But statistically[20] $F=-kT\ln Z$ and therefore, from (26) and (28),

$$K_1(T)=\sum_n \exp\left(-\frac{K_{0n}}{kT}\right)K_{1n}\Big/\sum_n \exp\left(-\frac{K_{0n}}{kT}\right). \qquad (29)$$

Upon making use of the ideas discussed in the text,

$$K_{0n}+K_{1n}(\alpha_1^2\alpha_2^2+\alpha_1^2\alpha_3^2+\alpha_2^2\alpha_3^2) =N\{k_{0n}+N^{-1}K_1(0)\langle\beta_{1n}^2\beta_{2n}^2+\beta_{1n}^2\beta_{3n}^2+\beta_{2n}^2\beta_{3n}^2\rangle\}, \qquad (30)$$

where k_{0n} and $N^{-1}K_1(0)$ are appropriate to one of the N atoms and the β's refer to the local magnetization about that atom.

For each low-energy eigenstate n, one may picture the local magnetization as making an angle Θ_n (defined by I_n/I_0) with the field direction. Thus, in analogy with (5),

$$K_{1n}=K_1(0)P_4(\cos\Theta_n). \qquad (31)$$

Finally, upon replacing sums by integrals, (29) goes over to

$$K_1(T)=K_1(0)\int f(\Theta)P_4(\cos\Theta)d\tau\Big/\int f(\Theta)d\tau. \qquad (32)$$

Zener assumed a random walk distribution function for $f(\Theta)$; Brenner, a molecular field function.

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[20] In reality the Gibbs' free energy is desired, since measurements are made at constant pressure. However, the difference between measurements at constant strain and constant pressure is negligible for most materials.

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Low-Temperature Magnetic Studies of Uranium Hydride, Uranium Deuteride, and Uranium Dioxide

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A study of magnetization as a function of temperature and magnetic field has been carried out for uranium hydride, uranium deuteride, and uranium dioxide at temperatures from 300°K to 1.3°K and in magnetic fields from 60 000 gauss down to zero field. The apparent saturation magnetization for the samples of beta-uranium hydride used is 1.18 ± 0.03 Bohr magnetons per atom of uranium and for one sample of uranium deuteride is 0.98 ± 0.03 Bohr magneton per atom of uranium. The magnetic moment of uranium dioxide, limited by what may be antiferromagnetic ordering, is about 0.025 Bohr magneton per atom of uranium at 35 000 gauss and 1.3°K. This result makes possible corrections for the moments of UH_3 and UD_3 on the basis of a known oxygen content or an estimate of the oxide impurity on the basis of apparent saturation. A high zero-field remanent magnetization (over 50% of the saturation magnetization for a spherical sample) is observed, attesting to the pronounced magnetic hardness of beta-uranium hydride. Analytic expressions have been worked out for magnetization as a function of temperature for zero magnetic field and 11 500 gauss, leading to a paramagnetic θ of 180°K and a ferromagnetic θ of 168°K. An estimate of 2×10^6 gauss is made for the molecular field in UO_2.

INTRODUCTION

In recent years, much interest has been shown in the overlap of wave functions as associated with exchange interactions, and how they foreshadow ferromagnetism and antiferromagnetism. The formerly conventional ferromagnetic and antiferromagnetic substances have been in the iron ($3d$ unpaired electrons) group; also the rare earth group ($4f$ unpaired electrons) has yielded ferromagnetic[1] and antiferromagnetic substances.[2] It is then of particular interest to study possible exchange interactions originating in $5f$ and $6d$ configurations in the actinide elements and their compounds. The discovery of a ferromagnetic transition in uranium hydride[3] at 173°K heightened the interest in the study of some of these interactions. Various low-field studies have been made of the magnetic properties of beta-uranium hydride. The susceptibility above the Curie temperature was studied by Trzebiatowski, Stalinski, and Sliwa,[3] by Gruen,[4] and later by Lin and Kaufmann.[5] Estimates of 2.9 Bohr magnetons per atom[4] were made from the low-field susceptibility measurements, using

$$\mu=C[\chi(T+\Delta)]^{\frac{1}{2}}. \qquad (1)$$

Here μ is the intrinsic moment, χ is the susceptibility, T the absolute temperature, and C and Δ are constants. In the neighborhood of 173°K, there is a more rapid increase in the susceptibility. This, together with hysteresis and direct zero-field magnetization measurements,[6] confirmed the strong ferromagnetism of

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[1] Banister, Legvold, and Spedding, Phys. Rev. **94**, 1140 (1954); Elliott, Legvold, and Spedding, Phys. Rev. **94**, 1143 (1954).

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[3] Trzebiatowski, Stalinski, and Sliwa, Roczniki Chem. **26**, 110 (1952); **28**, 12 (1954).

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[5] S. T. Lin and A. R. Kaufmann, Phys. Rev. **102**, 640 (1956).

[6] W. E. Henry and D. M. Gruen, Phys. Rev. **98**, 1200(A) (1955).

beta-uranium hydride. Gruen[4] also suggested $J=\frac{1}{2}$ for the uranium ion. The susceptibility values determined by the above authors[3–5] were used to estimate saturation magnetization by extrapolation from small magnetic fields. In Table I, the magnetization values so obtained are listed. From the experimentally determined values for the highest available fields, and the curvatures, some extrapolations to saturation were made; the moments thus obtained are low compared with moments calculated from neutron diffraction studies.[7] It was thus deemed advisable to analyze our previously obtained data further and to extend the magnetization measurements of beta-uranium hydride to higher fields. Also, in order to increase the chance of gaining further insight into the behavior of uranium ions, we have studied some of the magnetic properties of uranium deuteride and uranium dioxide. It is interesting to determine whether the deuteride, which has the same structure as the hydride, differs in properties in the ferromagnetic case as certain pairs of compounds do in the ferroelectric case. Even at the higher temperatures, there is a difference in the susceptibilities of uranium hydride and uranium deuteride. Corrections for UO_2 impurity were made by Gruen[4] to his susceptibility measurements of UH_3. These corrections gave him an improved value for the saturation magnetization even though, as he points out in his article, he had to extrapolate from low-field data. The other investigators[3,5] did not mention corrections for impurities. Although the intrinsic moment for UO_2 calculated by Dawson and Lister[8] from high-temperature susceptibility measurements is over 3 Bohr magnetons per atom of uranium, it seems to follow a Curie-Weiss law,

$$\chi=C/(T+\Delta), \tag{2}$$

with $\Delta=233$°K at the high temperatures. There are indications of an anomaly. Specific heat measurements by Jones, Gordon, and Long[9] show a peak at 28.9°K, perhaps corresponding to antiferromagnetic ordering at these lower temperatures. In the vicinity of the maximum, the specific heat curve is qualitatively similar to that calculated by Van Vleck.[10] The fit is not quantitative, but it is to be remembered that the Van Vleck calculation is for simple cubic and body-centered cubic structures, and for spin only. Thus, some deviation is to be expected because (1) UO_2 has a calcium fluorite structure[11] and (2) susceptibility measurements at high temperatures show the intrinsic moment to be over 3 Bohr magnetons per atom of uranium, indicating that there is only a partial quenching of the orbital angular momentum.[8] Also, the broadening of the specific heat hump may be due to so-called short-range ordering.[12] Recently, another indication of antiferromagnetic ordering has come from neutron diffraction studies[13] which revealed that at 77°K only the lines expected from a calcium fluorite structure were observed, whereas at 4.2°K additional lines appeared, indicating possible antiferromagnetic ordering. Recent unpublished magnetic studies[14] in low fields also indicate antiferromagnetic ordering.

TABLE I. Approach to the saturation magnetization of uranium hydride.

Source	Highest fields (gauss)	Method of determination	Highest measured moment[a]	Estimated saturation magnetization[a]
Trzebiatowski, Stalinski, and Sliwa[b]	6450	Calculated from susceptibility		0.7
Lin and Kaufmann[c]	21 000	Calculated from susceptibility		0.9
Gruen[d]	9000	Calculated from susceptibility		1.0
Naval Research Laboratory[e]	60 000	Direct moment (sample motion ballistic)	$1.18+0.03$	1.2
Shull and Wilkinson[f]	15 000	Calculated from neutron diffraction (not dependent on impurity content)	1.25 ± 0.2	1.25

[a] Bohr magnetons per atom of uranium.
[b] See reference 3.
[c] See reference 5.
[d] See reference 4.
[e] Results of present investigation.
[f] See reference 7.

In addition to studying the magnetization of uranium hydride, uranium deuteride, and uranium dioxide as a function of temperature and magnetic field, we study the remanent magnetization of uranium hydride and uranium deuteride. We attempt to replace extrapolated values of the saturation magnetization by actually measured values by applying higher magnetic fields than have been possible before.

EXPERIMENTAL PART

The measurement of magnetization of uranium hydride, uranium deuteride, and uranium dioxide was carried out as a function of temperature (from 300°K down to 1.3°K)[15–17] and in magnetic fields[18]

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[13] D. G. Henshaw and B. N. Brockhouse, Bull. Am. Phys. Soc. Ser. II, **2**, 9 (1957).

[14] Through private communication, it was learned that Dr. W. P. Wolf of Oxford has also observed a temperature-independent low-field susceptibility in the liquid helium range for UO_2; see a report of a low-field anomaly below 20°K by J. E. Goldman and A. Arrott, Bull. Am. Phys. Soc. Ser. II, **2**, 119 (1957); see also a preliminary report on the magnitude of the high-field magnetization of UO_2, W. E. Henry, Bull. Am. Phys. Soc. Ser. II, **2**, 237 (1957).

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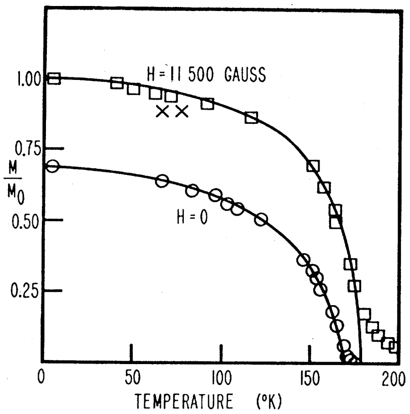

FIG. 1. Plot of relative magnetization (M/M_0) as a function of absolute temperature for $H=0$ and $H=11\,500$ gauss. M is the magnetization at temperatures T, and M_0 is the magnetization at absolute zero.

from 60 000 gauss down to zero field. A sample motion ballistic ensemble including a moment lift[19] was used. Pure iron was employed in the calibration. Samples were protected[19] and spherical[20,21] where the demagnetization factor cancels the Lorentz polarization in first approximation. The samples of beta-uranium hydride, uranium deuteride, and uranium dioxide were obtained from the Oak Ridge National Laboratory through the courtesy of Dr. M. H. Wilkinson. A sample of beta-uranium hydride was also obtained from the Argonne National Laboratory through the courtesy of Mr. Flotow and Dr. Gruen.

DISCUSSION OF RESULTS

The magnetization studies were carried out in three atomic environments for comparison. Two samples of uranium hydride compared favorably.

Uranium Hydride

Figure 1 shows a plot of the magnetization of uranium hydride as a function of temperature at 11 500 gauss and the remanent moment at $H=0$; normalization is at 1.3°K (taken as the absolute zero value, since there is less than a 0.2% change in the helium range). Analysis of the magnetization results is made in terms of a Brillouin-type function, which has been shown to apply up to over 99.8% saturation[22] in paramagnetic substances where the field components other than applied could be neglected. In the cases of exchange interaction, the effective field is compounded of the applied field and the projection of the molecular field. The molecular field projection is subtracted in the antiferromagnetic case[23] and enhances[24] the applied field in the ferromagnetic case. For uranium hydride, the energy which is put into the Boltzmann factor (which determines the extent of magnetization) is not linear in the applied field nor in the magnetization as is assumed in the Weiss treatment.[25] Using a modified Weiss treatment in which the energy is an even series in magnetization and keeping only the dominant even power, we represent the magnetization (M) as a function of temperature (T) with the equation:

$$M=M_0 \tanh\left[\frac{m(1-m^{2N})}{t}\right], \tag{3}$$

where M_0 is the magnetization at absolute zero, t is a reduced temperature (T/θ), θ is a Curie temperature, m is a reduced magnetization (M/M_0), and N is an integer.

For the $H=11\,500$ gauss case, we neglect the applied field, which is about 1% of the molecular field, in the formulation in Eq. (3). Here N is 5 and θ turns out to be 180°K. The upper curve in Fig. 1 shows a fit of the experimental points on the curve from $0.2M_0$ to M_0 except for points in the liquid nitrogen region where there is a suggestion of a departure, perhaps due to a double transition. The points (crosses) showing marked deviation were taken in a nitrogen bath which had oxygen contamination,[16] but the other points were taken without a liquid bath. Since this experiment was done, a pronounced double transition has been found in another substance.[26]

For $H=0$, we also use the modified Weiss treatment. Here $N=5$, as above, but θ is 168°K. This value of θ is also the extrapolated value of the Curie temperature (lower curve, Fig. 1) although the zero-field magnetiza-

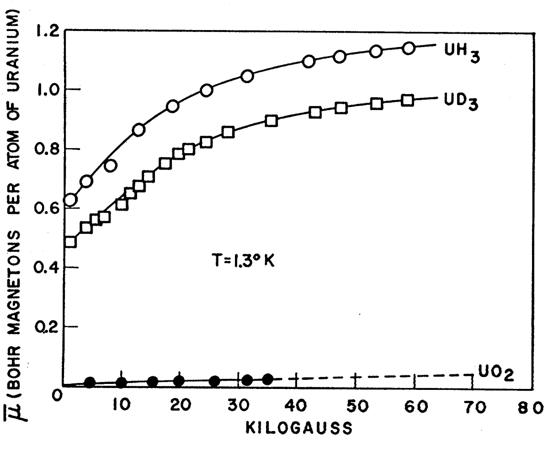

FIG. 2. Plot of magnetization as a function of magnetic field at $T=1.3$°K for uranium dioxide, uranium deuteride, and uranium hydride.

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[19] W. E. Henry, National Bureau of Standards Circular No. 519 (U. S. Government Printing Office, Washington, D. C., 1952), p. 237.

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tion curve has a small tail which comes down to zero at 173°K. Here, short-range order is probably indicated. It is also noticed that the low-temperature remanence is very high.

The magnetization of beta-uranium hydride as a function of magnetic field for the liquid helium temperature range is shown in Fig. 2. It is seen that the magnetization increases rather slowly with field (for a ferromagnetic) even at the low fields, perhaps a result of strong anisotropy fields. This would be consistent with partial quenching of the orbital angular momentum. At 60 000 gauss the magnetization seems to be approaching an asymptote slightly in excess of 1.18 Bohr magnetons per atom of uranium, in agreement with the results obtained by Shull and Wilkinson[7] using neutron diffraction. Nevertheless, this saturation magnetization is far short of the value expected for U^{+++} ($5f^3$ ground state) as determined for the chloride by Hutchison[27] and collaborators and for the fluoride by O'Brien[28]; U(IV) compounds have been studied[29] by Ghosh, Gordy, and Hill and by Hutchison and Herzfeld. Even if a hydrogen bridge structure is assumed, leading to an effective U^{++++}, one would expect a saturation magnetization of at least 2 Bohr magnetons per atom of uranium. Our low value of approximately 1.2 Bohr magnetons per atom of uranium for saturation magnetization in uranium hydride may be explained by assuming quasi-metallic behavior for the uranium hydride. In this case, the bottom of the antiparallel energy band could be lower than the top of the parallel band. On this basis, the statistical filling of the two bands could lead to a reduced and nonintegral value, 1.2. An example of a similar application of the band picture is seen for iron[30] where the reduction is from an expected 4 Bohr magnetons per atom of iron to 2.22. A recent alternative picture[31] is based on mixed states for iron in which $3d$ electrons are promoted to higher states.

Uranium Deuteride

The experimental results for the deuteride are qualitatively similar to those for the hydride, but quantitatively there are differences. There is a slight difference in the Curie temperature. The remanence is high as for the hydride. Assuming the same high purity in both cases, the absolute moment of uranium deuteride seems to be less, for all equal conditions of temperature and magnetic field, than that of the hydride. Figure 2 shows a plot of magnetization *vs* magnetic field at 1.3°K. The saturation magnetization approaches a value slightly above 0.98 Bohr magneton per atom as contrasted with 1.18 for uranium in the hydride. This departure could be due to a slight change in lattice constants by the slightly heavier deuterium or it could be an impurity effect. Figure 3 shows a plot of ratios of magnetization of UH_3 to magnetization of UD_3 as a function of magnetization of the uranium hydride at 1.3°K. If there were an inert (noninteracting and independent) impurity, macroscopically dispersed throughout the sample, this curve would be a horizontal line. While x-ray and neutron diffraction analyses[7] have suggested that the hydride and deuteride are relatively pure (their samples were used in this investigation), contamination is a possibility. Gruen[4] has shown that a few percent of oxide can appear in the preparation of the hydride.

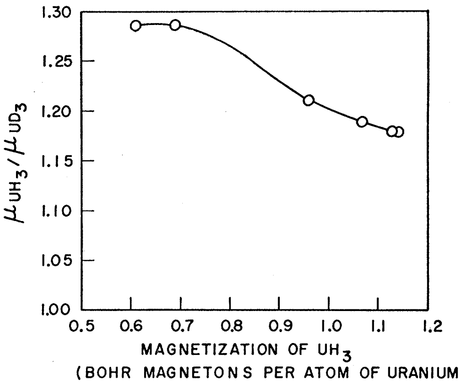

FIG. 3. Plot of the ratios of magnetizations $[\mu(UH_3)/\mu(UD_3)]$ of uranium hydride $[\mu(UH_3)]$ to the magnetization of uranium deuteride $[\mu(UD_3)]$ as a function of the magnetization of uranium hydride. The conditions are the same for both substances.

Uranium Dioxide

The high-temperature results are in qualitative agreement with values which could be calculated from low-field susceptibility measurements of Dawson and Lister.[8] At low temperatures, our measurements gave much lower moments than the 3 Bohr magnetons per atom of uranium implied in the low-field susceptibility measurements at high temperatures. We obtained only 0.025 Bohr magneton per atom of uranium even at 1.3°K and 35 000 gauss. Figure 2 shows the linear dependence of the magnetization of UO_2 on magnetic field, in which

$$M=7\times10^{-7}H \tag{4}$$

Bohr magnetons per atom of uranium, where H is the field in gauss. If the linear equation is assumed to hold up to saturation and if the saturation is assumed to be 2 Bohr magnetons per atom, the molecular field would be about 3×10^6 gauss.

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SUMMARY AND GENERAL REMARKS

The magnetization of uranium hydride and uranium deuteride has been measured as a function of temperature at constant magnetic fields and as a function of magnetic field at constant low temperatures. We have interpreted magnetization results on the basis of internal molecular fields. A strong remanence is obtained and may be associated with strong anisotropy fields (a possible result of partial quenching of the orbital angular momentum) as well as huge exchange interactions. The high saturation magnetization, 1.18 ± 0.03 Bohr magnetons per atom of uranium in UH_3, may be near the correct value and is in accord with the neutron diffraction value, which is not dependent on purity in first approximation. The lower apparent saturation magnetization for uranium deuteride may conceivably be due to change in interatomic distances from those in UH_3, but the possibility of contamination should be kept in mind, particularly since the magnetization of UO_2 is very small under the conditions for measuring saturation magnetization for the deuteride and hydride. Although the measurement of a magnetization of 0.025 Bohr magneton per atom of uranium in UO_2 at 1.3°K and 35 000 gauss can be explained in terms of antiferromagnetic ordering under a strong molecular field, some consideration should be given to a possible reduction in the intrinsic moment through splitting of the ground state by interactions similar to that in potassium ferrocyanide[32] in which application of the Pauli principle leads to restricted magnetization. In view of the small moment of UO_2, whatever the mechanism, it is possibly worthwhile to keep open the question of saturation magnetization of uranium hydride to see if an even higher value than 1.2 Bohr magnetons per atom can be determined from absolutely pure UH_3. Further work should be done to examine carefully the possibility of a real difference between the magnetization at absolute zero of uranium hydride and of uranium deuteride, as a possible difference is suggested also by unpublished work[33] which shows from specific heat measurements that the sub-Curie regions have different entropies.

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Piezoresistance Constants of *P*-Type InSb†*

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The change of resistance in uniaxial tension was measured for several single-crystal specimens of *p*-type InSb over the range 77°K to 350°K. The difference between the donor and acceptor concentrations for these specimens ranges from 3×10^{15} cm^{-3} to 7×10^{17} cm^{-3}. The piezoresistance coefficients were found to depend on impurity concentration. The elasto-Hall constant was measured at 77°K for the purest specimens and the experimental results indicate that, in the extrinsic range, the large piezoresistance is primarily due to stress induced changes in the tensor mobility of the holes. The shear coefficients were found to vary approximately linearly with T^{-1} in the extrinsic range. It is concluded that the valence band extrema occur at, or very near, $\mathbf{K}=0$ in the Brillouin zone with energy surfaces similar to those of Si and Ge.

1. INTRODUCTION

PIEZORESISTANCE measurements have recently been helpful in the study of the band structure of semiconductors.[1–5] Smith[1] points out that the anisotropy of the piezoresistance effect offers information concerning the directions in $\mathbf{K}$ space along which the energy extrema lie for a simple "many-valley" semiconductor. Theoretical predictions[5–9] have been made about the temperature dependence of the various components of the piezoresistance tensor for both the "many-valley" model and the "degenerate" model. With this in mind, the present work was undertaken with the hope that the results would shed some light on the band structure of *p*-type InSb.

The piezoresistance constants of *p*-type InSb were measured as a function of temperature and impurity concentration from 77°K to 350°K. The Hall constant and resistivity were measured as a function of tempera-

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† Based on work performed at The Institute for the Study of Metals and submitted to the University of Chicago in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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