Crystal structure and magnetic properties of UGaCo and UGaNi single crystals

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New uranium magnetic materials, UGaCo and UGaNi, have been discovered. The temperature and field dependences of the magnetization and the temperature dependences of the lattice parameters of the single crystals have been measured. It is shown that both compounds are highly anisotropic uniaxial ferromagnets. The magnetic properties are explained under the assumption that the 4*f* electrons are partially localized on the uranium ions and that the 3*d* metals are nonmagnetic.

1. INTRODUCTION

At the present time a great deal of attention is being given to investigations of actinide magnetic materials, in particular to those of uranium. It is well known that the magnetic properties of uranium compounds depend very strongly on the degree of localization of the 5*f* electrons.[1,2] If the 5*f* electrons are localized on the ions, the properties of the uranium compounds are similar to those of the rare earth metals—a huge magnetic anistropy and magnetostriction, and large coercive forces are observed. If the 5*f* electrons are collectivized, then magnetic ordering does not occur and the compound, as a rule, is a Pauli paramagnet like pure uranium. The degree of localization of the 5*f* spin density is to a large extent determined by the minimum separation (d_0) between the uranium ions. For small separations the 5*f* electrons are collectivized via 5*f*-6*d* hybridization. For $d_0 \approx 3.4$–3.5Å the 5*f*–6*d* hybridization is weakened in compounds of uranium with nonmagnetic partners and some of the 5*f* electrons remain localized on the uranium ions, which leads to a Curie-Weiss law for the paramagnetic susceptibility and to magnetic ordering. For example, in UGa_2, where $d_0 = 4.0$Å, the magnetic moment of uranium is close to the calculated value for the free ion, and an enormous magnetic anisotropy and magnetostriction are observed.[3]

In compounds of uranium with 3*d* metals, there exists another possibility for the collectivation of the 5*f* electrons; this is the occupation of the 3*d* band by the 5*f* electrons. In this case, the magnetic moment of the 3*d* metal decreases, as in UFe_2 (Ref. 4), or it completely disappears as in $UCo_{5.3}$ (Ref. 5), while the uranium ions have no magnetic moment or the moment is very small.

It is a matter of some interest to study the magnetic properties of the equiatom compounds UGaT (T = Co, Ni), where the minimum spacing between the uranium ions ($d_0 = 3.5$–3.6Å) is close to the "critical" value, at which the transition from the collectivized to the localized states of the 5*f* electrons occurs.

In this investigation we have observed for the first time magnetic ordering in the compounds UGaCo and UGaNi; we have produced single crystals and have studied their magnetic properties and their crystal structures.

2. EXPERIMENTAL METHOD

The components were melted in a water-cooled copper tray, under a helium atmosphere inside an electric arc furnace having a nonconsumable tungsten electrode. To ensure uniform mixing of the components, the ingot was turned upside down and remelted at least three times. The phase composition of the alloys that were produced was checked by x-ray diffraction. No noticeable nonuniformities of the phase composition over an ingot were observed. To increase the grain size, the ingots were remelted in a resistance furnace in an Alundum crucible in a helium atmosphere. By using experimentally chosen temperature gradients within the furnace and cooling rates it was possible to obtain a grain size of several millimeters. After checking and orientation of the grains by means of x-ray diffraction, single crystals with faces normal to the principal crystallographic axes were cut from them. The x-ray phase analysis showed that the ingots remelted in the resistance furnace were single-phase compounds having the FE_2P structure. The lattice parameters were measured directly on the single crystals from the α_1-004 and α_1-330 lines obtained with Fe radiation in a URS-50 IM diffractometer in a cryostat cooled by flowing helium, over the temperature range 5–300 K.

The magnetization was measured with a vibrating sample magnetometer in an electromagnet with a maximum field of 22 kOe, and by the induction method in pulsed fields up to 300 kOe (4.2–300 K). The hysteresis properties of UGaNi were also measured in the range 9–300 K with a vibrating sample magnetometer in a superconducting solenoid having a field up to 37 kOe.

3. CRYSTAL STRUCTURE

The crystal structure of UGaCo and UGaNi have been described in Ref. 6. It is of the Fe_2P structural type, space group $P\bar{6}m2$, (Fig. 1), and our investigations bear out this result. The values for the lattice parameters reported in Ref. 6 and our data for 300 K are in good agreement. The T-atoms (Co or Ni) occupy the sites occupied by phosphorous in Fe_2P, and the U and Ga atoms are arranged in the sites that in Fe_2P correspond to the two inequivalent iron sublattices. The coordinates of the atoms in the unit cell are:

1	T_1	$0, 0, 0;$
2	T_2	$^1/_3, ^2/_3, ^1/_2;\ ^2/_3, ^1/_3, ^1/_2;$
3	Ga	$x, 0, ^1/_2;\ 0, x, ^1/_2;\ 1-x, 1-x, ^1/_2;$
3	U	$y, 0, 0;\ 0, y, 0,\ 1-y, 1-y, 0.$

Thus, there are three UGaT formula units in the unit cell.

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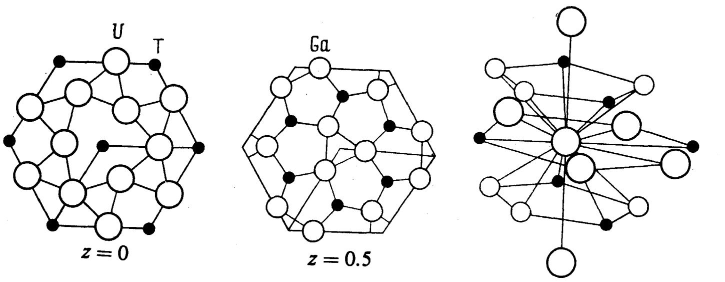

FIG. 1. Crystal structure of UGaT. Arrangement of atoms in the basal plane and in the immediate surroundings of the uranium atom.

All the uranium atoms occupy symmetry-equivalent sites, as do the gallium atoms, but the T-atoms occupy two inequivalent sites. The local symmetries of the atoms are: T_1, $\bar{6}m2$; T_2, $\bar{6}$; and U and Ga, mm. The structure parameters x and y can, with a high degree of accuracy, be determined from the possible arrangement of the atoms in the (100) plane in the spherical packing model, assuming atomic radii. According to our calculations, $x = 0.27 \pm 0.01$ and $y = 0.59 \pm 0.01$, and the minimum distance between the uranium ions is $d_0 = (1 - 3y + 3y^2)^{1/2} \cdot a = (3.52 \pm 0.04)\text{Å}$. Table I shows the calculated distances between the ions in the UGaNi crystal lattice along with the indicated number of nearest neighbors. The immediate neighborhood of the uranium atom, within a radius of ~ 4Å, is shown in Fig. 1. It can be seen that this region contains 18 atoms of different kinds and has low symmetry, which creates the necessary conditions for the existence of a strong crystal field with a preferred axis.

Measurements of the temperature dependences of the lattice parameters a and c and of the volume V of the unit cell for both compounds showed that the compounds exhibit anisotropic thermal expansion. The coefficient of linear thermal expansion in the basal plane, α_a, at 300 K is three times greater than that quantity in the direction of the axis, α_c (they are, respectively, $1.5 \cdot 10^{-5}$ deg^{-1} and $0.5 \cdot 10^{-5}$ deg^{-1}). No thermal expansion anomalies indicating phase transitions were observed. The dependence $V(T)$ has a normal Debye-type shape, with a Debye temperature ≈ 100 K.

4. MAGNETIC PROPERTIES OF UGaCo

Figure 2 shows the curves of magnetization and demagnetization along the [001] and [100] axes of the single crystal UGaCo at $T = 4.2$ K (the curves of magnetization along the [120] and other directions in the basal plane are the same as for the [100]). It can be seen that the easy axis of magnetization in UGaCo is the c axis, while in the basal plane the magnetization is practically zero, not only in a static field of 22 kOe (Fig. 2), but also in a pulsed field up to 300 kOe, and this result is indicative of the enormous magnitude of the magnetocrystalline anisotropy field in this compound.

The magnetic moment μ_0 per unit formula at 4.2 K is 0.56 μ_B. The temperature dependences of the magnetization, shown in Fig. 3, show that the large magnetocrystalline anisotropy is maintained over the entire region of the ferromagnetic state: In the [100] direction as the temperature $T_c = 51$ K is approached [the Curie temperature T_c and the specific spontaneous magnetization σ_s are obtained from the magnetization isotherms plotted in the coordinates $H/\sigma = f(\sigma^2)$] there is no marked increase in the magnetization in a field $H = 22$ kOe, a feature that is typical of ordinary highly anisotropic ferromagnets and is a consequence of a decrease in the anisotropy energy as the temperature is raised.

From Fig. 2 it can be seen that the single crystal UGaCo has a coercive force at 4.2 K of about 1 kOe and the hysteresis loop is nearly rectangular.1) The magnetic aftereffect commonly observed in highly anisotropic magnets at low temperatures (e.g.,[7] in Tb_3Co) is absent.

Since the magnetic moment practically does not deviate from the c axis even in a 300 kOe field normal to the c axis, the magnetostriction in this field does not exceed the error in the measurements ($< 10^{-5}$). The absence of any anomaly in $V(T)$ at T_c indicates that the spontaneous exchange volume magnetostriction in UGaCo is also small ($< 10^{-4}$).

5. MAGNETIC PROPERTIES OF UGaNi

Figure 4 shows the curves of the magnetization and demagnetization of the single crystal UGaNi at 4.2 K. It can be seen that, like UGaCo, UGaNi is a highly anisotropic magnetically uniaxial ferromagnet (the easy magnetization axis is the c axis). The value of μ_0 in UGaNi is twice as large (1.19

TABLE I. Interatomic distances and number of nearest neighbors in UGaNi.

Central Atom	Environment (Distances in Å and number of neighbors)			
	Ni_1	Ni_2	Ga	U
Ni_1	4.02—2	4.32—12	2.65—6	2.80—3 3.93—3
Ni_2	4.38—6	3.89—3 4.02—2	2.54—3	2.85—6
Ga	2.65—2	2.54—2	3.03—2 4.02—1 4.38—4	2.97—2 3.18—4
U	2.80—1 3.93—1	2.85—4	2.97—2 3.18—4	3.49—4 4.02—2

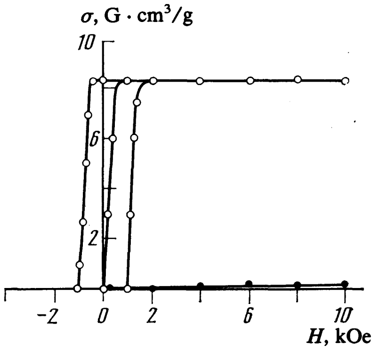

FIG. 2. Field dependence of specific magnetization σ of the single crystal UGaCo at 4.2 K. ○ denotes the magnetization curve and hysteresis loop in the [001] direction: ● denotes the magnetization curve in the [100] direction.

μ_B), and T_c (41 K, Fig. 5) is somewhat lower, than for UGaCo. In this case, too, the magnetic moment practically does not deviate from the c axis in fields up to 300 kOe. The spontaneous volume magnetostriction, as in UGaCo, is small ($< 10^{-4}$), as follows from the absence of an anomaly in $V(T)$ at T_c. Again, there is no marked linear magnetostriction upon application of a field of 300 kOe in the direction of hard magnetization.

Thus, the principal magnetic properties of UGaNi are close to those of UGaCo. However, the hysteresis properties of these compounds are radically different. First, the value of H_c at 4.2 K in UGaNi, as can be seen from Fig. 4, is considerably higher (~ 7 kOe). Second, in fields below H_c the magnetization of the thermally demagnetized single crystal practically does not increase, while in stronger fields there is a sharp increase. Third, in UGaNi there is a very strong magnetic aftereffect in fields close to H_c. Figure 6 shows an example of the relaxation process at $T = 9$ K. After magnetization by a field of 37 kOe, a reverse field of 3.5 kOe, close to H_c at this temperature, was applied, and beginning 30 seconds after the full amplitude of the field was established, the magnetization as a function of the time t was measured. As can be seen from Fig. 6, beginning from $t = 120$ sec $\sigma(t)$ is well described by the relation

$$\sigma(t) = \sigma(\infty) - [\sigma(\infty) - \sigma(0)] \exp(-t/\tau) \tag{1}$$

with a relaxation time $\tau = 360$ sec.

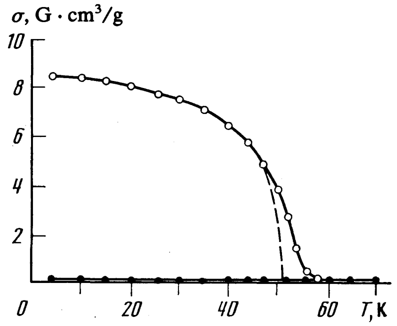

FIG. 3. Temperature dependence of specific magnetization of UGaCo. ○—in the [100] direction, $H = 10$ kOe; ●—in the [100] direction, $H = 22$ kOe; dashed line is the temperature dependence of the specific spontaneous magnetization σ_s.

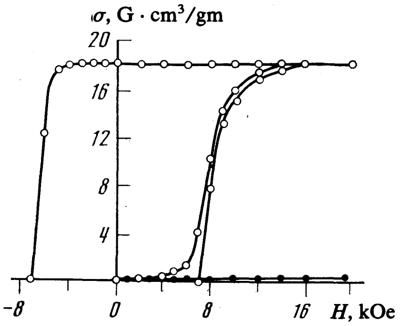

FIG. 4. Field dependence of specific magnetization of UGaNi. ○ denotes the magnetization curve and hysteresis loop in the [001] direction; ● denotes the magnetization curve in the [100] direction.

The temperature dependence of H_c, also shown in Fig. 6, is well described by the exponential function

$$H_c(T) = H_c(0) \exp(-kT/u) \tag{2}$$

with parameters $H_c(0) = 12$ kOe and activation energy $u = 11 \cdot 10^{-16}$ erg.

The principal magnetic and structural characteristics of UGaCo and UGaNi are given in Table II.

6. DISCUSSION OF RESULTS

As can be seen from the results presented here, both of the compounds that we have studied are highly anisotropic magnetically uniaxial ferromagnets having low values of μ_0 and T_c. Qualitatively, their magnetic properties are similar to those of UGa_2, in which the uranium has a localized component of spin density.[3] However, in UGaCo and UGaNi, the cobalt and nickel can supply an additional contribution to the magnetic moment. Therefore, in order to draw accurate conclusions concerning the nature of the magnetic moment, it is necessary to carry out neutron diffraction studies of the magnetic structure. However, from the fact that the exchange volume magnetostriction is close to zero, we can conclude that if there is a contribution from the collectivized $3d$-magnetism, it is very small. In the compounds of $4f$ and $5f$ metals with $3d$ metals, the presence of a nonzero magnetic moment on the $3d$ metal is accompanied by a large (to 10^{-2}) volume magnetostriction [e.g., R_2Fe_{17} (Ref. 8), UFe_2 (Ref. 4), $GdCo_2$ (Ref. 9), and RT_2 (Ref. 10)], whereas in compounds that do not contain a $3d$ metal [UGa_2 (Ref. 3)] or if $\mu_{3d} = 0$

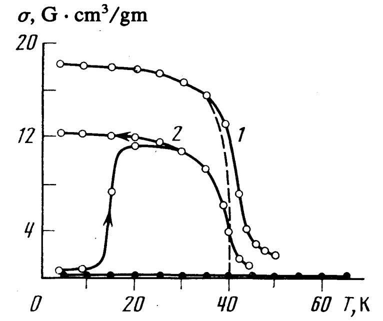

FIG. 5. Temperature dependence of specific magnetization of UGaNi at 4.2 K: ○ in the [001] direction, 1) $H = 10$ kOe, 2) $H = 1$ kOe; ● in the [100] direction, $H = 22$ kOe; the dashed line is σ_s.

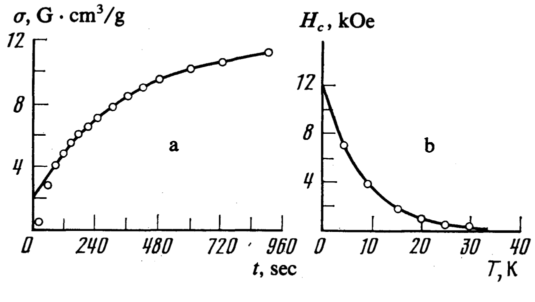

FIG. 6. Hysteresis properties of UGaNi: a) dependence of magnetization σ on time t ($T = 9$ K, $H = 3.5$ kOe, [001] axis). O denote the experimental values; solid line is the calculation from formula (1). b) temperature dependence of coercive force H_c in the [001] direction, O denote the experimental data, solid line is the calculation from formula (2).

[R_3Co (Ref. 11)], the bulk magnetostriction is small ($\lesssim 10^{-3}$). Evidently, the 7*s*, 6*d*, and some of the 5*f* electrons of the uranium in UGaT populate the 3*d* band, destroying the magnetic moment of the 3*d* metal. Since d_0 in these compounds is somewhat larger than the critical value (3.4–3.5Å), the 5*f*–6*d* hybridization does not lead to complete collectivization of the 5*f* electrons, and part of them remain localized on the uranium ions and give rise to the observed magnetic properties, in particular, the enormous energy of magnetocrystalline anisotropy.

The values of the magnetic moments, $0.6\mu_B$ in UGaCo and $1.2\mu_B$ in UGaNi are typical for uranium magnets having incomplete localization of the 5*f* electrons. It should be noted that μ_0 in UGaNi is about twice as large as in UGaCo. This may be because of the different degree of localization of the 5*f* spin density, and this difference may, in turn, be explained by two causes. First, Ni has one more electron per atom in the 3*d* band than Co has. Therefore, it takes fewer uranium 5*f* electrons to fill the band, and this means that a larger fraction of those electrons can be localized. Second, since the structure of UGaCo is somewhat more compact than that of UGaNi (see the values of the density ρ at 5K in Table II), and the U–U spacing in these compounds is close to critical, a small difference in the U-U spacing can have a large effect on the value of μ_0. It is evident that the value of μ_0 in these compounds must depend strongly on the pressure.

Because of the errors in the measurement of the magnetization in the hard direction, we can only estimate a lower bound of the magnetocrystalline anisotropy constant K_1 from the magnetization curves. We have assumed that in this direction $\sigma = 0$ at $H = 0$ and at $H = H_{\max}$ the value of σ is equal to the error in the measurements, and we have drawn a straight line through these points to the intersection with $\sigma = \sigma_s$. The minimum values of the anisotropy field H_A at 4.2 K estimated in this way are 1000 and 2000 KOe, and the anisotropy constants are $K_1 = \sigma_s \rho H_A / 2 = 5 \cdot 10^7$ and $22 \cdot 10^7$ erg/cm³ respectively for UGaCo and UGaNi; however, the actual values evidently are considerably larger. For more reliable estimates it is necessary to measure the magnetization in the hard direction in much larger magnetic fields ($H \gg 300$ kOe), in which the magnetic moment might deviate substantially from the easy axis of magnetization. It should be remembered, however, that in this case a difficulty arises in the calculation of the true anisotropy constants because of the deformation of the magnetic structure in the magnetic field, since the magnetic anisotropy field in UGaCo and UGaNi are of the same order of magnitude as the exchange field $H_{\rm ex} = kT_c/\mu_0$, equal, respectively, to 1400 and 500 kOe. Evidently, such a high magnetic anistropy energy in these compounds is due to the electrostatic interaction of the localized 5*f* spin density of the uranium ions with the crystal field of the lattice.

In highly anisotropic magnets, in which the magnetocrystalline anisotropy energy is comparable in magnitude with the energy of the exchange interaction, the domain walls can be very narrow and have a high intrinsic coercivity H_ω. The width δ of a domain wall, estimated from the relation $\delta \approx \pi (A/K)^{1/2}$ (where $A = kT_c/d_0$, k is the Boltzmann constant, and d_0 is the distance between the closest uranium atoms) is about 20 Å in UGaCo and 9 Å in UGaNi. In the case of UGaNi this is only 2–3 spacings between magnetically active ions. A narrow domain wall has an intrinsic coercivity $H_\omega = B \exp(-\pi\delta/l)$, where B is a quantity of the order of H_A and l is the wavelength of the Peierls potential, which we can set equal to the repeat distance of the structure in the direction perpendicular to the domain wall, i.e., the lattice parameter a.[12] For UGaNi the estimated value of H_ω is about 30 kOe, which, in order of magnitude, agrees with the extrapolated value of $H_c(0)$ (12 kOe, Fig. 6). The shape of the magnetization curve and the hysteresis loop, the exponential dependence $H_c(T)$, and the strong aftereffect, all of which are evidence for thermal fluctuational activation of the motion of the high-coercivity domain walls in UGaNi, correspond to the model of narrow domain walls. This same kind of hysteresis properties is seen, for instance, in Tb_3Co, for which the estimate $\delta \approx \pi (A/K)^{1/2}$ gives 9 Å, or 2–3 spacings between Tb ions, and $H_c = 24$ kOe.[7]

If in a similar manner we estimate H_ω in UGaCo, we get 80 Oe, which is an order of magnitude lower than the experimentally observed value (1 kOe). Thus, the narrow domain wall mechanism does not explain the hysteresis properties of

Table II. Principal structural and magnetic characteristics of UGaCo and UGaNi.

	UGaCo	UGaNi		UGaCo	UGaNi
a (5 K), Å	6.6657	6.7020	ρ (5 K), g/cm³	12.07	11.70
c (5 K), Å	3.9322	4.0115	ρ (300 K), g/cm³	11.96	11.60
a (300 K), Å	6.6910	6.7251	μ_0, μ_B	0.56	1.19
c (300 K), Å	3.9370	4.0162	T_C, K	51	41
c/a (5 K)	0.5899	0.5986	H_c (4.2 K), kOe	1.0	7.0
c/a (300 K)	0.5884	0.5972	min H_A (4.2 K), kOe	1000	2000

UGaCo. If we assume that in this compound the domain walls move readily during magnetization, while remagnetization occurs with relative difficulty, we can conclude that the hysteresis is due to the difficulty in the formation and growth of remagnetization nuclei.

7. CONCLUSION

In this investigation we have discovered two new highly anisotropic uranium-based magnets, having the Fe_2P-type hexagonal structure. We have made single crystals of these compounds and have studied their magnetic properties. Their magnetic moments are due mainly to the uranium ions, while the large magnetic anisotropy energy is associated with the localized state of the $5f$ electrons. The nature of the magnetic rigidity in the compounds UGaCo and UGaNi is different for the two cases. In the former of the compounds, the rigidity is due to the difficulty of formation and growth of the remagnetization nuclei, and in the latter it is a result of the high intrinsic coercivity of the narrow domain walls. To understand more deeply the origin of the magnetic properties of these compounds neutron diffraction studies of their magnetic structure are necessary.

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[1)] The remagnetization of a coarse-grained polycrystalline sample proceeds via large Barkhausen jumps corresponding to remagnetization of the individual grains.

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