Journal of the Physical Society of Japan
Vol. 51, No. 2, February, 1982, pp. 452–459

Mössbauer and X-Ray Study of $MnTe_2$

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(Received August 17, 1981)

Experiments on the Mössbauer effect of ^{125}Te and the X-ray diffraction for antiferromagnetic $MnTe_2$ were performed. Temperature dependence of the spin direction has been observed for a magnetic ordering of the first kind fcc lattice. The angle between the spin direction of Mn and the principal axis of electric field gradient increases from 23° at 4.2 K to 30° at 60 K and decreases to 0° at 70 K. Discontinuous changes are found in hyperfine field and quadrupole splitting at 60 K. An analysis of X-ray diffraction intensities for (742), (732) and (721) reflections shows that u parameter increases by 0.0015 at 60 K as temperature decreases and that Einstein temperature increases from 95 K to 105 K below 60 K. The crystallographic phase diagram of MnTe–Te system is given.

§1. Introduction

$MnTe_2$ is an antiferromagnetic semiconductor. Its Néel temperature is about 85 K[1,2,3] and its crystal structure is the pyrite type.[2] The neutron diffraction study for $MnTe_2$ by Hastings *et al.* shows that the magnetic ordering is the first kind of fcc lattice.[2] Pasternak and Spijkervet[3] measured the hyperfine field of Te, which is transferred from the neighboring Mn atoms, and revealed that the Mn spins in the first kind ordering are non-collinear and the direction of Mn spin makes an angle of about 30° at 4.2 K and nearly 0° at 77 K with the symmetry axis at Mn site. The temperature dependence of spin direction was not measured in detail. Hase *et al.*[4] studied theoretically an effect of the anisotropy energy on the first kind antiferromagnetic structure in the pyrite type crystal. They considered higher order spin interactions and explained qualitatively the change in spin direction of $MnTe_2$ below T_N.

We have made a Mössbauer measurement of ^{125}Te in $MnTe_2$ to investigate the temperature dependence of spin structure in detail. We have found anomalous changes in the spin direction and in the hyperfine field at 60 K below T_N. A part of these results was reported in ref. 5. To investigate the anomaly at 60 K in detail, we have made thermal expansion and X-ray diffraction experiments for $MnTe_2$. A weak anomaly has been found in a thermal expansion of $MnTe_2$ at 60 K,[6] although the pyrite structure remains unchanged on cooling down to helium temperature.[7]

This paper reports the detail of spin structure in the first kind fcc lattice and anomalies at 60 K.

§2. Experimental

2.1 *Sample preparation*

$MnTe_2$ crystallizes peritectically from the melt.[8] We have made a phase diagram for MnTe–Te system to prepare the samples for Mössbauer and X-ray measurements as follows.

The sample of $MnTe_2$ which had been sintered at 700°C for three days was sealed in an evacuated quartz ampoule, inside which carbon was coated. We heated the ampoule in a furnace, which was set vertically, at 800°C for three hours, and then cooled by moving down at a rate of 1 mm/hr through the furnace and rotating at a rate of about 50 rpm. The sample obtained is shown in Fig. 1. The X-ray diffraction patterns reveal that the parts I, II

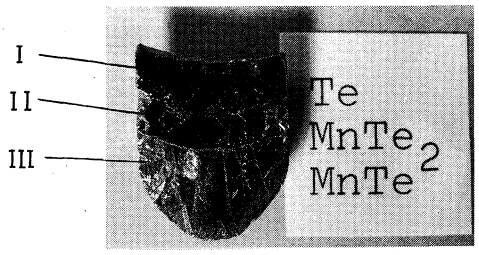

Fig. 1. The sample prepared by Bridgemann type method, separated into three parts. Each part I, II and III of the sample is confirmed to be Te, $MnTe_2$ and MnTe respectively by an X-ray diffraction.

and III are Te, $MnTe_2$ and MnTe respectively. A gravimetric analysis for the $MnTe_2$ and Te indicates that a point A in Fig. 2 locates at 16.4 at%Mn. A thermal analysis has been carried out form $MnTe_2$, which was sealed in an evacuated quartz vessel, using a differential thermal analyzer. It is confirmed that $MnTe_2$ forms peritectically at 742°C, with the liquidus temperature 760°C for 66.7 at%Te composition. A peak of Te appears in DTA curve and becomes larger and larger with thermal cycles. This verifies a presence of pertitectic line in the phase diagram. The peritectic temperature is in good agreement with that reported by Dudkin and Vaidanich,[8] but the liquidus temperature is lower by about 100°C than the temperature determined by them. From these results, one can derive a crystallographic phase diagram for MnTe–Te system as shown in Fig. 2. On the basis of this phase diagram, we started from the 88 at%Te composition to make a single crystal of $MnTe_2$. The starting material with the

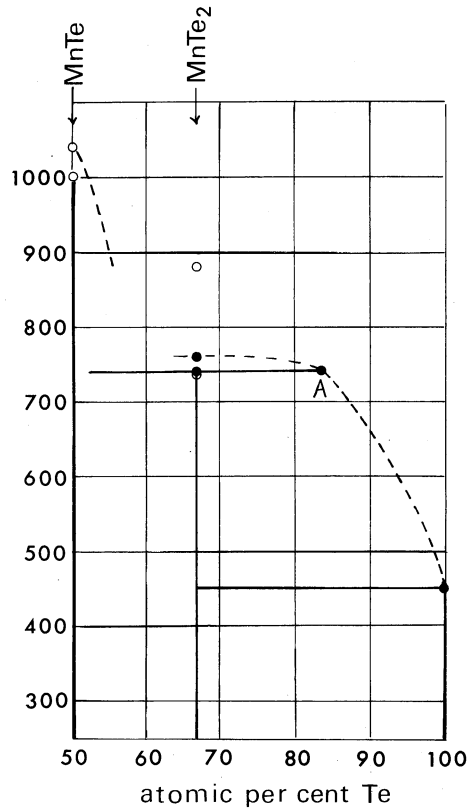

Fig. 2. Phase diagram for MnTe–Te system. The data for $MnTe_2$ by Dudkin and Vaidanich are shown by open circles.

calculated amounts of 99.99% purity Mn and Te was sealed in an evacuated quartz ampoule, coated with carbon on the inner surface. The ampoule was heated in a furnace at 780°C for three hours and was moved down at a rate of 1 mm/hr through the furnace, while the ampoule was rotated with the wire suspending it at a rate of about 50 rpm. The grown samples were $MnTe_2$ and Te. The sample of $MnTe_2$ were confirmed to be single crystal by Laue's X-ray pattern.

A polycrystalline sample which was used in Mössbauer experiment was prepared as follows. The stoichiometric amounts of 99.99% Mn and Te were sealed in an evacuated quartz ampoule, heated at 470°C for one day and at 650°C for one day, and cooled slowly. The procedure was repeated twice. We prepared the powdered sample for X-ray diffraction experiment by grinding single crystals described above. The lattice constant is 6.942 ± 0.004 Å for both samples for X-ray and Mössbauer experiments.

2.2 Experimental procedure

Mössbauer experiment of ^{125}Te was performed in the temperature range from 4.2 K to 100 K. The γ-ray source is 5 mCi ^{125}Sb in rhodium. All measurements were performed with the source kept below 77 K. The velocity scale was calibrated with a spectrum of metallic iron at room temperature. The temperature dependence of Mössbauer spectrum of ^{125}Te in $MnTe_2$ is shown in Fig. 3.

The X-ray diffraction were carried out using CuKα radiation by a step scanning method with an increment of 0.01 degree. Total counts of integrated intensity for a reflection are several tens of thousands. The temperature range was from 20 K to 300 K. We used the three reflections, that is, {(742), (821),} {(732), (651)} and {(721), (633), (552)} reflections, because they have strong intensity and high angle in 2θ. For convenience, we name those reflections (742), (732) and (721) respectively in this paper. A typical profile, which is for (742) reflection of $MnTe_2$, is shown in Fig. 4.

§3. Results and Analysis

3.1 Mössbauer effect

3.1.1 Mössbauer spectrum

Hyperfine field H, quadrupole splitting $E_{Q.S.}$ ($=e^2qQ/2$), angle between the spin direction

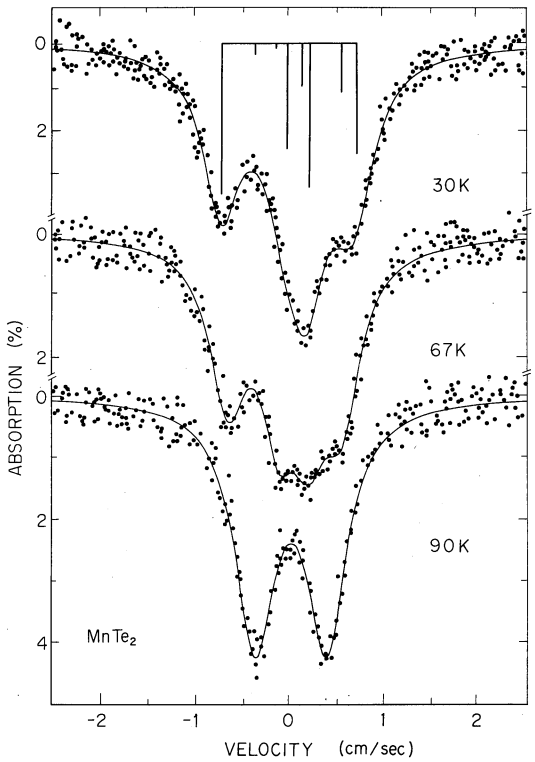

Fig. 3. Mössbauer spectra of ^{125}Te in $MnTe_2$.

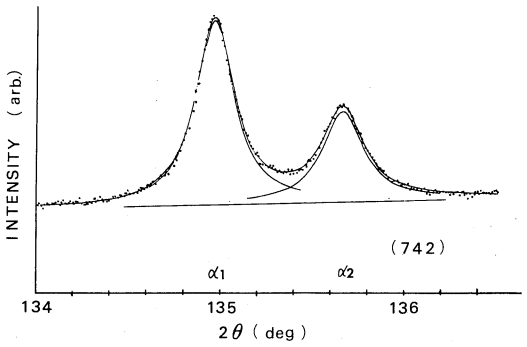

Fig. 4. X-ray diffraction pattern for (742) reflection in $MnTe_2$. The solid line shows the best fit curve. The computer fitting curves of the $K\alpha_1$, $K\alpha_2$ line and the back ground are also shown.

and the principal axis of electric field gradient φ, line width and absorption area (integrated absorption intensity) were determined by the least squares fitting of Mössbauer spectra.[9] The φ is the angle between the spin direction and the principal axis of electrical field gradient and have an effect on the magnetic hyperfine splitting of energy level for ^{125}Te nucleus.[9] Then φ can be determined from the Mössbauer spectrum for polycrystalline samples. On the contrary an angle between the spin direction and incident direction of γ-ray is averaged out in Mössbauer experiment for polycrystalline samples and then the angle can not be determined from the Mössbauer spectrum. Solid curve in Figs. 3 were obtained by a computer fitting.

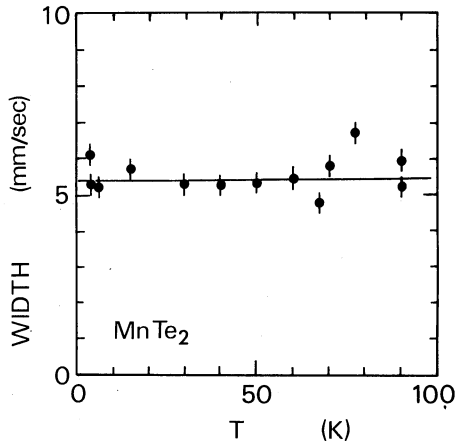

Fig. 5. Temperature dependence of the line width of Lorentzian in ^{125}Te Mössbauer spectrum.

3.1.2 Line width

The line width of the Lorentzian is 5.5 mm/s and constant in the experimental temperature range as shown in Fig. 5. This value is smaller by 2~3 mm/s than that of Pasternak and Spijkervet.[3]

3.1.3 Temperature dependence of H, $E_{Q.S.}$ and φ

Temperature dependences of the quadrupole splitting and the hyperfine field are shown in Figs. 6 and 7 respectively. The hyperfine field

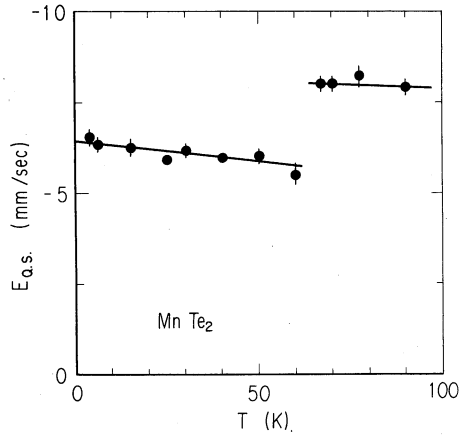

Fig. 6. Temperature dependence of the quadrupole splitting of ^{125}Te.

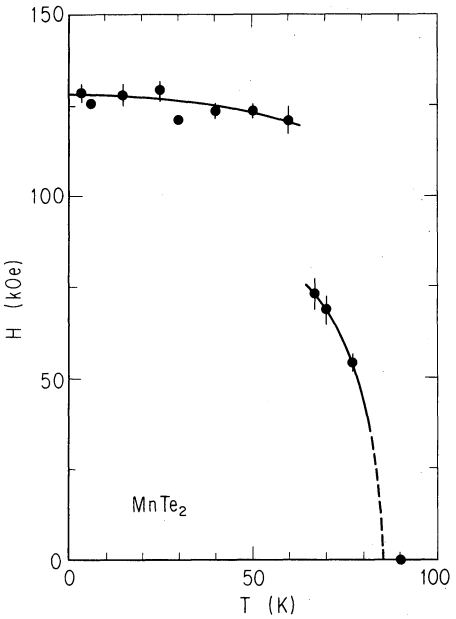

Fig. 7. Temperature dependence of the hyperfine field at ^{125}Te in $MnTe_2$.

disappears at about 85 K. The temperature is in agreement with the Néel temperature which was determined from magnetic susceptibility and resistivity measurements.[1,6,10] Both the quadrupole splitting and the hyperfine field change discontinuously at 60 K. The hyperfine field changes from 125 to 75 kOe and the quadrupole splitting from -5.8 to -8.0 mm/s at 60 K as temperature increases. These changes were not observed by Pasternak and Spijkervet.[3]

The temperature dependence of φ in $MnTe_2$ is shown in Fig. 8. The φ increases from 23° to 30° with increasing temperature up to 60 K. Above 60 K, φ decreases rapidly to 0°. This shows that the direction of Mn spin rotates rapidly toward a body diagonal direction with increasing temperature.

3.1.4 Temperature dependence of absorption area

The temperature dependence of absorption area is shown in Fig. 9. The absorption area is proportional to a recoil-free fraction f. Using Debye model, f is represented as follows,

$$f=\exp\left[-\frac{3E_R}{2k\Theta_D}\left\{1+4\left(\frac{T}{\Theta_D}\right)^{\Theta}\int_0^{\theta_D/T}\frac{y\,dy}{e^y-1}\right\}\right], \quad (1)$$

where E_R is a recoil energy. From a reasonable fitting, the Debye temperature of $MnTe_2$ was

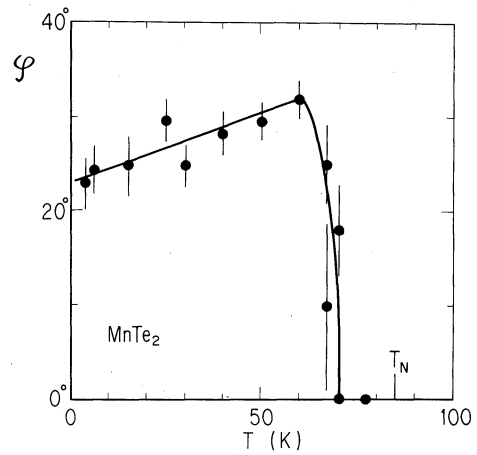

Fig. 8. Temperature dependence of the angle between the spin direction and the principal axis of electric field gradient, φ, in $MnTe_2$.

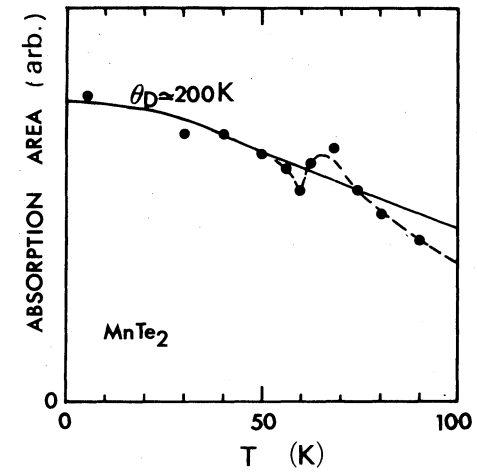

Fig. 9. Temperature dependence of the absorption area of ^{125}Te Mössbauer spectrum in $MnTe_2$. The solid curve shows the calculated temperature dependence of recoil-free fraction assuming $\Theta_D=200$ K. The broken line is for eye guide.

determined to be about 200 K at low temperature. The solid curve in Fig. 9 shows the calculated temperature dependence of recoil-free fraction assuming $\Theta_D=200$ K. The Debye temperature is in agreement with that determined from a specific heat measurement by Westrum and Grønvold,[7] which is about 220 K.[6]

A slight decrease in the absorption area was observed near 60 K, which might be due to a softning of atomic vibration. From the temperature dependence of the absorption area above 60 K, the Debye temperature above

60 K may become lower than 200 K.

3.2 *X-ray diffraction*

3.2.1 *Diffraction pattern*

A diffraction angle 2θ, whidth W and intensity I, were determined by a profile fitting using a least-squares method. The profile fitting method is described in detail elsewhere.[11] The solid curve in Fig. 4 is a best fit curve. The $K\alpha_1$, $K\alpha_2$ lines and the back ground, which were obtained by a computer fitting, are also shown in Fig. 4. The accuracy in a diffraction angle is 0.001° and an integrated intensity is determined within its statistical error.

The temperature dependence of lattice parameter $\Delta a/a$, determined from the observed 2θ, is in good agreement with that determined from the thermal expansion measurement for a polycrystalline $MnTe_2$[6] as shown in Fig. 10. The width of reflection profile depends on temperature. The changes of width from that at 300 K, $\Delta W/W$, are shown in Fig. 11. The $\Delta W/W$ due to the change of lattice parameter from room temperature to 4.2 K is probably in the order of 10^{-2}, which is much smaller than the observed change.[12] The observed

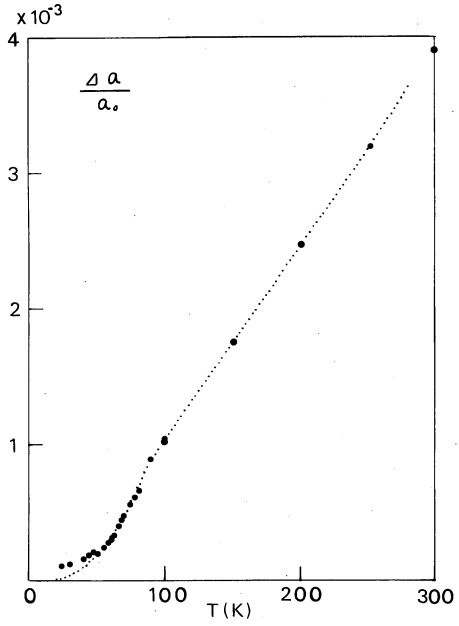

Fig. 10. Temperature dependence of the lattice parameter, $\Delta a/a$. The closed circles show the results from observed 2θ in X-ray diffraction. The dotted line shows the $\Delta a/a$ obtained from the thermal expansion experiment using a capacitance method (ref. 6).

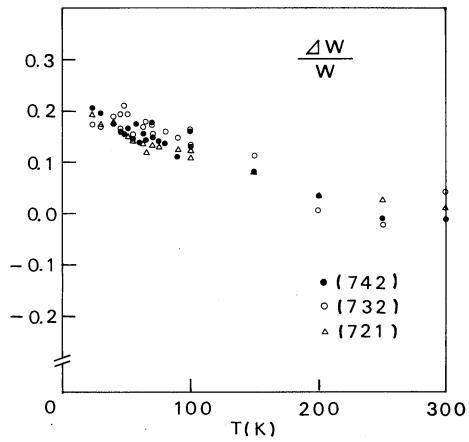

Fig. 11. Temperature dependence of the line width, W, of X-ray diffraction profiles. $\Delta W/W=[W(T)-W(300\text{ K})]/W(300\text{ K})$.

width is probably caused from some factors, for example strain in cryostat, in addition to a sample size. However, we are concerned about the integrated intensity. Generally an integrated intensity is not proportional to a width. We obtained the integrated intensity accurately by the computer fitting for the profile assuming the profile to be a Lorentzian shape.

3.2.2 *Temperature dependence of intensity*

The temperature dependence of integrated intensities is shown in Fig. 12. The intensity

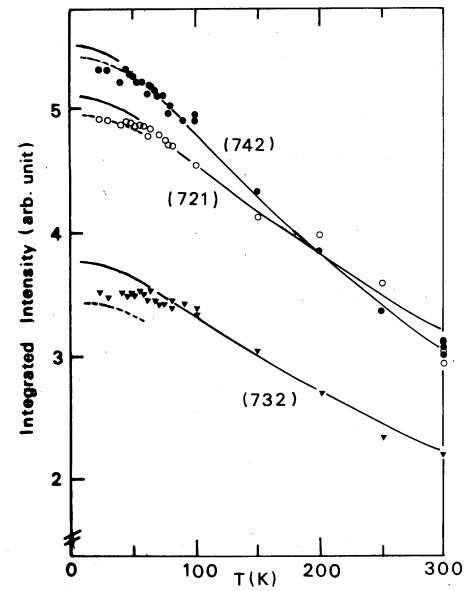

Fig. 12. Temperature dependence of integrated intensity. Solid curves show the calculated intensity for $\Theta_E=95$ K and $u=0.386$. Broken curves below 60 K show those calculated with $\Theta_E=105$ K and $u=0.3875$.

for each reflection does not show any sudden change at 60 K, as observed in Mössbauer parameters.

We compute the intensity of an X-ray reflection assuming that an atomic vibration is isotropic. The structure factor F_{Mn} for Mn, and F_{Te} for Te in $MnTe_2$ can be computed from the data of atomic structure factor of Te and Mn^{2+} and u parameter. The u parameter for $MnTe_2$ has been obtained as 0.386 at room temperature from X-ray and neutron diffraction measurements.[2,14] At a given temperature the intensity is modified by a Debye-Waller factor M due to a thermal vibration of atom. We represent the intensity of reflection in the following way for a convenience of computation,

$$I=I_0\,|\exp(-M_{Mn})F_{Mn}+\exp(-M_{Te})F_{Te}|^2, \quad (2)$$

where I_0 depends on 2θ. The Einstein model being assumed, the Debye-Waller factor is represented as

$$M_x=\frac{2h^2}{m_x k}\cdot\frac{\sin^2\theta}{\lambda^2}\cdot\frac{1}{\Theta_E(x)}\times\left\{\frac{1}{2}+\frac{1}{\exp(\Theta_E(x)/T)-1}\right\}, \quad (3)$$

x: Mn or Te,

where λ, m_x and $\Theta_E(x)$ are a wave length of X-ray beams, mass and Einstein temperature for Mn or Te atom. Though it would be possible that the Mn atoms oscillate with a different frequency from that of Te atoms, we assume $\Theta_E(\mathrm{Te})=\Theta_E(\mathrm{Mn})=\Theta_E$. Contributions from Mn atoms to the intensity for (742), (732) and (721) reflections are rather small and the value of $\Theta_E(\mathrm{Mn})$ has less effect on the intensities. The temperature dependence of the computed intensity for (742) reflection is shown in Fig. 13 for four cases as $\Theta_E=80$, 95, 110 and 150 K. The computed intensity at a given temperature increases and the slope decreases as Θ_E increases.

The temperature dependence of the intensities for three reflections were fitted with the same Einstein temperature. The best fit curves were obtained with $\Theta_E=95$ K when u is fixed to 0.386. The solid curves in Fig. 12 are the best fit curves. Temperature dependence of computed intensities for three reflections is in good agreement with observed ones above about 60 K. Below about 60 K, the observed intensities deviate gradually from the calculated intensities and have a more gentle slope than the intensities expected from $\Theta_E=95$ K. Intensity is expected to decrease when Θ_E decreases. On the other hand slope is expected to decrease when Θ_E increases. Then the observed results can not be explained by changing Θ_E alone. We need another reason which would explain the anomaly at 60 K. The intensity depends also on u parameter through the structure factor. The u dependence of the intensity at 10 K has been computed and is shown in Fig. 14 for $\Theta_E=105$ K. The intensity decreases as u increases near 0.386. Equation 2 is fitted to the temperature dependence and the intensity ratio of the three X-ray reflections with variable parameters Θ_E and u parameter. The best agreement is obtained when $\Theta_E=105$ K and $u=0.3875$. The curves for $\Theta_E=105$ K and $u=0.3875$ are shown as broken lines in Fig. 12 in the temperature range from 10 K to 60 K. The agreement is excellent for (742) and (721) reflections. For (732) reflection, the fitting is not so well as in (742) and (721). However the qualitative agreement is obtained; that is, the intensity becomes lower and the slope becomes gentle. The observed intensities do not change discontinuously at 60 K. It would be possible that near 60 K one of or both Θ_E and u parameter change gradually. Considering the result of Mössbauer experiment, we conclude that

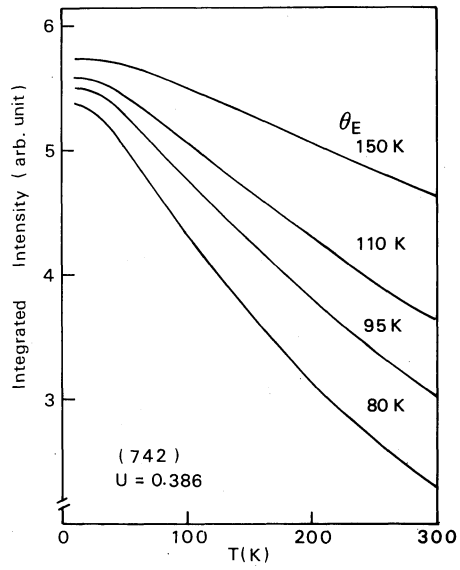

Fig. 13. Computed intensities for various Θ_E when $u=0.386$.

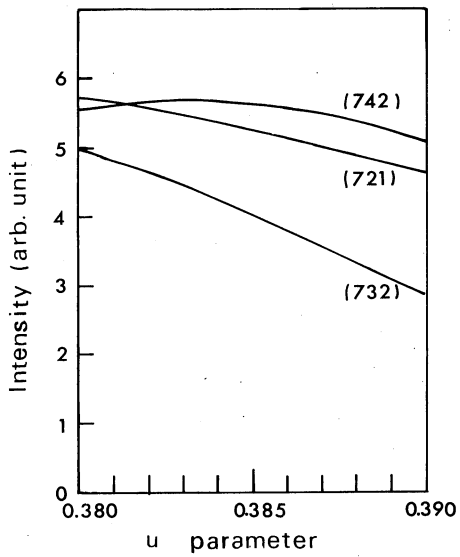

Fig. 14. U parameter dependence of reflection intensity when $\Theta_E=105$ K.

the u parameter changes suddenly at 60 K.

§4. Discussion

4.1 Magnetic structure

Hase *et al.* studied theoretically on the first kind antiferromagnetic structure in the pyrite-type crystal.[4] They considered the fourth order spin interactions and anisotropic energy. They found a solution where the angle φ, which was taken to be 30° at 0 K, decreased with increasing temperature and jumped to 0° discontinuously at $T/T_N=0.52$ under a condition that both the coefficient of anisotropy energy and the coefficient of fourth order interaction energy between localized spins were negative.

From the result of the present Mössbauer measurement, φ is 23° at 4.2 K and increases to 30° at 60 K. Above 60 K, Mn spins turn rapidly to the body diagonal direction.

The rapid change near 60 K below T_N in φ is explained qualitatively with the theory by Hase *et al.* but the decrease in observed φ below 60 K is contradictory to the theoretical result. The temperature variation of φ is due to the competition of the anisotropy energy with the fourth order isotropic spin interactions as described by them. The magnetic interaction in $MnTe_2$ is the superexchange interactions through Te atoms. Then the exchange constant varies as Mn–Te and Te–Te distances change. From our experimental results, the u parameter changes at 60 K. That is, Mn–Te distance decreases and the distance of Te–Te atoms, which make an anion pair, increases at 60 K as temperature increases. The exchange constant J should change at 60 K corresponding to the u change. In the theory by Hase *et al.* the temperature dependence in φ results from the temperature dependence of magnetic moment which is included in the term of spin interactions. The u parameter change at 60 K causes the change in magnitude of J and does not change the temperature dependence of spin interaction term. Then the decrease in φ below 60 K can not be explained due to the change in J alone, although the temperature at which φ jumps discontinuously may change. Another source would be required to explain the decrease in φ below 60 K.

4.2 Anomaly at 60 K

We discuss the anomaly at 60 K in $MnTe_2$. No anomaly appeared at 60 K in the electric resistivity and the magnetic susceptibility.[1,6] Lattice constant increases anomalously at 60 K as temperature increases. The amount of the increase is far less than that expected from a crystal lattice transformation or from a magnetic structure change[6] and the pyrite structure at room temperature remains unchanged on cooling down to low temperature.[7]

The hyperfine field and the quadrupole splitting change discontinuusly at 60 K. The hyperfine field at ^{125}Te is the transferred hyperfine field from the neighboring Mn spins and the quadrupole splitting is caused by the molecular nature of the Te^{1-}–Te^{1-} anion pair in $MnTe_2$.[3] Therefore both the hyperfine field and the quadrupole splitting are sensitive to the position of tellurium atoms in the crystal. U parameter decreases at 60 K from 0.3875 to 0.386 as temperature increases, considering our analysis on the temperature dependence of X-ray diffraction intensity. The change of hyperfine field and the quadrupole splitting at 60 K can be explained through the change of u parameter. The decrease at 60 K in the hyperfine field is explained by the consideration below. If ^{125}Te atom is put as a probe in $MnTe_2$, the transferred hyperfine field at ^{125}Te from neighboring Mn spins should be as shown in Fig. 15 from a symmetry consideration.

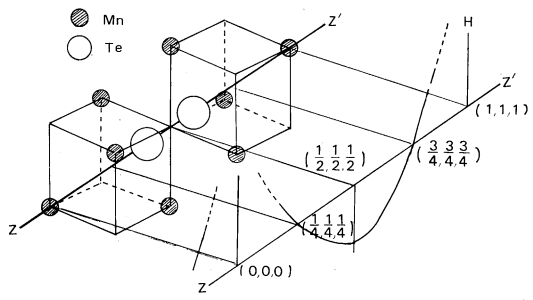

Fig. 15. Schematic representation of the hyperfine field, which is produced by the magnetic moments of Mn atoms on a body diagonal axis in $MnTe_2$. Te atoms lie on the body diagonal axis.

The hyperfine field is minimum at a center of the unit cell and maximum at a corner of the unit cell. At (1/4, 1/4, 1/4) and (3/4, 3/4, 3/4) positions, the hyperfine field is nearly cancelled out. The distance of Te–Te anion pair is $2\sqrt{3}\,(1/2-u)\cdot a$, where a is the lattice constant of $MnTe_2$. When Te atoms move from the position where u is 0.3875 to that where u is 0.386, the hyperfine field at ^{125}Te nucleus becomes weak.

The temperature dependence of Mössbauer absorption intensity predicts that the frequency of atomic vibration is higher below 60 K than above 60 K. The result is consistent with the change of Θ_E determined from X-ray intensity measurement.

§5. Summary

We have made Mössbauer and X-ray experiments for $MnTe_2$. The temperature dependence of spin direction for the first kind fcc lattice has been determined. The angle between the spin axis of Mn and the principal axis of electric field gradient increases from 23° at 4.2 K to 30° at 60 K and decreases to 0° at 70 K. The theoretical study by Hase *et al.* give a qualitative explanation of the discontinuous change in spin direction below T_N not taking into account any u parameter change. Experimentally, the u parameter in $MnTe_2$ changes at 60 K. The theory of Hase *et al.* would require some modification based on the change of u parameter.

The observed temperature dependence of X-ray intensities for (742), (732) and (721) reflections and the intensity ratio of these reflections are fitted to those calculated with variable parameters Θ_E and u parameter. When u is fixed to 0.386, Θ_E above 60 K is determined to be 95 K by the best fitting. Below 60 K, the observed intensities deviate gradually from the best fit curves. It is concluded from this deviation that at 60 K u parameter varies from 0.386 to 0.3875 and that Θ_E increases from 95 K to 105 K. The changes in u parameter and Θ_E mean that Te atoms which make an anion pair come close to each other below 60 K and a thermal vibration frequency increases below 60 K. Discontinuous changes in hyperfine field and quadrupole splitting for $MnTe_2$ have been found. The decrease in hyperfine field at 60 K is explained qualitatively from the decrease in u parameter at the temperature.

Acknowledgement

We would like to express their thanks to Dr. Y. Yamaguchi and Dr. H. Unoki for valuable discussions. We would like also to express their thanks to Mr. K. Matsumoto for use of a Bridgemann type furnace and to Mr. A. Negishi for his support on a differential thermal analysis.

References

1) A. Sawaoka and S. Miyahara: J. Phys. Soc. Jpn. **20** (1955) 2087.
2) J. M. Hastings, N. Elliott and L. M. Corliss: Phys. Rev. **115** (1959) 13: J. M. Hastings, L. M. Corliss and M. Blume: Phys. Rev. **B1** (1970) 3209.
3) M. Pasternak and A. L. Spijkervet: Phys. Rev. **181** (1969) 574.
4) I. Hase, H. Fukuda and A. Yoshimori: J. Phys. Soc. Jpn. **50** (1981) 774.
5) Y. Nishihara and S. Ogawa: J. Phys. (France) **40** (1979) C2–221.
6) N. Kasai, S. Waki and S. Ogawa: to be published in J. Phys. Soc. Jpn.
7) E. F. Westrum, Jr and F. Grønvold: J. Chem. Phys. **52** (1970) 3820.
8) L. D. Dudkin and V. I. Vaidanich: Sov. Phys.-Solid State **2** (1961) 1384.
9) Y. Nishihara: Bull. Electrotech. Lab. **39** (1975) 865.
10) O. Okada and S. Miyahara: J. Phys. Soc. Jpn. **20** (1955) 2087.
11) N. Kasai, Y. Nishihara, T. Kinoshita and Y. Yamaguchi: Bull. Electrotech. Lab. **44** (1980) 259.
12) I. Nitta: *X-Sen Kesshogaku* (X-Ray Crystallography) (Maruzen, Yokyo, 1959) [in Japanese].
13) *International Tables for X-Ray Crystallography* Vol. III p. 210, 211.
14) N. Elliott: J. Am. Chem. Soc. **59** (1937) 1958.