Magnetic properties, and the crystal and domain structures of the uranium intermetallic compound $UCo_{5.3}$

A. V. Deryagin and A. V. Andreev

Urals State University
(Submitted March 24, 1976)
Zh. Eksp. Teor. Fiz. **71**, 1166–1171 (September 1976)

The parameters of the unit cell are determined and the magnetic properties of single crystals of the intermetallic compound $UCo_{5.3}$ are investigated. The temperature dependences of the spontaneous magnetization (σ_s) and magnetocrystalline anisotropy constants (K_1') are measured at temperatures between 4.2°K and the Curie point (~360°K). The $K_1'(T)$ dependence is compared with that predicted by one-ion anisotropy models. A domain structure is observed in single-crystal plates of the compound and the density of the domain-wall energy is determined. The new material is a magnetically uniaxial and highly anisotropic ferromagnet and can be useful as a medium for recording information in magnetic domains.

PACS numbers: 75.30.Cr, 75.30.Gw, 75.60.Fk, 75.50.Cc

1. INTRODUCTION

It has by now been experimentally established that certain compounds of uranium with elements of groups III–VI of the periodic table have high values of magnetocrystalline anisotropy, magnetostriction, and coercive force.[1–3] Their Curie temperatures, however, are low (as a rule, lower than room temperature), owing to the relatively weak and apparently indirect exchange interaction via the conduction electron, in analogy with the situation in certain lanthanides enriched with rare-earth metals.[4] On this basis we can expect the dominant exchange interaction in uranides, as in other actinides containing a high concentration of magnetoactive ions of the iron-group metals, to be the d–d interaction, which is usually stronger, and the Curie temperature to be higher. An investigation of the magnetic properties of such compounds can be not only of academic but also of practical interest.

In accordance with the phase diagram,[5] the U–Co system has six intermetallic compounds: U_6Co, UCo, UCo_2, UCo_3, UCo_4, and $U_2Co_{11}(UCo_{5.5})$. We report here the first study of the crystal structure, the magnetic properties, and the domain structure of the intermetallic compound $UCo_{5.5}$, which is the richest in cobalt.

2. SAMPLES AND EXPERIMENTAL PROCEDURE

Alloys with a chemical composition close to $UCo_{5.5}$ were melted in alundum crucibles in a helium atmosphere. To establish more accurately the chemical composition of the compound two alloys were melted with an excess of cobalt and with a shortage of cobalt relative to the chemical composition $UCo_{5.5}$. An x-ray microanalysis with a JXA-5 microanalyzer has shown that the first of these alloys contains 92% of $UCo_{5.4}$ in the form of a free phase and 6% in the eutectic ($UCo_{5.4}$ + Co). The second alloy consisted of 90% $UCo_{5.2}$ and 10% of the eutectic ($UCo_{5.2}$ + UCo_4). Thus, the composition of the fundamental phase oscillated in the range from $UCo_{5.4}$ to $UCo_{5.2}$, probably as a result of the presence of a region of homogeneity of this compound. However, the difference in the chemical composition of the fundamental phase is small and exceeds the measurement error only insignificantly. For the sake of argument we assume that its composition is close to $UCo_{5.3}$. The two ingots consisted of single-crystal plates 5–100 μ thick and with area of several square millimeters.

The magnetic characteristics in the temperature interval 4.2–400 °K were measured with the aid of a vibration magnetometer in a superconducting solenoid with a magnetic field intensity of approximately 40 kOe and in pulsed fields up to 100 kOe using samples constituting a stack of seven to ten of the above-described single-crystal plates, which were oriented (when the stack was glued together) in a magnetic field. Since the easy-magnetization axis (EMA), as will be shown below, was perpendicular to the plane of the plates, such a packet constituted a single crystal from the magnetic point of view. The standard for the determination of the absolute value of the specific saturation magnetization of the investigated samples was a sample of electrolytic nickel (99.99) of the same dimensions and shape. Its magnetization was assumed to be 54.4 G-cm^3/g.

The first magnetocrystalline anisotropy constant (K_1) in the expression for the anisotropy energy $E_a = K_1 \sin^2\theta + K_2 \sin^4\theta$ (θ is the angle between the EMA and the magnetization vector) was determined from the expression for the anisotropy field ($H_a = 2K_1/I_s$), which was assumed equal to the field corresponding to the intersection of the initial linear section of the magnetization curve in the difficult direction and the straight line $\sigma = \sigma_s$: $K_1 = H_a I_s/2$ [erg/cm^3] or $K_1' = H_a\sigma_s/2$ [erg/g], $I_s = \sigma_s\rho$ (ρ is the density).

3. CRYSTAL STRUCTURE

The Laue patterns obtained in reflection from the plane of the plates belong to the Laue $3m$-class and show that a threefold symmetry axis is perpendicular to the plane of the plates. No symmetry axes of higher order have been observed. The rotation x-ray patterns obtained in a RKV-86 chamber in Mo K_α radiation have made it possible to determine the parameter a in the plane of the plate. The parameter c was determined with a URS-50 IM diffractometer in Fe K_α radiation by means of the set of (000l) reflections from the plane of

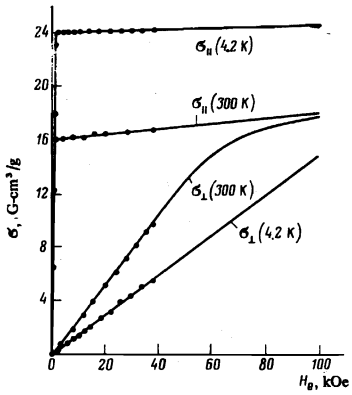

FIG. 1. Magnetization curves of the $UCo_{5.3}$ crystal along ($\sigma_\parallel$) and across ($\sigma_\perp$) the easy magnetization axis at temperatures 4.2 and 300 °K: points—static fields, solid lines—pulsed fields.

the plates. It turned out that $a = 4.76$ and $c = 36.49$ Å. Using these values, we indexed the rotation x-ray patterns about the axes $[10\bar{1}0]$ and $[21\bar{3}0]$. All the reflections can be assigned indices satisfying the law governing the extinction of the groups $R\bar{3}m$ and $R3m$. A more detailed determination of the crystal structure by the x-ray method is hindered by the sharply anisotropic shape of the crystal, which makes it difficult to determine quantitatively the intensities of the reflexes. The density measured by hydrostatic weighing the ingots was 11.1 g/cm³.

4. SPONTANEOUS MAGNETIZATION AND MAGNETIC ANISOTROPY

To determine the specific spontaneous magnetization (σ_s), the anisotropy field ($H_a = 2K_1'/\sigma_s$), the first magnetocrystalline anisotropy (K_1') and their temperature dependences, we measured the magnetization curves of single crystals of $UCo_{5.3}$ along and across the EMA in the temperature range from 4.2 °K to the Curie temperature (~ 360 °K). Figure 1 shows by way of example the data for 4.2 and 300 °K for static (up to 38 kOe) and pulsed (up to 100 kOe) fields. The value of $\sigma_s(T)$ was determined by extrapolating the strong-field section $\sigma_\parallel(H)$ to zero field. To determine the anisotropic field and from it the magnetic-anisotropy constants from the magnetization curves $\sigma_\parallel(H)$ and $\sigma_\perp(H)$ we subtracted from the values of $\sigma(H)$ the corresponding contribution made to the magnetization by the power process. As seen from Fig. 1, this contribution turned out to be large enough for the investigated compound.

Figure 2 shows the temperature dependence of the specific spontaneous magnetization σ_s. This dependence is of the typical, Weiss, type. The magnetic moment extrapolated to 0 °K was 2.4 μ_B for $UCo_{5.3}$ molecules, a value much lower than in rare-earth compounds with Co of the RCo_5 type. To explain this fact we propose that the uranium in the investigated compound is hexavalent and gives up these six electrons from the 7*s*, 6*d*, and the magnetoactive 5*f* electron shells to the electron 3*d* subband of cobalt, i.e., it is nonmagnetic. The spontaneous magnetization sets in as a result of the (Co–Co) exchange interaction. The experimental value of the magnetic moment at $T = 0$ °K per cobalt atom is 0.45 μ_B. On the other hand, if the uranium gives up in fact all six electrons to the 3*d* subband of cobalt without changing the structure of the 3*d* band, then there are an additional 1.15 electrons for each Co atom, and these lower the average magnetic moment of Co from 1.7 μ_B in the metallic cobalt to 0.55 μ_B in the compound $UCo_{5.3}$. This value of μ_{Co} is close to the experimentally observed value (0.45 μ_B). On the basis of these concepts one should expect μ_{Co} in the UCo_4 compound to equal 0.2 μ_B. In fact, according to our measurements down to 4.2 °K, this compound has no spontaneous magnetic moment ($\mu_{Co} = 0$). This shows that the situation is in fact more complicated and that at small values of the magnetic moment μ_{Co} the exchange Co–Co interaction becomes weaker and is no longer capable of splitting the electron 3*d* band of the cobalt. The situation is analogous in thorides $ThCo_5$ ($\mu_{Co} = 0.92$ μ_B) and Th_2Co_7 ($\mu_{Co} = 0$.[6,7] These questions, with REM compounds with iron-group metals as examples, are discussed in[4,7] and will not be touched upon here for lack of additional experimental data.

Figure 2 shows the temperature dependence of the field ($H_a = 2K_1'/\sigma_s$) and of the first constant (K_1') of the magnetocrystalline anisotropy. If the uranium ion is indeed nonmagnetic then it is obvious that the magnetic anisotropy is due only to the cobalt sublattice. We can then expect at $K_1' \gg K_2'$ the temperature dependence of K_1' to be described by the Akulov–Zener–Carr law:

$$\frac{K_1'(T)}{K_1'(0)} = \left(1 - \alpha \frac{T}{T_c}\right)\left[\frac{\sigma_s(T)}{\sigma_s(0)}\right]^{n(n+1)/2},$$

at $n = 2$ with account taken of the lattice thermal distortion characterized by the coefficient α, as was observed in experiment for pure cobalt.[8] Indeed, it is seen from Fig. 3 that the good agreement between the expected dependence and the experimental one in the entire range of temperatures of the magnetically-ordered state of the compound $UCo_{5.3}$. For comparison we present here the theoretical relations

$$K_1'(T)/K_1'(0) = \hat{I}_{5/2}[\mathcal{L}^{-1}(\sigma_s(T)/\sigma_s(0))]$$

in the quasi-classical approximation for a spin $S = \infty$[9] and with account taken of the quantization and the finite value of the spin ($S = 1$) within the framework of the molecular-field theory[10] ($\hat{I}_{5/2}$ is the normalized hyperbolic Bessel function; $\mathcal{L}^{-1}$ is the inverse of the Langevin function). It has turned out that they are also qualitatively close to the experimental relations. So satisfactory an agreement between theory and experiment seems somewhat surprising, inasmuch as the theoretical relations were obtained within the framework of the single-ion model of magnetic anisotropy of ferromagnets with lo-

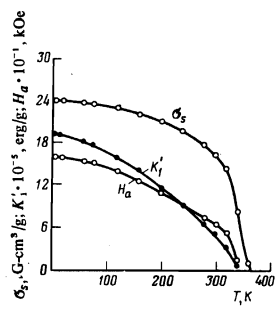

FIG. 2. Temperature dependence of the specific spontaneous magnetization (σ_s) of the first constant (K_1'), and of the magnetocrystalline anisotropy field ($H_a = 2K_1'/\sigma_s$) of the intermetallic compound $UCo_{5.3}$.

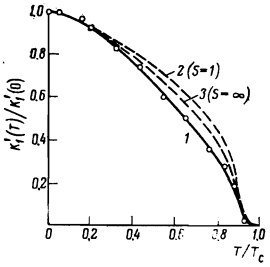

FIG. 3. Comparison of the experimentally obtained temperature dependence of the first magnetocrystalline anisotropy constant (points) and the theoretically expected values: 1—Akulov-Zener-Carr law: $K_1'(T)/K_1'(0) = (1 - 0.15\ T/T_c)\ [\sigma_s(T)/\sigma_s(0)]^3$, 2—theoretical dependence in the quasiclassical approximation $K_1'(T)/K_1'(0) = \hat{I}_{5/2}[\mathcal{L}^{-1}(\sigma_s(T)/\sigma_s(0))]$ at $S = \infty$; 3—the same as 2, but with allowance for the finite value and the effect of quantization of the spin ($S = 1$).

calized magnetic moments, and the experimentally observed decrease of the magnetic moment per Co ion, compared with pure Co, can be satisfactorily explained, as shown above, within the framework of the band model of magnetism.

5. DOMAIN STRUCTURE

The domain structure was investigated at room temperature with an MIM-8 microscope both in the demagnetized state of the samples and in a magnetic field, by the method of powder figures with the aid of the Kerr magneto-optical effect. Figure 4 shows by way of example a picture of the domain structure of a polycrystalline sample of the $UCo_{5.3}$ compound. It is easily seen that the domain structure is typical of magnetically uniaxial ferromagnets.

According to theoretical calculations,[11] for plates of magnetically uniaxial high-anisotropy ferromagnets ($K_1 \gg 2\pi I_s^2$) with EMA perpendicular to the surface of the plate, in the range of thicknesses from $l_1 = \gamma/2I_s^2$ to $l_2 = 32\gamma/I_s^2$ the domain structure should be simple, of the labyrinth type. In this interval of thicknesses, the width of the domains is $d = (\gamma l/1.7 l_s^2)^{1/2}$. Consequently, by measuring in experiment the equilibrium width of the domains d at a known thickness l, we can determine in the indicated interval of variation of l the density of the surface energy of the domain walls $\gamma \approx 4(AK_1)^{1/2} \approx 1.7 d^2 I_s^2/l_\gamma$ and from it the width of the wall $\delta \approx \pi(A/K_1)^{1/2} = \pi\gamma/4K_1$ and the exchange parameter $A \approx \gamma^2/16K_1$. To determine these quantities we investigated from two sides the domain structure of seven single-crystal plates with l ranging from 5 to 15 μ. It turned out that at all thicknesses the structure goes all the way through and is labyrinth-like, without additional domains (closing regions). The width of the domains increases with increasing thickness. At $l > 15$ μ the domain walls become wavy and additional domains appear. The value of γ for the different samples fluctuated from 0.8 to 1.2 erg/cm^2, and the calculated width of the wall was ~ 15 Å. Therefore the width of the exchange parameter was $A = 1.0 \times 10^{-8}$ erg/cm. This is lower by two orders of magnitude than the value $A \approx kT_c/a = 2 \cdot 10^{-6}$ erg/cm which is usually assumed in estimates (the distance a between the cobalt atoms was assumed to be 2.5 Å).

FIG. 4. Picture of the domain structure of a polycrystalline sample of $UCo_{5.3}$, displayed with the aid of the magneto-optical Kerr effect.

From the change of the contrast of the picture of the domain structure following rotation of the analyzer we estimated also the angle of the Kerr rotation of the plane of polarization for white light at room temperature. Its value was found to be 2–3°.

6. CONCLUSION

The intermetallic compound of uranium with cobalt, $UCo_{5.3}$, is a highly anisotropic ($K_1 \gg 2\pi I_s^2$) magnetically uniaxial ferromagnet. The high value of the anisotropy field ($H_a \approx 60$ kOe) at the lower value of the saturation magnetization ($4\pi I_s = 2.2$ kG) and at an "appropriate" value of the Curie temperature ($T_c = 360$ °K), the lower value of the end-point energy ($\gamma \approx 1$ erg/cm^2) and the large magneto-optical Kerr effect ($\varphi = 2–3°$) suggest this material, for example in thin-film form, as a medium for thermal magnetic recording of information in magnetic domains. A characteristic domain dimension is $d_0 = 2\gamma/\pi I_s^2 = 0.2$ μ.

The authors thank S. M. Zadvorkin, N. V. Kudrevatykh, and A. N. Maslov for help with the experiments.

[1]K. P. Belov, A. S. Dmitrievskiĭ, A. Zygmunt, R. Z. Levitin, and V. Tshebyatovskiĭ, Zh. Eksp. Teor. Fiz. **64**, 582 (1973) [Sov. Phys. JETP **37**, 297 (1973)].
[2]K. P. Belov, Z. Genko, A. S. Dmitrievskiĭ, A. Zygmunt, R. Z. Levitin, and Yu. F. Popov, Tr. Mezhdunarodnoĭ konferentsii po magnetizmu (Proc. Internat. Conf. on Magnetism MKM-73, VI, Nauka, 1974, p. 54.
[3]R. Z. Levitin, A. S. Dmitrievski, Z. Henkie, and A. Misiuk, Phys. Status Solidi [a] 27, K109 (1975).
[4]K. N. R. Taylor, Adv. Phys. 20, 551 (1971).
[5]O. S. Ivanov, T. A. Badaeva, R. M. Sofronova, V. B. Kishinevskiĭ, and N. P. Kushnir, Diagramma sostoyaniya i fazovye prevrashcheniya splavov urana (Phase Diagram and Phase Transitions of Uranium Alloys), Nauka, 1972.
[6]W. E. Wallace and J. T. Swearingen, J. Solid State Chemistry 8, 37 (1973).

[7]K. Buschow, Phys. Status Solidi [a] 7, 199 (1971).
[8]W. J. Carr, Jr., Phys. Rev. 109, 1971 (1958).
[9]E. Callen and H. B. Callen, Phys. Rev. 139, A455 (1965).
[10]A. A. Kazakov and V. A. Rotkina, in: Fizika metallov i ikh soedinenii (Physics of Metals and Their Compounds), Sverdlovsk, Ural Gos. Univ. 2, 187 (1974).
[11]J. Kaczer, Zh. Eksp. Teor. Fiz. 46, 1787 (1964) [Sov. Phys. JETP 19, 1204 (1964)]; IEEE Trans. Mag. 6, 442 (1970).

Translated by J. G. Adashko

The sound velocity in superconductors

I. É. Bulyzhenkov and V. I. Ivlev

L. D. Landau Institute of Theoretical Physics, USSR Academy of Sciences
(Submitted March 25, 1976)
Zh. Eksp. Teor. Fiz. **71**, 1172–1179 (September 1976)

We consider the influence of non-linear effects, which arise when sound propagates in a superconductor, on the temperature dependence of the sound speed. We show that the experimentally observed change in this behavior with increasing sound wave amplitude can be explained if we invoke a specific heating of the electron gas. Moreover, we show that the minimum in the temperature dependence of the velocity of transverse sound remains also in the "dirty" limit, in contrast to the result obtained using the two-fluid model of a superconductor.

PACS numbers: 74.20.Ef, 74.50.Nf, 63.20.−e

Recent experiment on sound in superconductors[1] have revealed a non-linear amplitude behavior of the sound velocity. The characteristic dip in the temperature dependence of the velocity below T_c was shifted to the higher temperature region when the sound amplitude increased. It is well known[2] that the presence of such a dip is connected with the appearance of superconducting currents which screen the lattice sound flux and which contribute to the force acting on the lattice. The fields which in that case occur depend on the state of the electrons. We shall in the present paper, as in an earlier one, [3] consider the heating of the electron gas by the sound wave which leads to a non-linear amplitude dependence of the sound velocity.

A survey of papers on the study of the sound speed in superconductors can be found in the monograph by Geĭlikman and Kresin. [4] We note merely that we shall show that in the limit $kl \ll 1$, where l is the mean free path of an electron connected with the scattering by impurities, the temperature dependence of the sound speed in the linear approximation is appreciably different from what follows from the simple two-fluid model of superconductivity used by Ozaki and Mikoshiba. [2]

1. SET OF EQUATIONS FOR A TRANSVERSE SOUND WAVE

We shall consider a sound wave propagating along the z-axis and the displacement vector is u_x. When we change to a comoving system of coordinates in which the lattice is at rest we must add to the electron Hamiltonian a part[5]

$$\mathcal{H}' = ec^{-1}vA_x n_x - iku_x pvn_x n_z + i\omega p n_x u_x, \tag{1}$$

$\mathbf{n}$ is a unit vector directed along the momentum. The second term is the deformation potential, and the third one is caused by the Stewart-Tolman effect.

If we take into account the force exerted by the electrons we can write the equation of motion of the lattice in the form

$$(\omega^2 - s_0^2 k^2) u_x + f_\omega(k)/Mn = 0, \tag{2}$$

where s_0 is the adiabatic sound velocity in a normal metal in agreement with Brovman and Kagan. [6] The volume force density f_ω refers to the laboratory system of coordinates. We shall assume u_x and A_x/c to be independent of the generalized coordinates[7] and the lattice force is then connected with the electron force through the simple relation:

$$f_x = -f_x^{el} = \frac{\partial \mathcal{H}'}{\partial u_x} + nm\omega^2 u_x. \tag{3}$$

The second term on the right is the inertial force which must be taken into account when we change to the laboratory system of coordinates. We can express Eq. (3) in terms of the electron Green function:

$$f_\omega(k) = \frac{ip^3}{\pi^2 v} \int \frac{d\varepsilon}{4\pi i} \int \frac{d^3p}{(2\pi)^3} (\omega - kvn_z) n_x G_{\varepsilon,\varepsilon-\omega}(p, p-k) + nm\omega^2 u_x, \tag{4}$$

which in the case of a normal metal goes over into the expression obtained by Kontorovich. [8] Using the Max-