

Magnetic Susceptibility of Manganese Selenide*

ROBERT LINDSAY
Rice Institute, Houston, Texas
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The susceptibility-temperature relation for the antiferromagnetic compound MnSe was measured over a range of temperatures between 70°C and -196°C. Evidence was found of a large thermal hysteresis and a dependence of susceptibility on field strength. A tentative theory is advanced to explain the thermal hysteresis in terms of three phases which possess different susceptibilities.

I. INTRODUCTION

THE susceptibility of a typical antiferromagnetic substance decreases with decreasing temperature below a certain critical temperature, and for most substances this susceptibility vs temperature relation is a reversible one. However, MnSe has been found by Squire,¹ Bizette and Tsai,² and by Haraldsen and Klemm³ to have several anomalies. Squire, who used a field strength of 700 gauss, obtained a larger maximum susceptibility and a higher indicated critical temperature than Bizette and Tsai, who made their measurements at a field strength of 30,000 gauss. Squire noted small magnetic hysteresis effects in the vicinity of the critical temperature when fields of the order of 10 gauss were applied. Bizette and Tsai observed a temperature hysteresis when the sample was cooled to -196°C and held at that temperature for a period of 12 hours or more and allowed to warm up. Some of the data of Haraldsen and Klemm showed a dependency of susceptibility on field strength. The experiments described below were made with the object of investigating some of these anomalies further.

II. EXPERIMENTAL

The apparatus was patterned after the ring balance devised by Sucksmith.⁴ A diagram of this system is shown in Fig. 1. The balance case was a rectangular brass box (*A*) mounted on a vibration damping frame (*B*). The ring (*C*), 6.0 cm in diameter, was made from a strip of phosphor-bronze 0.17 mm thick and 3.0 mm wide. The sylphon bellows (*D*) permitted vertical movement of the entire ring and suspended sample. A loop of copper wire (*E*), soldered to the ring at (*F*) and immersed in an annular oil bath (*G*) provided damping of vibrations. Two mirrors (*M*) were mounted on the ring so that the radius to each made an angle of 49 degrees with the horizontal. A beam of light from a fine horizontal wire filament (*H*), focused by an achromatic converging lens, was successively reflected by

the two mirrors and then emerged from the box. The image of the filament was viewed through a traveling microscope (*I*). When a vertical downward force acted upon the ring, this image was displaced upward because the slight distortion of the ring moved the mirrors.

The specimen container was a pharmaceutical gelatine capsule 11.04 mm long and 4.93 mm in diameter. It was suspended by a quartz fiber in the non-uniform part of the field of a Weiss electromagnet (*P-P*). Sidewise motion towards either pole-piece when the field was set up was prevented by a spiral spring (*J*) of fine copper wire cemented to a quartz rod (*K*). The plane of the spring was perpendicular to the quartz fiber.

The sensitivity of the system was 0.149 mm dyne and was found to be independent of temperature within the limits of the desired accuracy. A specimen of mass *m*, and susceptibility χ_m , when placed in a magnetic field of strength *H* and vertical gradient dH/dx experiences a force given by $F = \chi_m m H dH/dx$. The quantity $H dH/dx$ was determined by measurements on the standard paramagnetic salt $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$.⁵

Surrounding the lower portion of the Pyrex tube enclosing the suspension was a copper tube (*L*) of thickness $\frac{1}{8}$ in. with a bottom 1 in. thick. A small window was cut in the side to permit a view of the sample. This copper jacket provided uniform temperature over the specimen. After the balance chamber had been filled with dry helium at a pressure of one atmosphere, step-wise cooling was accomplished in the following fashion. Liquid nitrogen was forced into the surrounding Dewar flask a little at a time and allowed to evaporate. After a sufficiently low temperature had been reached, the necessary readings were quickly taken. The high thermal capacity of the copper tube and the good thermal insulation kept the temperature fairly constant. On the warming part of the cycle readings were taken as the temperature slowly increased after all the liquid nitrogen had evaporated. By injecting more liquid nitrogen into the flask at points along the warming cycle a closer approximation to equilibrium conditions could be obtained. For the attainment of temperatures above 25°C, a heating coil wrapped around the copper tube was used. All temperature measurements were made

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¹ C. F. Squire, Phys. Rev. **56**, 922 (1939).

² H. Bizette and B. Tsai, Compt. rend. **212**, 75 (1941).

³ H. Haraldsen and W. Klemm, Zeits. anorg. u. allgem. Chem. **220**, 183 (1934).

⁴ W. Sucksmith, Phil. Mag. **8**, 158 (1929).

⁵ L. C. Jackson, Trans. Roy. Soc. (London) (A) **224**, 1 (1924).

with a copper-constantan thermocouple, the junction being located close to the specimen.

The powder samples of MnSe came from a batch prepared by Kelley.⁶ The compound had been obtained by heating manganese and selenium in their proper combining ratio to a temperature at which the chemical reaction would take place and then the excess selenium was driven off.

III. RESULTS

The graph in Fig. 2 represents a typical run (although there were some runs with significant deviations from

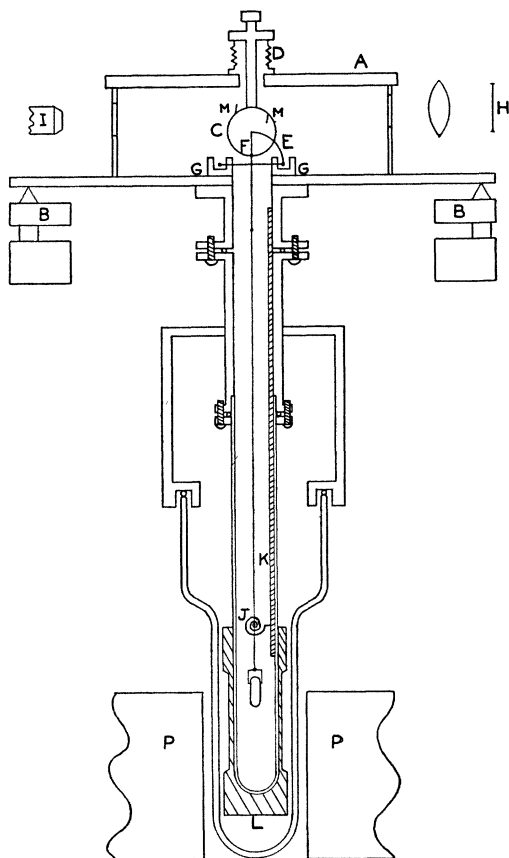


FIG. 1. Schematic diagram of susceptibility measuring apparatus.

this pattern). In all cases the cooling curve appeared to be influenced in some way by the previous temperature history of the sample, while the warming curve was a function of the length of time which the sample was held at low temperatures. For the data plotted in Fig. 2, the sample had previously been cooled to -196°C and then allowed to warm up to 28°C . The cooling curve (A) from 28°C to -55°C was almost linear. Between -55°C and -90°C there was a noticeable increase in slope followed by a gradual levelling off beyond -90°C . The curve showed a rather broad

maximum at -120°C and started dropping off quite steeply beyond -135°C . At -196°C it required 20 hours for final equilibrium to be reached.

When the sample was warmed to 70°C before cooling was started, the subsequent cooling curve showed a much smaller slope between 70°C and -60°C , while the maximum value of the susceptibility occurred at -135°C with a lower absolute value than in the case shown in Fig. 2. If held at -196°C sufficiently long, all samples, regardless of previous history, approached the equilibrium value shown in Fig. 2.

Curve (B) in Fig. 2 was obtained after the sample was held at -196°C for 20 hours and had then been allowed to warm up to 30°C . A period of 8 hours was required for this warming process. Curve (B) was reversible up to -25°C . A maximum in the vicinity of -100°C was noted. Above -25°C the curve ceased to be reversible. There was a slight rise up to a maximum at 10°C , during which the original cooling curve (A) was crossed and then the susceptibility decreased to approximately its original value at 28°C . Other runs indicated that the slope of the warming curve above 28°C was continuous with the slope of the prior cooling curve below that temperature. On one run, the warming was stopped at 13°C and the subsequent cooling curve was that shown in curve (C).

Figure 3 shows cooling curves taken on the same run for two different field strengths. The cooling was started at 25°C on a sample which had previously been cooled to -196°C . The higher values of susceptibility occurred with the lower value of the field strength. The maximum value of the susceptibility for 4300 gauss was higher than that in Fig. 2. The points at -196°C were taken after the sample had only been one hour at that temperature. The same sample was used in Fig. 3 as in Fig. 2.

IV. DISCUSSION

The cooling and warming cycle shown in Fig. 2 will be considered as representing typical behavior with the qualifications noted in the previous section. A tentative theory is advanced which considers the possibility of phase changes with temperature. The existence of three different phases is postulated which shall hereafter be referred to as I, II, and III. It is assumed that phase I predominates at room temperature. From room temperature to -55°C , the susceptibility is representative of phase I. The change in slope below -55°C is explained by saying that phase II starts to come in and has a relatively higher susceptibility than phase I. Below -135°C , phase III starts to form. The levelling off of the cooling curve between -115°C and -125°C represents antiferromagnetic behavior in phases I and II. The long time required for attaining equilibrium at -196°C suggests that the complete transformation of the other two phases into phase III is taking place. The warming curve taken after equilibrium has been reached is considered as being almost completely repre-

⁶ K. K. Kelley, J. Am. Chem. Soc. **61**, 203 (1939).

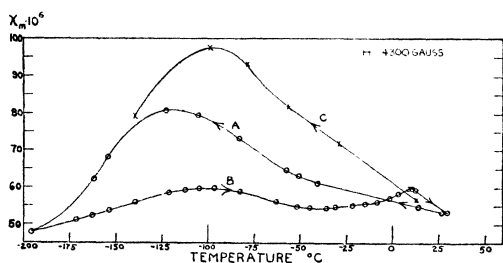


FIG. 2. (A) and (B): Cooling and warming curves showing thermal hysteresis. (C): Cooling curve obtained after warming of previously cooled sample is stopped at 13°C.

representative of phase III. The hump in the vicinity of -100°C indicates that phase III is antiferromagnetic with a critical temperature at about that point. Above -25°C phase III starts going back into phase II. This is evidenced by the gradual rise in the susceptibility up to 10°C and by the cessation of reversibility. At 10°C phase II is in preponderance. If curve (C), which was obtained when cooling was started at 13°C , can be taken as representative of phase II, then the data indicate that phase II has a higher maximum susceptibility than phase I and the critical temperature is higher than for phase I. When warming is continued above 10°C along curve (B), most of phase II passes back into phase I.

Modifications in crystal structure might be responsible for the changes in phase suggested above. The antiferromagnetic compounds MnO, FeO, NiO, and CoO⁷ 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 while CoO deforms to tetragonal symmetry. It is possible that similar changes take place in MnSe. The crystal structure of MnSe at room temperature has been studied by

⁷ J. S. Smart and S. Greenwald, Phys. Rev. **82**, 113 (1951).

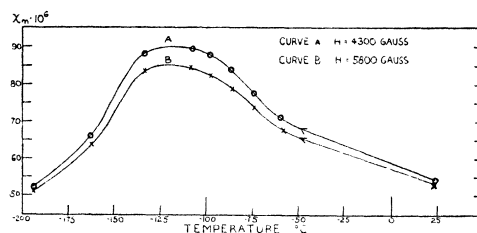


FIG. 3. Cooling curves showing dependence of susceptibility on field strength.

Baroni,⁸ who found three distinct structures depending on the method of preparation. MnSe α was a stable NaCl type while MnSe β and MnSe γ were unstable zincblende and wurtzite types, respectively, which both eventually passed back into the α -type. It is possible that these varying structures might be associated with the phase changes suggested above.

It is possible to correlate Kelley's measurements of the specific heat of MnSe⁶ with these magnetic measurements. Kelley measured the specific heat of a sample while it was slowly warming up from -196°C to room temperature. A very sharp peak was found in the vicinity of -25°C . On the warming curve for susceptibility it is noted that this is approximately the same temperature at which phase III is postulated as passing over into phase II. When specific heat measurements were made on a sample which had been cooled only to -45°C , no sharp peak was noted. This lack of anomaly would indicate no phase change, a fact which is consistent with the magnetic measurements in this range.

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⁸ A. Baroni, Z. Krist. **99**, 336 (1938).