small. Data were also taken for 10-ev ions, and these are shown in Fig. 2. Comparison of Figs. 2 and 3 shows clearly the anomalous behavior of Ne^+. At the lowest ion energies Ne^+ is Auger-neutralized and the upper energy limit of the N_0 function is approximately $E_i-2\varphi$ as for the other ions. As ion energy increases, a portion of the Ne^+ ions are resonance-neutralized and de-excited in a process of Auger de-excitation which has a higher yield (Fig. 1) and a larger kinetic energy maximum. Thus, for 40-ev ions (Fig. 3), the $E_i-2\varphi$ limit is clearly violated in the case of neon. These and related matters have already been discussed extensively in Sec. XI of reference 2.

The data presented here were taken under the same conditions of gas purity, vacuum conditions, and surface cleanliness of the target as in the previous work.[1]

PHYSICAL REVIEW VOLUME 104, NUMBER 2 OCTOBER 15, 1956

Magnetic Susceptibility of αMnS[†]

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(Received June 28, 1956)

The magnetic susceptibility of a powder sample of αMnS was measured from 90°K to 800°K by an absolute Gouy method. The Néel temperature was found to be 154°K. There was no evidence of thermal hysteresis and the susceptibility was independent of field strength over a range of fields between 2000 and 3000 oersteds. Two sets of Weiss-Curie constants fitted the data above the Néel temperature. Between the Néel temperature and 300°K, values of $\theta=490$°K and $C_M=4.40$ were calculated. Above 400°K, the respective values were 380°K and 3.90. It is suggested that the persistence of short-range ordering effects to temperatures well above the Néel temperature affects the value of these constants and that the values above 400°K are probably more representative.

INTRODUCTION

THE magnetic properties of αMnS (manganous sulfide, green, NaCl structure) have been studied by several investigators. Mehmed and Haraldsen[1] determined the susceptibility at several fixed temperatures between 90°K and 478°K. Bhatnagar[2] made a similar study between room temperature and 510°K. Squire[3] established that αMnS was antiferromagnetic with a Néel temperature of about 145°K. A subsequent investigation by Bizette[4] indicated a Néel temperature of 165°K. Anderson[5] observed two anomalies in the specific heat, one at 139°K and the other at 145°K, which have been correlated with the antiferromagnetic transition. Serres[6] measured the susceptibility from room temperature to 773°K.

For an antiferromagnetic substance the relationship, $\chi_M=C_M/(T+\theta)$, where $\theta>0$, describes the molar susceptibility above the Néel temperature; so, from the data in this temperature region, it is possible to calculate the values of θ and C_M. Values obtained by the various investigators are given in Table I. Other members of the manganese chalkogenide series have been investigated and found to be antiferromagnetic. MnSe and MnTe are somewhat unusual in that they show some thermal hysteresis effects in the vicinity of the Néel temperature.[7–9] In addition, field-dependent effects have been observed with MnSe.[8,10] So far, no such unorthodox behavior has been noted in the case of MnS.

TABLE I. Comparison of data obtained by different investigators for αMnS.

Investigator	Temperature range (°K)	Néel temperature (°K)	θ(°K)	C_M	μ_B
Mehmed and Haraldsen[a]	90–477	...	411	3.8	5.5
Serres[b]	293–773	...	459	3.45	5.27
Bhatnagar[c]	307–510	...	495	4.45	5.99
Bizette[d]	90–300	165	528	4.30	5.89
Squire[e]	90–300	145	...	...	...
Banewicz and Lindsay	90–400	154	490	4.40	5.96
	400–800	...	380	3.90	5.61

[a] See reference 1.
[b] See reference 6.
[c] See reference 2.
[d] See reference 4.
[e] See reference 3.

The purpose of this investigation was to make susceptibility measurements on a sample of MnS of known composition by an absolute method at several field strengths and over a wide enough temperature range to permit location of the Néel temperature and calcula-

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[†] Supported in part by a Frederick Gardner Cottrell grant from The Research Corporation.

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tions of the constants θ and C_M. It was also desired to investigate the possible existence of any thermal hysteresis effects such as are shown by MnSe and MnTe.

EXPERIMENTAL

The αMnS powder was obtained as a precipitate from a solution of manganese chloride when ammonia and hydrogen sulfide were added. The *p*H was controlled at 9.6 during the reaction. The resulting sulfide was dried and then heated in a vacuum to 1000°C to remove excess sulfur. The final particle size was estimated to be about 10 microns. Chemical analyses of the sample were made before and after the susceptibility runs. The manganese sulfide prepared by this method seemed to have a great affinity for water. It was found that the water taken up was driven off slowly starting at temperatures around 70°C and then more rapidly at temperatures above 400°C. The starting sample at low temperatures contained about 3% water. During the high-temperature measurements, this water was given up slowly. From the observed loss in weight of the sample and the analysis of the starting material, corrections to the susceptibility were made. The composition of the dried sample with respect to manganese and sulfur was 63.19% and 35.79% respectively as compared to the theoretical percentages of 63.15 and 35.85.

The manganese content of the sample was obtained by determining the weight of manganese sulfate formed by treating the sample with excess sulfuric acid and then heating to constant weight at about 475°C.[11] The sulfur content was obtained by oxidizing the sulfide to sulfate by fusion with sodium carbonate and potassium nitrate and then determining the sulfate by precipitation as barium sulfate.

The magnetic susceptibility measurements were made by an absolute Gouy method[12] with the sample suspension and balance enclosed so that the atmosphere within could be controlled. An analytical balance was converted into an electrodynamic balance by replacing one balance pan with a solenoid. The solenoid interacted with a permanent Alnico cylindrical bar magnet fixed to the base of the balance case. The body force was determined by measuring the current in the solenoid required to maintain the system in balance. It was possible to add and subtract calibrated weights to and from the balance by means of a special attachment to the balance case and thus to obtain current *vs* force calibrations during the runs without disturbing the sealed system. With this arrangement we could detect changes in body force of ±0.03 mg. Measurements of the mass of the sample, the length of the sample, and the magnetic field strengths provided the necessary additional data from which to calculate an absolute value for the magnetic susceptibility. Corrections were made for the diamagnetic susceptibility of the quartz tube which contained the sample.

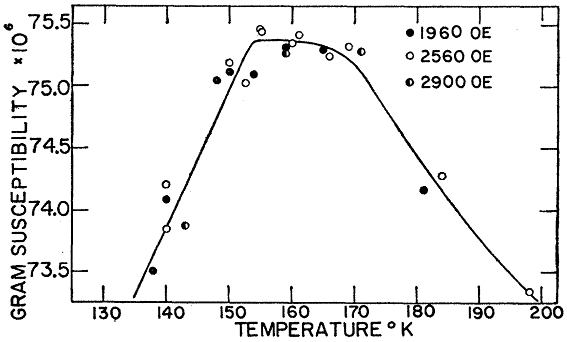

FIG. 1. The susceptibility of αMnS in the vicinity of the Néel temperature.

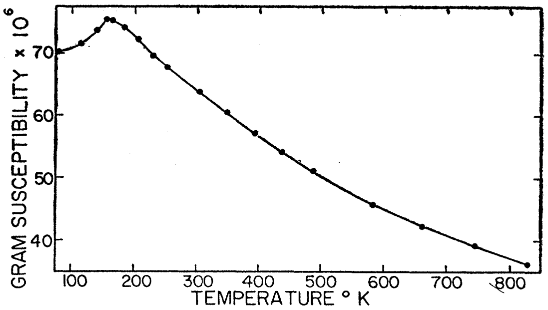

FIG. 2. The susceptibility of αMnS as a function of temperature. Points shown are averages obtained at two or more field strengths.

For temperatures below room temperature, the sample was suspended within a double-walled silvered Pyrex glass tube which was attached to the main balance case by a vacuum-tight seal. The space between the double walls was connected to another vacuum system. By injecting liquid nitrogen into a Dewar flask surrounding the double-walled tube and then regulating the inner vacuum, it was possible to obtain good temperature control. Temperatures were measured by two copper constantan thermocouples located at the extremities of the sample. Thermal equilibrium within the system was insured by maintaining a pressure of about one-half atmosphere of helium gas in the main balance enclosure.

For the high-temperature measurements, the sample was surrounded by a quartz tube. A bifilar winding of No. 22 Nichrome wire was used as the heating element. Temperatures were measured with a chromel alumel thermocouple.

RESULTS

The data obtained are shown in Figs. 1 and 2 and Table II. In Fig. 1, the points shown are those obtained both on heating and cooling and at three field strengths. We conclude there is no apparent thermal hysteresis

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TABLE II. Values of χ_M and $1/\chi_M$ used to calculate θ and C_M.

T°K	$\chi_M \times 10^6$	$1/\chi_M$
206	6360	157.2
222	6228	160.6
232	6125	163.3
253	5957	167.9
301	5596	178.7
348	5328	187.7
394	5027	198.9
437	4779	209.2
487	4502	222.1
582	4037	247.7
661	3749	266.7
745	3466	288.5
829	3205	312.0

and no detectable dependence of susceptibility on field strength within the limit of experimental precision. The break in the susceptibility curve occurs fairly sharply at 154°K, and we feel this represents the temperature at which the effective antiferromagnetic ordering occurs. In Fig. 2, the χ *vs* T relationship for the entire temperature range is shown. No apparent dependence on field strength was noted. In Table II are tabulated the values of χ_M from which the constants θ and C_M were calculated. In determining χ_M, account was taken of the intrinsic diamagnetic susceptibility of the anion and cation. Values of 38×10^{-6} and 20×10^{-6} per gram ion for S^{--} and Mn^{++} respectively were used.[13,14] In calculating θ and C_M, it was found that two sets of constants appeared to fit the experimental data. In the range from the Néel temperature up to 400°K, values of $\theta=490$°K and $C_M=4.40$ were found, whereas for temperatures above 400°K the values were $\theta=380$°K and $C_M=3.90$. These values are included in Table I along with similar results by other investigators listed for comparison.

DISCUSSION

The results of the low-temperature investigations indicate that αMnS does not display the unorthodox thermal hysteresis behavior of MnSe and MnTe. There is no detectable field-dependent susceptibility in the range 2000 to 3000 oersteds. Another point of interest is the comparison of these results with those obtained by others. The apparent Néel temperature is satisfying in that it falls between the two previously reported values. The susceptibility peak shows no anomalies corresponding to the double hump in the specific heat curve. It is seen by reference to Table I that there is considerable variation in the values of θ and C_M obtained by other investigators. The difference between values in the low- and high-temperature range might be due to the persistence of short-range ordering effects to temperatures considerably above the actual Néel temperature. Wangsness,[15] on the basis of antiferromagnetic resonance experiments, has suggested that such a persistence occurs. It is conceivable that representative values of θ and C_M can only be found at the higher temperatures and that only the data above 400°K should be considered for comparison. Unfortunately, even then the agreement is not satisfactory. Therefore, even small differences in chemical composition might be significant. The samples used by Mehmed and Haraldsen and also Bhatnagar were reported to be very close to stoichiometric perfection, yet considerable differences exist between these data. The number of lattice defects as influenced by previous heat treatment might also be a factor which has an important bearing on the observed magnetic behavior.

It is also possible that differences in particle size might be responsible for the variations in results on MnS obtained by various workers. A dependence of susceptibility on particle size has already been noted for NiO.[16] In the region above room temperature there seemed to be a tendency for our susceptibility values to decrease somewhat (1∼%) following prolonged exposure to high temperatures. It is interesting to speculate that this decrease might be due to an enlargement of particle size resulting from a partial sintering at the higher temperatures.

It will be noted that the value of the permanent magnetic moment, μ_B, of 5.61 Bohr magnetons obtained in the high-temperature region in this work lies somewhat below the theoretical value of 5.92 corresponding to a spin of 5/2 for the Mn^{++} ion. If such a value is truly representative, then it indicates that the number of unpaired electrons is actually less than 5. Perhaps this is due to hybridization which takes place because of the partially covalent character of the bond.

ACKNOWLEDGMENTS

We would like to acknowledge the valuable assistance of Mr. Robert Powers, Mr. Neal Moore, and Mr. Hugh Melrose during various stages of this experiment.

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