Metamagnetism of the actinide hydride $Th_2Co_7H_5$

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The magnetic properties and thermal expansion of single crystals of Th_2Co_7 and its hydride $Th_2Co_7H_5$ have been investigated. It was found that the paramagnetism of the original compound Th_2Co_7 was replaced by antiferromagnetic ordering with a Néel temperature of 90 K after hydrogen absorption. This is probably due to a reduction in the valence of Th and to a change in the density of states at the Fermi level. A metamagnetic phase transition occurs when a magnetic field is applied along the *c* axis of the hydride $Th_2Co_7H_5$. The *H–T* magnetic phase diagram of the hydride is constructed, and the spontaneous magnetostriction and Debye temperature are determined.

INTRODUCTION

The hydrides of intermetallic compounds of rare-earth or actinide metals and 3*d* transition metals have attracted considerable attention in recent years because hydrogen absorption leads to a radical alteration of the physical properties of the original compound.[1,2] Absorption of hydrogen is accompanied by an increase in the interatomic separation and may lead to an alteration of the crystal structure, right up to the formation of the amorphous state.[3,4] The essential feature of this situation is that hydrogen absorption frequently leads not only to a change in the magnetic moment of the original compound, but also to a change in the type of magnetic order.

Many intermetallic compounds of thorium and 3*d* transition metals absorb considerable amounts of hydrogen at relatively low pressures at room temperature, forming stable hydrides.[5] From the standpoint of magnetic properties, the compound Th_2Co_7 occupies an intermediate position along the series of intermetallic compounds of thorium and cobalt: compounds with the greater concentration of cobalt ($ThCo_5$ and Th_2Co_{17}) are ferromagnetic, whereas those with lower concentrations of cobalt (ThCo and Th_7Co_3), including Th_2Co_7, are paramagnetic. This is explained by the different filling of the 3*d* band by electrons of the tetravalent thorium.[6] It is therefore interesting to examine how absorbed hydrogen, which has a considerable effect on the band structure of the original compound, affects the magnetic properties of the actinide Th_2Co_7.

Until recently, all measurements of the physical properties of the hydrides of intermetallides of rare-earth and actinide metals with 3*d* transition metals have been performed on powdered specimens because the absorption of hydrogren results in the disintegration of the ingot of the original compound. In this paper, we report the first study of the crystal structure and magnetic properties of the single-crystal actinide Th_2Co_7 and its $Th_2Co_7H_5$.

METHOD OF MEASUREMENT AND SPECIMENS

The original compound Th_2Co_7 was produced in an electric-arc furnace, using a permanent tungsten electrode in a helium atmosphere. The single crystals were produced by recrystallization annealing: the Th_2Co_7 ingots were first fused in the arc and then annealed at 1000 °C for 170 hours. Single-crystal specimens in the form of 2-mm diameter disks were then cut from large ingot grains. X-ray data indicated that the subgrain disorientation angle in these specimens did not exceed 3°. X-ray and metallographic analysis showed that the concentration of subsidiary phases was not more than 3%. Hydrogen absorption was produced at room temperature by the methods described in a previous paper.[7]

Magnetization was measured by the inductive method at temperatures in the range 4.2–300 K, using pulsed magnetic fields up to 160 kOe, and by the vibration magnetometer method in static fields up to 24 kOe in the same temperature range. The magnetization was determined to within 5% in pulsed fields and 3% in static fields.

The thermal expansion of single-crystal Th_2Co_7 and $Th_2Co_7H_5$ was investigated in the temperature range 5–300 K, using Fe K_α radiation and an x-ray diffractometer. The crystal-lattice parameters *a* and *c* were determined from the (400) and (00.24) reflections of Th_2Co_7 and the (400) and (00.28) reflections of $Th_2Co_7H_5$. The uncertainty in the measured lattice parameters was 10^{-4}.

EXPERIMENTAL RESULTS

The isothermal graph of pressure against absorbed-hydrogen concentration in the actinide Th_2Co_7 showed that the resulting hydride $Th_2Co_7H_5$ was in the single-phase state with maximum hydrogen concentration at room temperature.[5] X-ray diffraction by the crystal lattice showed that its Ce_2Ni_7-type hexagonal structure remained after hydrogen absorption. The 17.7% increase in the volume *V* of the unit cell was entirely due to the increase in the parameter *c*, whereas the parameter *a* was almost unaffected (see Table I). This type of isotropic lattice expansion during hydrogen absorption was previously observed in a compound with a tetravalent rare-earth component (Ce_2Co_7) for which the parameter *c* was found to increase[8] by 21% at practically constant *a* in the case of the hydride ($Ce_2Co_7H_6$). We note that x-ray diffraction data indicated that the original compound was reinstated when the hydride $Th_2Co_7H_5$ was held in a vacuum at 200 °C for one hour.

Figure 1 shows the temperature dependence of the molecular magnetic moment of single-crystal Th_2Co_7 and

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TABLE I. Basic characteristics of single-crystal Th_2Co_7 and Th_2Co_7H5

Compound	a, Å 300 К	c, Å 300 К	V, Å^3 300 К	T_N, К	μ_m, μ_B 4,2 К	α_a, 10^{-5} К$^{-1}$ 300 К	α_c, 10^{-5} К$^{-1}$ 300 К	T_D, К	λ_a, 10^{-4} 4,2 К	λ_c, 10^{-4} 4,2 К	λ_V, 10^{-4} 4,2 К
Th_2Co_7	4,9290	24,658	518,80	–	–	2,6	0,3	320	–	–	–
$Th_2Co_7H_5$	4,9306	29,013	610,85	90	1,4	1,0	1,0	600	–7	–7	–20

$Th_2Co_7H_5$ in different crystallographic directions in static magnetic fields. For the original compound Th_2Co_7, the functions $\mu_m(T)$ are identical along the c axis and in the basal plane. The corresponding susceptibility was small throughout the temperature range under investigation (Fig. 1, curve 1). Magnetization curves obtained for this compound in fields up to 160 kOe take the form of straight lines passing through the origin (Fig. 2, curve 1). It follows from these data that Th_2Co_7 is a paramagnetic compound, as noted previously in Ref. 6.

Absorption of hydrogen by the original compound Th_2Co_7 leads to a substantial change in its magnetic properties. The function $\mu_m(T)$ for the hydride $Th_2Co_7H_5$ along its c axis is shown in Fig. 1 for different magnetic fields (curves 3–7). Curve 7′ was obtained after the specimen was cooled down in a magnetic field $H = 20$ kOe, and differs from the other curves obtained after cooling in zero field. Figure 2 shows magnetization isothermals for these single crystals in pulsed magnetic fields at 4.2 and 40 K. When the hydride was magnetized along the c axis at temperatures below 90 K, it was found that the magnetization rose abruptly in a certain critical-field range $H_1 - H_2$, and this was accompanied by magnetic hysteresis which disappeared for temperatures $T \geqslant 40$ K. Figure 3 shows the temperature dependence of the critical fields H_1 and H_2. The molecular magnetic moment of $Th_2Co_7H_5$ induced by the magnetic field is $\mu_m = 1.4\mu_B$ at 4.2 K. Extrapolation of the magnetization curve in the basal plane at $T = 4.2$ K to the molecular magnetic moment induced along the c axis gives $H^{bp} \simeq 220$ kOe. The small increase in magnetization on the $\mu_m(H)$ curve for the hydride at 4.2 K in a magnetic field of 14 kOe is probably due to the liberation of a small amount of the magnetic phase with a high Co concentration, which occurs as a result of the rapid hydrogen-absorption reaction.[9] However, x-ray analysis did not reveal the presence of this phase.

Figure 4 shows the temperature dependence of the lattice parameters a and c, and of the unit-cell volume V, referred to the corresponding values at 300 K, for the original compound Th_2Co_7 (curve 1) and the hydride $Th_2Co_7H_5$ (curve 2). It is clear that the considerable anisotropy in thermal expansion that was observed in Th_2Co_7, for which the thermal expansion coefficient α_a in the basal plane was greater by an order of magnitude than the expansion coefficient α_c along the c axis, was practically totally absent in the hydride (see Table I). The volume thermal expansion coefficient was appreciably lower in the case of the hydride.

For solids that do not undergo phase transition as the temperature is varied, the thermal expansion can be described in accordance with the Grüneisen law by the formula

$$V(T)=V(0)+ATF(T_D/T), \tag{1}$$

where A is a constant, T_D is the Debye temperature, and

$$F(T_D/T)=\frac{1}{T}\int_0^T C_V\,dT$$

is a function tabulated in Ref. 10 for different values of T_D/T. For Th_2Co_7, the function $V(T)$ is described by (1) throughout the temperature range with $T_D = 320$ K. We note that the value of T_D deduced from the measured longitudinal and transverse sound-propagation velocities in the single-crystal Th_2Co_7, is in good agreement with the value deduced from the function $V(T)$. For the hydride Th_2,Co_7H_5, the function $V(T)$ is also described by (1), but with $T_D = 600$ K and only for $T > 90$ K. The Debye temperature for $Th_2Co_7H_5$ could not be determined by acoustic methods because of the considerable attenuation of sound waves in this compound. Below 90 K, the measured function $V(T)$ departs from the Debye curve, and this is explained by the relatively high negative isotropic spontaneous magnetostriction resulting from magnetic ordering (see Table I).

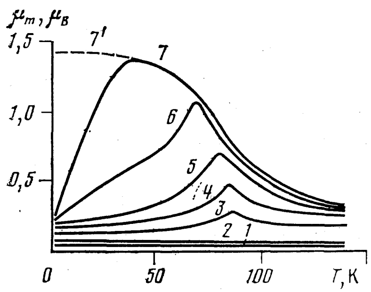

FIG. 1. Temperature dependence of the molecular magnetic moment of single-crystal Th_2Co_7 for $H \parallel c$, $H = 6$ kOe (curve 1) and single crystal $Th_2Co_7H_5$ for $H \perp c$, $H = 6$ kOe (curve 2); $H \parallel c$, 2 kOe (curve 3); $H \parallel c$, 6 kOe (curve 4); $H \parallel c$, 10 kOe (curve 5); $H \parallel c$, 14 kOe (curve 6); $H \parallel c$, 20 kOe (curve 7).

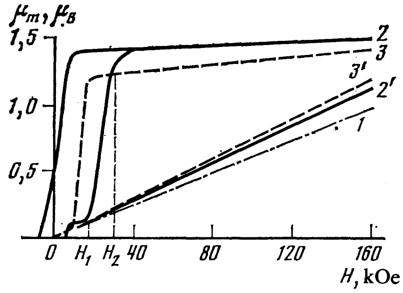

FIG. 2. Magnetization curves for different crystallographic directions in single-crystal Th_2Co_7 at $T = 4.2$ K, $H \parallel c$ (curve 1) and single-crystal $Th_2Co_7H_5$ for $T = 4.2$ K (curve 2, $H \parallel c$ and curve 2′, $H \perp c$) and at $T = 40$ K (curve 3, $H \parallel c$ and 3′, $H \perp c$).

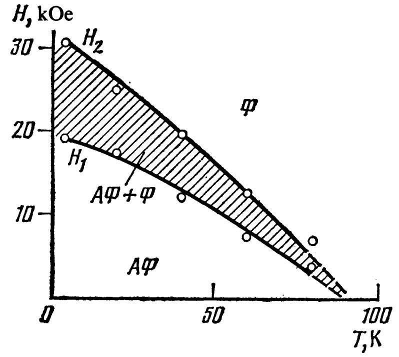

FIG. 3. H-T magnetic phase diagram for the compound $Th_2Co_7H_5$ along the c axis.

DISCUSSION

Neutron diffraction and magnetic studies have shown that hydrogen absorption by compounds of the form R-Co (R is a rare-earth or actinide element) leads to a reduction in the magnetic moment of cobalt and a weakening of intrasublattice exchange interactions in the case of tetravalent R (Ref. 2 and 7). Recent studies of single-crystal Y_2Co_7 and its hydride $Y_2Co_7H_6$ (Ref. 7), whose structure (Gd_2Co_7-type lattice) differs from that of Th_2Co_7 only by the packing of the R_4Co_{14} structure blocks along the c axis,[11] have shown that hydrogen absorption leads to the replacement of ferromagnetic by antiferromagnetic ordering. The uniaxial ferromagnet Y_2Co_7 ($T_C = 639$ K, $\mu_m = 9.6\mu_B$) becomes the antiferromagnet $Y_2Co_7H_6$ after hydrogen absorption ($T_N = 470$ K, $\mu_M = 6.5\mu_B$), in which the application of the magnetic field along the c axis leads to a first-order ferromagnetic phase transition. It is important to note that, like thorium, yttrium is nonmagnetic but, in contrast to the tetravalent thorium, it is trivalent.

The effects of hydrogen on the magnetic properties of a tetravalent nonmagnetic component R have been investigated[12] for Ce_2Co_7. It was found that hydrogen absorption led to a rise in the Curie temperature from 50 K for Ce_2Co_7 to 233 K for the hydride Ce_2Co_7H, and to a rise in the molecular magnetic moment from $0.9\mu_B$ to $3.8\mu_B$ at 4.2 K. The values of μ_m must be regarded as very approximate because the measurements were performed on powder specimens.

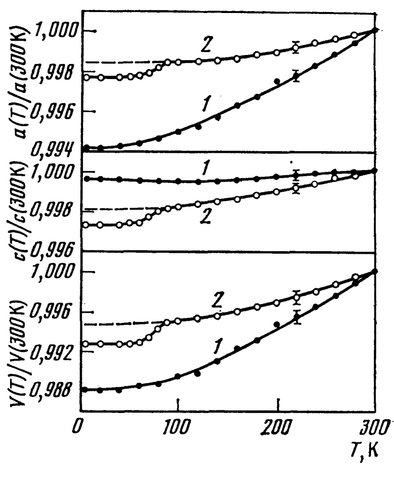

FIG. 4. Temperature dependence of the lattice parameters a and c and the unit cell volume V of the original compound Th_2Co_7 (curve 1) and the hydride $Th_2Co_7H_5$ (curve 2) referred to the values of a, c, and V at 300 K.

Our magnetic studies of single-crystal Th_2Co_7 and $Th_2Co_7H_5$ have shown that the absorption of hydrogen leads to the replacement of paramagnetism with antiferromagnetism. Application of a magnetic field along the c axis of the hydride in the critical range H_1–H_2 gives rise to first-order metamagnetic phase transition from the antiferromagnetic to the ferromagnetic phase. The criterion for metamagnetism is the inequality $H_a > H_{\rm ex}$ where $H_{\rm ex}$ is the effective field of the intrasublattice exchange interaction and H_a is the effective magnetic anisotropy field.[13] The critical field H_1 for the metamagnetic transition is approximately equal to $H_{\rm ex}$, i.e., $H_{\rm ex} \simeq H_1 \simeq 20$ kOe for the hydride at 4.2 K. On the other hand, magnetization of the metamagnet at right angles to the antiferromagnetic axis results in saturation in the field $H_a + H_{\rm ex}$ where for this particular hydride $H_a = H^{\rm bp} - H_{\rm ex} \simeq 200$ kOe. Thus, $H_a \gg H_{\rm ex}$ for $Th_2Co_7H_5$, i.e., the metamagnetic criterion is satisfied for this compound.

Since thorium is nonmagnetic, the values of μ_m and T_N for $Th_2Co_7H_5$ are determined by the magnetic moment of cobalt and the Co–Co exchange interaction. The original compound Th_2Co_7 has given nonequivalent positions of cobalt atoms. Not all the atoms acquire a magnetic moment after hydrogen absorption, but the magnitude of μ_m can be used to determine only the mean magnetic moment per cobalt atom, and the result turns out to be $0.2\mu_B$.

The magnetic behavior of R_2Co_7 with nonmagnetic R is satisfactorily described by the band d-magnetism model: the appearance of the magnetic moment of the d subsystem depends on the extent to which the relatively narrow d band is filled. In the band model, the necessary condition for the appearance of ferromagnetism is the Stoner criterion $IN(\varepsilon_F) \geqslant 1$, where I is the exchange interaction integral and $N(\varepsilon_F)$ is the density of states at the Fermi level. In compounds with tetravalent R, i.e., Th_2Co_7 and Ce_7Co_7, the d band is probably almost completely filled, so that Th_2Co_7 is a paramagnet and Ce_2Co_7 a ferromagnet with low magnetization and Curie temperature. In Y_2Co_7, in which the yttrium has one fewer valence electron, the $3d$ band is not completely filled and the density of states at the Fermi level is high, so that this compound has high Curie temperature and magnetization.

Hydrogen absorption is accompanied by an increase in the interatomic separation and a change in the density of conduction electrons, which leads, in all cases, to a reduction in the magnetic ordering temperature and in the magnetic moment of cobalt in R-Co systems with tetravalent R. Hydrogen absorption by compounds with tetravalent R is probably accompanied by a reduction in the valence of Ce and Th from four to three, or to intermediate valence, which leads to an increase in the density of states at the Fermi level. The Stoner criterion can therefore be satisfied for the actinide hydride $Th_2Co_7H_5$, and magnetic ordering takes place. A similar change in valence probably occurs during hydrogen absorption by other (Ce, Th) $3d$ compounds: the Curie temperature and the magnetization are found to increase in Ce_2Co_7 (Ref. 12) and $CeFe_2$ (Ref. 14), and paramagnetism is replaced with ferromagnetic ordering in $CeCo_3$ (Ref. 12) and Th_6Mn_{23} (Ref. 15).

The experimentally confirmed increase in the Debye temperature during hydrogen absorption by a factor of about two may be due to an increase in the density of atoms in the unit cell and the fact that the vibrational energies of the hydrogen atoms are large in comparison with the vibrational energies of the metal atoms.[16] However, we cannot exclude the possibility that a reduction in temperature is accompanied by a gradual ordering of hydrogen over the different types of interstice. If this process does actually occur, formula (1) is not valid for the hydride $Th_2Co_7H_5$, and the value of T_D determined from this expression is not correct.

CONCLUSION

We have obtained for the first time single crystals of the actinide compound Th_2Co_7 and its hydride $Th_2Co_7H_5$. We have found that hydrogen absorption leads to the replacement of paramagnetism in the original compound with antiferromagnetic ordering in the hydride ($T_N = 90$ K). The application of a magnetic field along the *c* axis of the hydride $Th_2Co_7H_5$ is accompanied by a first-order metamagnetic phase transition and magnetic hysteresis. We have found that thermal expansion becomes isotropic relative to the crystallographic axes after hydrogen absorption. Magnetic ordering in the hydride is accompanied by considerable negative isotropic spontaneous magnetostriction of exchange origin.

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