Magnetic and magnetoelastic properties of the band metamagnet $ThCo_5$

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We investigated the magnetization of the intermetallic single crystal $Th_{0.965}Co_{5.07}$ in strong pulsed magnetic fields up to 320 kOe in the temperature interval 4.2–300 K. From a comparison of the fields of the metamagnetic transition occurring when the $Th_{0.965}Co_{5.07}$ single crystal is magnetized either along the hexagonal axis (easy-magnetization direction) or in the basal plane we determined the magnetic-anisotropy constants of the cobalt in two nonequivalent positions in the crystal lattice, and observed that the anisotropy of the cobalt in the 3*g* sites is substantially larger than the anisotropy of the cobalt in 2*c* sites. Investigations of the magnetostriction of the $Th_{0.965}Co_{5.07}$ single crystal along the easy magnetization axis in the temperature interval 4.2–400 K in pulsed magnetic fields up to 200 kOe, as well as x-ray investigation of the crystal-lattice parameters of the compounds $Th_{0.965}Co_{5.07}$ and $Th_{0.950}Co_{5.10}$, have made it possible to calculate the constants of the magnetoelastic coupling both within the cobalt subsystems and between two nonequivalent cobalt subsystems. The results are in good agreement with analogous investigations of RCo_2 compounds, thus confirming that $ThCo_5$ and RCo_2 have like magnetic and magnetoelastic properties and that the magnetism in these compounds is of the band type.

INTRODUCTION

Interest in investigations of the intermetallic compound $ThCo_5$ is due to its strongly pronounced band metamagnetism.[1–3] the gist of this phenomenon, which is observable also in other intermetallic compounds, such as RCo_2 (R is a rare earth or Y), is the following. If the magnetic moments are due to collectivized electrons (band magnetism) (in $ThCo_5$ these are the 3*d* electrons of the cobalt hybridized with the 6*d* electrons of the thorium), the singularities of the structure of the energy band (location of the Fermi level on the descending section of the plot of the density of states) causes a dependence of the magnetic moment on the magnetic field, shown by curve 1 of Fig. 1. When the effective magnetic field reaches a certain critical value H_{cr}, the magnetic moment increases jumpwise, i.e., a transition from the "paramagnetic" to the "ferromagnetic" state takes place in the field H_{cr}.

The compound $ThCo_5$ has an hexagonal crystal structure of the $CaCu_5$ type (space group $P6/mmm$). A characteristic of this structure is alternation of layers of two types, perpendicular to the hexagonal axis. One such layer consists only of cobalt atoms that make up a planar hexagonal network (Kagome network). In the other layer the thorium atoms are located at the center of a hexagon made up of cobalt atoms. Thus, all the thorium atoms in the $ThCo_5$ structure are in crystallographically equivalent positions, and the cobalt atoms occupy two nonequivalent positions—the so-called 3*g* positions (point group *mmm*) in the layers of the first type and 2*c* positions (point group 6*m*2) in the layers of the second type.[5]

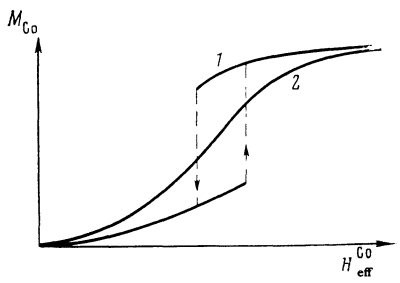

FIG. 1. Schematic plot of the dependence of the magnetic moment of cobalt on the effective field H_{eff} in $ThCo_5$ at various temperatures: 1—$T=0$ K, 2—$T\gtrsim 150$ K.

Neutron-diffraction investigations[2] have shown that the magnetic moments in the 2*c* and 3*g* sites are parallel to one another.

Some of the thorium atoms of $ThCo_5$ can be replaced by a "dumbbell" of two cobalt atom; this brings about a rather appreciable homogeneity region. Accordingly, the general formula of this compound can be written in the form $Th_{1-x}Co_{5+2x}$ ($0\leqslant x\leqslant 0.09$) (Ref. 6).[1)]

An interesting feature of the $ThCo_5$ compounds is that by varying the cobalt concentration within the homogeneity region it is possible to influence the *d*-band and the exchange parameters and alter thereby the magnetic properties of the $ThCo_5$.[3]

For cobalt atoms in the 2*c* sites, the effective exchange field H_{eff} exceeds H_{cr}, so that the 2*c*-site cobalt in all the $ThCo_5$ compounds is ferromagnetic inside the homogeneity region. For the 3*g*-cobalt atoms the effective field exceeds H_{cr} only when a certain critical concentration of the cobalt is reached. By varying thus the cobalt concentration inside the homogeneity region it is possible to obtain at the cobalt atoms in the 3*g* sites an effective field that is either stronger or weaker than the critical H_{cr} (i.e., the cobalt in the 3*g* sites can be either in a paramagnetic or in a ferromagnetic state).

For example, neutron diffraction investigations 2 have shown that in the compound $Th_{0.965}Co_{5.07}$ the magnetic moment of the ferromagnetic cobalt in the 2*c* sites is 1.21 μ_B, and the magnetic moment of the paramagnetic cobalt in the

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3g sites is $0.96\mu_B$ (so large a magnetic moment of the paramagnetic cobalt is due to magnetization by the ferromagnetic subsystem). It is clear that application of an external magnetic field on this compound can cause a metamagnetic transition of the paramagnetic cobalt in the 3g sites into the ferromagnetic state. In fact, such a transition was observed in $Th_{0.965}Co_{5.07}$ at temperatures ~ 150 K in a field oriented along the hexagonal axis (easy-magnetization direction)[1,2]: when the critical field is reached ($H_{cr} \approx 60$–80 kOe) a magnetization jump is observed and can reach 30% of the saturation magnetization.

Our aim was to investigate the influence of magnetic anisotropy on the metamagnetic-transition field. In addition, we investigated the magnetoelastic properties of $ThCo_5$ compounds and compared the results with those of analogous investigations of RCo_2 band metamagnets.[7]

PROCEDURE. SAMPLES

Magnetic fields up to 320 kOe were obtained by discharging a capacitor bank through a multiturn solenoid. The magnetic-field pulse duration was ≈ 15 ms. The magnetization was measured by a standard inductive method, and the relative error was 5%. The magnetostriction was measured by a glued-on quartz piezoelectric pickup, the error in the determination of the absolute value of the magnetostriction was 25%, and the resolution was 5%. The x-ray measurements were made in $K\,Fe_{\alpha_1}$ radiation, using the reflections 004 and 400, the absolute accuracy in the determination of the crystal lattice parameters was within 10^{-3} Å, and the resolving power was $2\cdot10^{-4}$ Å.

The samples were obtained by melting the initial materials in an arc furnace on a cold hearth in an argon atmosphere.

INFLUENCE OF MAGNETIC ANISOTROPY ON THE METAMAGNETIC TRANSITION IN $ThCo_5$

The features of magnetization of $Th_{0.965}Co_{5.07}$ in the hard magnetization direction (perpendicular to the hexagonal axis) have not yet been sufficiently well studied. A metamagnetic transition is expected to occur also at the latter magnetic-field orientation, although the transition field H_{cr} should be considerably stronger since the contribution of the magnetic anisotropy to H_{eff} is negative and is of the order of the anistropy field H_A. The fields needed to observe this transition could not be attained in Ref. 1. We have investigated the magnetization of single-crystal $Th_{0.965}Co_{5.07}$ in the hard magnetization direction. Figure 2 shows the magnetization curves of this single crystal both in the easy ($\mathbf{H}\|c$) and in the hard ($\mathbf{H}\perp c$) directions. The magnetization curves for the easy magnetization direction, the magnetization jump is observed in considerably stronger fields. The metamagnetic-transition field at 4.2 K amounts to 240 kOe.[2)] The increase of H_{cr} for magnetization in the hard direction can be qualitatively attributed to the influence of the magnetic anisotropy on the metamagnetic transition, but it is impossible to carry out a quantitative analysis within the framework of such a simple model. Indeed, whereas the anisotropy field of this compound is approximately 120 kOe, and H_{cr} for magnetization along the hexagonal axis is approximately 65 kOe, the metamagnetic transition in a field applied perpendicular to the easy magnetization axis should be observed at 185 kOe, i.e., much less than the experimental 240 kOe.

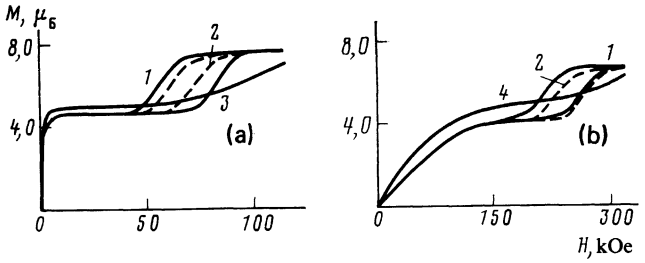

FIG. 2. Magnetization curves of single-crystal $Th_{0.965}Co_{5.07}$ in the easy-magnetization direction (a) and in the hard magnetization direction (b) at various temperatures: 1—$T = 4.2$ K; 2—$T = 70$ K; 3—$T = 150$ K; 4—$T = 160$ K.

To explain the increase of H_{cr} in the hard magnetization direction it must be taken into account that the measured anisotropy field characterizes the total magnetic-anisotropy energy of the crystal:

$$H_A = 2(3K_{3g} + 2K_{2c})/(3M_g + 2M_c), \quad (1)$$

and the increase of the critical field is due to the anisotropy field that acts on the cobalt in the paramagnetic 3g sites:

$$H_A{}^{3g} = 2K_{3g}/M_g \quad (2)$$

(here K_{3g} and K_{2c} are the magnetic anisotropy constants of cobalt per ion, while M_g and M_c are the magnetic moments of the cobalt in the 3g and 2c sites, respectively).

The experimental results allow us to estimate the anisotropy constants of the cobalt in different nonequivalent positions. Using the values of H_{cr} at $\mathbf{H}\perp c$ (240 kOe) and at $\mathbf{H}\|c$ (65 kOe) as well as the values given above for the magnetic moments of cobalt a different nonequivalent positions, we find that $K_{3g} = 4.9\cdot10^8$ erg/mol and $K_{2c} = 1.8\cdot10^8$ erg/mol at 4.2 K. It follows thus from our data that the magnetic anisotropy of the cobalt in 2c sites is much lower than in 3c sites. We note that the situation in YCo_5 is reversed: the anisotropy of the cobalt is larger in the 2c sites than in the 3g sites.[8] This difference is apparently due to the different states of the thorium and yttrium in these compounds. According to Ref. 6, the thorium in $ThCo_5$ is tetravalent and hence gives up two electrons to the d band, while yttrium in YCo_5 is trivalent and gives up to the d band only one electron. The d bands are therefore differently filled in $ThCo_5$ and YCo_5, and this leads to a different anisotropy of the cobalt in these compounds.

It must be recognized that the foregoing calculation of the anisotropy constants is approximate. It does not take into account the possible onset of a noncollinear magnetic structure upon magnetization in the difficult direction, nor the dependence of the magnetic moment of the cobalt on the direction (this dependence makes the saturation magnetization in $Th_{0.965Co\,5.07}$ at 4.2 K, in fields both stronger and weaker than H_{cr}, larger in a field parallel to the hexagonal axis than in a field perpendicular to this axis).

The temperature dependences of the metamagnetic-transition fields at $\mathbf{H}\|c$ and $\mathbf{H}\perp c$ are shown in Fig. 3. It can be seen that with rising temperature H_{cr} increases somewhat

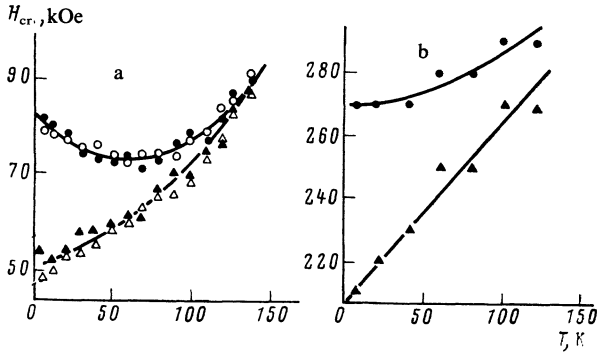

FIG. 3. Temperature dependences of the magnetic transition fields of the compound $Th_{0.965}Co_{5.07}$ at $\mathbf{H}\|c$ (a) and $\mathbf{H}\perp c$ (b): ● and ▲—from magnetization measurements, ○ and △—from magnetostriction measurements, circles and triangles—metamagnetic-transition field for increasing and decreasing magnetic field, respectively.

for both directions of the external magnetic field, and the hysteresis of the transition fields is strongly decreased. The decrease of the hysteresis with temperature can apparently be attributed to the insignificant change of the *d*-electron density of states with change of temperature, which leads in turn to a "smearing" of the metamagnetic form of the cobalt magnetization curve at sufficiently high temperatures (see curve 2 of Fig. 1). The metamagnetic transition vanishes then in the 3*g* sites and the magnetic moment of the cobalt at these sites approaches that at the 2*c* sites (in a 48-kOe field the magnetic moment of cobalt is 1.19 μ_B and 1.06 μ_B in the 2*c* and 3*g* sites, respectively[2)].

MAGNETOELASTIC PROPERTIES OF $ThCo_5$

It is well known that the magnetic ordering of cobalt in intermetallic compounds is accompanied by a large bulk magnetostriction.[9] To study the magnetoelastic properties of the cobalt in $ThCo_5$ compounds we measured the magnetostriction of $Th_{0.965}Co_{5.07}$. Figure 4 shows the longitudinal magnetostriction of a single crystal of this compound in the easy magnetization direction. It can be seen that at $H < H_{cr}$ the magnetostriction is small and has a discontinuity on the order of $1.2\cdot10^{-3}$ in the field H_{cr} at 4.2 K. The discontinuity decreases with rising temperature and becomes completely smeared out above ~150 K. The temperature dependences of the transition fields, determined from the magnetostriction data, agree with the analogous dependences obtained from magnetization measurements (see Fig. 3).

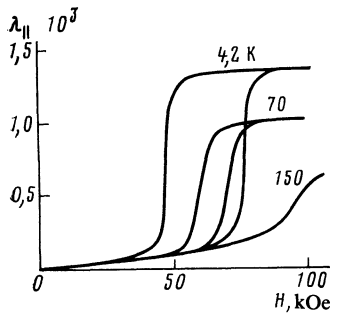

FIG. 4. Longitudinal magnetostriction $\lambda_{\|}$ in the easy-magnetization direction vs the magnetic field of single-crystal $Th_{0.965}Co_{5.07}$ at various temperatures.

Owing to the great experimental difficulties (the size of the crystal used in the experiments was ≈ 1 mm^3) we were unable to investigate the transverse magnetostriction of the single-crystal $Th_{0.965}Co_{5.07}$. Measurements made on polycrystals have shown that the discontinuity of the longitudinal magnetostriction in the field H_{cr} is approximately equal to the discontinuity of the transverse magnetostriction. Thus, this is predominantly bulk magnetostriction.

It can be seen from Fig. 4 that in weak fields ($H < H_{cr}$) the longitudinal magnetostriction of $Th_{0.965}Co_{5.07}$ is weak and linear in the field. Since the measurements are carried out in the easy magnetization direction, so that the magnetic moments of the cobalt are parallel to the applied field, the magnetostriction observed in weak fields is due to the change of the magnetic moment of the cobalt in the field. Our measurements have shown that the temperature dependence of $d\lambda_{\|}/dH$ ($H < H_{cr}$) of $Th_{0.965}Co_{5.07}$ goes through a broad maximum in the same region, 100–200 K, where (according to our data and those of Ref. 1) the saturation magnetization and the susceptibility of th paraprocess in $Th_{0.965Co\,5.07}$ go through a maximum.[2]

We have also investigated the crystal-structure parameters of $Th_{0.965}Co_{5.07}$, as well as of $Th_{0.950}Co_{5.10}$ (in the latter, according to the data of Ref. 3, the cobalt is in a ferromagnetic state in both nonequivalent positions). The measurements were made in the temperature interval 5–800 K. In the paramagnetic region, the lattice parameters are linear in the temperature, but below the Curie temperature (T_C) (according to magnetic measurements, this temperature is 540 and 650 K for the first and second compounds, respectively) deviations from linearity occur and are due to magnetoelastic interaction. Figure 5 shows the temperature dependence of the bulk magnetoelastic anomalies $\omega = (V_{un} - V_0)/V_{un}$ (V_0 is the unit-cell volume extrapolated from the paramagnetic temperature region in accord with the Debye relation, and V_{un} is the unit-cell volume) of the investigated compounds.[3)] It can seen that in $Th_{0.965}Co_{5.07}$

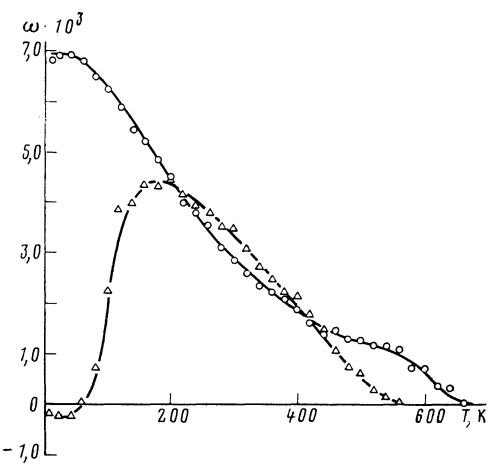

FIG. 5. Temperature dependence of magnetic-volume anomaly of the compounds $Th_{0.965}Co_{5.07}$ (△) and $Th_{0.950}Co_{5.10}$ (○).

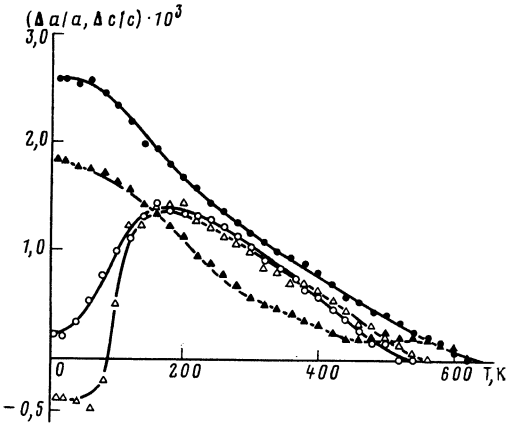

FIG. 6. Temperature dependence of spontaneous linear magnetostriction along the hexagonal axis ($\Delta c/c$—circles) and in the basal plane ($\Delta a/a$—triangles) of the compounds $Th_{0.965}Co_{5.07}$ (light symbols) and $Th_{0.950}Co_{5.10}$ (dark).

the magnetoelastic anomaly at $T < 150$ K is substantially less than in $Th_{0.950}Co_{5.10}$. In addition, in the first of these compounds an anomaly is observed in the temperature dependence of $\omega(T)$: the magnetoelastic bulk effect decreases sharply below approximately 100 K. The magnetoelastic anomalies on the temperature dependences of the lattice parameters $a(T)$ and $c(T)$ also decrease in this temperature region.

The difference between the values of the bulk magnetoelastic effect of the two investigated compounds can be attributed to the fact that the 3g-cobalt in them is in different magnetic states, paramagnetic in $Th_{0.965}Co_{5.07}$ and ferromagnetic in $Th_{0.950}Co_{5.10}$. The decrease of the magnetic-bulk anomaly in $Th_{0.965}Co_{5.07}$ can be related to the decrease, at $T \lesssim 150$ K, of the magnetic moment of the cobalt in the 3g sites.[2]

The exchange magnetostriction of an hexagonal crystal is described by two magnetostriction coefficients, $\lambda_1^{\alpha,0}$ and $\lambda_2^{\alpha,0}$, which characterize the magnetoelastic strains in the basal plane and along the hexagonal axis, respectively.[10] The obtained experimental data make it possible to estimate these coefficients for both compounds. If the parameters a and c of the crystal structure of the investigated compound is extrapolated from the paramagnetic region in accord with the Debye law, we obtain for $Th_{0.965}Co_{5.97}$, from the difference between the measured and extrapolated values of a and c at 5 K,

$$\lambda_{1s}^{\alpha,0} = -0.38\cdot10^{-3}, \quad \lambda_{2s}^{\alpha,0} = 0.21\cdot10^{-3}$$

and for $Th_{0.950}Co_{5.10}$

$$\lambda_{1s}^{\alpha,0} = 1.75\cdot10^{-3}, \quad \lambda_{2s}^{\alpha,0} = 2.53\cdot10^{-3}.$$

In the general case the exchange-magnetostriction coefficients $\lambda_1^{\alpha,0}$ and $\lambda_2^{\alpha,0}$ are expressed in terms of the coefficients n_{cc} and n_{gg} of the magnetoelastic coupling within the 2c and 3g subsystems, as well as in terms of the magnetoelastic coupling constant n_{cg} that characterizes the magnetoelastic interaction between the subsystems. For example, $\lambda_2^{\alpha,0}$ can be represented in the form

$$\lambda_2^{\alpha,0} = \Delta c/c = (2n_{cc}M_c^2 + 3n_{gg}M_g^2 + 6^{1/2}n_{cg}M_cM_g)/3V_{un} \quad (3)$$

(in this form, the expression takes into account the number of magnetoactive atoms per unit volume).

It can be assumed in the simplest case that the structure of the d band for cobalt in the 3g and 2c sites is the same. We put therefore $n_{cc} = n_{gg} = n$. Moreover, for further simplification we determine n by using the results of an investigation of the magnetostriction of the exchange-enhanced paramagnets YCo_2 and $LuCo_2$ (Ref. 7) and assume that the magnetoelastic-coupling constant in $ThCo_5$ is the same as the analogous constant in YCo_2, viz., 0.28 Å$^3/\mu_B^2$ at 5 K (n was recalculated here to allow for the difference between the atomic volumes of YCo_2 and $ThCo_5$).

We then have for the spontaneous magnetostriction along the hexagonal axis

$$\lambda_{2s}^{\alpha,0} = [n(2M_c^2 + 3M_g^2) + 6^{1/2}n_{cg}M_cM_g]/3V_{un}, \quad (4)$$

for the magnetostriction of the paraprocess in a field $H < H_{cr}$

$$d\lambda_2^{\alpha,0}/dH = [2n(2M_c\chi_c + 3M_g\chi_g) + 6^{1/2}n_{cg}(M_c\chi_g + M_g\chi_c)]/3V_{un} \quad (5)$$

(χ_g and χ_c are the susceptibilities of cobalt in 2g and 2c sites), and for the magnetostriction discontinuity in the metamagnetic transition

$$\Delta\lambda_2^{\alpha,0} = \{n[\Delta(2M_c^2) + \Delta(3M_g^2)] + 6^{1/2}n_{cg}\Delta(M_gM_c)\}/3V_{un} \quad (6)$$

(Δ in the right-hand side denotes the increment of the corresponding quantity in the metamagnetic transition).

Using the value of $\lambda_{2s}^{\alpha,0}$ obtained by us for $Th_{0.950}Co_{5.10}$ and the data of Ref. 2 on the magnetic moments of cobalt, $M_c = M_g = 1.58\ \mu_B$ at 4.2 K, we obtain from Eq. (4) the value $n_{cg} = -0.46$ Å$^3/\mu_B^2$.

With the same values of the coefficients n and n_{cg} we can describe satisfactorily the magnetoelastic phenomena in $Th_{0.965}Co_{5.07}$. Thus, putting[2] $M_c = 1.21\ \mu_B$, $M_g = 0.96\ \mu_B$, $\chi_g = 7.9\cdot10^{-4}\ \mu_B$/kOe, $\chi_c = 6.1\cdot10^{-4}\ \mu_B$/kOe, we find that at 4.2 K we have for this compound $\lambda_{2S}^{\alpha,0} = 9.9\cdot10^{-4}$ and $d\lambda_2^{\alpha,0}/dH$ amounts to $1.3\cdot10^{-8}$ kOe^{-1}.

Using the fact that, according to Ref. 3, $M_g = M_c = 1.6\ \mu_B$ in fields stronger than H_{cr}, we obtain for the magnetostriction discontinuity a value $1.5\cdot10^{-3}$ close to the experimental $1.2\cdot10^{-3}$. We note that the calculation, in Ref. 2, of $d\lambda_2^{\alpha,0}/dH$ and $\lambda_{2S}^{\alpha,0}$ as functions of the temperature, using data on the magnetic susceptibility and the magnetic moments of cobalt in different nonequivalent positions, describes the experimental temperature dependences of these characteristics only semiquantitatively.

This discrepancy between theory and experiment should not seem surprising, since the theoretical model is quite approximate. It sets out from the rather crude assumption that the two cobalt subsystems in $ThCo_5$ and the cobalt subsystem in RCo_2 can be described by the same magnetoelastic-coupling constant. By rejecting this approximation, and also by taking into account the temperature dependence of the magnetoelastic-coupling constants (this dependence, as shown in Ref. 7, is substantial in RCo_2 compounds), the agreement between theory and experiment can be considerably improved.

We are convinced, however, that this refinement is not justified, since the available experimental data are in many cases not accurate enough. This pertains primarily to the Debye temperature used by us, to the values of the magnetic moments of cobalt,[2] (magnetic and neutron-diffraction measurement data yield, e.g., for $Th_{0.965}Co_{5.07}$, saturation moments 4.6 μ_B and 5.3 μ_B respectively,[1,2] and the causes of this discrepancy are not quite clear), etc. At the same time, the crude model used for the calculation is sufficient to draw the following principal conclusion: Magnetoelastic effects in $ThCo_5$ and RCo_2 are of like nature and can be described in the band model of magnetism.

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[1)]The compositions of specific compounds will be given in this form, but the compound in general will be designated $ThCo_5$. We note that in other papers the specific compounds are designate $ThCo_{5+h}$, i.e., it is assumed that one formula unit contains one thorium atom. We, however, shall use the form $Th_{1-x}Co_{5+2x}$ even when referring to other papers.

[2)]Here and elsewhere H_{cr} is taken to be the mean value the magnetization-discontinuity fields for increasing and decreasing H.

[3)]Owing to the strong damping, we were unable to determine the Debye temperatures of the $ThCo_5$ compounds by the ultrasonic method. We used in the calculation the value $\Theta_D = 300$ K, which is close to those obtained for $CeCo_5$ (310 K) and Th_2Co_7 (270 K).

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