Journal of Alloys and Compounds, 189 (1992) 187–190
JALCOM 363

Thermal expansion anomalies and spontaneous magnetostriction in Tm_2Co_7

A. V. Andreev, S. M. Zadvorkin and E. N. Tarasov
Permanent Magnets Laboratory, Institute of Physics and Applied Mathematics, Ural State University, 620083 Ekaterinburg (Russian Federation)

(Received April 28, 1992)

Abstract

The temperature dependencies of the lattice parameters and magnetization have been studied in the intermetallic compound Tm_2Co_7. Magnetic ordering is accompanied by spontaneous magnetostriction in the basal plane and along the c axis (2.0×10^{-3} and 2.7×10^{-3} respectively at 5 K). This corresponds to a volume effect $\omega_s=6.6\times10^{-3}$. The Tm atoms on the quasi-cubic sites are considered to be responsible for the spin reorientation from the uniaxial type of magnetic anisotropy above 45 K to the cone of easy axes below this temperature, which is explained by magnetoelastic effects. In the cone range a large orthorhombic distortion ϵ (up to -3.5×10^{-3} at 5 K) is observed. The additional volume anomaly $\Delta\omega_s=-1\times10^{-3}$, which accompanies spin reorientation, can be explained by the anisotropy of the magnetic moments of the thulium and cobalt sublattices.

1. Introduction

The intermetallic compounds R_2M_7 (R≡rare earth metal, M≡Co or Ni) are interesting representatives of 4f–3d magnets. They have been found to display various types of magnetic anisotropy and to undergo spontaneous and field-induced spin reorientation phase transitions [1–3]. In Fig. 1 the rhombohedral structural modification of R_2Co_7 (the Gd_2Co_7 type of structure, space group $R\bar{3}m$) forming for heavy R is presented. The R atoms occupy two non-equivalent sites: R_1 with hexagonal local environment (as in RCo_5 compounds) and R_2 with quasi-cubic local environment (as in RCo_2 Laves phases, with some distortion). The total magnetocrystalline anisotropy energy is a result of the competition of the R_1, R_2 and cobalt sublattice contributions. Strictly speaking, five cobalt sublattices exist in these compounds (Fig. 1); however, the common cobalt sublattice could be a good approximation [2].

In the present paper we report the results of thermal expansion measurements of Tm_2Co_7 in comparison with magnetic data, as a continuation of the systematic research of spontaneous magnetostriction of R_2Co_7 [4].

2. Experimental details

The Tm_2Co_7 alloys (Tm, 99.9%; Co, 99.99%) were prepared in an induction furnace in alumina crucibles under a protective argon atmosphere. The ingots were remelted in an electric resistance furnace with a high temperature gradient to increase the grain size. According to X-ray and metallographic analysis, the ingots contained less than 3% of extraneous phases. Samples in the form of cubes of side $a\approx2$ mm were cut out from large grains of the ingots. The surfaces of the samples were polished parallel to the (001), (100) and (110) atomic planes. The misorientation of subgrains over samples was about 10°, so that they could not be considered as single crystals but strongly aligned polycrystals.

The thermal expansion was investigated by X-ray diffractometry in a cryostat in the temperature range 5–340 K and in a high-temperature chamber between 290 and 900 K. Cr Kα radiation was used for the investigation. The lattice parameter a was determined from the (2,2,0) reflection and the parameter c from the (0,0,30) reflection. This gave a Bragg angle 2θ larger than 130° and consequently the relative error of a and c determination was 7×10^{-5}.

For the determination of the magnetostrictive deformations, the temperature dependencies of the lattice parameters and the cell unit volume $V=a^2c3^{1/2}/2$ were extrapolated from the paramagnetic range 800–900 K to the range of the ferromagnetic state. The method of extrapolation has been described in ref. 4. The value of the Debye temperature, necessary for extrapolation, is taken to be equal to 300 K, as determined for other R_2Co_7 compounds from acoustic measurements [4].

0925-8388/92/$5.00

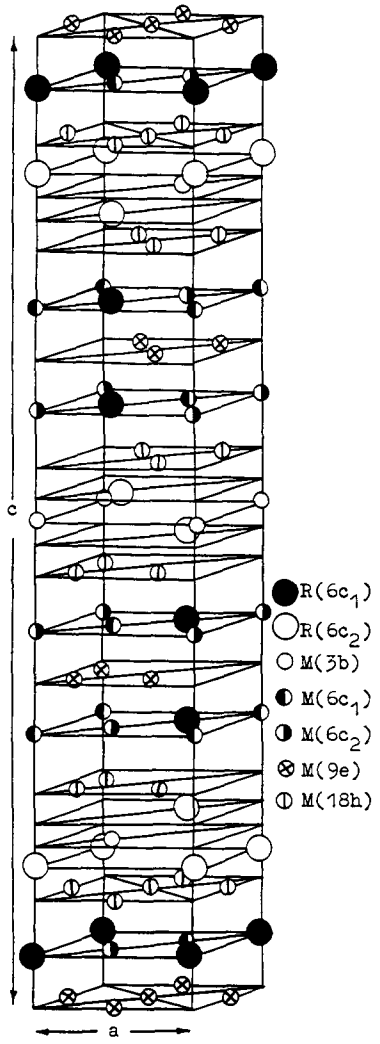

Fig. 1. Crystal structure of the Gd_2Co_7 type. The rare earth atoms R_1 have a hexagonal RCo_5 local environment; the R_2 atoms have a quasi-cubic RCo_2 environment.

The magnetization measurements along and perpendicular to the c axis (with the above-mentioned 10° accuracy in orientation) were carried out using a vibrating sample magnetometer in a magnetic field up to 2.2 T from 4.2 to 800 K.

3. Results and discussion

The temperature dependence of the spontaneous molar magnetic moment M along the c axis is shown in Fig. 2. One can see that the compound is a ferrimagnet with Curie temperature $T_C = 640$ K and $M_c = 2.8$ μ_B/f.u. (the value at 4.2 K; f.u., formula unit). There is a compensation point at 80 K. The compound has uniaxial magnetocrystalline anisotropy above 45 K and in this range M_c is actually equal to the value of M_s. A spin reorientation from uniaxial anisotropy to a cone of easy magnetization axes has been observed below

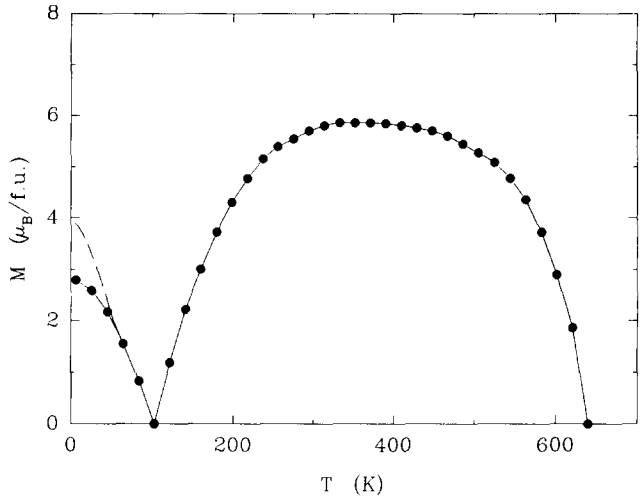

Fig. 2. Temperature dependence of the spontaneous magnetic moment M_c as measured along the c axis. The dashed line represents the spontaneous magnetic moment M_s along the easy magnetization direction, obtained from its projections parallel and perpendicular to the c axis below the spin reorientation temperature of 45 K.

45 K. In this temperature range M_c is equal to the projection of M_s on the c axis. From the projections of M_s parallel and perpendicular to the c axis, the values of M_s and of the cone angle Θ between the easy direction and the c axis were determined. $M_s = 4.0$ μ_B at 4.2 K and its temperature dependence is shown in Fig. 2 by a dashed line. Owing to considerable misorientation of subgrains, the Θ value was estimated as $45° \pm 15°$ at 4.2 K.

Figure 3 shows the temperature dependencies of the lattice parameters. During cooling from the paramagnetic range, the $a(T)$ and $c(T)$ curves deviate from the Debye extrapolation. The relative differences between the experimental and extrapolated values, $\lambda_a = (a - a_0)/a_0$ and $\lambda_c = (c - c_0)/c_0$, represent the spontaneous magnetostriction in the basal plane and along the c axis respectively. Both deformations are positive and increase monotonically with cooling in the uniaxial anisotropy range ($T > 45$ K). Extrapolation from this range to 0 K gives $\lambda_a(0) = 2.3 \times 10^{-3}$ and $\lambda_c(0) = 3.0 \times 10^{-3}$. This corresponds to a volume effect $\omega_s(0) = 7.5 \times 10^{-3}$. The actual values of λ_a, λ_c and ω_s at the lowest temperatures are equal to 2.0×10^{-3}, 2.7×10^{-3} and 6.6×10^{-3} respectively. The difference will be discussed below. The compensation point does not display itself in the $a(T)$ and $c(T)$ dependencies, since the compensation of the magnetic moments of the sublattices is not a phase transition.

In the cone range, at the spin reorientation, the rhombohedral lattice of the compound undergoes a large orthorhombic distortion within the basal plane and should be described by using a third lattice parameter b. The distortion $\epsilon = (b/3^{1/2} - a)/a$ is negative

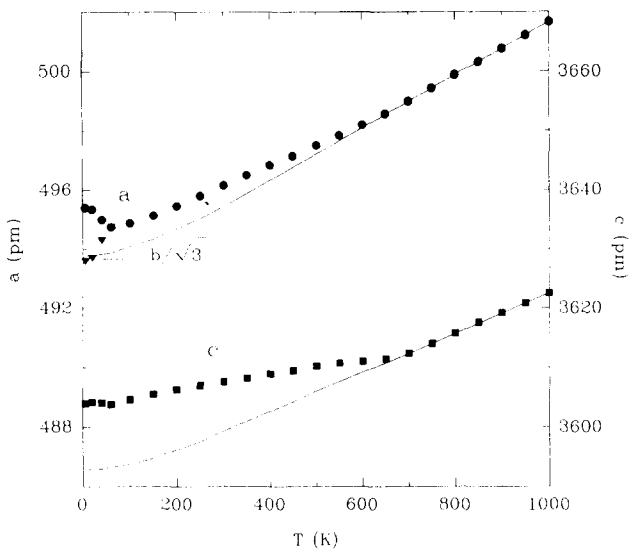

Fig. 3. Temperature dependencies of the lattice parameters a and c. Below 45 K the lattice undergoes orthorhombic distortion and a third parameter b should be used. The lines are extrapolations of the $a(T)$ and $c(T)$ curves from the paramagnetic range to the ferrimagnetic one.

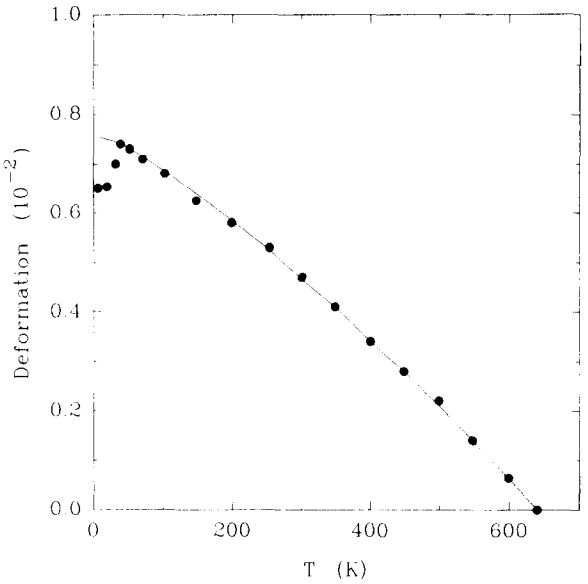

Fig. 4. Temperature dependence of the spontaneous volume magnetostriction ω_s. The line is an extrapolation of the $\omega_s(T)$ curve from the uniaxial magnetocrystalline anisotropy range to the cone anisotropy range.

and reaches -3.5×10^{-3} at 4.2 K. A similar distortion was observed in Nd_2Co_7 and Tb_2Co_7 [4] and indicates a huge so-called γ magnetostriction in these compounds. Limiting ourselves to the first term in the expression for the γ magnetostriction [5], the distortion can be described as

$$\epsilon = \lambda^{\gamma,2} \sin^2\Theta \qquad (1)$$

where $\lambda^{\gamma,2}$ is a second-order γ magnetostriction constant. It is already known that the next term (with a fourth-order constant) makes a considerable contribution to the γ magnetostriction [4]. However, the contributions were separated in ref. 4 using better single crystals, while here $\lambda^{\gamma,2}$ can only be estimated from the obtained values of ϵ and Θ as -7×10^{-3} at 5 K.

In Fig. 4 the spontaneous volume magnetostriction ω_s *vs.* temperature is presented. One can see that the spin reorientation is accompanied by an additional volume effect reducing ω_s by about 1×10^{-3}, distributed nearly isotropically over the main axes. Such an effect was not observed in Nd_2Co_7 and Tb_2Co_7, where the spin reorientation influences only the linear, but not the volume deformation.

As a usual approximation, the crystal structure of R_2Co_7 compounds can be considered by packing hexagonal structural blocks RCo_5 and cubic ones RCo_2 along the common hexagonal (trigonal for RCo_2) axis according to the scheme $2RCo_5+2RCo_2=2R_2Co_7$. The hexagonal $TmCo_5$ part contributes the uniaxial anisotropy to the total magnetocrystalline anisotropy of the Tm_2Co_7 compound; the magnetic moments of thulium and cobalt are along the c axis. The cubic Laves phase $TmCo_2$ has four equivalent easy magnetization axes of the <111> type. In Tm_2Co_7 one of these axes in a cubic block coincides with the c axis and the magnetic moment of the cubic part should choose this axis under the influence of the uniaxial $TmCo_5$ environment. The other axes deviate by an angle of 70° from c axis. In the scheme presented, there is no reason for any spin reorientation in Tm_2Co_7.

In order to explain the spin reorientation, we must take into account the fact that the $TmCo_2$ blocks in Tm_2Co_7 are not exactly cubic. In the hexagonal description of $TmCo_2$, $a=503$ pm, but it is only 495 pm in Tm_2Co_7 (Fig. 3). This means that $TmCo_2$ blocks are compressed perpendicular to the c axis. $TmCo_2$ has a huge magnetostriction constant λ_{111} (about -5×10^{-3} [6]) and it is important that the magnetostriction is negative. Therefore, owing to a reverse magnetostrictive effect, the mechanical stress directs the magnetic moments in the $TmCo_2$ blocks to the <111> axes under 70° from the c axis of Tm_2Co_7 and produces a non-collinearity between the two thulium sublattices. Such competition leads to the observed cone of easy axes at low temperatures. Since the cubic anisotropy decreases with increasing temperature much more strongly than the uniaxial one, the compound becomes uniaxial above 45 K. The same situation can be expected in the Sm_2Co_7 and Er_2Co_7 compounds, where the signs of the Stevens coefficients α and β determining the signs of the anisotropy and magnetostriction constants of the R ions are the same. In $SmCo_2$, $\lambda_{111}=-5\times10^{-3}$ [7] and we have already observed a similar spin reorientation in Sm_2Co_7 [8]. The Er_2Co_7 compound has

not been carefully studied. It is possible that a spin reorientation in this compound is not realized because of the relatively low value of λ_{111} in $ErCo_2$ (-2.5×10^{-3} [9]).

Several compounds are known in which the spin reorientation is accompanied by a volume anomaly (Tm_2Fe_{17} [10], $Nd_2Fe_{14}B$ [11]). This is explained by an anisotropy of the values of the magnetic moments. The volume magnetostriction of R–T compounds can be described (neglecting the weakest R–R exchange interaction) by the expression

$$\omega_s = n_{TT}\mu_T^2 + n_{RT}\mu_T\mu_R \quad (2)$$

where n_{TT} and n_{RT} are the magnetoelastic coupling coefficients within the T sublattice and between the R and T sublattices respectively (T≡3d metal). If the values of the magnetic moments depend on the orientation, the change in ω_s can be given as

$$\Delta\omega_s = (2n_{TT}\mu_T + n_{RT}\mu_R)\Delta\mu_T + n_{RT}\mu_T\Delta\mu_R \quad (3)$$

In the iron compounds mentioned above, n_{RT} is negligible and $\Delta\omega_s$ is determined by the first term in (3). In R–Co compounds with heavy R metals, both interactions give considerable positive contributions to ω_s. A careful neutron diffraction study of $TbCo_5$ showed that at the spin reorientation the values of $\Delta\mu_{Tb}$ and $\Delta\mu_{Co}$ have different signs [12]. Therefore the first and second terms in eqn. (3) cancel each other and we did not detect any $\Delta\omega_s$ in this compound [13]. The same cancellation apparently takes place in $NdCo_5$, Nd_2Co_7, $DyCo_5$ and Tb_2Co_7 [4, 13]. The observed anomaly leads us to suggest that in Tm_2Co_7, at the spin reorientation, $\Delta\mu_{Tm}$ and $\Delta\mu_{Co}$ have the same sign. Such a suggestion can be checked by a neutron diffraction study. We can expect a similar anomaly in the $\omega_s(T)$ dependence at the spin reorientation in Sm_2Co_7.

4. Conclusions

Thermal expansion and magnetization studies of the Tm_2Co_7 compound showed that magnetic ordering is accompanied by positive spontaneous magnetostrictive deformations in the basal plane (λ_a) and along the c axis (λ_c), which at the lowest temperatures reach the values 2.0×10^{-3} and 2.7×10^{-3} respectively. This corresponds to a spontaneous volume magnetostriction $\omega_s = 2\lambda_a + \lambda_c = 6.6\times10^{-3}$. The compound undergoes a second spontaneous magnetic transition, a spin reorientation, from the uniaxial type of magnetic anisotropy above 45 K to a cone of easy axes below this temperature. The Tm atoms on the quasi-cubic sites are considered to be responsible for the spin reorientation, which is explained as being due to magnetoelastic effects. In the easy cone range a large orthorhombic distortion ϵ (up to -3.5×10^{-3} at 5 K) is observed and the value of the γ magnetostriction constant is estimated as $\lambda^{\gamma,2} = -7\times10^{-3}$. An additional volume anomaly $\Delta\omega_s = -1\times10^{-3}$ accompanies the spin reorientation as a consequence of the anisotropy of the magnetic moments of the thulium and cobalt sublattices.

References

1 A. V. Deryagin, N. V. Kudrevatykh and E. N. Tarasov, in *Alloys of Rare and Refractory Metals with Special Physical Properties*, Nauka, Moscow, 1979, p. 142 (in Russian).
2 N. V. Kudrevatykh, A. V. Deryagin, E. N. Tarasov, A. V. Andreev and S. M. Zadvorkin, in *Alloys of Rare and Noble Metals with Special Physical Properties*, Nauka, Moscow, 1983, p. 54 (in Russian).
3 E. N. Tarasov, *Ph.D. Thesis*, Ural State University, Sverdlovsk, 1987 (in Russian).
4 A. V. Andreev, M. I. Bartashevich, A. V. Deryagin, S. M. Zadvorkin and E. N. Tarasov, *Sov. Phys.–JETP, 67* (1988) 771.
5 A. E. Clark, in E. P. Wohlfarth (ed.), *Ferromagnetic Materials*, Vol. 1, North-Holland, Amsterdam, 1980, p. 531.
6 A. V. Andreev and S. M. Zadvorkin, unpublished result, 1984.
7 A. V. Korolev, V. S. Gaviko, N. V. Mushnikov and A. V. Andreev, *Phys. Met. Metall., 69* (2) (1990) 88.
8 A. V. Andreev, M. I. Bartashevich, E. N. Tarasov, T. Goto, M. Yamaguchi, *Physica B.*, submitted for publication.
9 A. V. Andreev, A. V. Deryagin, S. M. Zadvorkin, V. N. Moskalev and E. V. Sinitsyn, *Phys. Met. Metall., 59* (3) (1985) 57.
10 A. V. Andreev, F. R. de Boer, T. H. Jacobs and K. H. J. Buschow, *Physica B, 175* (1991) 361.
11 A. V. Andreev, A. V. Deryagin, S. M. Zadvorkin and S. V. Terentiev, *Sov. Phys.–Solid State, 27* (1985) 987.
12 A. N. Pirogov, V. V. Kelarev, A. S. Ermolenko, V. V. Chuev, S. K. Sidozov, A. M. Artamonova, *Sov. Phys.-JETP, 56* (1982) 804.
13 A. V. Andreev, A. V. Deryagin and S. M. Zadvorkin, *Sov. Phys.–JETP, 58* (1983) 566.