Magnetic Properties of UMn_2*

S. T. Lin and A. R. Kaufmann†
Massachusetts Institute of Technology, Cambridge, Massachusetts
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The magnetic properties of UMn_2 have been investigated for the temperature range from 360°K down to 4.2°K. Below room temperature the magnetization curves are slightly bent toward the field axis and below 230°K the sample showed a small remanence. The susceptibility against temperature curve shows a λ-type anomaly at 260°K and a steep increase at about 4°K. The hysteresis loops are not symmetrical with respect to the origin and the degree of asymmetry depends upon either the temperature or whether the sample was cooled in magnetic field or without field. From some evidence, UMn_2 is classified as an antiferromagnetic material with a small parasitic ferromagnetism which may arise from uncompensated sublattice moments or uncompensated domain wall magnetization.

I. INTRODUCTION

Gordon[1] found that UMn_2 is antiferromagnetic and UFe_2 is ferromagnetic. As UMn_2 and UFe_2 are isostructural[2] it has been thought that the study of the ternary alloys of these three elements, which have the chemical formula UM_2 may reveal some interesting information concerning the electronic structure, electronic interaction, and magnetic properties. The equipment Gordon used seemed inadequate to produce accurate results. He only made three measurements below room temperature for UMn_2. The lowest temperature he used was 77°K. It was decided to study the binary alloy, UMn_2, in more detail first. We find some interesting phenomena: (1) UMn_2 really shows some evidences of antiferromagnetism but the critical temperature is about 260°K instead of 300°K as Gordon found. (2) Below 230°K the material shows a very small remanence and unfamiliar hysteresis. (3) In the region of liquid helium temperatures there is a very steep increase in susceptibility.

II. PREPARATION AND STRUCTURE OF UMn_2

The materials used for the sample were of the highest purity available. Uranium was obtained from the Atomic Energy Commission and manganese from Foote Mineral Company. The hydrogen content in uranium is about 2 ppm (parts per million); in manganese about 7 ppm. The quantities of materials according to the formula UMn_2 were melted together in vacuum by an induction furnace in a crucible of beryllium oxide. As the vapor pressure of manganese is very high, the melted material was held at about 1300°C for a short time and then cooled down naturally to room temperature.

The intermetallic compound UMn_2, which has metallic luster, is very brittle. It crystallizes in a face-centered cubic lattice with lattice constant 7.1628 ± 0.0014 A and density 12.57 g/cc. The compound is isostructural with $MgCu_2$, the C-15 structure type.[2]

III. METHOD OF MEASUREMENT

The technique and equipment used for the present work were the same as has been described by the authors[3] in their previous work, except for the cryostat for low temperatures. The cryostat, made of metal, is based upon the principle of utilizing the liquid helium gas to cool a massive coil of copper tubing which in turn cools the guided tube of the vacuum chamber and the working space. The temperature is controlled by the pumping speed of the helium gas through the copper coil. The cryostat can produce any intermediate temperature between liquid nitrogen and liquid helium for long periods of time.

UMn_2 oxidizes readily. To prevent oxidation the sample used was made of small chips instead of powder. The Pyrex container of the sample was evacuated and sealed in helium atmosphere.

IV. EXPERIMENTAL RESULTS

A. Magnetization Curve

The magnetization curves for the temperature range from 273.7°K down to 4.2°K have been obtained. The data are tabulated in Table I and are plotted in Fig. 1. Above room temperature the magnetization is proportional to the field strength. Below that temperature the magnetization curves are slightly bent toward the field axis, and below 230°K the data show a small remanence. In order to eliminate the effect of this residual magnetism, the sample was cooled from room temperature down to the desired temperature without applying any field before the beginning of the measurement. It is to be noted in the figure that the positions of the curves between 77°K and 260°K are inverted and switched back again above 260°K. The curve at helium temperature is very high but the remanence is low. If the sample was cooled in a magnetic field (say 7000 oe) the mag-

* This work was carried out under contract with the U. S. Atomic Energy Commission.
† Present address: Nuclear Metals, Inc., Cambridge, Massachusetts.
[1] P. Gordon, thesis, Department of Metallurgy, Massachusetts Institute of Technology, 1949 (unpublished).
[2] Baenziger, Rundle, Snow, and Wilson, Acta Cryst. **3**, 34 (1950).
[3] S. T. Lin and A. R. Kaufmann, Revs. Modern Phys. **25**, 182 (1953); Phys. Rev. **102**, 640 (1956).

TABLE I. Specific magnetization of UMn_2 at various magnetic field strengths for various temperatures in units of emu/g.

Field in kilo-oersteds \ T	4.2°K	11.5°K	28°K	77°K	123.9°K	180°K	250.2°K	260.2°K	273.7°K
0.351	0.0035	0.0024	0.0020	0.0020	0.0021	...	0.0024	0.0025	0.0023
1.052	0.0104	0.0069	0.0065	0.0062	0.0064	0.0066	0.0071	0.0073	0.0073
2.150	0.0207	0.0137	0.0129	0.0125	0.0126	0.0135	0.0142	0.0148	0.0145
3.509	0.0344	0.0233	0.0221	0.0211	0.0215	0.0231	0.0238	0.0243	0.0244
7.018	0.0699	0.0473	0.0442	0.0425	0.0431	0.0453	0.0475	0.0494	0.0487
10.527	0.1037	0.0710	0.0659	0.0630	0.0641	0.0677	0.0712	0.0738	0.0729
12.282	0.1207	0.0822	...	0.0732	0.0744	0.0778	...	...	...
14.036	0.1361	0.0934	0.0870	0.0834	0.0846	0.0880	0.0947	0.0982	0.0971

netization curve beyond that field strength was higher than the corresponding one when cooled without field. Two sets of the curves are shown in Fig. 2.

B. Susceptibility

The susceptibility at each temperature was obtained by taking the slope of the corresponding isotherms at high fields and the data are tabulated in Table II without applying diamagnetic correction. The susceptibility-temperature curve, Fig. 3, shows two anomalies: a λ-type maximum at 260°K and a steep increase at helium temperature. The first anomaly suggests that UMn_2 is an antiferromagnetic material with critical temperature 260°K. Gordon[1] found that the transition was around 300°K but his data seemed inadequate to determine it accurately. The second anomaly, the steep increase in susceptibility around helium temperature, is common to many substances but the interpretation is quite controversial.

C. Hysteresis

Figure 4 shows some typical hysteresis loops which are dissimilar to those of ordinary ferromagnetic materials. The shape of the loop is like a compass needle and its area is bounded by four segments of almost straight lines. The remanence is very small and the coercive force is high. The most unusual thing is that the hysteresis loop including the remanence, the coercive force, and the maximum moments at the two tips is not symmetrical with respect to the origin. The degree of asymmetry depends upon either the temperature or whether the sample was cooled in the magnetic field or without field. A separate article will be published at a later date to describe in detail this unusual hysteresis shift.

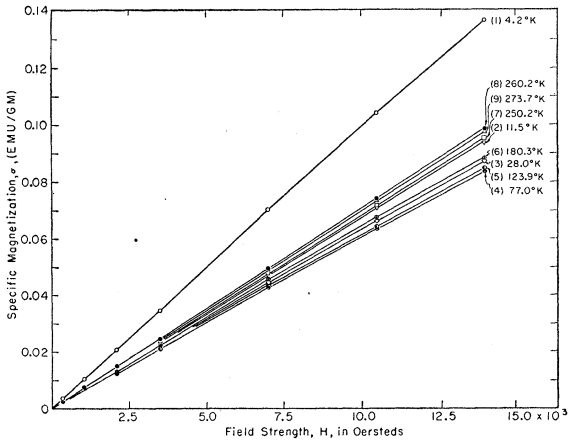

FIG. 1. Variation of magnetization with field.

V. DISCUSSION OF RESULTS

UMn_2 may be classified as an antiferromagnetic material from the following evidence: (1) The susceptibility-temperature curve is very similar to that of α-manganese itself except that the transition temperature is shifted to higher temperature and the maximum is much more defined. α-manganese has been confirmed

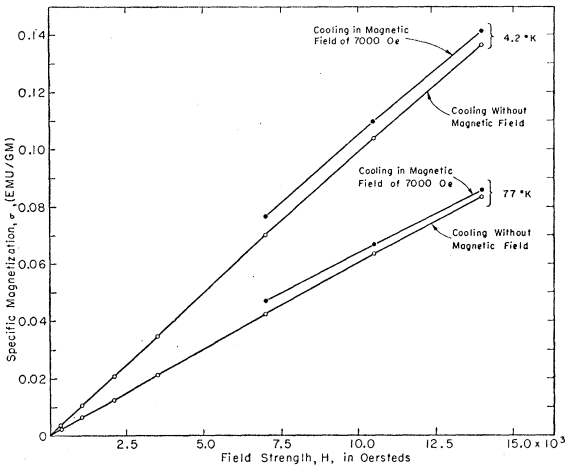

FIG. 2. Variation of magnetization with field (including two pairs of curves).

as an antiferromagnetic material by neutron diffraction.[4] (2) Li[5] has used the Bethe-Weiss method[6] to derive an accurate high-temperature theory of antiferromagnetism. The curve of X_{T_c}/X_T against T/T_c (where X_{T_c} is the susceptibility at the critical temperature T_c) for UMn_2 is close to his theoretical curve for a simple cubic lattice, which is shown in Fig. 5. For comparison, the

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[5] Y. Y. Li, Phys. Rev. **84**, 721 (1951).
[6] H. A. Bethe, Proc. Roy. Soc. (London) **A150**, 552 (1935); P. R. Weiss, Phys. Rev. **74**, 1493 (1948).

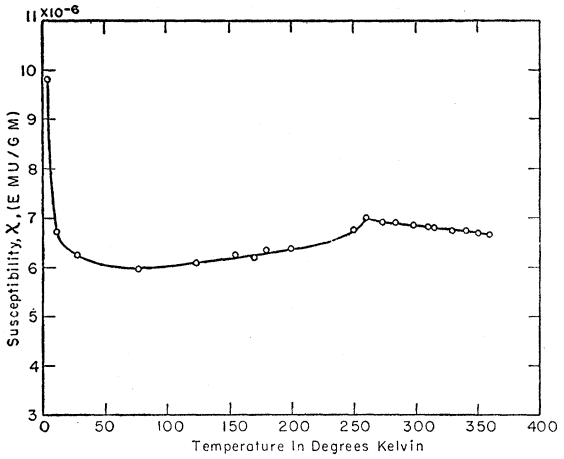

FIG. 3. Susceptibility as a function of temperature.

curves from Van Vleck's theory[7] and from experimental data on MnO of Bizette *et al.*[8] are also presented. Although the agreement of UMn_2 to the theory is a little worse than that of MnO, it should be remembered that the comparison is of a qualitative nature instead of a quantitative one because the antiferromagnetic structure of UMn_2 is not definitely known and the high-temperature range is very limited. From this crude comparison it is also seen that the experimental data of UMn_2 agree better with the Bethe-Weiss theory of antiferromagnetism than with the molecular field theory. It would be advisable to clarify this point by neutron diffraction.

From the experimental results, UMn_2 displayed a very small ferromagnetism which behaves very peculiarly. The origin of this small ferromagnetism is not understood since the sample is very pure. It is conceivable that small amounts of UH_3, which is ferromagnetic, could give the observed effect. In fact, one sample of

TABLE II. Magnetic susceptibility of UMn_2 for various temperatures in units of emu/g.

Temperature in degrees kelvin	$10^6 \times$susceptibility
4.2	9.83
11.5	6.71
28	6.25
77	5.99
123.9	6.08
155.3	6.26
170	6.21
180.2	6.36
199.8	6.40
250.2	6.76
260.2	7.01
273.7	6.93
284	6.92
298.3	6.88
310	6.82
315.3	6.82
321.8	6.80
330.8	6.77
341.7	6.75
350.6	6.72
359.8	6.69

UMn_2 which was known to contain 70 parts per million of hydrogen did exhibit an appreciable remanence. The hydrogen content of the uranium used to make the alloy was only 2 ppm and that of the manganese was about 7 ppm. This very small quantity of hydrogen could combine with uranium to form UH_3. We expected that part of the hydrogen would come out in the period of preparation of the sample because the preparation was carried out in vacuum at high temperature. After the magnetic study was finished, the sample was analyzed for hydrogen. The result showed that the hydrogen content in the sample was less than 1 ppm. It may be concluded that the effect of UH_3 must be negligibly small and that the observed trace of ferromagnetic behavior is a characteristic of UMn_2 itself. Furthermore,

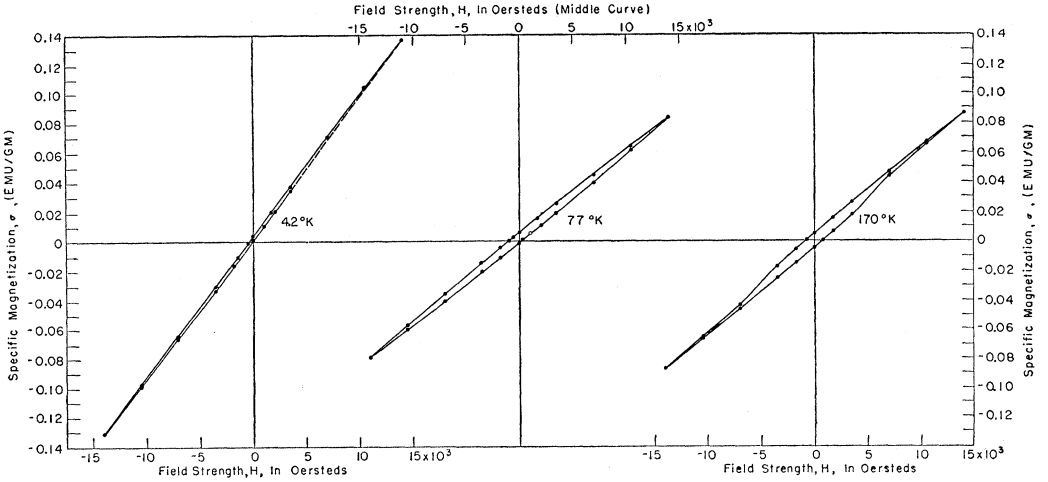

FIG. 4. Hysteresis loops at different temperatures.

[7] J. H. Van Vleck, J. Chem. Phys. **9**, 85 (1941).
[8] Bizette, Squire, and Tsai, Compt. rend. **207**, 449 (1938).

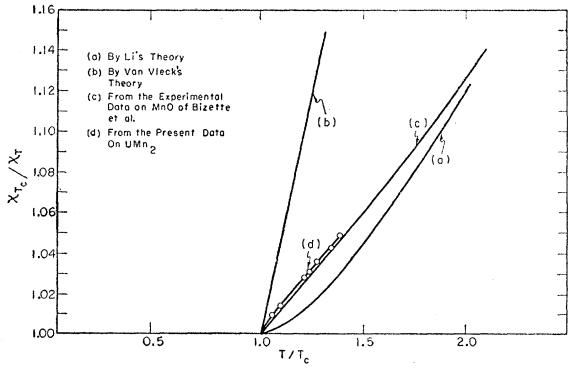

FIG. 5. Reciprocal susceptibility *vs* temperature.

the hysteresis shift of uranium hydride[9] is entirely different from that observed on this sample. Another criterion is that for ordinary ferromagnetic impurities the hysteresis loop should be symmetrical with respect to the origin. UMn_2 shows a peculiar hysteresis shift. The area of the hysteresis loop is maximum at about 180°K. At liquid helium temperature the loop area and the remanence are reduced greatly but the susceptibility increase is very high. A few other materials have been investigated by us and it appears that this small ferromagnetism and its peculiar hysteresis shift may be a property of some antiferromagnetic materials. The origin of the small ferromagnetism could be from either the uncompensated sublattice moments or the uncompensated domain wall magnetization[10] or it could be that the antiferromagnetic domain has an inherent hysteresis.

The so-called paramagnetic critical temperature, θ, was found to be about 1977°K by extrapolating the linear portion of the $1/X$–T curve above T_c to the temperature axis. The value of θ/T_c is then about 7.6. If the experiment was extended to a higher range of temperature, θ/T_c could be a little smaller but the value is still unusually high. From the known experimental data on antiferromagnetic salts, the highest value of θ/T_c for MnO seems to be 5. The high value of θ indicates that the internal field[11] which is responsible for the antiferromagnetism must be very high. This may explain qualitatively the asymmetry of the hysteresis loop since the applied field would need to be very high to reverse the direction of any small ferromagnetism due to uncompensated sublattice moments or the uncompensated domain wall magnetization. Another experimental fact, which supports this argument, is that the hysteresis is symmetrical near the critical temperature and the degree of asymmetry increases with decreasing temperature. This phenomenon is concordant with the theory of antiferromagnetism according to which the antiferromagnetic coupling is weaker near the transition temperature and stronger at lower temperatures.

As far as the authors are aware, no hysteresis loop for antiferromagnetic material has ever been reported except a brief account for MnSe by Squire.[12] The loop of MnSe is very similar to that of UMn_2. Squire claimed that at very low temperature there was no hysteresis. From our data the area of hysteresis decreases with decreasing temperature. Near or at absolute zero the loop area could be reduced to zero. That may be the reason why Squire could not detect the hysteresis of MnSe at very low temperature.

According to the customary procedure the number of Bohr magnetons per molecule were found to be about 6.6 from the slope of the $1/X$–T curve above T_c. Owing to the lack of information concerning the definite electronic configuration and the bonding character of the material, this value was not corrected for diamagnetism.

The phenomenon of steep increase in susceptibility around liquid helium temperatures seems to be quite common to many materials, such as pure manganese,[13] dilute Cu-Fe alloy,[14] dilute Cu-Ni alloy,[15] and even extremely pure copper.[14] $MnCl_2$ also shows a rise in susceptibility at very low temperature below the transition region.[16] Some authors have interpreted the increase as being due to impurities. Although it is difficult to disprove this argument, the interpretation seems not to be unique. This phenomenon could be a property of the material itself. We have tried CoO even with 0.2% ferromagnetic impurities. Its susceptibility did not show an anomaly at liquid helium temperature. For the case of UMn_2 the susceptibility increases very steeply at about 4°K. The remanence at that temperature decreases substantially.

ACKNOWLEDGMENTS

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[9] A detailed description of the phenomenon will be published at a later date.

[10] Y. Y. Li, Phys. Rev. **101**, 1450 (1956); Helen M. A. Urquhart and J. E. Goldman, Phys. Rev. **101**, 1443 (1956).

[11] J. Samuel Smart, Revs. Modern Phys. **25**, 327 (1953).

[12] C. F. Squire, Phys. Rev. **56**, 922 (1939).

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[14] Bitter, Kaufmann, Starr, and Pan, Phys. Rev. **60**, 134 (1941).

[15] Pugh, Coles, Arrott, and Goldman, Phys. Rev. **105**, 814 (1957).

[16] R. B. Murray and L. D. Roberts, Phys. Rev. **100**, 1067 (1955).