MAGNETIC PROPERTIES OF THE β-MODIFICATION OF URANIUM HYDRIDE AND DEUTERIDE

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Submitted to JETP editor August 10, 1961

J. Exptl. Theoret. Phys. (U.S.S.R.) 42, 375-382 (February, 1962)

The magnetization and paramagnetic susceptibility and also the magnetocaloric effect in the β-modifications of UH_3 and UD_3 are investigated. The molar magnetizations of these compounds at liquid helium temperatures differ only slightly; it is about 6% higher in UH_3 than in UD_3, which contradicts the results of Henry.[4] The Curie points were determined from the temperature dependence of the spontaneous magnetization (181° K for UH_3 and 177.5° K for UD_3) and from the maximum of the magnetocaloric effect (182.0° K for UH_3 and 178.4°K for UD_3). The magnetocaloric effect at the Curie temperature in UH_3 is 1.4 ± 0.15 times greater than the corresponding value in the deuteride. For both compounds the magnetic susceptibility obeys an expression of the type given in (2), the values of the constants being given in (3). It is shown that there is no contradiction between the calorimetric measurements[5,6] and the results of the magnetic investigations carried out in the present work.

INTRODUCTION

THE discovery of ferromagnetism in the compounds UH_3 and UD_3[1] has led to considerable interest in the study of their thermal and magnetic properties. The hydride and deuteride of uranium are the first ferromagnets in which an element of the actinide group - uranium - is the carrier of the magnetic moment. The physico-chemical properties of these compounds have been studied in considerable detail.[2] UH_3 and UD_3 have a cubic lattice with eight uranium atoms in the unit cell and the lattice constant a is 6.632 Å for UH_3 and 6.625 Å for UD_3. These compounds are the first to provide the possibility of observing a change in magnetic properties of a substance connected with a change in isotopic constitution. In addition, the inconsiderable difference in the lattice parameters must, in general, lead to an appreciable difference in the magnitudes of the exchange integrals, which will show up directly in a shift of Curie point in uranium deuteride compared with that of the hydride. One of the authors[3] showed the existence of an isotopic shift in the Curie point. Henry[4] observed a large (up to 30%) difference in the magnetization of UH_3 and UD_3 at helium temperatures, which varied slightly with magnetic field.

We must point out that the data of different authors on the magnetic and thermal properties of uranium hydride and deuteride do not agree among themselves. For example, a study of the heat capacities of UH_3 and UD_3[5,6] led to the conclusion that the magnetization of uranium hydride and deuteride were the same at low temperatures, in contradiction to Henry's data.[4] Authors who have studied the paramagnetic susceptibility of uranium hydride[1,7,8] derived considerably different magnitudes for the constants of the Curie-Weiss law, although the susceptibilities are close to one another in absolute magnitude and in their temperature dependence.

The chief problem of the present work is the further study of the magnetic properties of UH_3 and UD_3 and also an elucidation of the reasons for the considerable difference between the values of the magnetocaloric effect in uranium hydride and deuteride.[3]

THE SPECIMENS

The uranium hydride and deuteride were prepared at a temperature of 250 — 255° C by the direct reaction of metallic uranium of 99.80% purity with hydrogen or deuterium, obtained by the decomposition of UH_3 or UD_3 previously prepared.[2] Control of the composition of the specimens was achieved by the weights of the original reagents and of the compound. It was found that after the metal had reacted to the extent of about 90% the reaction rate slows down appreciably and a considerable time of hydrogenation (of the order of 30 — 40 hr) is required to obtain specimens of the stoichiometric composition. The measurements were made on specimens which had reacted with

hydrogen (or deuterium) up to not less than 98%, and no correction was made for the unreacted uranium. Under the hydrogenation conditions described only the β -modification of UH_3 is always formed.[9]

Specimens of UH_3 or UD_3 were contained in a spherical glass ampoule of diameter ~ 15 mm (weight of specimen in the ampoule $3 - 4$ g) for investigations of the magnetization in the ferromagnetic temperature region. Cylindrical glass ampoules 2.5 mm in diameter and 85 mm high (weight about 2 g) were used for measurement of the paramagnetic susceptibility.

After filling with uranium hydride (or deuteride) powder, the ampoules were pumped out, filled with spectroscopically pure helium at a pressure of $200 - 300$ mm Hg, and sealed. The whole manipulation with the specimens was carried out under a special sealed cover in an atmosphere of pure argon.

EXPERIMENTAL METHOD

The magnetic field was produced by a water-cooled electromagnet with which fields up to 29 kOe could be obtained in a 30 mm gap with 40 mm diameter pole pieces.

The measurements of the magnetization were made with the usual inductance method. The temperature of the specimen was measured by a chromel-kopel thermocouple, the hot junction of which was in contact with the wall of the ampoule containing the specimen. The cold junction of the thermocouple was maintained at the temperature of melting ice. The measuring coils were immersed in either liquid helium or liquid nitrogen, for making measurements at 4.2° K and 77.8°K, inside an ordinary glass helium cryostat in close proximity to the specimen. A ballistic galvanometer was used to measure the magnetization. Calibration of the system was carried out with carbonyl nickel and electrolytic iron. The agreement of the results of the measurements on nickel and iron with tabulated data was within $\sim 0.3\%$. The overall error in the measurements was about 1%.

The Gouy method was used for studying the paramagnetic susceptibility of UH_3 and UD_3. A micro-analytic balance, placed under the vacuum cover, was used for this purpose. An electromagnetic method was used for compensating the inclination of the balance from the equilibrium position. The accuracy of measurement was $\sim 2\%$.

Since UH_3 and UD_3 are always obtained in the form of a fine (and moreover, pyrophoric) powder, a suitable arrangement for investigating the mag-

netocaloric effect in such specimens was developed. This consisted of the following elements: an electromagnet to obtain sufficiently strong magnetic fields, a metal vacuum system with diffusion and forevacuum pumps and a constant current compensation system for measuring the temperature of the specimen.

The main part of the vacuum system, in which the specimen and measuring chrome-kopel thermocouple are placed, is shown in Fig. 1. An ionization gauge was connected on one side to the aluminum case with four flanges through rubber vacuum seals. On the other side a long (1.5 m) aluminum tube of 70 mm diameter connected with a diffusion pump trap. A thin-walled (0.2 mm) stainless steel tube of internal diameter 19 mm was joined to the bottom of the case. A glass or thin-walled (0.1 mm) German-silver tube carrying the speci-
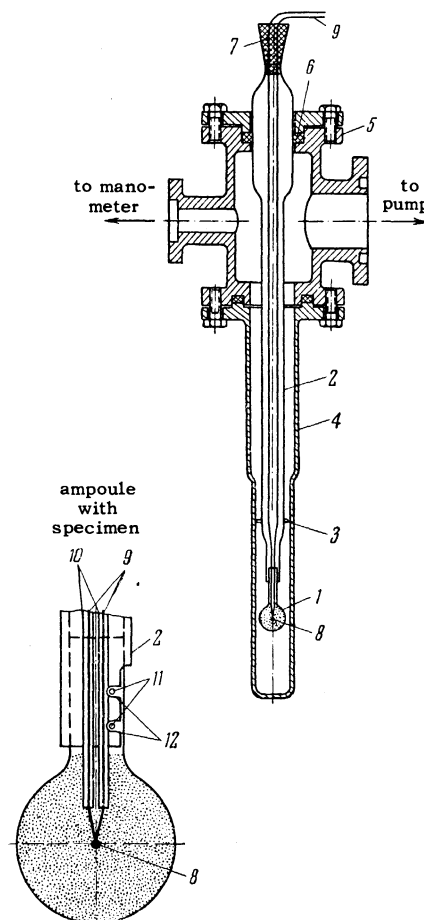

FIG. 1. The arrangement for fixing the specimen and measuring thermocouple into the apparatus for studying the magnetocaloric effect in powders: 1 — ampoule with specimen, 2 — specimen holder, 3 — centring projections on the holder, 4 — tube, 5 — head with flanges, 6 — rubber packing, 7 — picene, 8 — thermocouple junction, 9 — thermocouple leads, 10 — quartz capillaries, 11 — projections on the ampoule, 12 — transverse grooves on the holder.

men was led in through the upper opening through a rubber vacuum packing. The adiabatic experimental conditions for observing the magnetocaloric effect were achieved by maintaining a low pressure in the vacuum system $(2-5) \times 10^{-6}$ mm Hg and by the negligible heat conductivity of the holder.

No correction was made for the heat capacity of the ampoule or for the heat flow along the holder tube. Heat contact between the powder specimen and the working junction of the thermocouple turned out to be completely reliable for accurate measurement of the magnetocaloric effect.

It was shown in special control experiments with nickel (Curie point 365° C) and MnSb (Curie point 315°) that the measurement of the magnetocaloric effect in powders of these materials agreed within an accuracy of $10-15\%$ with values obtained on bulk specimens.

It was shown in the same experiments that thermal equilibrium between the thermocouple and specimen at 180° K was achieved in 30 sec for the case of uranium hydride or deuteride and in $4-5$ sec for nickel at 640° K. The method described for measuring the magnetocaloric effect in powders was very convenient for studying this effect in other materials, and one specimen could be changed for another in $20-30$ min. The magnetocaloric effect was measured on various materials (MnBi, MnSb, CrTe, FeC_3 etc.) in the same apparatus in the temperature range from 77 to 900° K (the specimen ampoules were made of quartz for the high temperatures).

For measurements of the magnetocaloric effect and magnetic susceptibility, the vapor from liquid nitrogen was used for cooling the specimens down to 150°K. This passed through a coil surrounding the tube with the cooled specimen. In this case the specimen temperature was regulated and stabilized by changing the power in the evaporator which determined the rate of evaporation of nitrogen from the supply dewar. One 15 liter dewar was enough for maintaining the temperature of a specimen continuously around 170° K for $3.5-4$ hours. The specimen temperature could be stabilized so that the temperature drift was 0.005° in the course of $4-6$ min.

RESULTS AND DISCUSSION OF THE MEASUREMENTS

The results of the measurements of the magnetization of UH_3 and UD_3 at liquid helium and liquid nitrogen temperatures are shown in Fig. 2.
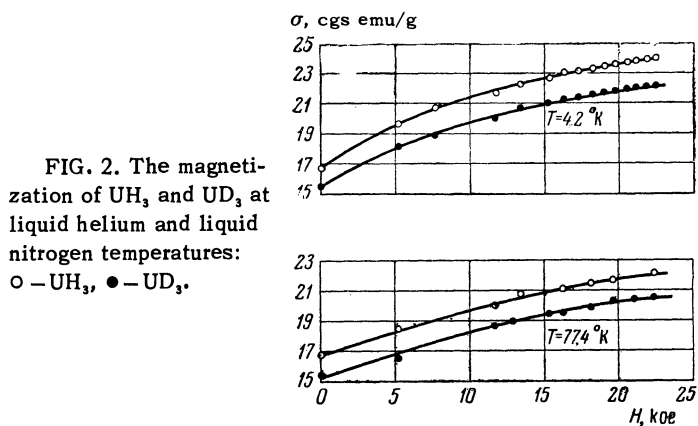

FIG. 2. The magnetization of UH_3 and UD_3 at liquid helium and liquid nitrogen temperatures: $\circ - UH_3$, $\bullet - UD_3$.

Cooling the helium bath from 4.2 to 1.8°K did not lead to any change in the magnitude of the magnetization of UH_3 or its dependence on the external magnetic field. Henry[4] also showed that no noticeable change takes place in the magnetization over the range of helium temperatures.

It can be seen from Fig. 2 that the molar magnetization of UH_3 exceeds the corresponding value for UD_3 in the same external fields by 6% at 4.2 and 77.4° K. According to our data this difference in the magnetization of UH_3 and UD_3 is completely independent of external magnetic field. One of the specimens of UD_3 had a magnetization slightly greater than the mean value shown in Fig. 2. In this case the ratio of molar magnetization of UH_3 and UD_3 was 1.04. The absence of any dependence of the ratio of molar magnetizations of uranium hydride and deuteride on magnetic field and also the small (only about 6%) difference in magnitude of these magnetizations is in sharp contradiction with Henry's data.[4]

The value of the magnetization of UH_3 in a field of 20 kOe at 4.2°K, obtained in the present work, differs insignificantly from the value of σ (UH_3) found in Henry's work[4] and also by Lin and Kaufman,[8] while the magnetization σ (UD_3) (see Fig. 2) is 20% greater than found by Henry.[4] In so far as the evaluation of the magnetic components of the specific heat of UH_3 and UD_3[6] indicate indirectly that the magnetizations of uranium hydride and deuteride should be the same at low temperatures or at any rate should differ only slightly, we are inclined to consider that Henry's conclusions about the large difference between the magnetizations of uranium hydride and deuteride are incorrect; that is that the values of σ (UD_3) given by him are considerably smaller than the true values.

The magnetization of uranium hydride and deuteride was also studied in the temperature

range from 80 to 210° K in fields from 18 to 29 kOe. The spontaneous magnetization of UH_3 and UD_3 near the Curie point (see Fig. 3) was determined by extrapolation of the lines of constant magnetization to zero field (the T-H curves method) and from the magnetocaloric effect. The temperature dependence of the square of the spontaneous magnetization σ_S, determined by the T-H curves method leads to the Curie temperatures Θ_f (UH_3) = 181.0° K and Θ_f (UD_3) = 177.5° K, which are in good agreement with data from the magnetocaloric effect.[3]

It follows from Fig. 3 that the ratio σ_S (UH_3)/σ_S (UD_3) at the same relative temperatures in the region of the phase transition is 1.17, which is considerably greater than the ratio σ (UH_3)/σ (UD_3) at temperatures below 80° K.

It can be deduced, from a comparison of these two facts, that the temperature dependence of the spontaneous magnetization of the two compounds is somewhat different.
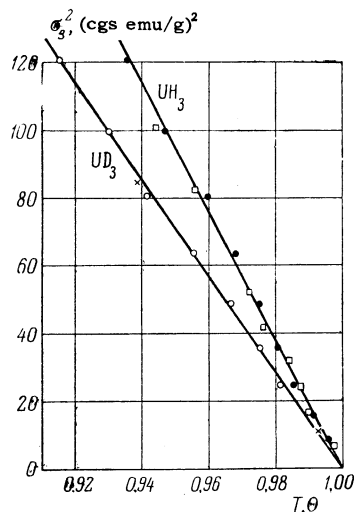
FIG. 3. The temperature dependence of the square of the spontaneous magnetization of UH_3 and UD_3 near the Curie temperature: $\bullet, o$ — from the T − H curves, $\square, \times$ — from the magnetocaloric effect.

The results of measurements of the magnetization of UH_3 and UD_3 in a field of 20 kOe are shown in Fig. 4; for comparison, the values of σ (at H = 20 kOe) for UH_3 from Lin and Kaufman's work[8] are shown. It can easily be seen that the slopes of the tangents to the σ (T) curves at the Curie points are different. This slope of the tangents, i.e. $(\partial\sigma/\partial T)_H$ is in fact completely determined by the temperature dependence of the spontaneous magnetization, shown in Fig. 3. The values of $(\partial\sigma/\partial T)_H$ at H = 18 − 29 kOe at the Curie point is 0.47 CGS emu/g-deg for UH_3 and 0.38 cgs emu/g-deg for UD_3.

Using the expression for the magnetocaloric effect

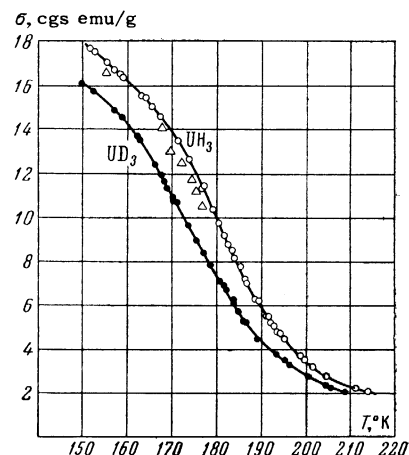$$\Delta T = -\frac{T}{C_H}\left(\frac{\partial \sigma}{\partial T}\right)_H \Delta H, \tag{1}$$

FIG. 4. The temperature dependence of the magnetization of UH_3 and UD_3 in a magnetic field of 20 kOe. Lin and Kaufman's data[8] for UH_3 (triangles) are shown for comparison.

we can evaluate the magnitude of the magnetocaloric effect at the Curie point from the total specific heats measured by Abraham et al[6] and the values of $(\partial\sigma/\partial T)_H$ given above. Such a calculation will naturally be approximate since the heat capacity of a substance in a magnetic field must, in general, be somewhat different from that in the absence of a field. The heat capacity of uranium deuteride is greater than that of the hydride, due to the different contribution from the hydrogen and deuterium.[6]

It thus follows from our measurements of $(\partial\sigma/\partial T)_H$ and the calorimetric data that the value of the magnetocaloric effect at the maximum for uranium hydride must be 1.35 times greater than the corresponding value for the deuteride.

The results of the measurements of the magnetocaloric effect carried out earlier and given in part in [3] are shown in Fig. 5. The additional investigations of the magnetocaloric effect, carried out on a large number of specimens, were made to determine accurately the positions of the Curie points and the relative magnitude of the magnetocaloric effect in these compounds.

These studies showed that the relative difference in the maxima of the magnetocaloric effect amounts to 1.4 ± 0.15. The values obtained for the magnetocaloric effect are somewhat lower than expected from (1). We explain this by the influence of the heat capacity of the glass ampoule, thermocouple, and insulating capillaries, which was not taken into account. The error due to this could reach 20%. The Curie temperatures, determined from the mean position of the maxima of the magnetocaloric effect for many specimens, are the following:

$$\Theta_f (UH_3) = 182.0° K, \qquad \Theta_f (UD_3) = 178.4° K.$$
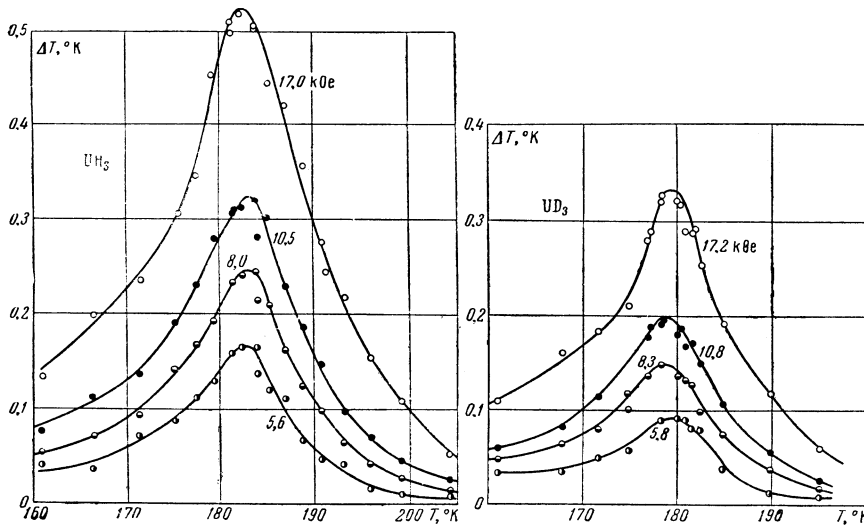
The difference in Curie temperatures of UH_3 and

FIG. 5. The magnetocaloric effect in UH₃ and UD₃.

UD$_3$ were determined with an accuracy of 0.5° K, while the error in determining the absolute value of the Curie temperature is ~1.0°K. An error in determining the absolute value of the magneto-caloric effect does not influence the determination of the spontaneous magnetization and only leads to a corresponding lowering of the value of the constant molecular field. In general, the determination of the spontaneous magnetization from the magneto-caloric effect in powders can lead to errors in determining σ_s because of the different demagnetizing factors for the different powders. However, near the Curie point, as can easily be shown, this error does not usually exceed 0.1 — 0.2% of the value of the spontaneous magnetization.

The paramagnetic susceptibility of uranium hydride and deuteride was measured at temperatures from 200° to 500°K in fields up to 12 kOe. The temperature dependence of the reciprocal of the susceptibility of UH$_3$ is shown in Fig. 6. The $1/\chi$ (T) curve for UD$_3$ has a similar appearance.

The considerable departure of the experimental data from the Curie-Weiss law is noticeable. We therefore tried to express the dependence of the susceptibility of both compounds over the whole temperature range by a relation of the form

FIG. 6. The temperature dependence of the inverse of the paramagnetic susceptibility of UH₃; χ_{mol} = 0.624/(T − 176.1) + 40 × 10⁻⁵.

$$\chi_{mol}= C_{mol}/ (T - \Theta_p) + \chi_0, \qquad (2)$$

where χ_0 is the temperature independent part of the susceptibility. Treatment of the experimental data by the method of least squares yields the following constants in (2):

$$C\,(\mathrm{UH_3}){=}C\,(\mathrm{UD_3}) = 0.624;$$
$$\chi_0\,(\mathrm{UH_3}) = \,+\,40\cdot10^{-5};\chi_0\,(\mathrm{UD_3}) = \,+\,43\cdot10^{-5};$$
$$\Theta_p\,(\mathrm{UH_3}) = 176.1°\,\mathrm{K};\quad \Theta_p\,(\mathrm{UD_3}) = 175.2°\,\mathrm{K}. \qquad (3)$$

Comparison of the data on the paramagnetic susceptibility[1] with (2) leads to the same values of the constants. As is well known, the temperature dependence of the inverse susceptibility of a number of ferromagnets, such as pure nickel, is described by (2). However, the values of χ_0 usually found[10] are considerably less than those found in UH$_3$ and UD$_3$. Leaving open the question of the source of the large value of χ_0 in UH$_3$ and UD$_3$, we only note that a whole range of elements of the actinide group have an anomalous temperature dependence of the paramagnetic susceptibility; for example, the susceptibility of metallic uranium is independent of temperature in the range 200 — 400° K and has a value of the order of +40 × 10⁻⁵ (per g-atom).

CONCLUSIONS

1. The investigation of the magnetization and magnetocaloric effect in β-UH$_3$ and β-UD$_3$ showed the existence of an isotopic shift in the Curie point, equal to $\Delta\Theta_f = \Theta_f\,(\mathrm{UH_3}) - \Theta_f\,(\mathrm{UD_3}) = +3.5 \pm 0.5°\mathrm{K}$.

2. The magnetization of uranium hydride, per gram-molecule of the substance, exceeds the corresponding value for the deuteride by a small amount (6%) at low temperatures.

3. The considerable difference in the magnitudes of the magneto-caloric effect for UH$_3$ and UD$_3$ at the Curie point is mainly produced by two causes:
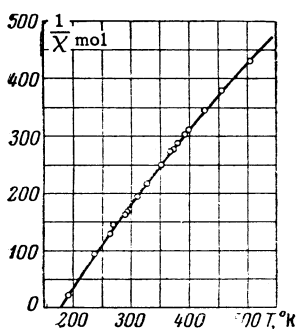
first, the magnitude of the temperature derivative of the magnetization $(\partial\sigma/\partial T)_H$ in UH_3 is larger than in UD_3, which is connected with the temperature variation of the spontaneous magnetization of these compounds and, secondly, the heat capacity of UD_3 exceeds the heat capacity of UH_3 due to the different contribution from deuterium and hydrogen to the heat capacity.

4. The disagreement of the ratio $\sigma(UH_3)/\sigma(UD_3)$ = 1.08, measured at low temperatures, with the value $\sigma_s(UH_3)/\sigma_s(UD_3)$ = 1.17 in the region of the Curie point, indicates directly that the temperature dependence of the spontaneous magnetization is different in the two compounds.

5. The small difference of the magnetic moments of UH_3 and UD_3 in the ferromagnetic temperature region, is completely absent in the paramagnetic $[C_{mol}(UH_3) = C_{mol}(UD_3)]$. The paramagnetic Curie points Θ_p of uranium hydride and deuteride are practically the same.

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