

Magnetic Properties of Beta-Uranium Hydride*

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A thorough magnetic investigation of beta-uranium hydride has been carried out. The curve of reciprocal paramagnetic susceptibility against temperature generally follows the Curie-Weiss law and shows the same curvatures near the Curie point and at high temperatures as do the data for the ferromagnetic elements above their Curie points. A considerable number of magnetization curves have been obtained for a wide range of temperatures. Three methods were used for deducing the spontaneous magnetization for comparison. The curve of reduced spontaneous magnetization against reduced temperature lies very close to the curves of iron, nickel, and cobalt. The paramagnetic Curie temperature, 173°K, is about 8°K lower than the ferromagnetic Curie point. The number of electron spins per molecule obtained from the saturation magnetization and from the temperature dependence of the paramagnetic susceptibility shows the same discrepancy as do the ferromagnetic elements. Three hysteresis loops at about 161.1°K, 75°K, and 4.2°K and the coercive forces from about 170°K down to 4.2°K have been obtained. The magnetocrystalline anisotropy constants for the whole low-temperature range calculated from the magnetization curves and from the coercive forces agree in order of magnitude.

INTRODUCTION

PURE ferromagnetic elements are much simpler for theoretical studies than alloys because no alloying complexities and inhomogeneities of constituents are introduced and the exchange interactions are also much simpler. For example, from many studies¹ of ferromagnetic alloys it has been evident that alloys (with almost no exception, at least for binary nickel alloys) do not obey the law of corresponding states² predicted by the quantum modification of Curie-Weiss theory. But this law applies much better to the pure elements Fe, Ni, and Co. Even for these elements the experimental data still show significant deviations from the theoretical predictions. In general, the experimental values of the reduced magnetic moments are lower at low temperatures and higher at high temperatures than the theoretical results. If more ferromagnetic elements could be found we would have greater opportunity to test the law.

Beta-uranium hydride has recently been reported to be ferromagnetic.³ Although the hydride is not an element, it is a definite compound with metallic properties. Another advantage is its low Curie point which makes the paramagnetic state easier to study. Gruen⁴ has measured its paramagnetic susceptibility above the Curie temperature and Henry and Gruen⁵ its saturation magnetization at low temperatures. The results seem not entirely consistent with those obtained by Trzebiatowski

and his collaborators.³ It is worth while to make a thorough study of this new material.

PREPARATION AND STRUCTURE OF URANIUM HYDRIDE

The uranium hydride samples were prepared with hydrogen generated from a larger batch of uranium hydride, obtained by the reaction of tank hydrogen with scrap uranium turnings. The tubes containing the sample and the scrap were connected by ground glass joints to a glass line which included a mercury bubbler, serving also as a manometer. The glass line could be connected by a stopcock either to vacuum or to a tank of hydrogen.

The big sample for high-temperature measurement was prepared in a flat-bottom Pyrex tube of 8-mm i.d. This sample tube was at the end of a long tube, whose other end was provided with a ground glass joint. Turnings from electrolytic uranium were etched with 1:1 nitric acid, rinsed with water and acetone, air-dried, weighed (1.00 g), and placed in the glass tube which was immediately connected to the line. The tube containing the uranium scrap was already connected to the line before the connection of the tube containing the sample. The system was evacuated, following which the hydrogen was admitted and the scrap heated for hydriding. Cessation of hydriding of the scrap was followed by evacuation before hydriding of the sample. The sample was hydrided twice, with intermediate decomposition. Hydriding was in the range of 250–300°C maintained in a Hevi-Duty split-tube furnace, readily maneuvered around either the charge or scrap tube. In this temperature range the hydride should come out in the form of beta-uranium hydride.⁶

The progress of hydriding and dehydriding of the samples could be observed. Hydriding appeared quite rapid, but an additional two-hour exposure to hydrogen

* This work was carried out under contract with the U. S. Atomic Energy Commission and presented in part at the Conference on Magnetism and Magnetic Materials, Pittsburgh, Pennsylvania, June, 1955.

¹ J. J. Went, *Physica* **17**, 596 (1951); D. J. Oliver and W. Sucksmith, *Roy. Soc. Proc. (London)* **A219**, 1 (1953).

² This is the well-known universal relation between $\sigma_0 T / \sigma_{\infty, 0}$ and T / θ_f , $\sigma_0 T$ being the spontaneous magnetization at $T^\circ\text{K}$, $\sigma_{\infty, 0}$ the absolute saturation moment, and θ_f the Curie temperature in $^\circ\text{K}$.

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

⁴ D. M. Gruen, Chemistry Division, Argonne National Laboratory (private communication).

⁵ W. E. Henry and D. M. Gruen, *Phys. Rev.* **98**, 1200(A) (1955).

⁶ Mulford, Ellinger, and Zachariasen, *J. Am. Chem. Soc.* **76**, 297 (1954).

was provided to ensure complete hydriding. Suitable hydrogen pressure, observed on the bubbler, was maintained by heating the scrap. The sample was sealed under the vacuum obtained by the cooling and rehydriding of the scrap.

The main feature of the preparation of the small sample for low-temperature measurement was the incorporation of a closely fitted plunger which could be manipulated through a Wilson seal so as to reach the bottom of the sample tube. This plunger permitted compacting of the hydride; its lowermost portion was sealed with the sample in the tube to minimize the dead space remaining above the hydride. This sample tube was prepared from Pyrex tubing drawn down to a bore of 35 mils. (The outer diameter was about 2 mm). The uranium wire fitted loosely in this tube, having a diameter of 18 mils. It was $\frac{7}{16}$ in. long and weighed 29.5 mg.

Hydrogen was generated in the usual way from a larger batch of uranium hydride prepared from scrap uranium turnings and tank hydrogen. After the first hydriding, the uranium wire was decomposed. The second and final hydriding was then carried out for over five hours. The plunger was then brought to bear on the sample. The tube was sealed under an atmosphere of hydrogen with the lowermost portion of the plunger remaining in the tube and minimizing the dead space above the sample. The glass immediately above the sample tube was recovered and analyzed to check against the possible loss of uranium if the sample was blown upward during the intermediate dehydriding.

Uranium hydride⁷ forms a compound, UH_3 , of definite composition with metallic properties. The bonding between uranium and hydrogen plays a predominant role and the metal-metal bonds are almost lacking.

The hydride is cubic, $a = 6.631 \text{ \AA}$, with two types of uranium atoms per unit cell, two atoms at 000, $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ and six atoms at $\frac{1}{4}$, 0, $\frac{1}{2}$; $\frac{1}{2}$, $\frac{1}{4}$, 0; 0, $\frac{1}{2}$, $\frac{1}{4}$; $\frac{3}{4}$, 0, $\frac{1}{2}$; 0, $\frac{1}{2}$, $\frac{3}{4}$; $\frac{1}{2}$, $\frac{3}{4}$, 0; the hydrogens lie in distorted tetrahedra, equidistant from four uranium atoms. Each uranium atom has twelve nearest hydrogen atoms. The x-ray density is 10.92 g/cc.

THE MAGNET

The newly designed Helmholtz magnet⁸ has been used for all the measurements above and below the Curie point. As the field and the gradient of the magnet are separately controlled, the Curie method was adopted to measure the intensity of magnetization below the Curie point by using a small gradient of a few oersteds per centimeter. In this way the whole sample was in an almost uniform field and hence in stable equilibrium. The main field was calibrated by the usual search coil and the gradient by a special differential coil. The two coils making up the differential coil were carefully

designed to measure fields at their respective center points. The two coils were wound on a single agate frame. The distance, about $\frac{1}{4}$ in. between the two centers, was accurately measured. The constants of the coils were calibrated by the proton resonance method. The fields and gradients calibrated by search coils were checked by using the conventional standards such as Mohr's salt and pure iron. The results were in very good agreement. During each measurement the main field was kept constant and the gradient was changed in polarity. The correct force on the specimen was taken as the difference of the forces for the two directions of the gradient divided by two. The advantages of this method are to eliminate the errors due to variation of the initial reading of the balance, buoyancy differences, and condensation at very low temperatures. The most important advantage is to eliminate completely the small gradient of the main field, which varies with the load and nonuniform water cooling. Sometimes under unfavorable conditions the absolute values of each single reading with different polarity of the gradient could be very different, but the mean differences are still the same. It is believed that the accuracy of this method of measurement is very high.

THE MICROBALANCE

A primary standard is desirable for the measurement of force on the specimen. It was decided that the measurement should be carried out in vacuum and therefore a special microbalance, designed and constructed by the Ainsworth Company,⁹ was procured. The sensitivity of the balance is 5 micrograms and the capacity about 25 grams.

By using simple worm and gear arrangements it is possible to manipulate 201 milligrams of multiriders from outside of the vacuum chamber. This is accomplished by several shafts which emerge from the vacuum chamber through Wilson seals and which are coupled to the worm gears by step joints.

THE FURNACE

A water-cooled molybdenum furnace was used for the production of high temperatures. The No. 20 s.w.g. molybdenum wire was wound on a grooved alundum tube about 1 in. i.d., $1\frac{1}{8}$ in. o.d., and 24 in. long. The winding was about 12 in. in length. The grooved tube was covered with alundum cement and was surrounded by two alundum tubes and two thin molybdenum sheets alternately. The molybdenum sheets served as radiation shields and at the same time helped to equalize the temperature throughout the length of the furnace. The whole system was put in a water-cooled brass jacket. The temperature was regulated by the usual mechanical controller and measured by a platinum-platinum and 10 percent rhodium thermocouple which was fixed inside and at the middle of the grooved alundum tube. Within

⁷ R. E. Rundle, J. Am. Chem. Soc. **69**, 1719 (1947); **73**, 4172 (1951).

⁸ S. T. Lin and A. R. Kaufmann, Revs. Modern Phys. **25**, 182 (1953).

⁹ W. Ainsworth and Sons, Inc., Denver 2, Colorado.

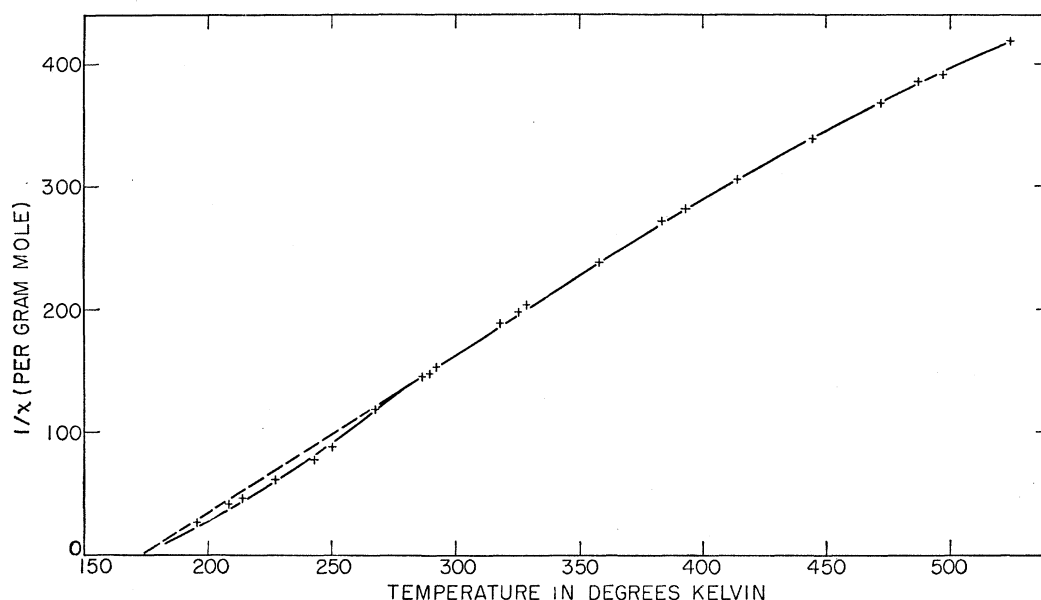


FIG. 1. Variation of susceptibility above the Curie temperature.

about 1 in. of the middle of the winding, the temperature was very uniform.

THE DEWAR

All the temperatures between room and liquid nitrogen temperature were obtained by a liquid nitrogen Dewar and a heater installed in the Pyrex guide tube which formed a part of the vacuum chamber and was inserted in the Dewar. The heater was made out of a copper tube about 7 in. long which was wound with No. 30 B. and S. Ga. enameled constantan wire. By repeatedly adjusting the height of the liquid nitrogen surface and the current of the heater, the temperature could be kept constant for several hours without difficulty. Liquid helium temperature was obtained by a Pyrex liquid helium Dewar installed inside the liquid nitrogen one. The Dewars were conveniently arranged for refilling. The temperature was measured by a copper-constantan thermocouple which was soldered to the copper heating chamber.

EXPERIMENT

A. Experimental Results of the Measurements above the Curie Point

Susceptibility measurements have been carried out for the temperature range from 191°K up to 572°K. Except near the lower extremity of this temperature range, the susceptibility values are independent of the magnetic fields up to 12 000 oersteds. The results, corrected for container and diamagnetism of uranium ions, are shown in Fig. 1.

The curve of reciprocal susceptibility against temperature is concave at high temperatures and convex toward the temperature axis near the Curie point. The

middle part of the curve is almost a straight line. Although many paramagnetic substances satisfy the Curie-Weiss law almost completely, this general type of curvature is the usual characteristic of ferromagnetic elements above their Curie points. Fallot¹⁰ carefully measured the susceptibility of Ni above its Curie temperature and obtained a $1/\chi - T$ curve which is very similar to the present one. According to Stoner's¹¹ treatment based on collective electron theory, the $1/\chi - T$ curve near the Curie point should be convex toward the temperature axis. But it should be noted that in the present case the curve lies beneath the extended straight line from the linear part of the curve instead of above it as predicted by the theory. An attempt has been made to fit the concave part of the curve at high temperatures to the formula

$$\chi - \alpha = C/(T - \theta_p), \quad (1)$$

but no suitable value of α could be found to account for the major part of the curve.

The extrapolated straight line from the linear part of the curve meets the temperature axis at about 173°K, which is considered to be the paramagnetic Curie temperature, θ_p .

B. Method and Experimental Results of the Measurements Below the Curie Point

1. Method of Measurement

As the conventional standard ballistic method is not convenient for measurements at high fields and low

¹⁰ M. Fallot, *J. phys. radium* **5**, 153 (1944).

¹¹ E. C. Stoner, *Proc. Roy. Soc. (London)* **A165**, 372 (1938); *Phil. Mag.* **25**, 899 (1938); *Proc. Roy. Soc. (London)* **A169**, 339 (1939); *Phil. Mag.* **28**, 527 (1939).

temperatures, the intensity of magnetization has been measured by the Curie method by using a small gradient combined with the main field. The advantages of the present method are: (1) use of a very small sample; (2) no need to take the sample out of the field or to turn off the field, which is very inconvenient for high fields; (3) no need to put the sample in a cyclic state for each change of field as required by some other methods; (4) convenience of working at very low temperatures. The disadvantages are (a) the poor stability at very high fields, as a result of which the maximum field used was about 21 000 oersteds (b) inaccuracy of measurements at very low fields because a gradient, although small, must be used.

Before the beginning of the measurement at each temperature, the sample was warmed to room temperature to eliminate residual magnetism. In order to deduce the spontaneous magnetization from $H-T$ curves for constant magnetization, extensive data have been taken and a large number of isotherms at very small temperature intervals have been obtained. The data are too extensive to publish. Only a few of the magnetization curves are shown in Fig. 2 for clarity. All the measurements were not corrected for the demagnetizing force.

2. Deduction of Spontaneous Magnetization

Three methods of deduction of the spontaneous magnetization have been used and the results are shown in Fig. 3. Curve I was obtained by linear extrapolation from the isotherms at high fields to $H=0$. Curve II was calculated from the isotherms by using the formula

$$\sigma_{H,T} = \sigma_{0,T} + aH - b/H^2, \quad (2)$$

applied to high fields. Curve III was obtained from linear extrapolation of $H-T$ curves for constant magnetization at high fields to $H=0$.

Since the magnetizations are far from saturation,

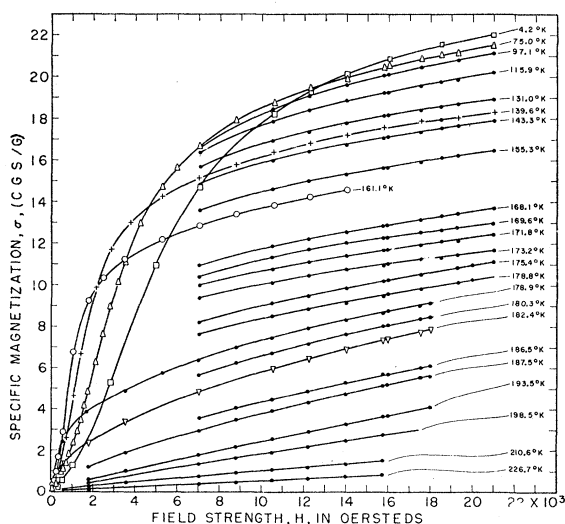


FIG. 2. Variation of magnetization with field.

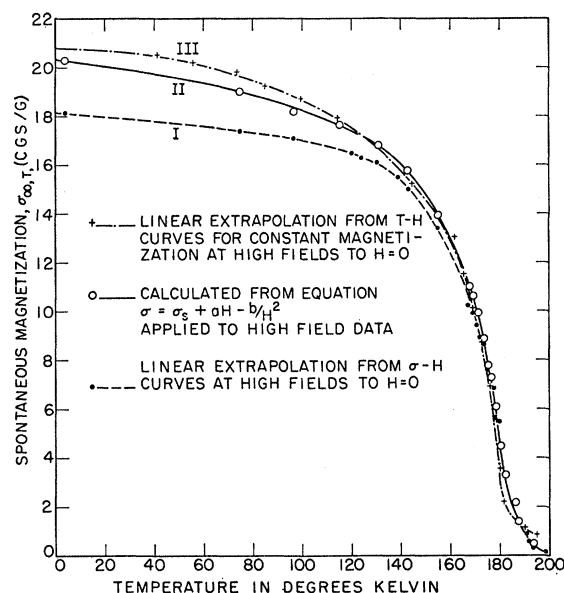


FIG. 3. Variation of magnetization with temperature.

Curve I lies beneath Curve II, especially at low temperatures. The method of obtaining Curve I is eventually equivalent to that of Curve II with the term b/H^2 omitted. However, in the present case the fields are not high enough for the term b/H^2 to be neglected. It is interesting that Curves II and III are very close to each other. This may indicate that both methods could be applied to the present case. It has been well established that the term b/H^2 is due to the magnetocrystalline anisotropy, which opposes the rotation of the magnetization vector toward the external field direction. The calculated values of b and hence the anisotropy constant K are fairly large. This indicates that the term b/H^2 can not be neglected and explains why Curve I lies beneath Curve II, especially at lower temperatures at which the anisotropy constants are higher.

3. Test of the Law of Corresponding States

The absolute saturation magnetization $\sigma_{\infty,0}$ was obtained at low temperatures by plotting $\sigma_{T,0}$ from Curve III of Fig. 3 against T^2 and linearly extrapolating to $T^2=0$. The value was found to be 20.8 cgs units per gram. The ferromagnetic Curie point θ_f was obtained by plotting $\sigma_{\infty,T}^2$ against T and linearly extrapolating to $\sigma_{\infty,T}^2=0$. The value obtained was 181°K. The curve of the reduced spontaneous magnetization against the reduced temperature obtained from the values of $\sigma_{\infty,T}$, θ_f , and Curve III, is shown in Fig. 4. Since the reduced curve derived from Curve II of Fig. 3 is almost the same as that from Curve III, it is omitted for clarity. For comparison, the data for iron, nickel, and cobalt, and the theoretical curve for $J=\frac{1}{2}$, are also shown in the same figure. The curve for UH_3 lies very close to those for the ferromagnetic elements.

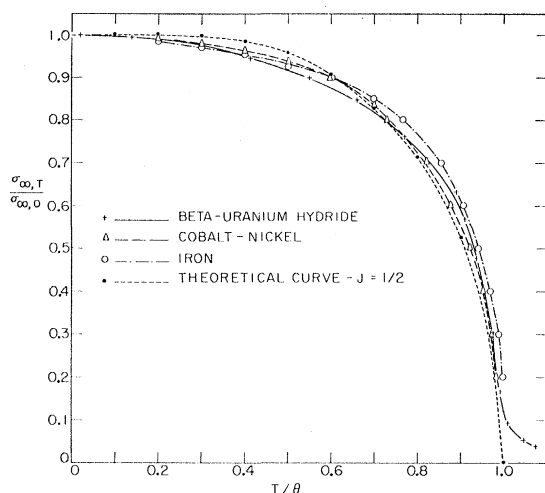


FIG. 4. Temperature dependence of the saturation magnetization of beta-uranium hydride, iron, cobalt, and nickel, as compared with theory.

4. Hysteresis Loops and Coercive Forces

The Curie method has been used for hysteresis measurements. The sample used here was the same one that was used in magnetization measurements. Since it was not convenient to reverse the polarity of both generators, only about 16 000 oersteds was used for the maximum field strength and about 4 oersteds per cm for the gradient. The coercive forces have been measured from about 191°K down to 4.2°K and three typical hysteresis loops were determined at 4.2°K, 75°K, and 161°K. The coercive force data are shown in Fig. 5. For comparison, the three loops are shown in Fig. 6. The peculiar features are the big loops and the high coercive forces, especially at helium temperature. The coercive force decreases rapidly with increasing temperature at low temperatures. The general appearance of the curve of coercive force as a function of temperature is very

TABLE I. Characteristics of the ferromagnetic elements and beta-uranium hydride.^a

	Fe	Co	Ni	Gd	β -UH ₃
Z	26	27	28	64	92
A	55.84	58.94	58.69	157.3	(atomic number of U) 241.1 (molecular weight)
Ferromagnetic					
θ_f , °C	770	1120	358	16	-92
σ_0	221.7	162	57.6	254	20.8
q_f	2.217	1.71	0.605	7.14	0.898
Paramagnetic					
temp. range, °C	...	{1230	{500	{90	{7
θ_p , °C	820	{1450	{850	{366	{117
C_A	1.268	1.228	0.322	7.84	0.783
$\frac{1}{3}(r+2)(q_p)r$	3.37	3.27	0.86	20.9	2.09

^a Z, atomic number; A, atomic weight; θ_f , ferromagnetic Curie temperature; σ_0 , specific saturation magnetization extrapolated to absolute zero; q_f , corresponding number of parallel electron spins; T range, range over which the relation $C_A/(T-\theta_p)$ holds approximately; θ_p , paramagnetic Curie temperature; C_A , Curie constant per gram atom; $(q_p)r$, corresponding number of electron spins, coupled to give a carrier moment of $r\mu_B$ (for Gd, if $r=7$; $q_p=6.97$).

similar to that for fine particles of Ni obtained by Weil and Marfause,¹² but the magnitude is about ten times larger.

DISCUSSION OF RESULTS

From the absolute saturation value $\sigma_{\infty,0}$, the number of electron spins per molecule, f , may be immediately calculated:

$$f = \sigma_{\infty,0} M / M_B = 20.8 \times 241.09 / 5.585 \times 10^3 = 0.898,$$

where M is the molecular weight of UH₃, and M_B the Bohr magneton value per mole. Since the reduced spontaneous magnetization curve (Fig. 4) is very close

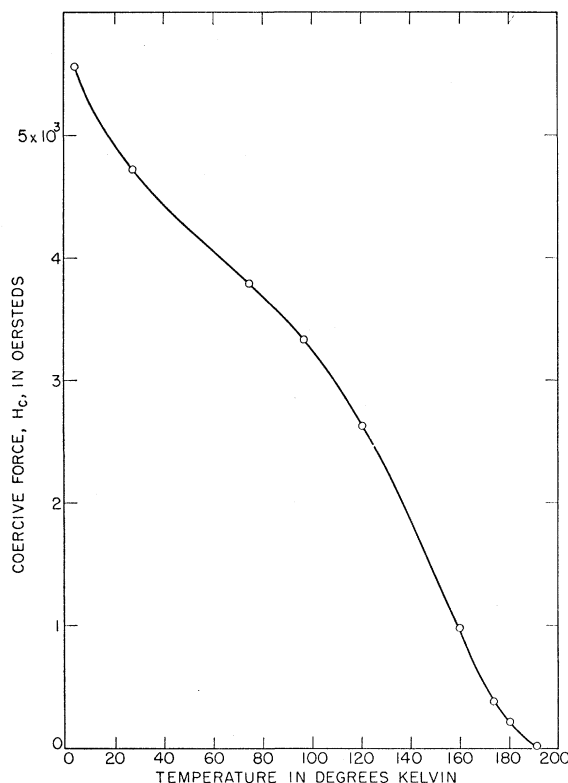


FIG. 5. Dependence of the coercive force on the temperature.

to the theoretical curve with $J = \frac{1}{2}$, the ferromagnetism of UH₃ at low temperatures is evidently due to independent electron spins. According to Stoner's¹³ suggestion, the number of electron spins per atom $(q_p)r$ calculated from the paramagnetic susceptibility on the assumption that each carrier consists of r spins in parallel coupling can be expressed as follows:

$$\frac{1}{3}(r+2)(q_p)r = RC_A / M_B^2 = 2.665C_A,$$

where R is the gas constant per mole, C_A the Curie-Weiss constant per mole, and M_B is the gram molecular Bohr magneton. Knowing the number of spins in parallel

¹² L. Weil and S. Marfause, J. phys. radium 8, 358 (1947).

¹³ E. C. Stoner, Repts. Progr. Phys. 11, 79 (1946-47).

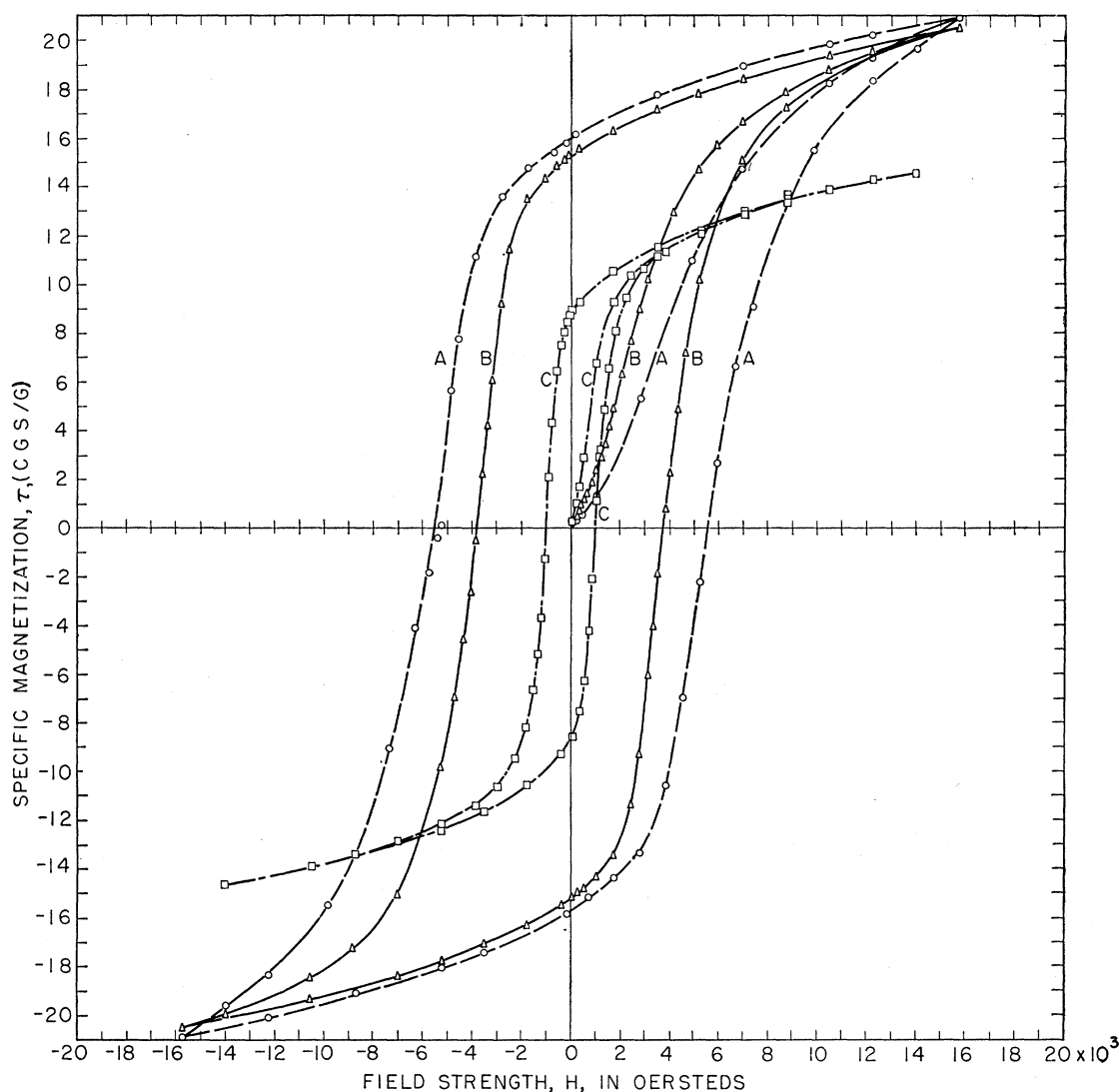


FIG. 6. Hysteresis loops at different temperatures: (1) 4.2°K; (2) 75.0°K; (3) 161.1°K.

coupling, we can calculate the number of electron spins $(q_p)_r$ per atom. For comparison of the full magnetic behavior of UH_3 with that of the other ferromagnetic elements, we reproduce the table compiled by Stoner¹³ and put the new data in it. (See Table I.)

It is to be noted that the difference θ_p and θ_f for UH_3 is smaller than for the other elements, but in the case of UH_3 $\theta_f > \theta_p$ which is contrary to the situation for the other elements. But this is not the only case. Ferrocobalts show the same behavior. Now it would be better to emphasize here that owing to the different intensities of magnetization of the ferromagnetic and paramagnetic states it would be very difficult to use the same sample for all the measurements. The samples for low-temperature and high-temperature measurements were different although the uranium used for both samples was very pure (but from different sources), and the packing

density for the low-temperature experiment was much higher than that for the high-temperature experiment. We wonder whether these different packing densities and the different sources of the samples may cause some difference in Curie temperatures.

Since the same sample has been used for coercive force and magnetization measurements for different temperatures, we can compare the magnetocrystalline anisotropy by these two different methods. For an ensemble of single-domain particles of cubic crystals, like iron, oriented at random, Néel¹⁴ obtained an expression for the coercive force

$$H_c = 0.64K/I_s, \quad (3)$$

where K is the magnetocrystalline anisotropy constant related to the magnetocrystalline energy by the

¹⁴ L. Néel, *Compt. rend.* **224**, 1488 (1947).

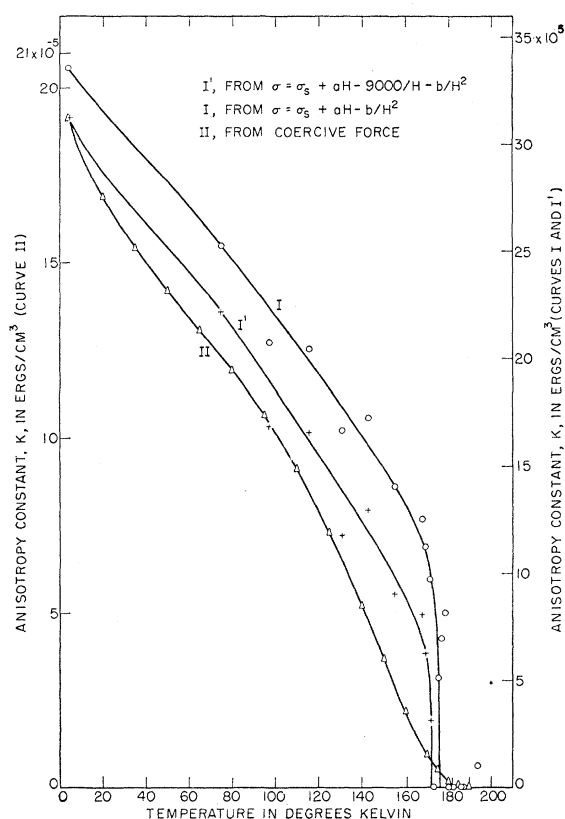


FIG. 7. Dependence of the anisotropy constant on the temperature.

equation

$$W = K(\alpha^2\beta^2 + \beta^2\gamma^2 + \gamma^2\alpha^2),$$

where α , β , and γ are the direction cosines of the spontaneous magnetization with respect to the three axes of the cubic crystal, and I_s is the saturation magnetization per cc.

Since UH_3 has been reported as having a cubic structure, Eq. (3) may be used for estimating the order of magnitude of the anisotropy constant K . The values obtained are plotted in Fig. 7 (Curve II). As mentioned previously, the term b/H^2 has been interpreted as due to the effect of magnetocrystalline anisotropy. In polycrystalline material with grains (cubic) oriented at random, the constant b^{15} may be calculated by averaging over all possible orientations. The result is

$$b = 0.0762K^2/I_s. \quad (4)$$

Using the values of b calculated by fitting Eq. (2) to the magnetization, and Eq. (4), we can estimate the value of K for comparison with that obtained from Eq. (3). The results are shown in Fig. 7 (Curve I). The two sets

of values agree in order of magnitude. From about 130°K down to liquid helium temperature, the general form of the two curves is similar but the absolute values of Curve I are about two times larger than that of Curve II. In the neighborhood of the Curie point, the deviations are still larger.

It should be noted that the accuracy of Curve I is worse than that of Curve II. This is also evident from the scatter of points around Curve I, especially in the neighborhood of Curie point.

We have tried to use the more general formula

$$\sigma = \sigma_0 + aH - C/H - b/H^2 \quad (5)$$

to fit the curve, but the data are not accurate enough to permit the use of four parameters so the constant obtained was very irregular. From the work of Polley¹⁶ for nickel, the constant C is almost constant for a large range of temperature. We fixed a suitable value of 9×10^3 for C and then solved the general equation for the other three parameters. The results are that the values of σ_∞, r change slightly, and the $K-T$ Curve I' (see Fig. 7) obtained from constants b in Eq. (5) is closer to Curve II.

From the general agreement of the values of K from Eqs. (3) and (4), we may conclude that the high coercive force is accounted for by the high magneto-crystalline anisotropy.

Figure 3 indicates that the spontaneous magnetization calculated by applying the general formula (5) to high magnetic fields is in good agreement with that obtained from the linear extrapolation of the $H-T$ curve for constant magnetization at high fields.

The experimental result showing in Fig. 4 that the UH_3 curve lies very close to the curves of iron, nickel, and cobalt indicates that the modified quantum Curie-Weiss theory can be applied successfully not only to the pure ferromagnetic elements but also to the ferromagnetic compounds. However, the agreement between the theory and the present experiment is as unsatisfactory in detail for uranium hydride as for the other ferromagnetic elements. The curve of $1/\chi$ against T above the Curie point is not completely linear as predicted by the theory. The reduced spontaneous magnetization curve shows deviations from the theoretical one, and the number of electron spins per molecule obtained from the saturation magnetization and from the temperature dependence of paramagnetism are not in agreement.

ACKNOWLEDGMENTS

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¹⁵ N. S. Akulov, Z. Physik **69**, 822 (1931); R. Raus, Ann. Physik **15**, 28 (1932).

¹⁶ H. Polley, Ann. Physik **36**, 625 (1939).