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Thermal Expansion of $MnTe_2$

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The thermal expansion of $MnTe_2$ has been measured. A small anomaly in thermal expansion has been observed at 60 K, which is probably due to a change of internal parameter of crystal. The coefficient of thermal expansion has been separated into lattice, magnetic and Schottky contributions. The magnetic entropy associated with an antiferromagnetic ordering is computed from the observed coefficient of thermal expansion to be (10.8 ± 0.18)J/K·mol. It is concluded that in $MnTe_2$ zero field splitting of the ${}^6S_{5/2}$ is small. The Grüneisen constant for Schottky contribution is negative.

§1. Introduction

$MnTe_2$ is an antiferromagnetic compound with a pyrite structure.[1] The Néel temperature, T_N is 85 K. $MnTe_2$ is a semiconductor with a narrow band gap.[2] It was found from a magnetic susceptibility measurement at high temperatures that in $MnTe_2$ there are five unpaired electrons with parallel spins per Mn^{2+} center.[1] Westrum and Gronvøld[3] measured the specific heat of $MnTe_2$. They estimated from the magnetic contribution to the specific heat that the magnetic entropy associated with antiferromagnetic ordering was only a fraction of the value R ln 6 which was expected for randomization of five manganese 3d electrons over the state ${}^6S_{5/2}$.

The magnetic ordering was studied by several investigators by means of neutron diffraction and Mössbauer effect.[1,4–6] The magnetic structure of $MnTe_2$ is a non-collinear and a first kind ordering of fcc lattice below T_N.

Discontinuous changes in the quadrupole splitting and the hyperfine field in Mössbauer spectrum of ${}^{125}Te$ were observed at 60 K below T_N by Nishihara and Ogawa.[6] However, any anomalous change has not been observed observed at 60 K in other measurements for electric and magnetic properties of $MnTe_2$. We supposed that the discontinuous changes in the quadrupole splitting and the hyperfine field in Mössbauer spectrum are due to a lattice origin.

We have measured a thermal expansion of $MnTe_2$ from 4.2 K to 280 K. A thermal expansion due to the antiferromagnetic ordering has been observed. From the magnetic thermal expansion the magnetic entropy has been computed to be about 73% of R ln 6.

A little anomaly has been observed in thermal expansion at 60 K, where the change in Mössbauer parameter was observed. We report in the present paper the data of thermal expansion, a result of analysis about the magnetic contribution and a Schottky type contribution due to an excited state.

§2. Experimental

Powder sample was prepared as follows. The stoichiometric amounts of manganese and tellurium, of which purity are both 99.99%, were sealed in an evacuated quartz ampoule, heated at 470°C for 24 hours and at 650°C for 24 hours and cooled slowly. The sample was ground and sintered by the same procedure as above once more. A sample used for thermal expansion measurement was prepared in a cylindrical shape by pressed at 400°C in vacuum and sintered 650°C for about one day in an evacuated quartz ampoule. The sample size is 10.90 mm in diameter and 15.10 mm long.

A thermal expansion was measured by the three terminal capacitance method using a copper differential cell.[7] The sensitivity was about 8×10^{-7} in $\Delta l/l$. We had improved the cell used in a previous measurements[7] by using spring washers for all copper screws to avoid an inhomogeneous thermal expansion of cell. The copper cell was calibrated previously

against a copper sample which had been prepared from the same copper block with the cell. The thermal expansion of the copper cell against the copper sample is in good agreement with reported data of thermal expansion of copper.[8,9] Then we assumed that the absolute value of thermal expansion of our copper cell is the same as those reported by Car *et al.* and by Rubin *et al.*[8,9] The absolute value of thermal expansion for a sample is obtained after correcting for the thermal expansion of the copper cell. An error in a thermal expansion comes from the experimental error in measurement and from that included in the data of thermal expansion of copper. The total error in the absolute value of $\Delta l/l$ is less than 1×10^{-5}.

The measurement was done continuously from 4.2 K to 280 K as temperature elevated at a rate of about 3 deg/hr. A Au–0.07 at% Fe vs KP thermocouple thermometer was used for temperature measurements.

The electrical resistivity was measured by a four probe method and the magnetic susceptibility was measured by the Faraday method using a Cahn RG electrobarance.

§3. Experimental Results and Discussion

The experimental result of thermal expansion after correction for the copper cell is shown in Fig. 1. The large expansion below about 85 K corresponds to the antiferromagnetic ordering.

3.1 Anomaly at 60 K

An anomalous expansion has been observed at 60 K. This anomaly corresponds with the discontinuous change at 60 K observed in Mössbauer parameter. The temperature dependence of this anomalous expansion was slightly different for different runs. An example of the observed thermal expansion of $MnTe_2$ in the neighborhood of 60 K is shown in an insertion in Fig. 1. The anomalous change of lattice parameter $\Delta l/l$ is about 4×10^{-6}. The amount is far less than that expected for a crystal lattice transformation or for a magnetic structure change.

The electrical resistivity and the magnetic susceptibility of $MnTe_2$ have been measured carefuly in the neighborhood of 60 K. No anomaly is found in both the measurements. The result of electrical resistivity measurement

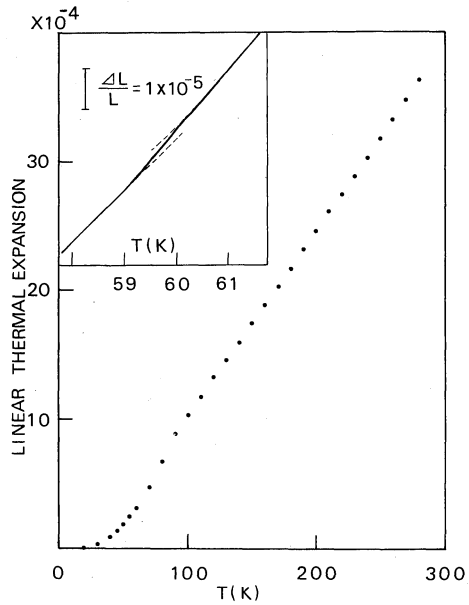

Fig. 1. Thermal expansion of $MnTe_2$. The insertion shows an example of the observed thermal expansion in the neighborhood of 60 K. The anomalous change near 60 K is about 4×10^{-6}.

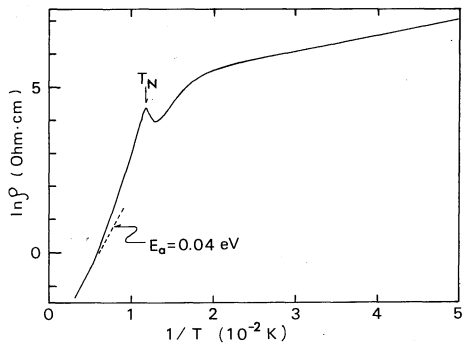

Fig. 2. Electrical resistivity vs resiprocal temperature for $MnTe_2$. The energy separation from ground state to excited state E is twice an activation energy E_a, $E=2E_a$.

is shown in Fig. 2. The result of magnetic susceptibility, uncorrected for diamagnetism, is shown in Fig. 3. It is in good agreement with that by Okada and Miyadai.[10]

Discontinuous changes in the quadrupole splitting and the hyperfine field in Mössbauer spectrum of ^{125}Te were observed at 60 K.[6] The hyperfine field at ^{125}Te is the transfered hyperfine field from the nearest neighbor Mn and the quadrupole splitting is caused by the molecular nature of the Te^{1-}–Te^{1-} anion pair in $MnTe_2$.[5] Therefore both the hyperfine field

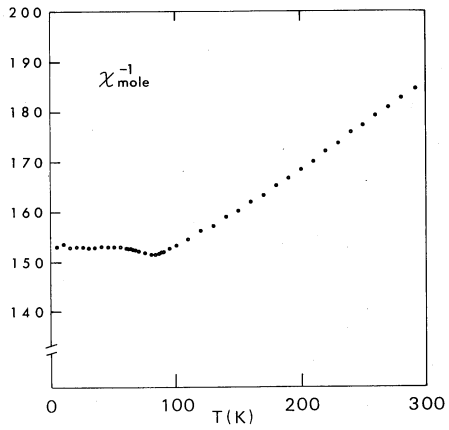

Fig. 3. Inverse susceptibility, χ^{-1}_{mole}, vs temperature for $MnTe_2$.

and the quadrupole splitting are sensitive to the position of tellurium atoms in the crystal. In $MnTe_2$ the pyrite structure remains unchanged on cooling down to low temperature.[1,3] Without a change of crystal symmetry, Te atom can move relatively against Mn atom changing the internal parameter of crystal, u parameter. While, a distance between Te atoms, which make an anion pair, is given by $2\sqrt{3}(1/2-u)\cdot a$. When the u parameter in $MnTe_2$ changes at 60 K, the quadrupole splitting and the hyperfine field change. The lattice constant of $MnTe_2$ is also expected to change a little with the change of u parameter. The anomaly in thermal expansion at 60 K is probably due to the change of u parameter. Thus, a change of the u parameter is one of the possible causes of the anomaly at 60 K.

There is another possibility. According to ref. 6, the angle between the direction of Mn spin and the symmetry axis at Mn site, θ, increases from about 23° to 30° with increasing temperature up to 60 K and above this temperature θ decreases rapidly to 0°.[6] Hase *et al.*[11] studied theoretically an effect of the anisotropy energy on the first kind antiferromagnetic structure in the pyrite-type crystal, in which higher order spin interactions were taken into consideration. They found a solution where the angle θ, which is 30° at 0 K, decreased with increasing temperature and jumped to 0° discontinuously at $T/T_N=0.52$ when both the coefficient of anisotropy energy and the coefficient of fourth order interaction energy between localized spins were negative. This transition is a first order transition.[11] A discontinuous change in thermal expansion would appear associated with the transition.

We can not conclude, only from the experimental data of thermal expansion, which of, or both, the above two possible mechanisms is the cause of the anomaly in thermal expansion at 60 K. An X-ray diffraction experiment for $MnTe_2$ is in progress to measure a temperature dependence of the u parameter.

3.2 Coefficient of thermal expansion

The experimental data of the coefficient of thermal expansion, α, are shown in Fig. 4. The α is contributed from lattice vibration, magnetic interaction and excited energy level,

$$\alpha=\alpha_{lattice}+\alpha_{magnetic}+\alpha_{Schottky}.$$

There is no electronic contribution to α in $MnTe_2$, because $MnTe_2$ is a semiconductor. The electronic energy state of $MnTe_2$ has a low lying excited energy level. The energy separation of the excited state from the ground state in $MnTe_2$, E, is 0.08 eV from the electrical resistivity above 150 K as shown in Fig. 2. The E is in good agreement with those by Brostigen and Kjekshus[2] and by Sawaoka and Miyahara.[12] There should be a Schottky type contribution to the coefficient of thermal expansion from this excited state, $\alpha_{Schottky}$. The specific heat of $MnTe_2$ has also a Schottky contribution.[3]

We have analyzed the observed α and evaluated each contribution as follows. A

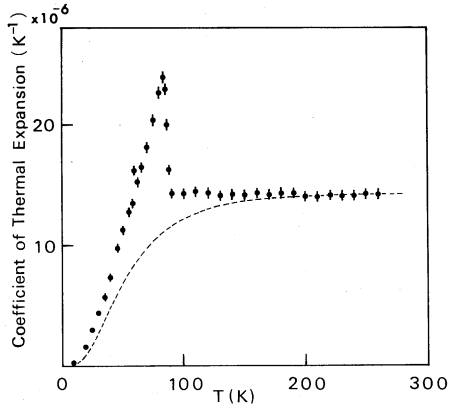

Fig. 4. Coefficient of thermal expansion of $MnTe_2$, α. The sum of estimated lattice contribution and Schottky contribution to the coefficient of thermal expansion is shown by a broken curve.

coefficient of thermal expansion is related thermodynamically with a specific heat, C; $\alpha=(\kappa/3V)\gamma C$, where V, κ and γ are a volume, compressibility and Grüneisen constant respectively. The relations between each contribution to the coefficient of thermal expansion and the specific heat are represented as follows,

$$\alpha_{\text{lattice}}=\left(\frac{\kappa}{3V}\right)\gamma_{\text{lattice}}C_{\text{lattice}},$$

$$\alpha_{\text{Schottky}}=\left(\frac{\kappa}{3V}\right)\gamma_{\text{Schottky}}C_{\text{Schottky}},$$

$$\alpha_{\text{magnetic}}\equiv\alpha_{\text{m}}=\left(\frac{\kappa}{3V}\right)\gamma_{\text{magnetic}}C_{\text{magnetic}}.$$

If there is not α_{Schottky} and the Grüneisen constant is independent of temperature, α above T_{N} is proportional to the lattice specific heat, which can be represented approximately by the Debye specific heat function. The observed α above T_{N} seems almost independent of temperature. The lattice thermal expansion above T_{N} should be suppressed by the Schottky contribution. That is, the γ_{Schottky} is negative as in the case of CeTe.[13]

To separate the α far above T_{N} into α_{lattice} and α_{Schottky}, we need the Debye temperature of $MnTe_2$. The Debye temperature of $MnTe_2$ has not been reported. Then we have evaluated the Debye temperature from the data of specific heat by Westrum and Gronvøld as follows.[3] In the case where there is a contribution of Schottky anomaly, the specific heat is represented as follows,

$$C=3C_{\text{Debye}}(\theta_{\text{D}}/T)+\delta C+C_{\text{Schottky}},$$

where δC is a correction due to the thermal expansion. We can compute the $\delta C(\equiv 9V\alpha^2T/\kappa)$ from the observed thermal expansion and C_{Schottky} from E. C_{Schottky} contributes less than 4% of total specific heat in the temperature range of this analysis. Subtracting δC and C_{Schottky} from the observed specific heat, we evaluated a likely value of θ_{D} as 220 K.

The compressibilities are 6.9×10^{-7} bar^{-1} and 9.6×10^{-7} bar^{-1} for FeS_2 and NiS_2 respectively.[14,15] Both FeS_2 and NiS_2 have the same pyrite structure as $MnTe_2$. Generally a compressibility is larger as a Debye temperature is lower. The Debye temperature is 605 K for FeS_2 and 445 K for NiS_2.[16] We presumed the compressibility of $MnTe_2$ to be 13×10^{-7} bar^{-1}, which is computed by a extrapolation assuming a proportionality between a compressibility and θ_{D}, since there is no experimental value of the compressibility of $MnTe_2$.

Using the specific heat data discussed above and the compressibility, we have estimated that $\gamma_{\text{lattice}}=+2.4$ and $\gamma_{\text{Schottky}}=-3.0$ in order to fit best the observed α above T_{N}. The residual of the coefficient of thermal expansion is represented as $\alpha_{\text{m+u}}$. The temperature dependence of $\alpha_{\text{m+u}}$ is shown in Fig. 5. The anomaly at 60 K is probably due to the change of internal parameter of crystal as discussed at §3.1. The $\alpha_{\text{m+u}}$ includes a contribution from the anomaly in addition to the magnetic contribution. A magnetic entropy associated with an antiferromagnetic ordering, S_{m} is related to a magnetic specific heat, C_{m}, as

$$S_{\text{m}}=\int_0^\infty (C_{\text{m}}/T)\,\mathrm{d}T.$$

This equation is rewritten using a relation $C_{\text{m}}=(3V/\kappa\gamma_{\text{m}})\alpha_{\text{m}}$, as

$$S_{\text{m}}=\frac{3V}{\kappa\gamma_{\text{m}}}\int_0^\infty \frac{\alpha_{\text{m}}}{T}\,\mathrm{d}T,$$

where γ_{m} is a magnetic Grüneisen constant. Assuming that a contribution from the anomaly at 60 K is negligibly small compared with the magnetic contribution, S_{m} is computed from the observed $\alpha_{\text{m+u}}$ to be $(1.3\pm0.1)R$. It is rather in good agreement with the expected value of S_{m} for spin 5/2 considering an uncertainty in $\alpha_{\text{m+u}}$.

Westrum and Gronvøld estimated the S_{m} of $MnTe_2$ from their specific heat data.[3]

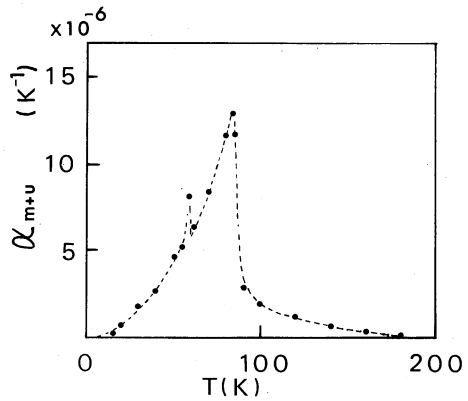

Fig. 5. The magnetic contribution to α for $MnTe_2$ including the anomaly at 60 K which is discussed in the text.

Their value of S_m is only a fraction of the value $R \ln 6$. They interpreted the result in terms of a large zero field splitting of $\pm 3/2$ and $\pm 5/2$ levels from $\pm 1/2$ level. They considered that the energy separation from $\pm 1/2$ level, E/k, is 180 K for $\pm 3/2$ level and 800 K for $\pm 5/2$ level.

It is concluded from our result of S_m that the zero field splitting of the ${}^6S_{5/2}$ state is small and all d levels are occupied. This conclusion is supported from the result by Okada *et al.*[17] that Mn^{2+} ions in pyrite-structure ZnS_2 are in a high spin state ${}^6S$ and the uniaxial crystal field parameter is 0.151 ± 0.001 cm^{-1}.

§4. Summary

We have measured the thermal expansion of $MnTe_2$, analyzed the coefficient of thermal expansion and separated into three contributions α_{lattice}, α_{Schottky} and α_{magnetic}. The Grüneisen constant for Schottky contribution, γ_{Schottky} is negative. The magnetic entropy have been computed from the coefficient of thermal expansion to be (10.8 ± 0.8)J/K·mol. It is concluded that zero field splitting of the ${}^6S_{5/2}$ state is small.

We have found a small anomaly at 60 K, which is probably due to a change of internal parameter of crystal.

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