 2. — Temperature dependence of the reciprocal molar susceptibility.

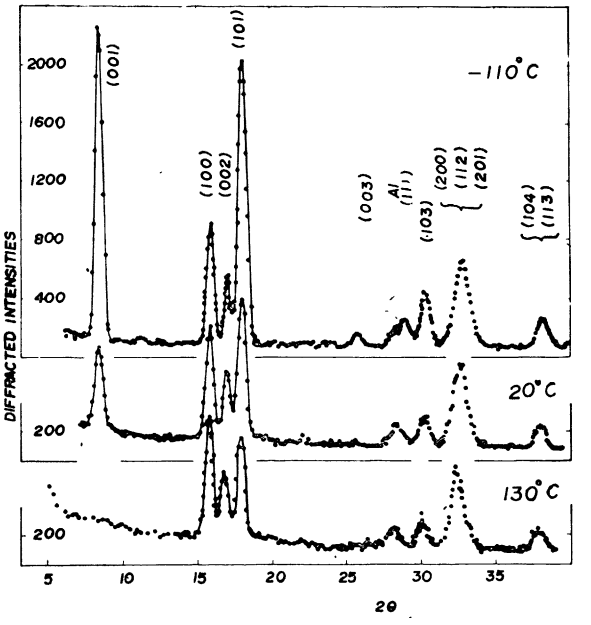

FIG. 3. — Neutron diffraction patterns of MnTe measured at — 110 °C, room temperature and 130 °C.

the spin quantum number should be 5/2. It implies that each manganese ion should have five unpaired electrons in MnTe.

In order to confirm the effect of oxidation, the magnetic susceptibility has been measured with the specimen sealed in low vacuum. The results are very similar to those observed by Uchida et al. showing an appreciable hysteresis in heating and cooling which is not observed in the case of high vacuum. Therefore, it is concluded that lower values reported for S might be due to contamination by oxide and ditelluride.

5. **Neutron diffraction results.** — Neutron diffraction patterns, measured at — 110 °C, room temperature and 130 °C and shown in figure 3, were obtained with the powder specimen type neutron diffractometer of JAERI. The pattern taken at — 110 °C corresponds to the nearly saturated antiferromagnetic state and that taken at 130 °C to the paramagnetic state. Their difference pattern is shown in figure 4. The room temperature pattern shows the intermediate state, where the ordering of the magnetic spins is incomplete.

The observed peaks are indexed in the chemical unit cell of the nickel arsenide structure which contains two metal and metalloid atoms as shown in figure 7. The four peaks assigned as (001), (003), (111), and (113) are purely magnetic because they appear in the difference pattern but not in the high temperature pattern. On the other hand, the (100) and (002) reflections are purely nuclear, because they appear in the high temperature pattern but not in the difference pattern. The (101),

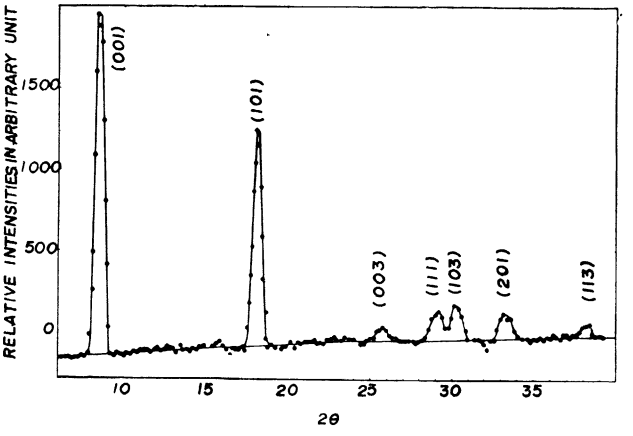

FIG. 4. — Difference pattern showing the magnetic contribution at — 110 °C.

(103), and (201) reflections are both nuclear and magnetic. Peaks corresponding to a unit cell larger than the chemical one are not observed throughout the whole temperature range. In general, magnetic lines are observed only when l is odd and lines with even l are purely nuclear. This implies an antiferromagnetic structure in which the sign of spins alternates along the c-axis with the period c_0. Considering the facts that the intensity of the magnetic superlattice line (001) is most pronounced and that the (101) reflection is also verys trong, the spin direction is probably perpendicular to the c-axis.

Intensities for the nuclear scattering were calculated for MnTe at 130 °C by using the coherent

nuclear scattering amplitudes of -0.36×10^{-12} cm for Mn and 0.56×10^{-12} cm for Te, and a Debye temperature of 217 °K calculated from specific heat measurements [16]. The calculated as well as observed intensities of the nuclear scattering are shown in figure 5 in which they were normalized to the (100) reflection. It is also assumed in the calculation that the preferred orientation does not exist for the neutron diffraction specimen although it was observed in the X-ray pattern.

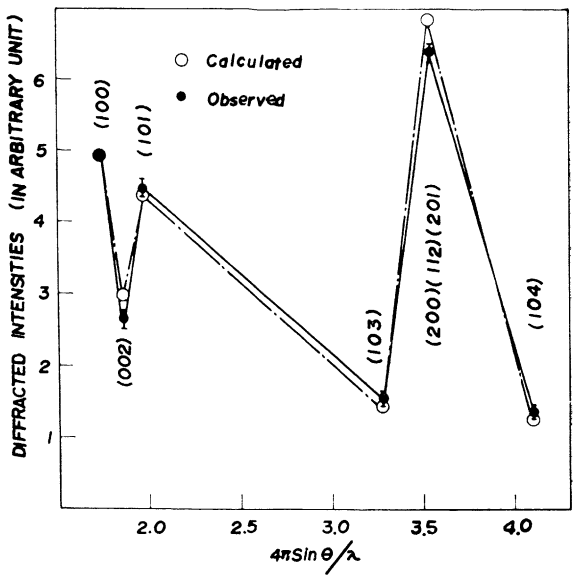

FIG. 5. — Comparison between the observed and the calculated intensities of the nuclear reflections. The intensities are normalized by (100) reflection.

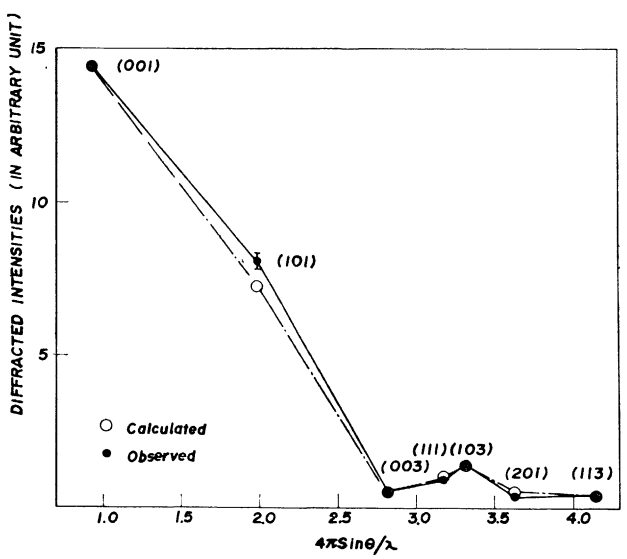

FIG. 6. — Comparison between the observed and the calculated intensities of the magnetic reflection. The intensites are calculated by using the from factor proposed by Hastings, Elliott and Corliss.

The agreement between calculated and observed intensities is almost satisfactory except that the observed (002) reflection is slightly smaller than calculated.

The magnetic contribution was calculated by using the average form factor of Hastings, Elliott and Corliss [17]. The experimental values (after Debye-Waller correction) are shown figure 6. The agreement is satisfactory and confirms the validity of the magnetic structure model drawn in figure 7.

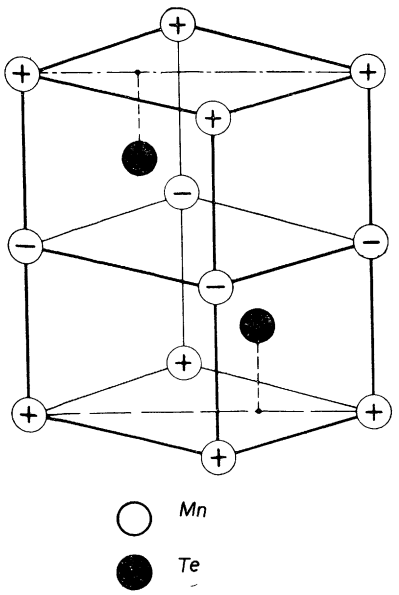

FIG. 7. — Antiferromagnetic structure model of MnTe.

The magnetic scattering amplitudes at 20 °C, — 110 °C, and 148 °C are 0.51, 0.98 and 1.07×10^{-12} cm respectively and the spin quantum number obtained by the extrapolation of the Brillouin curve is $S = 4.6/2$ for this specimen.

6. **Discussion.** — The first conclusion derived from the present investigation is that MnTe has a simple antiferromagnetic structure with spins in c-plane as is shown in figure 7. This conclusion strikingly contradicts Doroshenko et al. [10] who propose a complex magnetic structure. The discrepancy is probably due to the difficulty of the sample preparation as is described in section 2 and 3. The present conclusion is, however, consistent with magnetic anisotropy measurements. Two-fold symmetry of the torque curve has been observed in the plane including the c-axis and six-fold symmetry in that perpendicular to the c-axis, suggesting that the spins lie in c-plane. Six-fold symmetry changes into two-fold, after the stress-anneal [8] or field-cooling [6] implying that the spin direction should be unique in these specimens and should not be triangular

[9]. Such a behaviour of the magnetic anisotropy is well explained by considering that the crystal is composed of three kinds of magnetic domains with the magnetic structure shown above. The second conclusion concerns the magnetic form factor deduced from our experimental results and shown in figure 8. The theoretical atomic form

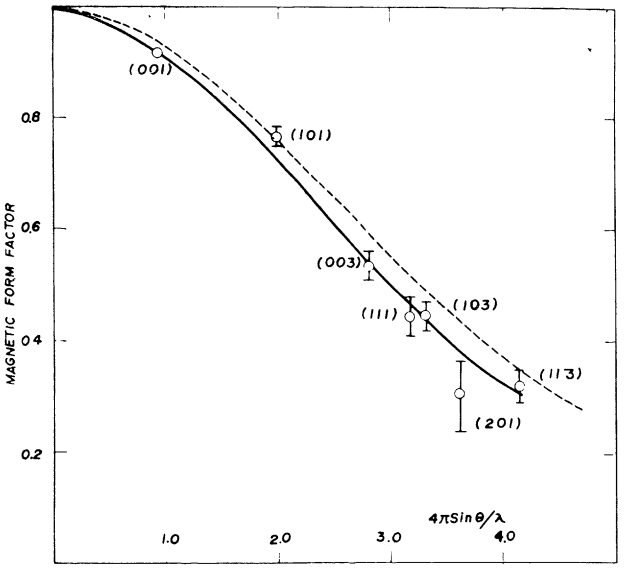

FIG. 8. — The magnetic form factor of manganese ions in MnTe. The dotted curve shows the theoretical value by Watson et al. and the solid one the experimental value by Hastings et al.

factor for 3d electrons in free Mn^{2+} ion calculated by Watson and Freeman [18] and the experimental curve obtained by Hastings, Elliott and Corliss [17] by averaging the observed values for several manganese compounds are shown in the same figure for comparison. These curves are similar to each other so that the electron distribution is almost spherical but slightly expanded from that of the free ion. A small bump is observed in the (101) reflection beyond the experimental error, but it is probably explained by assuming that the specimen has a slight preferential orientation in which the basal plane of any crystallite tends to align horizontally. This tendency shows up in figure 6 as a disagreement between the observed and calculated intensities of the (002) reflection.

According to the magnetic measurement. the Mn ion in MnTe should have five unpaired electrons and the ground state $^6S_{5/2}$. Since this electronic state is hardly influenced by the crystalline field, the deformation from the spherical distribution should be quite small. However the existence of covalent bonds anticipated from the electrical resistivity should deform the electronic distribution. By the present experiment, an anisotropic deformation of the electronic distribution has not been observed within the experimental accuracy, but experiments to measure the form factor more precisely on single crystalls of MnTe and other manganese compounds are now in progress.

A model of chemical bonds in MnTe has been proposed by Pearson [19] explaining both magnetic and electrical properties of MnTe. His model assumes that manganese and tellurium ions should be monovalent and are bound together by p^3 resonating bonds and that five d-electrons form the electronic shell with magnetic moment. The present experimental study does not provide a direct proof or disproof of Pearson's theory but agrees in that the spin quantum number is probably 5/2 and that the unpaired spin distribution is nearly spherical. The obtained value $S = 4{,}6/2$ is considerably smaller than 5.0/2 obtained from magnetic susceptibility measurement. If one assumes that the smaller value of the observed (002) reflection is due to preferred orientation, in the present specimen, the correction can be easily made to obtain $S = 4.8/2$ which is still below 5.05/2. The reason of this discrepancy is not known but Takei, Cox, and Shirane have recently found a similar tendency in CrSb but not in MnSb [20]. It is also planned to measure the magnetic moment at liquid helium temperature to confirm this effect.

8. **Conclusion.** — The neutron diffraction study of a carefully prepared MnTe specimen reveals (1°) that the spin structure of MnTe is the simple antiferromagnetic structure shown in figure 7 (2°) that the unpaired electronic distribution is nearly spherical and (3°) that the spin quantum number is 4.6/2 or 4.8/2 which is compared with 5.05/2 obtained from susceptibility measurements.

9. **Acknowledgments.** — The authors express their hearty thanks to Mr. H. Motohashi and to Mr. N. Minakawa for their technical assistance in X-ray and neutron diffraction analysis and to Drs. Y. Obata and Y. Takagi for their discussions.

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