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Magnetic properties and spin-reorientation phase transitions in intermetallic compounds $Nd_{1-x}U_xCo_5$

A. V. Deryagin, A. V. Andreev, and V. A. Reĭmer

Urals State University

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The crystal structure of powders and the magnetic moments and magnetocrystalline anisotropy of single crystals, as functions of the uranium concentration and the temperature, have been investigated for the compounds $Nd_{1-x}U_xCo_5$. For comparison, the results of similar investigations are presented for $Y_{1-x}U_xCo_5$. In the compounds studied, the uranium is apparently nonmagnetic and gives up all electrons from its $5f$, $6d$, and $7s$ electronic shells to the $3d$ band of the cobalt, thereby decreasing the value of its mean magnetic moment. By variation of the uranium concentration, it is possible to vary substantially the temperature range of spin-reorientation magnetic phase transitions.

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1. INTRODUCTION

In recent years, a large number of uranium compounds have been synthesized, and their crystal structure and magnetic properties have been studied.[1] Some general rules have been established for the appearance of magnetism in them, as it depends on the U-U distance in the crystal lattice. In particular, it has been shown that in compounds of uranium with nonmagnetic elements, in which the U-U distance is larger than ~3.5 Å, the uranium ions possess a magnetic moment that is due to the unfilled $5f$ electronic shell. In such compounds, high values of the magnetocrystalline anisotropy and of the magnetostriction may be observed in consequence of electrostatic interaction of the $5f$ shell with the crystalline field of the ligands,[2,3] as in the rare-earth metals and their alloys. At smaller U-U distances, the $5f$ electrons, together with the $6d$ and $7s$ electrons, apparently become collectivized, and the uranium ion (U^{6+}) is nonmagnetic. But so far there have been very few investigations devoted to clarification of the behavior of uranium in intermetallic compounds with rare-earth (R) and $3d$ transitional (T) metals, and of its effect on the values of the magnetic moment and magnetocrystalline anisotropy of these compounds. It is therefore of interest to study the magnetic properties of quasibinary compounds of the type $R_{1-x}U_xCo_5$. As is well known,[4] high-anisotropy alloys of the type RCo_5 are now widely used as magnetically hard materials. And those in which a spin-reorientation magnetic phase transition occurs on change of temperature[1)] ($NdCo_5$, $PrCo_5$, $TbCo_5$, etc.) many find application as thermally sensitive elements (for example, in thermomagnetic generators [6] or thermometers [7]), or as media for thermomagnetic registration of information on magnetic domains.[8]

The present paper reports the results of an investigation of the crystal structure, magnetic moment, magnetocrystalline anisotropy, and spin-reorientation phase transitions in monocrystals of the quasibinary compounds $Nd_{1-x}U_xCo_5$. For comparison, magnetic properties are presented for monocrystals of $Y_{1-x}U_xCo_5$.

2. EXPERIMENTAL METHOD

The $R_{1-x}U_xCo_5$ ($0 \leqslant x < 1$) alloys were melted in an induction furnace in alundum crucibles, in a helium atmosphere. The phase composition of the alloys was monitored by metallographic, x-ray, and thermomagnetic methods. An x-ray determination of the lattice parameters of powder specimens of the alloys was made on a diffractometer URS-50IM, in K_α Fe radiation. For measurement of the magnetic properties, the following were used: a vibration magnetometer with static field up to 100 kOe ($77\text{ K} \leqslant T \leqslant 1000\text{ K}$), a pulse solenoid with field up to 100 kOe ($4.2 \leqslant T \leqslant 300\text{ K}$), and a torque magnetometer with field up to 28 kOe ($77\text{ K} \leqslant T \leqslant 300\text{K}$).

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3. CRYSTAL STRUCTURE

As is well known, the compounds RCo_5 possess a homogeneity region within which the crystal lattice parameters and the magnetic properties vary.[4] Therefore for measurement of the concentration dependences of the lattice parameters and of the magnetic characteristics, alloys were used that contained a small amount (2 – 3%) of the neighboring phase R_2Co_7. Such an amount of a secondary phase is barely noticeable in x-rays, and the diffraction patterns of alloys with $0 \leq x \leq 0.6$ corresponded to single-phase compounds with structure of the $CaCu_5$ type. The concentration dependence of the lattice parameters a and c and of the ratio c/a at room temperature are shown in Fig. 1. The ratio c/a increases with increase of x and reaches 0.84 at $x = 0.6$, whereas all intermetallic compounds known to us with the $CaCu_5$ structure have c/a within the range 0.73–0.83. The value $c/a = 0.84$ is apparently critical for existence of the $CaCu_5$ structure. For $x > 0.6$, the quasibinary alloys investigated are two-phase; that is, a solubility limit is observed for uranium in RCo_5. A similar phenomenon, it is known,[9] is traced also in compounds RCo_5, where with increase of the atomic number of the elements the ratio c/a increases and the temperature range of stability of the $CaCu_5$-type structure decreases: $TmCo_5$ ($c/a = 0.826$) is obtained only in the form of traces of a second phase for extremely rapid cooling of the alloy, while Yb and Lu do not form such compounds at all.

The x-ray density of the single-phase alloys also varies linearly with the uranium concentration and agrees well with the value of the density measured by hydrostatic weighing of the specimens (Fig. 1).

4. MAGNETIC MOMENT AND CURIE TEMPERATURE

For measurement of the magnetic characteristics, from the single-phase alloys of compositions $x \leq 0.6$ monocrystalline specimens, in the form of spheres of diameter about 2 mm, were obtained by rounding off coarse grains of the ingots on an abrasive disk. The specimens were tested for monocrystallinity and oriented with their crystallographic axes in the required direction with respect to the magnetic field by x-ray methods. The misorientation of subgrains in them did not exceed 5°. Measurements of the magnetization curves were made along axis [100], [120], and [001] over the temperature range 4.2–1000 K. From these data were determined the spontaneous magnetization σ_s, the magnetocrystalline anisotropy constants K_1 and K_2, and the Curie temperature T_c.

Figure 2 shows the concentration dependence of the magnetic ordering temperature and of the molecular magnetic moment $\mu_m(4.2\ K)$ for the compounds $Nd_{1-x}U_xCo_5$ and $Y_{1-x}U_xCo_5$. As is evident, both quantities decrease linearly with increase of the uranium concentration. The ferromagnetic type of $\mu_m(T)$ relation for the monocrystals of these compositions indicates absence of antiferromagnetic ordering between the magnetization of the Co sublattice and the magnetic moments of the other components in the alloys. Therefore the decrease of $\mu_m(x)$ with increase of uranium concentration is due to a decrease of the magnetization of the Co sublattice and to a small or zero moment of the uranium ions, as in $UCo_{5.3}$.[10] This is possible if we suppose that the uranium ions in the compounds studied are hexavalent and give up all six electrons from the $5f$, $6d$, and $7s$ electronic shells to the $3d$ electronic band of the Co. In this case, if we suppose that there are two vacancies in the $3d^-$ band of cobalt and 0.3 in the $3d^+$ band [11] and that the Y and Nd ions give up three and four electrons, respectively, to the $3d$ band, then for

$$\mu_{Co} = {}^1/_5[\mu_m - (1-x) g J_R \mu_B],$$

where g is the Landé factor and J_R is the total moment of the rare-earth ion, we get the value $1.7\mu_B$ in YCo_5 and $1.5\mu_B$ in $NdCo_5$; these are close to the experimental values, 1.64 and 1.39 respectively.

With replacement of Y^{3+} and Nd^{4+} ions by U^{6+}, there occurs an increase of the number of additional electrons (z) in the $3d$ band per Co ion. This must cause a decrease of μ_{Co} linearly with increase of z, since for $z = 2.3$ electrons per Co atom the value of μ_{Co} is zero. The expected relation $\mu_{Co}(z) = (2.3 - z)\mu_B$ is shown dotted in Fig. 3. The qualitative agreement of the experimental $\mu_{Co}(z)$ relation with the calculated shows that in all probability the

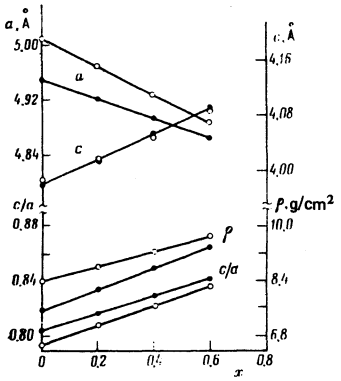

FIG. 1. Concentration dependence of the lattice parameters, the density, and the ratio c/a in the systems of compounds: ○—$Nd_{1-x}U_xCo_5$; ●—$Y_{1-x}U_xCo_5$ ($T = 300$ K).

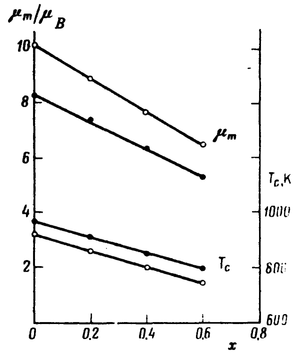

FIG. 2. Concentration dependence of the Curie temperature and of the molecular magnetic moment of the compounds: ○—$Nd_{1-x}U_xCo_5$; ●—$Y_{1-x}U_xCo_5$ ($T = 4.2$ K).

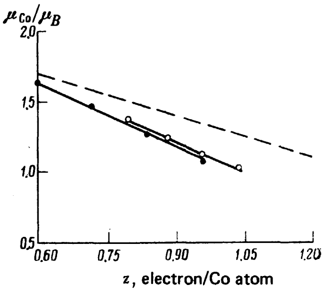

FIG. 3. Variation of μ_{Co} with number of additional electrons in the 3d band per cobalt atom. Points, experimental results (T=4.2 K); dotted line, $\mu_{Co}=(2.3-z)\mu_B$. ○—$Nd_{1-x}U_xCo_5$; ●—$Y_{1-x}U_xCo_5$.

decrease of μ_{Co} is actually due to filling of the $3d$ band by uranium electrons. A more accurate treatment of the results must take into account the details of the band structure of the compounds RCo_5, its change on introduction of U^{6+}, and polarization of the conduction electrons by the magnetically active ions.

5. MAGNETOCRYSTALLINE ANISOTROPY AND SPIN-REORIENTATION PHASE TRANSITIONS

Figure 4 shows the temperature dependence of the magnetocrystalline anisotropy constants (K_1 and K_2) for the compounds of various chemical compositions investigated, as determined from magnetization curves in the hard and easy directions by the method of Sucksmith and Thompson.[12] The alloys $Y_{1-x}U_xCo_5$ are magnetically uniaxial over the whole temperature range. The constant K_2 is very small for alloys of all compositions. Since neither Y nor U carries a magnetic moment, it may be supposed that the magnetic anisotropy of these compounds is caused entirely by anisotropy of the Co sublattice.

The compounds $Nd_{1-x}U_xCo_5$ are magnetically uniaxial in the high-temperature range, since here their anisotropy is determined mostly by the anisotropy of the Co sublattice, as in $Y_{1-x}U_xCo_5$. But in the low-temperature range, the anisotropy of neodymium-rich compounds is caused chiefly by anisotropy of the neodymium ions resulting from electrostatic interaction of their $4f$ electronic shell with the crystalline field of the ligands. At T=4.2 K, in compounds with $0\leqslant x\leqslant 0.6$, there are six axes of easy magnetization of the type [100], lying in the basal plane of the crystal. The value of the anisotropy constant K_4, which describes anisotropy of the magnetization in this plane, is ~5 · 10⁶ erg/cm³ for $NdCo_5$ at T=4.2 K; this is substantially higher than the result of Frederick *et al.*[13] (~1 · 10⁶ erg/cm³). The data for K_1 and K_2 at x=0 agree, within the limits of experimental error, with the results of other workers [14–16] and at the same time are lower by about a factor of two than the data of Ref. 13.

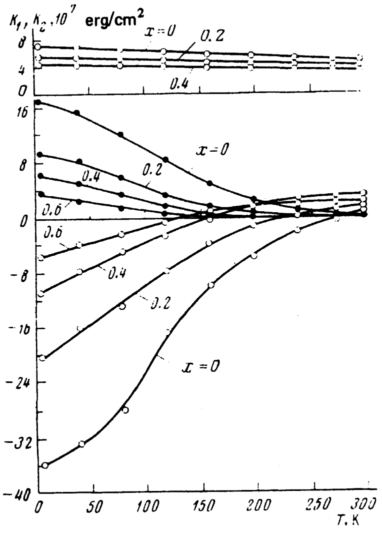

FIG. 4. Temperature dependence of the anisotropy constants of monocrystals of compounds $Nd_{1-x}U_xCo_5$ (below) and $Y_{1-x}U_xCo_5$ (above) of various compositions: ○—K_1; ●—K_2.

With rise of temperature, in consequence of a change in the relation between K_1 and K_2, quasibinary compounds containing neodymium undergo a reorientation of the axis of easy magnetization (AEM): specifically, a departure of the AEM from the basal plane and an approach to the c axis. The variation of the angle φ_0 between the AEM and the c axis, determined from magnetic measurements with a torque magnetometer, on rise of temperature is shown in Fig. 5 for compounds $Nd_{1-x}U_xCo_5$ of various chemical compositions. These data for $\varphi_0(T)$ agree satisfactorily with those calculated from the measurement of $K_1(T)$ and $K_2(T)$:

$$\varphi_0(T)=\arcsin[-K_1(T)/2K_2(T)]^{1/2}. \quad (1)$$

Thus by introduction of uranium into the compound $NdCo_5$, it is possible to shift the temperature range of the spin-reorientation magnetic phase transition (plane–cone–axis). At uranium concentration x=0.6, the anisotropy of the R sublattice has been so weakened that anisotropy of the "easy plane" type is not guaranteed even at T=4.2 K, and over the whole temperature range of the magnetically ordered state of this compound there is only the single phase transition cone-axis.

On the assumption that the anisotropy of the cobalt sublattices in the compounds $Nd_{1-x}U_xCo_5$ and $Y_{1-x}U_xCo_5$

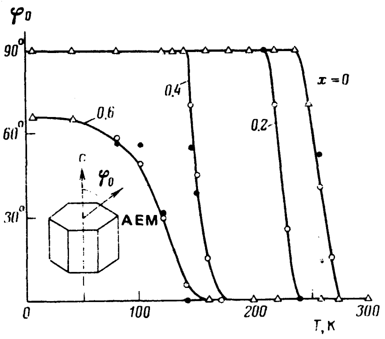

FIG. 5. Temperature dependence of the angle of orientation of the axis of easy magnetization (φ_0) for the compounds $Nd_{1-x}U_xCo_5$; ○—points obtained from measurements with a torque magnetometer; ●—points obtained with formula (1); Δ—the points obtained by both methods coincide.

at the same x differs insignificantly, it is possible, by subtracting from the anisotropy constants of $Nd_{1-x}U_xCo_5$ (K_{1Nd} and K_{2Nd}) the corresponding anisotropy constants of $Y_{1-x}U_xCo_5$ (K_{1Y} and K_{2Y}) at the same x, to determine the value of the anisotropy coefficient k_2^0 per Nd ion:

$$k_2^0 = -[{}^2/_3(K_{1Nd}-K_{1Y}) + {}^{16}/_{21}(K_{2Nd}-K_{2Y})]V/(1-x).$$

Here V is the volume of the elementary cell; in the $CaCu_5$ structure, it is occupied by one formula unit. The temperature variations of the anisotropy coefficient for various uranium concentrations are shown in Fig. 6. Also shown there is the theoretical relation

$$\frac{k_2^0(T)}{k_2^0(0)} = L_2^{(J)}\left[\frac{\xi_0\sigma_{Co}(T)}{T}\right], \tag{2}$$

which describes the temperature behavior of $k_2^0(T)$ of the neodymium ion for $x=0$ according to the single-ion anisotropy model.[17] In this expression, $\sigma_{Co}(T)$ is the relative magnetization of the cobalt sublattice, ξ_0 has the meaning of energy of exchange interaction of the neodymium ion with the cobalt environment at $T=0$ K, and $L_2^{(J)}(x)$ differs from a normalized hyperbolic Bessel function $I_{5/2}(x)$[18] by allowance for quantization of the total moment. The experimental relation for $x=0$ agrees well with the theoretical curve with $\xi_0=480$ K. This value coincides with ξ_0 for Nd_2Co_{17}.[19] For the other compositions, the drop of $k_2^0(T)$ occurs faster, and the value of ξ_0 is somewhat lower. No analysis of the temperature and concentration dependence of $k_2^0(T, x)$ was made, both because of the difficulty of taking into account the effect of deformation of the magnetic structure under the influence of the magnetic field and because of the large error in the determination of K_2.

Figure 7 shows the concentration dependence of the anisotropy constants of the compounds $Nd_{1-x}U_xCo_5$ at 4.2 K. Shown also for comparison are the analogous relations for the compounds $Nd_{1-x}Y_xCo_5$, taken from Ref. 14. It is seen that the relation for $Nd_{1-x}U_xCo_5$ is nonlinear and different from that for $Nd_{1-x}Y_xCo_5$. It was found possible to interpret these relations satisfactorily within the framework of the single-ion anisotropy model with allowance for change of the lattice parameters, as was done [20] for Dy-Gd alloys. In the nearest-neighbor approximation in the R sublattice, with the effective charge of the cobalt ion equal to zero,[21] the following expression can be derived for the relative value of the anisotropy coefficient of an ion:

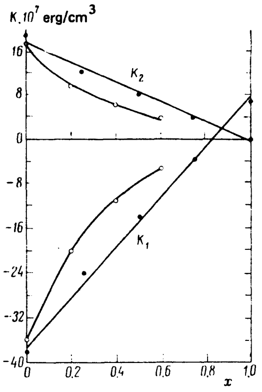

FIG. 7. Concentration dependence of the anisotropy constants K_1 and K_2 at $T=4.2$ K: ○—$Nd_{1-x}U_xCo_5$; ●—$Nd_{1-x}Y_xCo_5$.[14]

$$\frac{k_2^0(x)}{k_2^0(0)} = 1-3\left[\left(\frac{a_0}{c_0}\right)^3 - \frac{\Delta c(x)}{c_0} - \frac{3}{2}\frac{\Delta a(x)}{a_0}\right]\left[\left(\frac{a_0}{c_0}\right)^3 - \frac{3}{2}\right]^{-1}, \tag{3}$$

where $\Delta c(x)$ and $\Delta a(x)$ are the changes of the lattice parameters measured from the parameters a_0, c_0 at $x=0$. If we assume that the relative change of the lattice parameters with change of concentration is the same at 0 K as at room temperature, then the relation (3) for the compounds $Nd_{1-x}U_xCo_5$ and $Nd_{1-x}Y_xCo_5$ will have the form shown by the dotted lines in Fig. 8. As is seen, the agreement of the experimental results with the calculated is quite satisfactory.

Thus the temperature and concentration dependences of the anisotropy of the rare-earth element in $Nd_{1-x}U_xCo_5$ find their explanation within the framework of the single-ion anisotropy model.

6. CONCLUSION

The alloys $R_{1-x}U_xCo_5$ (R = Nd, Y) are single-phase solid solutions of uranium in the intermetallic compounds RCo_5, with a structure of the $CaCu_5$ type, up to concentration $x=0.6$.

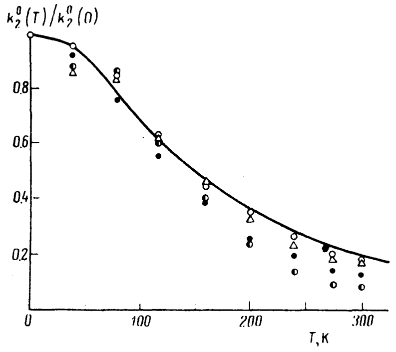

FIG. 6. Experimental temperature dependence of the relative anisotropy coefficient of the neodymium ion in a compound $Nd_{1-x}U_xCo_5$; ○—$x=0$; Δ—$x=0.2$; ◐—$x=0.4$; ●—$x=0.6$. The solid curve is the theoretical, with $\xi_0=480$ K, according to (2).

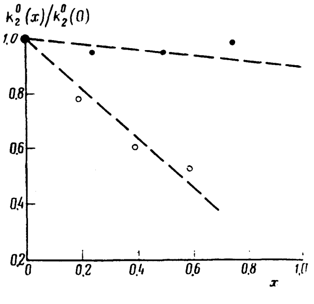

FIG. 8. Concentration dependence of the relative anisotropy coefficient of the neodymium ion: ○, in $Nd_{1-x}U_xCo_5$; ●—in $Nd_{1-x}Y_xCo_5$.[14] Points, experimental data ($T=4.2$ K); dotted line, relation according to (3), which takes into account the change of lattice parameters with concentration.

The uranium ions in these compounds carry no magnetic moment. The electrons of the external shells of uranium are collectivized and apparently fill the 3d band of cobalt; this leads to a decrease of the magnetic moment per cobalt ion. The decrease of the magnetic moment of the cobalt with introduction of uranium leads, in the compounds investigated, to a lowering of the Curie temperature, since in them the Co-Co exchange interaction is dominant and determines the value of the magnetic ordering temperature.

The magnetic anisotropy of the compounds $Nd_{1-x}U_xCo_5$ is single-ion ($x \leq 0.6$) and is caused by electrostatic interaction of the 4f electronic shell with the crystalline field of the ligands. The deviation of the concentration dependences of the anisotropy constants from linearity is due to change of the value of the crystalline field as a result of change of the lattice parameters of the compounds $Nd_{1-x}U_xCo_5$ with introduction of uranium. The temperature variation of the anisotropy coefficients can also be satisfactorily explained within the framework of this model.

By replacement of neodymium by uranium in the compounds $Nd_{1-x}U_xCo_5$, it is possible to change to a significant degree the temperature range of the spin-reorientation magnetic phase transitions, which is determined by the change with temperature of the relation between the values of the magnetic anisotropy constants of the R sublattice. This possibility may be useful in the development of magnetic materials for devices that use the effects of spin-reorientation phase transitions. The extension of the magnetically uniaxial state in the direction of low temperatures is also favorable for the purpose of using such compounds as magnetically hard materials at temperatures near room temperature.

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