Magnetic and Thermal Properties of UI_3 at Liquid Helium Temperatures*

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Previous measurements of the magnetic susceptibility of UI_3 revealed a susceptibility maximum near 3.2°K of antiferromagnetic character, and a second susceptibility maximum at 1.5°K which is strongly depressed by an applied magnetic field of only 5 to 10 oersteds. The specific heat of UI_3 has now been measured from 1.2° to 4.2°K. These measurements show a λ-type anomaly of magnitude 10 joules/mole-deg at 2.61°K which is interpreted as arising from the antiferromagnetic transition. The behavior of the entropy and specific heat curves indicates an extensive short-range order above the antiferromagnetic transition point. The lower temperature susceptibility anomaly is tentatively interpreted as a manifestation of the growth of long-range antiferromagnetic order.

SUSCEPTIBILITY MEASUREMENTS

THE magnetic susceptibilities of UCl_3, UBr_3, and UI_3 have recently been measured from 77° to ~500°K by Dawson.[1] In the region near room temperature and above the susceptibilities of these compounds followed the Curie-Weiss law. In the case of UI_3, the susceptibility followed a Curie-Weiss law in the temperature region 200°–400°K, with a measured Weiss constant of about 5°K; this small Weiss constant suggests the possibility of a magnetic ordering transition at liquid helium temperatures.

In order to investigate the magnetic properties of UI_3 at very low temperatures, Roberts, Lavalle, and Erickson[2] measured the differential magnetic susceptibility of polycrystalline UI_3 in the region 1.1°–4.2°K. These measurements were carried out with a mutual inductance bridge which has been described previously.[3] The susceptibility curves are reproduced here in Figs. 1 and 2 along with some additional new data. These data were obtained as before[2] with an oscillating measuring field of about 2 oersteds amplitude and a frequency of 500 cycles per second. The temperature of the sample was obtained from liquid helium vapor pressure mealsurements using the 1948 temperature scale[4] with corrections given by Erickson and Roberts.[5] The bridge caibration was determined at 77°K using the absolute susceptibility as measured by Dawson at that temperature. The results of our measurements show a well-defined susceptibility maximum at 3.2°K, characteristic of a transition to the antiferromagnetic state. In addition to the 3.2°K maximum, the susceptibility displays further anomalous behavior in that both the reactive component (χ') and the resistive component (χ'') pass through a maximum near 1.5°K. The 1.5°K maximum in both components of the susceptibility is strongly depressed by applied magnetic fields of 5–10 oersteds, while the 3.2°K maximum is relatively field independent.

The open and closed circles in Figs. 1 and 2 represent data points taken on two different samples of UI_3 which were prepared by different chemical processes[2] from materials of high purity. The very good agreement between these two samples is taken as evidence that this anomalous susceptibility behavior is an inherent property of UI_3, and suggests, in particular, that the exceptional behavior near 1.5°K is not due to impurity effects. It is interesting to note that the lower temperature susceptibility maximum would not have been observed if the usual strong magnetic field Gouy method had been used rather than the above bridge procedure.

SPECIFIC HEAT MEASUREMENTS

In order to extend the study of the properties of UI_3 at liquid helium temperatures, the specific heat of polycrystalline UI_3 has been measured from 1.2°–4.2°K by the usual techniques of low temperature calorimetry. The over-all procedures and apparatus used will be described elsewhere.[6] The temperature scale used in the specific heat measurements is that noted in reference 5. The sample of UI_3 used in the specific heat measurements (0.1041 mole) was part of a large sample prepared at the time of the susceptibility studies. The sample had been stored in a sealed glass container in an atmosphere of helium gas prior to its use in the specific heat experiments. It was handled at all times in an atmosphere of dry, inert gas to prevent chemical decomposition or contamination. This sample was prepared by reacting uranium metal, in the form of a powder, with iodine gas at a high temperature. This preparation has been previously described in the literature.[7] The UI_3 was in the form of a powder with

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[1] J. K. Dawson, Atomic Energy Research Establishment, Report C/R 578, September, 1950 (unpublished). See also J. Chem. Soc., 429 (1951).

[2] Roberts, Lavalle, and Erickson, J. Chem. Phys. **22**, 1145 (1954).

[3] Erickson, Roberts, and Dabbs, Rev. Sci. Instr. **25**, 1178 (1954).

[4] H. Van Dijk and D. Shoenberg, Nature **164**, 151 (1949).

[5] R. A. Erickson and L. D. Roberts, Phys. Rev. **93**, 957 (1954). These corrections are in accord with the temperature scale adopted at the Paris Low Temperature Conference, September, 1955.

[6] R. B. Murray, paper on specific heat of $MnCl_2$ (to be published).

[7] J. J. Katz and E. Rabinowitch, *The Chemistry of Uranium* (McGraw-Hill Book Company, New York, 1951).

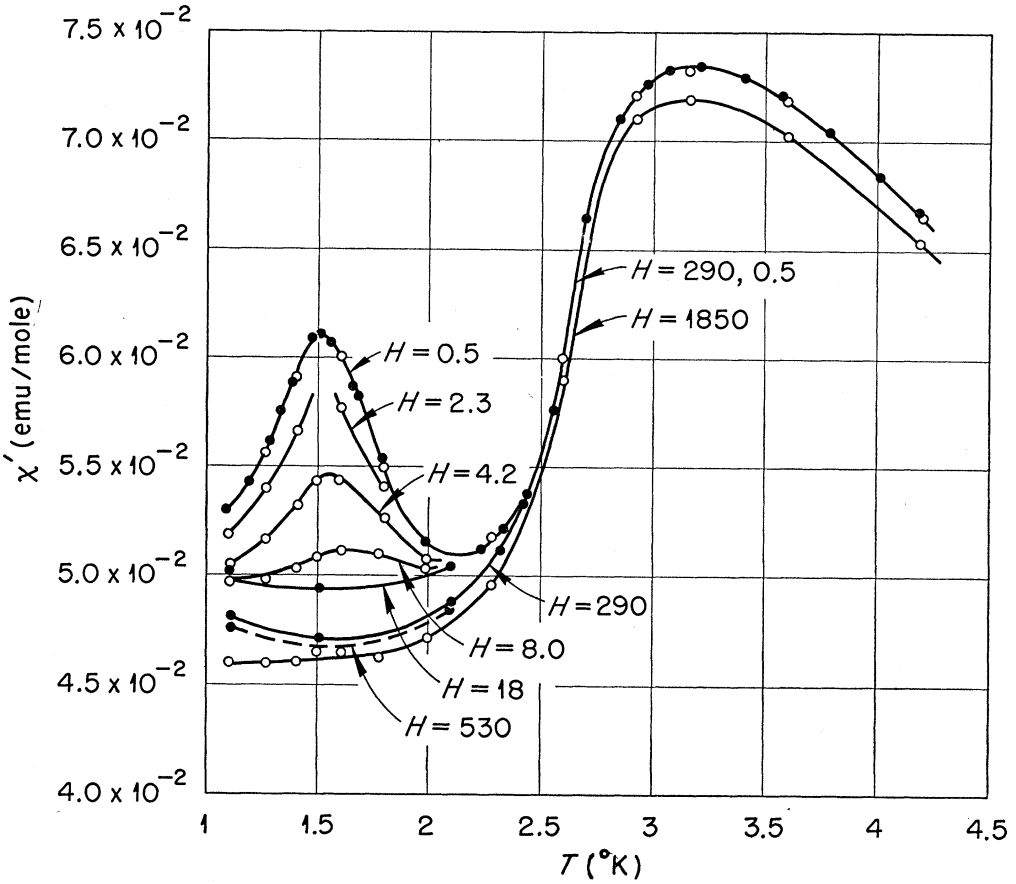

FIG. 1. Reactive component of the differential magnetic susceptibility of polycrystalline UI_3 as a function of temperature and applied magnetic field. The applied field H was parallel to the oscillating measuring field. H is in oersteds.

average particle size $\sim\frac{1}{4}$ mm. The UI_3 samples used in the susceptibility and specific heat studies were prepared by D. E. Lavalle of this laboratory.

The copper calorimeter cup used in the UI_3 experiments is shown schematically in Fig. 3. This cup was gold-plated on the inside to prevent any chemical reaction between the sample and copper wall. A thin-wall, gold-plated, copper sleeve was bonded to the bottom of the calorimeter cup with Araldite cement. A heater coil of Constantan wire was insulated from and bound to the outside of the sleeve with Araldite. The carbon resistance thermometer was prepared from a $\frac{1}{2}$-watt Allen-Bradley resistor by grinding away the external insulating cover. This unit (47 ohms at room temperature) was cemented to the wall of the cup and was covered by the UI_3 specimen. Helium exchange gas at a pressure of 20 cm Hg at room temperature was sealed inside the cup to insure thermal equilibrium. In the measuring process the sample was heated over temperature increments ranging from 20 to 100 millidegrees.

The results of the specific heat measurements are shown in Fig. 4 and in Table I. The data points given here represent the molar specific heat of UI_3, the specific heat of the calorimeter cup, thermometer, etc., having been subtracted from the measured points. This correction, which amounted at most to only 2% of the total specific heat at 4.2°K, was calculated from known specific heats of the components of the calorimeter assembly.

The specific heat maximum at 2.61°K (Fig. 4) is interpreted as arising from the onset of long-range antiferromagnetic order, and is thus to be associated with the susceptibility maximum observed at 3.2°K (Fig. 1).

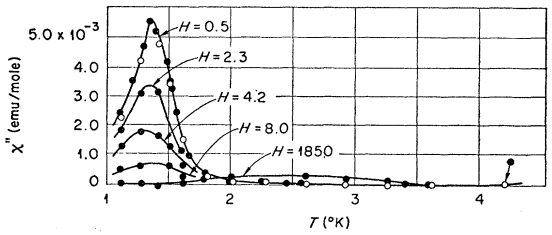

FIG. 2. Resistive component of the differential magnetic susceptibility of polycrystalline UI_3 as a function of temperature and applied magnetic field. The applied field H was parallel to the oscillating measuring field. H is in oersteds.

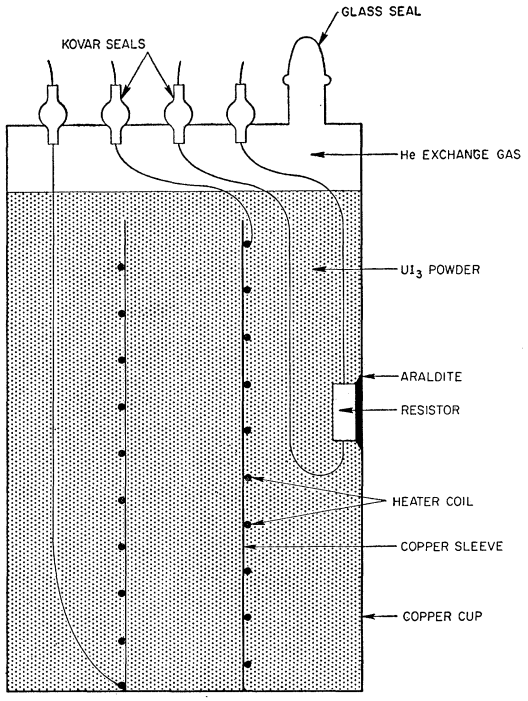

FIG. 3. Calorimeter cup assembly for specific heat measurements.

Below 2.61°K the specific heat exhibits a very sharp fall which is characteristic of cooperative transitions. No evidence of thermal hysteresis effects was found. Above 3°K, the specific heat behaves in a rather unusual manner, decreasing very slowly with increasing temperature. As no specific heat data are available at temperatures above 4.2°K, it is not possible to establish with any accuracy the lattice contribution to the specific heat in the liquid helium region. By comparison with the lattice specific heat of other compounds at liquid helium temperatures, however, we may estimate the order of magnitude of the lattice specific heat to be ~0.1 to 0.2 joule/mole-deg at 4°K. With this estimate the lattice specific heat amounts to about 3 to 6% of the total specific heat at 4°K. Thus it does not seem reasonable to account for the large specific heat above 3° as arising from the lattice contribution.

No indication of a second specific heat anomaly was found in the neighborhood of 1.5°K, the temperature at which the susceptibility shows a second maximum.

CALCULATION OF THE ENTROPY

Since the specific heat of UI_3 was found to be extremely small near 1°K, the total contribution to the entropy below 1° arising from this ordering process is assumed to be negligible, and we may correspondingly evaluate the entropy by numerical integration of the specific heat data between 1.2° and 4.2°K. The results of the entropy calculation are shown in Fig. 5. The entropy calculated in this manner includes, of course, the small contribution from the lattice. For a completely disordered system of electronic moments the minimum entropy per mole is $R\ln 2$, corresponding to $J=\frac{1}{2}$, where J is the effective angular momentum quantum number. Reference to Fig. 5 shows that at 4.2°K only about one half of this minimum has been achieved. At 2.61°K, where the specific heat passes through its maximum, the calculated entropy is only 0.2 $R\ln 2$.

DISCUSSION OF THE SPECIFIC HEAT AND SUSCEPTIBILITY ANOMALIES

The ground-state electronic configuration of the U^{+++} ion in UI_3 is not known and thus the maximum entropy of disorder, $R\ln(2J+1)$, cannot be predicted. The fact that the calculated entropy is only $0.2R\ln 2$ at the transition point shows nevertheless that the electron system is still only partially disordered at that temperature. This unusually small value of the entropy at the transition point (2.61°K) is in distinct contrast with the predictions of the molecular field theory and indicates that there is an extensive short-range order persisting at temperatures well above the transition point. Correspondingly, the very gradual fall in the specific heat above 3°K may be associated with the slow decay of this short-range order. Such a small entropy at the transition temperature as well as the large, almost temperature-independent magnetic specific heat immediately above the transition point, is unusual.

As mentioned previously, the susceptibility anomaly at 3.2°K, Fig. 1, is interpreted as arising from a transition to the antiferromagnetic state. This conclusion is based on the fact that (1) the susceptibility demonstrates a well-defined maximum which is nearly field independent, and (2) the specific heat exhibits a λ-type transition characteristic of cooperative ordering. In view of the evidence of an extensive short-range order, it is not surprising that the peak in the specific heat occurs at a somewhat lower temperature than does the susceptibility maximum, since the specific heat anomaly presumably occurs with the onset of long-range magnetic ordering, whereas the susceptibility would be affected by the extensive short-range order above this transition.

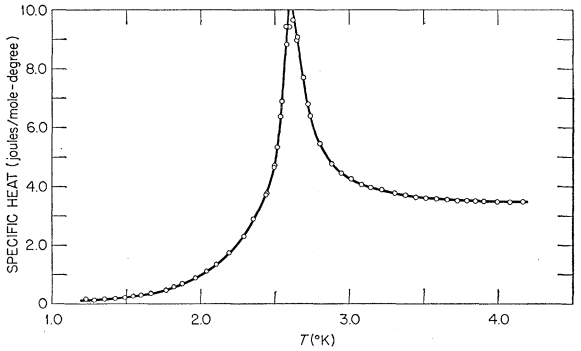

FIG. 4. Molar specific heat of UI_3 as a function of temperature.

Turning now to the susceptibility anomaly near 1.5°, we note that the magnitude of the 1.5° susceptibility peak is of the same order as the antiferromagnetic maximum at 3.2°K. The extreme field dependence of the susceptibility near 1.5° indicates that this effect is also of a cooperative nature, since the susceptibility of a system of noninteracting moments would be unaffected by such small applied fields. In addition, the fact that the susceptibility is depressed by these small fields suggests that the ordering is, at least in part, of a weakly "ferromagnetic" nature.

The presence of a large out-of-phase susceptibility component, χ'', Fig. 2, is to be associated with a phase lag between the applied measuring field and the induced moment. This behavior is characteristic of ordinary ferromagnetic materials (e.g., iron) suggesting further an analogy between the 1.5°K susceptibility anomaly and a type of "ferromagnetic" behavior.

The extreme sensitivity of the susceptibility at 1.5°K to small magnetic fields has been noted above. We now observe that, as the applied steady field attains larger values the susceptibility appears to approach a lower limit. This occurs at fields in the vicinity of 1850 oersteds. The susceptibility in the neighborhood of the antiferromagnetic maximum at 3.2°K was found to be essentially field independent; it then seems reasonable to ascribe the strong field limiting susceptibility near 1.5°K to the residual antiferromagnetic properties of the system. This strong field limit of the antiferromagnetic susceptibility extrapolated to 0°K is about 0.6 times its maximum value at 3.2°K. Thus there appears to be a correlation with the Van Vleck two-sublattice model of antiferromagnetism,[8] which predicts a ratio of $\frac{2}{3}$. It does not seem justifiable, however, to conclude on this basis alone that the antiferromagnetic order in UI_3 is of a simple two-sublattice type. Rather, we note the qualitative similarity in the behavior of the residual antiferromagnetic susceptibility observed here, and that predicted by the Van Vleck theory.

If we ascribe differences between the 1850 oersted curve and the curves in lower fields, Fig. 1, as due to the "ferromagnetic" behavior, it is possible to determine this incremental susceptibility, denoted by S, as a function of field. A plot of S *vs* H at 1.5°K is shown in Fig. 6. The corresponding magnetization (at 1.5°K) as a function of field is obtained by integrating S as a function of H and is shown in Fig. 7. This integration neglects the small (about one percent) contribution from the resistive component. By integrating this susceptibility to large fields it was found that the incremental moment appears to saturate at $M_{sat} \approx 0.6$

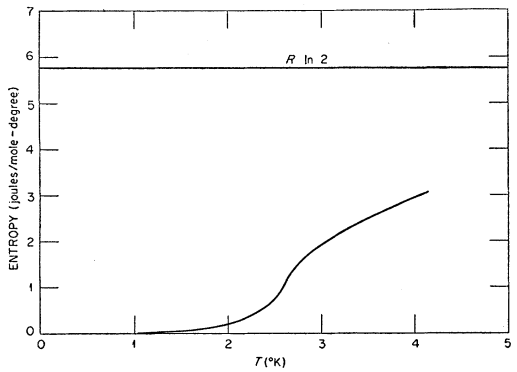

FIG. 5. Entropy of UI_3 as a function of temperature.

[8] J. H. Van Vleck, J. Chem. Phys. **9**, 85 (1941).

TABLE I. Molar specific heat of UI_3.

T (deg K)	C_{meas} (joules/mole-deg)
Experiment Number 1	
1.230	0.173
1.287	0.129
1.355	0.175
1.424	0.172
1.490	0.212
1.547	0.250
1.598	0.293
1.663	0.359
1.766	0.496
1.820	0.575
1.875	0.679
1.963	0.882
2.042	1.11
2.105	1.33
2.191	1.72
2.291	2.30
2.363	2.89
2.439	3.72
2.500	4.71
2.537	6.39
Experiment Number 2	
2.443	3.78
2.518	5.35
2.579	8.84
2.648	8.96
2.721	6.81
2.803	5.47
2.883	4.77
2.949	4.45
3.015	4.26
3.083	4.07
3.144	3.97
3.229	3.84
3.306	3.78
3.377	3.71
3.446	3.64
3.517	3.60
3.589	3.58
3.659	3.55
3.724	3.52
3.790	3.53
3.846	3.50
3.904	3.50
3.992	3.48
4.079	3.46
4.164	3.48
2.496	4.65
2.548	6.90
2.576	9.44
2.599	9.43
2.622	9.66
2.651	9.09
2.691	7.71
2.737	6.40

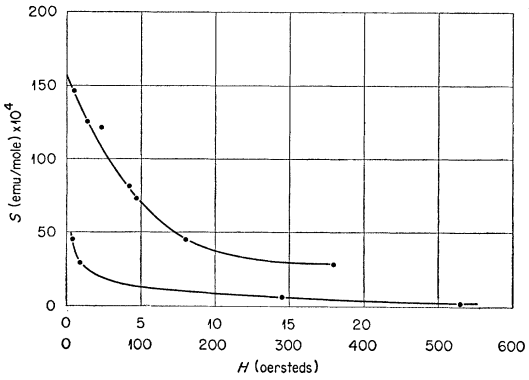

FIG. 6. "Ferromagnetic" susceptibility of UI_3 as a function of applied field H at 1.5°K.

emu/mole (at 1.5°K) or an average moment of 10^{-24} emu per U^{+++} ion. This is quite small, being of the order of 10^{-4} Bohr magneton. This ratio of 10^{-4} should be taken as an approximate value, since we have assumed that the residual antiferromagnetic susceptibility is field independent. This is not strictly true, as the susceptibility near 3°K is in fact depressed somewhat by fields greater than about 300 oersteds and a large contribution to the area under the S *vs* H curve, Fig. 6, comes at large fields. This calculation, nevertheless, should indicate the correct order of magnitude.

Because of the approximate nature of the above calculation, we do not present detailed results for M_{sat} as a function of temperature. We note, however, that the extreme field sensitivity of the susceptibility first appears at a temperature just below the temperature of maximum specific heat and displays a trend toward increasing magnetization with decreasing temperature. Thus, the extreme field sensitivity of the susceptibility and the growth of long range antiferromagnetic order are simultaneous phenomena in temperature and are possibly correlated. In this connection it is also interesting to note that with small applied fields the phase angle $\theta=\arctan\chi''/\chi'$ also increases with decreasing temperature below about 2.6°K.

Referring to the specific heat measurement, we note that there is only one specific heat anomaly, although there are two susceptibility maxima. This suggests either that both of the susceptibility peaks are associated with the same ordering process, or that one of the susceptibility maxima (presumably that at 1.5°) results from the ordering, perhaps by some new process, of relatively few moments.

Weak ferromagnetic properties are often found to accompany antiferromagnetic transitions. Néel[9] has suggested a possible explanation of this for crystals of a layer lattice structure, of which UI_3 is an example, by postulating the existence of antiferromagnetic domains. These antiferromagnetic domains are considered by Néel to consist of ferromagnetic sheets of alternating spin orientation with a corresponding zero net magnetization. The boundary between two antiferromagnetic domains is considered to be a region (a few layers in thickness) in which the spin phase shifts by 180 degrees, giving rise to an uncompensated net spin, of a ferromagnetic nature, in the separating wall. On the basis of Néel's picture, the growth of magnetization in the separating walls, and thus of the "ferromagnetic" effects, would be expected to be simply correlated with the growth of long-range antiferromagnetic order throughout the crystal. In the case of UI_3, the observed parasitic "ferromagnetism" begins to grow in at temperatures just below the 2.61°K antiferromagnetic specific heat anomaly as previously noted. Thus there is an interesting parallel between Néel's suggestion of ferromagnetic walls separating antiferromagnetic domains and the observed behavior of UI_3. It must be noted, however, that this picture of Néel does not provide a unique interpretation of these measurements.

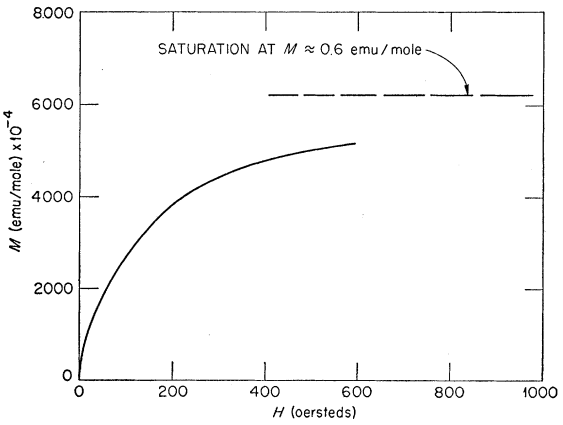

FIG. 7. "Ferromagnetic" moment of UI_3 as a function of applied field H at 1.5°K.

ACKNOWLEDGMENTS

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[9] L. Néel, Brussels Conference, 1954 (unpublished).