with an inverse ninth power law. Their results are reproduced in Fig. 7 for comparison. Curve I is a plot of A as a function of $1/\mu$ for the model with rigid spheres, and curve II is the corresponding plot for the model with an inverse ninth power law.

As the drift velocity is increased, the parameter C approaches the ratio m_1/m_2, $1/\mu$ becomes large, and the parameters D_∞ and D_9 approach the corresponding values in Tables III and IV. In the case of rigid spheres, the velocity then varies directly, and the mobility inversely as the square root of E/p. If the repulsive force obeys the inverse ninth power law, the velocity varies directly as the two-thirds power of E/p, and the mobility varies inversely as the cube root of E/p.

Although the theory is not exact, the general formulae should not be seriously in error.

Chapman,[10] Enskog,[11] and Pidduck[2] have shown that at low E/p the error is no greater than a few percent. Comparison with experiment,[12] however, indicates that the repulsive force varies with distance to a higher power than nine. The correct law may eventually be found through accurate measurements of the scattering and retardation of ion beams. The use of classical cross sections also introduces error at low velocities, and at low temperatures, but this is less important at high velocities where classical and quantum theories converge.

The writer takes pleasure in thanking Professor Leonard B. Loeb for several stimulating discussions of this subject.

[10] S. Chapman, Phil. Trans. A217, 115 (1917).
[11] D. Enskog, *Kinetische Theorie der Vorgänge in mässig verdünnten Gasen*, Inaugural Dissertation, Upsala, 1917.
[12] A. F. Pearce, Proc. Roy. Soc. A155, 490 (1936); A. V. Hershey, preceding paper.

Antiferromagnetism in Some Manganous Compounds*

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The temperature dependence (300°K to 40°K) of the magnetic susceptibility of the following Mn^{++} salts has been measured: MnO, MnS, MnSe, MnTe. A λ-point transition at low temperatures makes the susceptibility break away from a Weiss-Curie law and decrease with lowering temperatures. Each salt has its characteristic transition temperature, increasing with increasing molecular weight. Evidence for field dependence of the susceptibility and for magnetic hysteresis has been found. It seems likely that an exchange force is the cause of the transition from paramagnetism to antiferromagnetism.

INTRODUCTION

THE paramagnetic susceptibility of salts usually obeys a Weiss-Curie law: $\chi = C/(T - \Theta)$ where the constant C is the Curie constant, T the absolute temperature, and Θ the point where the straight line $1/\chi$ intersects the temperature axis. Deviations from this law have been observed in several salts[1] at low temperatures. The

experiments described in this paper are on the following Mn^{++} salts: MnO, MnS, MnSe, MnTe. At a temperature, characteristic for each salt, the susceptibility breaks away from the Weiss-Curie law and decreases with lowering of temperature.

Kelley[2] has measured the specific heat of Mn, MnSe, and MnTe; in the latter two compounds he has found a hump or abnormal specific heat. Measurements on MnO and MnS by Millar[3] and Anderson[4] each show a hump in the specific

[1] M. and B. Ruhemann, *Low Temperature Physics* (Cambridge, 1937), Chapter II.

[2] K. K. Kelley, J. Am. Chem. Soc. 61, 203 (1939).
[3] R. W. Millar, J. Am. Chem. Soc. 50, 1875 (1928).
[4] Anderson, J. Am. Chem. Soc. 53, 476 (1931).

heat curve. The hump in each case is quite large and the transition temperature or λ point occurs at: 116°K for MnO, 140°K for MnS, 247°K for MnSe, 307°K for MnTe. It is evident that the temperature of the hump occurs higher the greater the mass of the combining atom.

Using the same sample of MnO and MnS as had been used for the specific heat studies, Ellefson and Taylor[5] looked for structure changes but found no change. Only an abnormal expansion in the λ region was detected. Ruhemann[6] independently made similar studies on MnO and reported a sodium chloride type structure above and below the transition with only a rapid but continuous expansion through the λ region.

The first accurate susceptibility measurements were made on MnO by Bizette, Squire and Tsai.[7] They showed that the susceptibility abruptly changed from the Weiss-Curie law at T_λ and decreased continuously as the temperature was lowered. Below the transition the susceptibility varied with the measuring field. The sample was freshly prepared by reducing the manganese oxalate with hydrogen at a very high temperature. Analysis showed no impurities with respect to iron or sulfur.

EXPERIMENTAL

The compounds MnS, MnSe, MnTe were obtained from Kelley.[2] The degree of purity is very satisfying—in particular Kelley reports the MnSe on analysis to be 99.35 percent pure, based on its manganese content; and 99.48 percent pure, based on its selenium content. The method for measuring the susceptibility was to
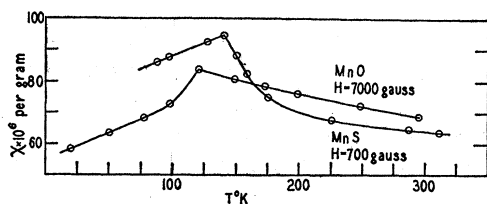

FIG. 1. Magnetic susceptibility per gram against temperature for MnO (from reference 7) and for MnS.

[5] B. S. Ellefson and N. W. Taylor, J. Chem. Physics 2, 58 (1934).
[6] B. Ruhemann, Sow. Phys. 7, 590 (1935).
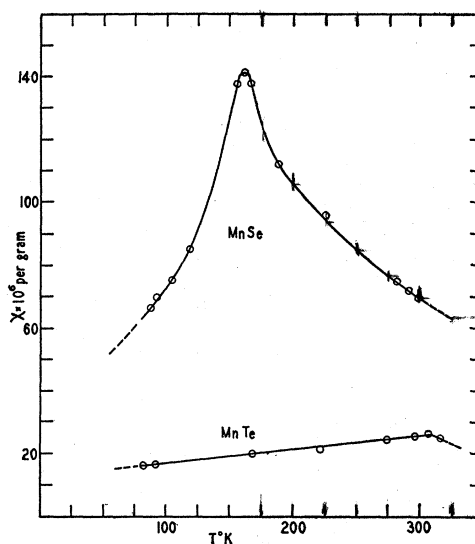[7] H. Bizette, Squire and Tsai, Comptes rendus 207, 449 (1938).

FIG. 2. Magnetic susceptibility per gram against temperature for MnSe and MnTe.

determine the force on a sample placed in a nonhomogeneous field. The modification for low temperature measurements is due to de Haas, Wiersma and Kramers.[8] In these experiments, approximately 3 grams of the powder was placed in the weighing tube. The nonhomogeneous field was 700 gauss at its maximum intensity. The force pulling the sample into the field was of the order 100 milligrams; a force of 1 milligram could be easily detected on the balance. The calibration for the absolute value of the susceptibility was done with $NiCl_2$ whose value has been carefully determined.[9] With the calibration, measurements on $NiSO_4$ gave a value at 298°K which agreed with reported[9] values to within 2 percent. Temperatures were measured by thermocouples in all these experiments.

Figures 1 and 2 show the magnetic susceptibility plotted against the temperature for the Mn^{++} compounds studied. A large number of points were taken and the experimental runs were repeated several times in complete agreement. Constant temperature baths of CO_2 in alcohol, of O_2, and of N_2 furnished fixed points at which temperature equilibrium was insured. Intermediate values were obtained by allowing the rate of cooling to proceed very slowly.

[8] de Haas, Wiersma and Kramers, Physica 1, 1 (1933).
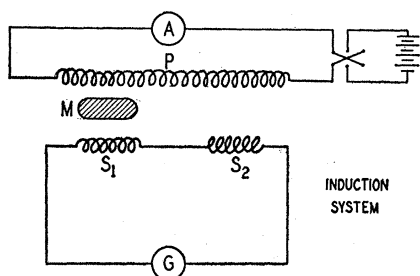[9] A. Serres, Ann. de Physique 20, 441 (1933).

FIG. 3. Circuit for measuring magnetic susceptibility. The two secondaries, S_1 and S_2 are wound equal and opposite.

Supercooling—i.e., causing the transition point to occur at a lower temperature than reported for the C_p values, is the result of rapid cooling. Kelley found similar supercooling effects on the C_p measurements of MnSe.

The large change in the susceptibility of MnSe was easily detected by another technique. A 15-cm long solenoid of 2 cm diameter formed the primary coil (P) to an induction system (see Fig. 3). Two identical coils S_1 and S_2 (3000 turns each) were wound on the primary in such a way that their direction of winding was opposite to one another. When a current is passed through the primary coil, the induced e.m.f. of S_1 is equal and opposite to that of S_2. The induction system was placed in a liquid N_2 bath so that the resistance of the coils was reduced. Removing a single turn on one of the secondaries would produce an unbalancing action which could just be detected by the ballistic galvanometer G. Placing the paramagnetic salt, M, into the space of S_1 has the effect of increasing the induced e.m.f. of coil S_1. Thus with the coils perfectly balanced, the throw of the galvanometer is proportional to the magnetic susceptibility. Fig. 4 shows the deflection on the galvanometer scale plotted against temperature when 10 grams of MnSe is placed in coil S_1. With a current in the primary sufficient to give a field of 3 gauss, one obtains curve "a"; for 5 gauss, curve "b"; and for a 10-gauss measuring field, one obtains curve "c."

A reversing switch was put into the primary coil circuit for the purpose of detecting hysteresis effects.[10] In curve "c" of Fig. 4 the upper curve (marked with dashes) represents the throw of the

10 Kurti, Lainé and Simon, Comptes rendus 204, 675 (1937).

galvanometer upon first reversing the primary current. All subsequent deflections caused by sending the primary current in the same direction fall on the lower curve. The magnitude of the current in the primary was kept constant. Similar upper and lower curves were observed in "a" and "b" but only the lower values are plotted. The measurements were taken every 5-degree interval on both curves and the curves were repeatedly reproduced. Measurements as low as 40°K were obtained by the adiabatic desorption of hydrogen gas from activated charcoal; the susceptibility continues to fall off at lower temperatures.

Figure 5 shows the same type of curve for MnSe measured with completely new coils. It is interesting to observe that the hysteresis effect vanishes after an appreciable temperature interval on each side of the transition. The points establishing the curves are not shown; the points plotted on the curve represent the observed deflection when an additional field of 7, 14, 21, 28, and 35 gauss was superimposed steadily by means of an external solenoid. Had a microscopic piece of soft iron been the cause of the hysteresis, it might possibly have become saturated in such an additional field. In any case the hysteresis arising from such an impurity would not vanish at low temperatures. It is difficult to see how the copper coils (Fig. 3) could give rise to the hysteresis; three different coils, wound on different Pyrex tubes, gave identical results.

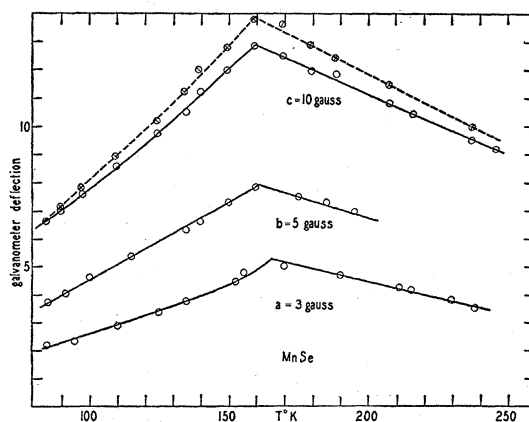Finally in Fig. 6 is shown one of the hysteresis loops which was measured close to the λ-point.

FIG. 4. Deflection of galvanometer in cm against temperature. MnSe.

The circle marks represent the first time around the loop and the x marks the second time around. The coordinates are the galvanometer deflection against the measuring field of the primary. A similar loop was measured on MnS with the difference that the magnitude of deflection—i.e., width of the loop at the center, was about one-fifth as large.

DISCUSSION

The transition phenomenon appears to be the result of antiferromagnetism. Upon examining the susceptibility curves we may make the following remarks: Since the Mn^{++} ions are in the ^6S state, the spin alone contributes to the paramagnetism. On the high temperature side of the transition, the spins are free to orient with the magnetic field; while on the low temperature side, they are locked antiparallel. Thus as one lowers the temperature towards $0°K$ the susceptibility approaches zero. The λ-point is simply a Curie point where paramagnetism becomes antiferromagnetism.

It seems likely that such antiparallel orientation can be identified with an exchange force; and as the temperature increases a point is reached where there is sufficient kT energy to set free the spins. This means that the extra binding force due to the exchange will disappear and so the crystal expands during the liberation. The extra specific heat would naturally occur in such a process.

FIG. 6. Deflection of galvanometer in cm against measuring field in gauss. MnSe.

The hysteresis which is observed in the neighborhood of the Curie point cannot be explained on any such simple basis. Certainly with spins antiparallel there can be no permanent magnetic moment; at low temperatures well away from the Curie point there is no hysteresis. Just why the relaxation time should be abnormally long for the spin system to go from a state of magnetization to one of zero moment is not at all clear. Simon[10] has observed hysteresis effects in Fe—alum at 0.034°K.

Kramers[11] has pointed out the possibility of exchange coupling between magnetic ions being sometimes less drastic than an exponential function of their distance apart; coupling via the excited states of the intermediate (normally nonmagnetic) atoms is possible. The experimental fact that the Curie point is higher, the greater the mass of the combining atom indicates that the exchange force is perhaps not greatly diminished by increasing the distance between Mn^{++} ions. It is not obvious that here is a transition of the third kind, corresponding to an order-disorder in spin space.

The author is greatly indebted to Dr. Kelley, Bureau of Mines, U. S. A. for the manganous salts used in this research, and for discussions with staff members at the University of Pennsylvania.
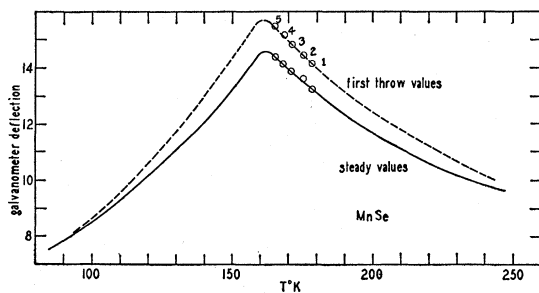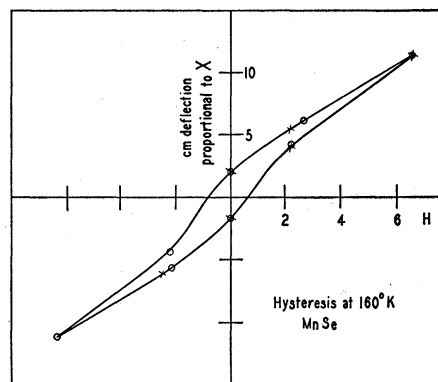

FIG. 5. Deflection of galvanometer in cm against temperature. MnSe. The points plotted have additional field in same direction as measuring field. 1, 7 gauss; 2, 14 gauss; 3, 21 gauss; 4, 28 gauss; 5, 35 gauss.

[11] H. A. Kramers, Physica 1, 182 (1933).