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Magnetic Properties of Manganese Selenide

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Measurements of magnetic susceptibility and electrical resistivity have been made on the antiferromagnetic compound MnSe in a temperature range covering both of magnetic ordering and paramagnetic regions. The curves of the susceptibility and the resistivity obtained show a large thermal hysteresis and a sharp transition at the Néel temperature. The cooling and warming curves appear to be influenced in some way by the previous thermal history of the sample. The value of the magnetic disorder resistivity in the cooling process is $1.5\times10^4\Omega$ cm.

§1. Introduction

MnSe is known to be antiferromagnetic and magnetic susceptibility measurements have been made by several investigators.$^{1-3)}$ Lindsay$^{3)}$ found a thermal hysteresis of the magnetic susceptibility which he attributed to a crystallographic phase change. The Néel temperature from susceptibility data is found at about 130 K when going down in temperature but on warming it is apparently considerably higher.

Measurements of the paramagnetic resonance of MnSe were made by Maxwell and McGuire.$^{4)}$ They found that the Néel temperature was uncertain because of a thermal hysteresis and probably did not lie below 110 K.

Kelly$^{5)}$ has made measurements of the specific heat of MnSe in the warming process and found a very sharp peak in the vicinity of 248 K. When specific heat measurements were made on a sample which had been cooled only to 228 K, no sharp peak was noted.

According to neutron diffraction measurements of Shull, Strauser and Wollan,$^{6)}$ MnSe has a spin ordering of the second kind similar to MnO, in which the spins alternate in sign along each cube edge. The spin axis was not explicitly mentioned, but if it is the same as in MnO, it is perpendicular to the unique [111] direction defined by the ordering.$^{7)}$

The crystal structure of MnSe at room temperature has been studied by Baroni,$^{8)}$ who found three distinct structures depending on the method of preparation. MnSeα was a stable NaCl type while MnSeβ and MnSeγ were unstable zincblende and wurtzite types, respectively, which both eventually passed back into the α-type. The antiferromagnetic compounds MnO, FeO and NiO$^{9)}$ have been shown to have, like MnSe, a NaCl type structure above the critical temperature. Below their critical temperatures, MnO, FeO and NiO undergo deformations to rhombohedral symmetry.

Andressen and Rotterud(10) have carried out a careful study of the temperature variation of the neutron powder diffraction diagram. It has been found that a gradual transition to a hexagonal phase started at about 160 K. However, a small part transforms at this temperature, and it is not until the temperature has decreased to 138 K that an abrupt change takes place. The transformation seems to stop at an intermediate stage and no further change is observed. The final product does not appear to consist of two separate phases but can rather be described as a hexagonal phase exhibiting stacking faults.

The resistivity of MnSe has been measured by Palmer(11) and by Murakami.(12) They found a thermal hysteresis of the resistivity.

These measurements have revealed the magnetic structure, magnetic transition temperatures and crystal structures, but it is not sufficient to make clear the magnetic properties of MnSe. It is interesting to study the thermal hysteresis of the magnetic susceptibility and of the electrical resistivity.

§2. Preparation of Specimens

The specimens of MnSe used were prepared by solid-vapour reaction. The reactants were weighed in the stoichiometric quantities. Manganese metal, 99.995% in purity, was introduced in the form of chips into a quartz tube. A constriction was then made by melting the tube above the metal chips. After cooling, selenium pellets, 99.999% in purity, were introduced above the constriction. Direct solid contact of the reactants was thus prevented. After evacuating the system, the open end of the tube was sealed off, and the whole was inserted into a silicon carbide furnace. The furnace zone adjacent to the ampoule containing manganese was heated at 700°C, and the temperature of the outer zone containing selenium was maintained at about 300°C for a week, and then the temperature of the inner zone was raised to 1200°C for the complete reaction. The entire reaction period involved from eight to ten days. After a slow cooling in the furnace, polycrystal lumps of MnSe were obtained. This was ground to the specimens for experiments on the magnetic susceptibility and the electrical resistivity. For measurement of the electrical resistivity, the sample was shaped into the rectangular parallelepipeds, about $10 \times 1 \times 1$ mm^3. The completeness of the reaction was ascertained by X-ray powder diffraction work. At room temperature MnSe obtained was single phase with the NaCl structure.

§3. Experimental Results

3.1. *Magnetic Susceptibility*

The magnetic susceptibility was measured by means of the automatic magnetic balance which utilized the differential transformer displacement meter for the conversion of displacement to electricity. The block diagram of this system is show nin Fig. 1.

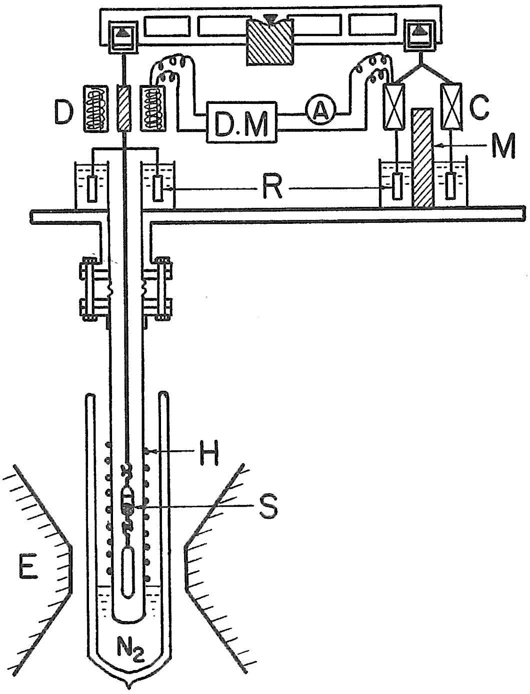

Fig. 1. Block diagram of a magnetic balance.

The displacement of the specimen S, which results from the action of an applied field on the specimen, is transferred to the core of the differential transformer D, so that the corresponding voltage is induced in the differential transformer displacement meter D. M. The induced voltage is feed back negative to the coil C which enclosed a piece of permanent magnet M, so that reverse displacement is introduced to the coil system so as to balance the original displacement. The balancing current in the coil C is obviously in proportion to the magnetic moment of the specimen and is read by the milliamperemeter A. The oil dampers R are used to prevent the forced vibration of C and S. The diameter of the tips of the electromagnet E is 80 mm and the gap between them is 45 mm. The highest field obtained was 4.2 kOe. The force acting on the specimen was detected in a weight range from 0.2 dyne to 4×10^3 dyne, and it corresponded to the susceptibility in a range from 10^{-7} emu to 2×10^{-3} emu for a sample weight of 0.5 gram.

In the actual measurements, the magnetic-field gradient was calibrated by use of a standard ferrous ammonium sulphate for the present specimen. The temperatures at which the measurement was made ranged from 77 to 870 K. The temperatures from 77 K to room temperature were obtained by the cold gas evaporated from liquid nitrogen and by the control of the electric current flowing in the non-inductive heater H. The temperatures above room temperature were obtained by controlling the current of electric furnace. The temperatures of the specimen were determined with a gold cobalt-copper thermocouple below the room temperature and a platinum-platinumrhodium thermocouple above it.

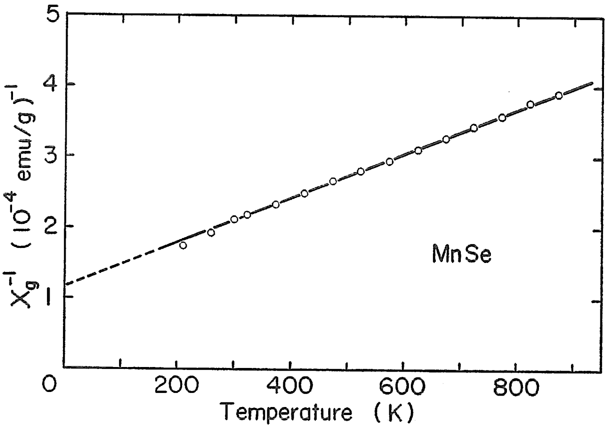

Fig. 2. Inverse susceptibility versus temperature for MnSe.

In Fig. 2, the reciprocal of the paramagnetic susceptibilities for MnSe is plotted as a function of temperature. At temperatures except near the transition temperature, it well followed the Curie-Weiss law. On the basis of the results in Fig. 2, the effective number of Bohr magnetons n_{eff} and paramagnetic Curie temperature θ_p are estimated as follows. The n_{eff} and θ_p are 5.88 μ_B and -373 K, respectively. The value of n_{eff} is fair agreement with the theoretical value of $n_{eff}=5.92\ \mu_B$ for Mn^{++}.

Fig. 3 shows the magnetic susceptibility per gram, χ_g, measured in the applied field

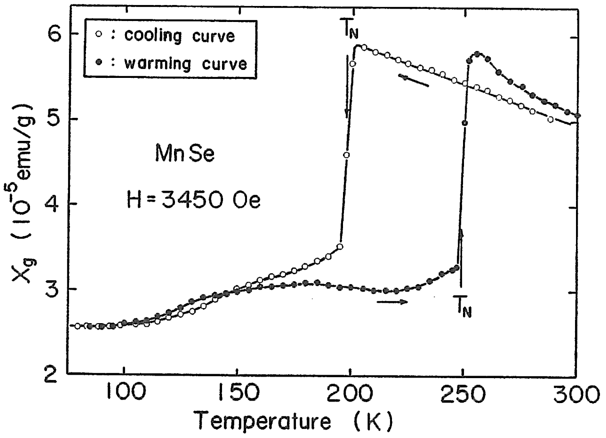

Fig. 3. Magnetic susceptibility of MnSe for decreasing and increasing temperature.

of 3450 Oe, as a function of temperature for MnSe. The cooling and warming cycle was obtained by the first measurement, starting from a virgin state of the sample. These curves show a large thermal hysteresis, and it is evident that a remarkably sharp transition occurs at the Néel temperature. According to an expedient definition, the Néel temperature T_N is defined as an inflection point near the boundary between the paramagnetic and antiferromagnetic regions. The Néel temperatures obtained in the cooling and warming processes are 197 K and 249 K, respectively. The Néel temperature thus obtained in the warming process is in good agreement with 248 K determined by Kelley.[5] When susceptibility measurements were made on a sample which had been cooled only to 205 K, no thermal hysteresis was noted. But below 205 K, the thermal hysteresis was observed.

Figs. 4–(a) and 4–(b) show the magnetic susceptibility per gram as a function of

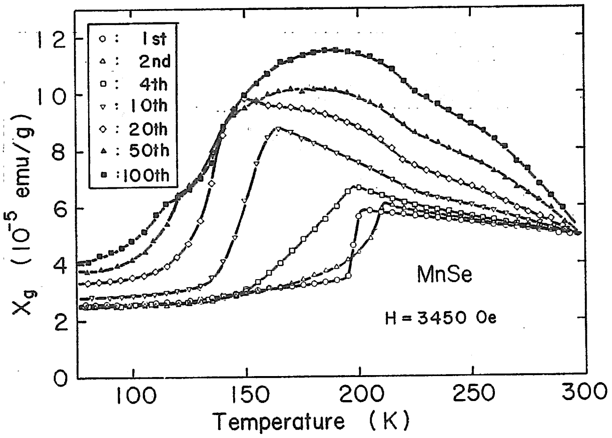

Fig. 4–(a). Magnetic susceptibility of MnSe for decreasing temperature.

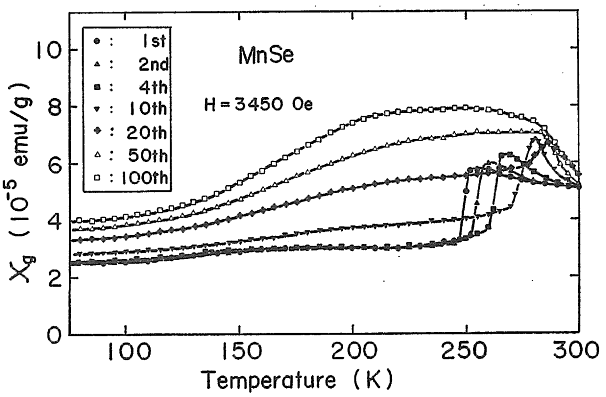

Fig. 4–(b). Magnetic susceptibility of MnSe for increasing temperature.

temperature in the cooling and warming processes, respectively. For the data plotted in these figures, the sample had previously been cooled to 77 K and then allowed to warm up to room temperature. In all cases the cooling and warming curves appear to be influenced in some way by the previous thermal history of the sample. In the cooling process shown in Fig. 4–(a), the Néel temperatures, T_N, decrease with increasing the times of the measurements. On the contrary, in the warming process, T_N increase with increasing the times of the measurements. The maximum values of the susceptibility increase with increasing the times of the measurements. The curves of the 20th measurement show a broad maximum and are similar to that of Lindsay.[3] At room temperature all the values of susceptibility approach its original value. The sample was heated again at 800°C for two days after the 100th measurement had been made. The cooling and warming curves obtained from the sample were very similar to those of the first measurement shown in Fig. 3.

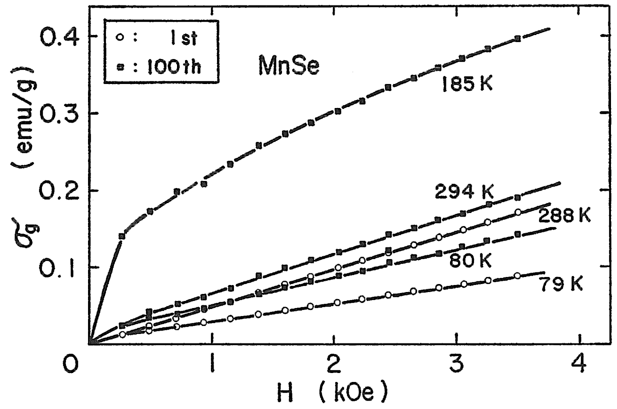

Fig. 5. Magnetic moment per gram, σ_g, as a function of applied field.

Fig. 5 shows the magnetic moment per gram, σ_g, versus applied field for MnSe. Except for the magnetization curve of the first measurement at 288 K, the curves do not vary linearly with applied field. It may be assumed to be the result of the existence of induced moment.

3.2. *Electrical Resistivity*

The electrical resistivity for MnSe have been measured by the standard four-probe method with current reversal. For the probes the copper wires, 0.2 mm in diameter, were used and they were welded on the samples by spot welding. The size of the cross-section area of the specimen and the length between two potential probes were measured with an accuracy of ±1/500 mm, using a travelling microscope. In the present experiments, the measurements have been made in a range from 77 K to room temperature.

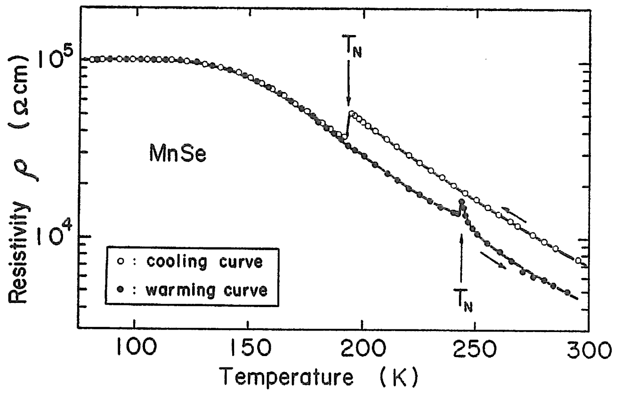

Fig. 6. Electrical resistivity of MnSe for decreasing and increasing temperature.

The electrical resistivities versus temperature for MnSe are shown in Fig. 6. The cooling and warming cycle was obtained by the first measurement, starting from a virgin state of the sample. The resistivity curves show a behavior similar to that of semiconductors and an abrupt change at the Néel temperature. Below 120 K, the resistivity is nearly independent of temperature. The activation energy obtained from the cooling curve at room temperature is 0.20 electron volt. This value is in good agreement with that determined by Kasaya[13] but in disagreement with that by Palmer.[11]

§4. Discussion

In the paramagnetic range, MnSe in its stable form has the rocksalt structure with the metal atoms forming a face-centered cubic lattice. When the measurements were made on a sample which had been cooled below the Néel temperature, a thermal hysteresis was observed, and this result may be due to a transition of the crystal structure. It may possibly start that a NaCl phase is transformed into a hexagonal phase at the Néel temperature which is defined as the critical temperature at which a paramagnet transforms to an antiferromagnet. However, only a small part may transform at this temperature, and it is not until the temperature has decreased to 120 K that an abrupt change takes place. The transformation seems to stop at an intermediate stage being described as a hexagonal phase exhibiting stacking faults. In the warming process, the rocksalt phase may not be re-established in precisely the same manner, and at room temperature the complete transformation of the hexagonal phase into the rocksalt phase may not be taking place. The hexagonal phase may have a relatively higher susceptibility than the rocksalt phase. If the sample had been heated again at 800°C sufficiently long, it, regardless of the previous thermal history, approached the virgin state as shown in Figs. 3 and 6.

Heikes[14] have discussed the electrical resistivity of the magnetic compounds.

According to his model, the antiferromagnetic compound is a semiconductor. MnSe is a high-resistivity semiconductor and its resistivity at room temperature is roughly estimated at 7×10^3 Ωcm. The activation energy obtained from the cooling curve at room temperature is 0.20 electron volt. The resistivity curves show an anomaly at the Néel temperature. The resistivity of MnSe can be written as a sum of three contributions

$$\rho = \rho_0 + A \exp\left(\frac{V}{k_B T}\right) + \rho_{mag},$$

where the first term is the residual resistivity, the second is the resistivity of a semiconductor discussed by Heikes and the third is the magnetic disorder resistivity studied by Kasuya.[15] The anomaly of the resistivity curves at the Néel temperature is that of the magnetic disorder resistivity. The value of ρ_{mag} in the cooling process is 1.5×10^4 Ωcm.

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References

1) C. F. SQUIRE: Phys. Rev. **56** (1939) 922.
2) H. BIZETTE and B. TSAI: Compt. Rend. **212** (1941) 75.
3) R. LINDSAY: Phys. Rev. **84** (1951) 569.
4) L. R. MAXWELL and T. R. MCGUIRE: Revs. Modern Phys. **25** (1953) 279.
5) K. K. KELLEY: J. Am. Chem. Soc. **61** (1939) 203.
6) C. G. SHULL, W. A. STRAUSER and E. O. WOLLAN: Phys. Rev. **83** (1951) 333.
7) W. L. ROTH: Phys. Rev. **110** (1958) 1333; **111** (1958) 772.
8) A. BARONI: Z. Krist. **99** (1938) 336.
9) J. S. SMART and S. GREENWALD: Phys. Rev. **82** (1951) 113.
10) A. F. ANDRESSEN and H. ROTTERUD: Acta Cryst. **a25** (1969) s250.
11) W. Palmer: J. Appl. Phys. **25** (1954) 125.
12) M. MURAKAMI: Bull. Fac. Engr. Hiroshima Univ. **2** (1953) 67.
13) M. KASAYA: Phys. Letters. **55A** (1976) 365.
14) R. R. HEIKES: Phys. Rev. **99** (1955) 1232.
15) T. KASUYA: Prog. Theor. Phys. **16** (1956) 45.