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PHASE TRANSITIONS INDUCED IN $HoCo_3Ni_2$ SINGLE CRYSTALS

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The magnetic studies of temperature and field induced phase transitions were performed on single crystals of $HoCo_3Ni_2$ compound. The rotational-type spin reorientation was found between $T_{SR1} = 160$ K and $T_{SR2} = 200$ K. In the vicinity of T_{SR1} two different field induced transitions were observed: the first order moment reorientation type transition in the basal plane and the spin reorientation from the easy plane to the c-axis with simultaneous increase in spontaneous magnetization. The intersublattice molecular field coefficient as well as the magnetization anisotropy of Ho sublattice were determined. The observed magnetic behaviour was analysed within the framework of the spin-reorientation model, taking into account the change of the intrinsic states of rare-earth ions caused by their huge anisotropy energy. The thermal variation of the anisotropy constants of the studied compound is also presented.

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1. Introduction

In the past years considerable efforts have been made to explain anomalous temperature and field dependencies of the magnetization in $R(Co,T)_5$ (where T = Ni, Cu) intermetallics with heavy rare-earth elements (R) [1–4]. Extremely large magnetocrystalline anisotropy comparable with the exchange energy, together with the competition between anisotropies of both magnetic sublattices existing in Pr, Nd, Tb, Dy, and Ho compounds leads to many peculiarities, e.g., spin-reorientation transition (SRT), noncollinearity of the magnetic structure, and negative jump of the spontaneous magnetization during the reorientation process. The substitution of cobalt by nickel is often used in investigation of magnetic phase transitions in these compounds. Such a replacement allows to change both the compensation temperature and the temperature range of the SRT.

In the paper the investigations of temperature and field induced phase transitions in $HoCo_3Ni_2$ single crystals are presented. Some magnetic properties of $HoCo_3Ni_2$ compound have already been reported [5, 6]. However, the results obtained in both works on polycrystalline samples are not fully consistent. It especially concerns the magnitude of the rare-earth anisotropy in low temperatures. Moreover, there is no information on magnetic field induced transitions. In the present paper two different kinds of phase transitions induced by the magnetic field at the temperature of the beginning of SRT were observed (spin-flop transition in the basal plane and complete spin reorientation from the easy plane to hexagonal axis). It made possible to determine simultaneously the intersublattice molecular exchange field coefficient n_{HoCo} as well as magnitude of magnetization anisotropy. A quantitative analysis of the obtained results was performed on the basis of spin-reorientation and magnetization anisotropy hypotheses. It allowed us to evaluate the anisotropy of rare-earth sublattice as well as to get good accordance between the experimentally observed and theoretically calculated thermal variation of the spontaneous magnetization of Ho sublattice. The temperature dependence of the anisotropy constants in the range of 4.2–300 K was also determined using the Sucksmith–Thompson procedure.

2. Experiment

The single crystals of the $HoCo_3Ni_2$ compound were grown under argon atmosphere by the Czochralski method, using a high-frequency technique with a water-cooled crucible. The X-ray diffraction patterns confirmed that the ingot obtained was single phase of the $CaCu_5$ type of hexagonal crystal structure. The ingot was sparkly cut into parallelepipeds with dimensions of 5 mm×4 mm×4.5 mm. The magnetization measurements were carried out by means of ballistic method in steady fields up to 70 kOe. The field was applied successively parallel to the a[100], b[120], and c[001] crystallographic axes of the ortohexagonal cell. The magnetic isotherms were measured in the temperature range of 4.2–300 K. Some additional magnetization measurements in fields up to 50 kOe and in the temperature range 165–205 K were performed with the SQUID magnetometer. This was done to examine more precisely the magnetic moment rotation in the SRT range.

3. Analysis and discussion

The temperature dependence of the magnetizations, M_a, M_b, and M_c, measured along three crystallographic axes at effectively zeroth field, is shown in Fig. 1. These results clearly demonstrate that the easy directions are the a-axes below $\approx$ 160 K and the c-axis above $\approx$ 200 K. Between indicated temperatures the direction of easy magnetization rotates continuously in the a–c plane. The temperature dependence of the angle Θ between the easy direction and the c-axis is given in Fig. 2. The saturation magnetization and the angle Θ were calculated from the following relations: $M_S = (M_a^2 + M_c^2)^{1/2}$, $\sin\Theta = M_a/M_S$ or $\cos\Theta = M_c/M_S$. The above described behaviour of the easy axis is the result of the competition

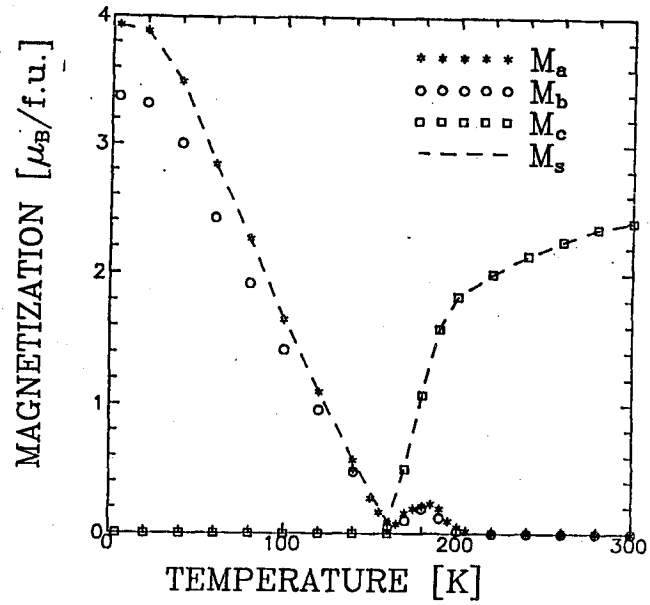

Fig. 1. Temperature dependence of magnetizations measured along main crystallographic axes (M_a, M_b, and M_c) in $HoCo_3Ni_2$ single crystal.

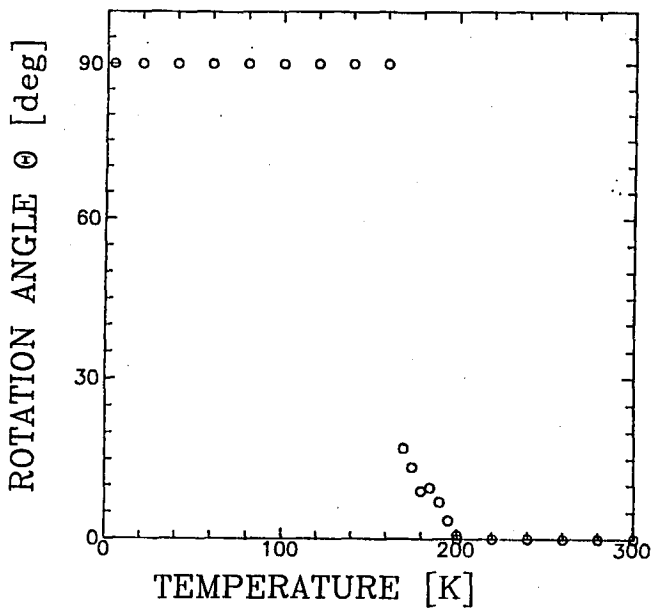

Fig. 2. Temperature induced rotation of spontaneous magnetization in the a–c plane of $HoCo_3Ni_2$ single crystal (Θ is the angle between easy direction and c-axis).

between anisotropies of both magnetic sublattices. It can be analysed by minimizing the expression for the anisotropy energy of hexagonal system. In the case of collinear sublattice moments this energy is given as follows:

$$E_A = K_1 \sin^2\Theta + K_2 \sin^4\Theta + K_3 \sin^6\Theta + K_4 \sin^6\Theta p \cos 6\phi, \quad (1)$$

where $K_i = K_i^{Ho} + K_i^{Co}$ stands for anisotropy constants, Θ and ϕ are the polar and azimuthal angles of the effective magnetization with respect to the [001] and [100] crystallographic directions, respectively. Nickel is practically non-magnetic in RT_5 compounds, because its $3d$ band is completely filled up by the sd electrons of the rare-earth metal. Simultaneously, the magnetic interactions due to rare-earth sublattice are too weak (except at very low temperatures) to induce a magnetic moment of the nickel atoms [6].

It was found that the magnetization compensation of the both sublattices occurs at $T = 160$ K, i.e. exactly at the beginning of the spin-reorientation range. Another characteristic feature of the temperature dependence of spontaneous magnetization is its sharp jump in narrow SRT region. The value of M_S at the beginning of the reorientation range ($T_{SR1} = 160$ K) is smaller than at its end ($T_{SR2} = 200$ K) by 1.75 μ_B/f.u. Such steep change of M_S cannot be attributed only to the temperature decrease in magnetization of R sublattice according to the Brillouin function. The observed jump could be explained by the existence of anisotropy of the spontaneous magnetization of both magnetic sublattices. Such effect was reported earlier in RCo_5 compounds with R = Dy, Tb [7]. In order to obtain deeper insight into this effect the field induced phase transitions occurring in $HoCo_3Ni_2$ single crystals were closely studied.

At low temperatures $T < T_{SR1}$ the spontaneous magnetization lies in the basal plane. The magnetic moment is strongly stabilized around one of the easy a-directions, when the in-plane, sixfold anisotropy K_4 is large. The external magnetic field, applied along the a- or b-axes, produces only a small rotation of ferrimagnetic moment connected with slight deviations of sublattice moments from their antiparallel alignment. This behaviour reflects the fact that exchange and anisotropy energies are comparable (as it is shown later). Similar situation occurs for the magnetic field parallel to the c-axis. In this case the ferrimagnetic moment is insignificantly deflected away from the easy plane. This deflection is strongly limited by basal plane anisotropy, which is expressed as $K_\perp = -(K_1 + 2K_2 + 3K_3)$. In both cases the deflection becomes larger as temperature approaches T_{SR1}, because both K_4 and $|K_\perp|$ decrease distinctly with the increase in temperature. In the vicinity of the compensation point also the deviation of sublattice moments from their antiparallel alignment becomes significant.

At temperature $T > T_{SR2}$ the applied magnetic field produces similar changes in the sublattice moments arrangement, i.e. the rotation and induced noncollinearity. There were observed no differences of the magnetic isotherms obtained in fields applied along the a- and b-axes. It indicates that sixfold anisotropy is negligible in this temperature range.

Two different kinds of field induced phase transitions were observed at the temperatures close to the compensation point. They were the most distinct at $T = 160$ K, where the compensation point and the beginning of the SRT coincide ($T_{SR1} = T_{comp}$). The magnetization curves measured at $T = 160$ K along the a, b

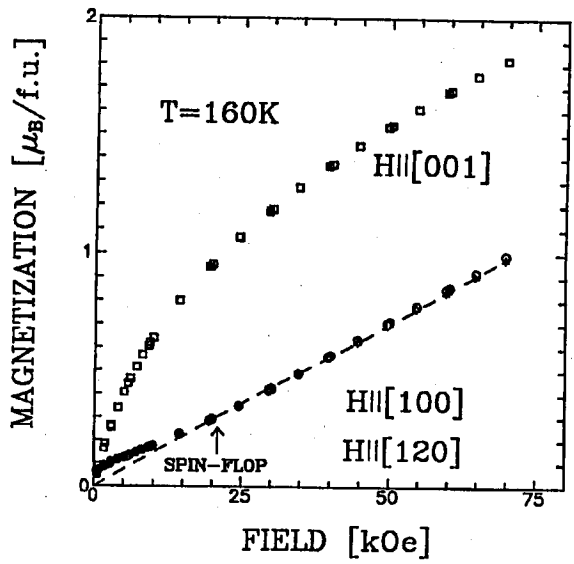

Fig. 3. Magnetic isotherms of $HoCo_3Ni_2$ single crystal along the *a*-, *b*- and *c*-axes at compensation point ($T_{comp} = T_{SR1}$).

and *c* crystallographic axes are shown in Fig. 3. Two different cases can be distinguished:

1) Magnetic field in the basal plane.

In the field lower than 20 kOe the character of magnetization curve is determined by a small noncollinearity of sublattice-moments arrangement. The ferrimagnetic moment can easily rotate, because the sixfold anisotropy is negligible at this temperature. Therefore, it orients itself along the external magnetic field. The small canting of ferrimagnetic structure is simultaneously induced. It increases gradually with the field growth. The characteristic increase in the slope of magnetization curve appears in the field of about 20 kOe. It is interpreted as the first order moment reorientation (FOMR) transition. The competition between magnetostatic and exchange energy leads to flopping of magnetic structure from the direction parallel to the applied field to the perpendicular one, with simultaneous canting of the sublattice moments. The stability region of this new arrangement is bounded by two critical fields [4, 8]:

$$H_{1,2}^{crit} = n_{RT} \cdot |M_R \mp M_T|, \tag{2}$$

where n_{RT} is the intersublattice molecular exchange coefficient. In this region the susceptibility is equal to $1/n_{RT}$. The precise determination of the intersublattice molecular field coefficient from the slope of the magnetization curve above 20 kOe gives $n_{HoCo} = 4.78\ \mathrm{K}/\mu_B^2$.

The FOMR-type transition was also observed in the temperature range 140–180 K. The critical field H_1^{crit} increases significantly with the temperature going away from T_{SR1}. It is worth to stress that below T_{SR1} the FOMR-type tran-

sition occurs in the basal plane, whereas above this temperature a flopping of a cone-like structure, existing in SRT range, takes place.

2) Magnetic field parallel to the c-axis.

In this case the magnetization curve demonstrates the anomalous field dependence. The most striking feature is the large value of the magnetic moment induced by low field at the compensation point. This effect can be mainly attributed to the magnetization anisotropy of Ho sublattice. It can be proved that at the beginning of the SRT region $K_{\perp} = 0$ in HoT_5 compounds. Hence, even a low magnetic field applied along c-axis can easily deflect the magnetic moment from the basal plane. Three processes occur simultaneously under action of this field: the rotation of M_S, the change of its magnitude, and the canting of ferrimagnetic structure.

The magnetic moment of Ho sublattice decreases during rotation towards the c-axis [6, 9]. Therefore, its basal-plane anisotropy is also reduced, which promotes further rotation. The magnetization anisotropy of the Co sublattice is smaller than that of the Ho sublattice [10]. The magnetic moment of Co sublattice increases during the rotation from the basal plane to the c-axis, so its axial anisotropy also increases. Therefore, the field applied parallel to the c-axis induces the transition with rotation of magnetic structure from the basal plane to the c-axis and with the simultaneous change of modulus of magnetization vector.

As it is seen in Fig. 3, this rotation is complete in the field of about 4 T, when the curvature of magnetization curve disappears. The further, linear increase in induced magnetic moment is mainly attributed to the canting of rare-earth and cobalt sublattice moments. Above the field of 4 T this isotherm is practically parallel to that obtained for $H \parallel a$. Therefore, the magnetization anisotropy in $HoCo_3Ni_2$ at 160 K can be directly determined from the distance between both magnetic isotherms in the fields greater than 4 T. The obtained value of magnetization anisotropy, $\Delta M(160\,\mathrm{K}) = M_c(160\,\mathrm{K}) - M_a(160\,\mathrm{K})$, is equal to 0.85 μ_B/f.u.

It is interesting to compare the magnetization anisotropy values obtained both from field induced phase transitions and from temperature induced ones. Precise calculations were done using the theory of Yermolenko et al. [9] and taking into account the rearrangement of energy levels of rare-earth ion under influence of the magnetic anisotropy of the R sublattice. If the mixing of the R-ion states is negligible, this theory gives the following relations for the free energy of RT_5 compound and for the temperature dependence of the magnetization of the rare-earth sublattice:

$$F = -I_{HoCo}\cos(\Theta_{Ho} - \Theta_{Co}) + k_{Ho}\cos^2\Theta_{Ho} - k_{Co}\cos^2\Theta_{Co}, \tag{3a}$$

$$\langle m^l\rangle = \frac{\sum_{m=-J}^{J} m^l \exp\{[n_{HoCo}M_{Co}(T)mA + (1/2)K_{Ho}m^2B](1/k_BT)\}}{\sum_{m=-J}^{J} \exp\{[n_{HoCo}M_{Co}(T)mA + (1/2)K_{Ho}m^2B](1/k_BT)\}}, \tag{3b}$$

$$A = \cos(\Theta_{Ho} - \Theta_{Co}), \quad B = 1 - 3\cos^2\Theta_{Ho},$$

$$I_{HoCo} = N_{Ho}n_{HoCo}M_{Co}(T)\langle m\rangle,$$

$$k_{Ho} = (1/2)N_{Ho}K_{Ho}[3\langle m^2\rangle - J(J+1)], \tag{3c}$$

where Θ_{Ho} and Θ_{Co} are the angles between the c-axis and corresponding sublattice moments, n_{HoCo} is the parameter of intersublattice exchange, m is a projection of the Ho-ion moment on the direction of the Ho-sublattice moment; k_{Ho} and k_{Co} are the anisotropy constants per formula unit for both magnetic sublattices, K_{Ho} is the microscopic anisotropy constant per ion of Ho. N_{Ho} stands for the number of unit cells per unit volume being equal to 1.21×10^{22} cm^{-3} [11].

At first the temperature variation of holmium sublattice magnetization, $M_{Ho}(T)$, was evaluated under the assumption of collinear moment configuration. The following expression was used:

$$M_{Ho}(T) = |M_S(T) \pm M_{Co}(T)[1 - p(T)\sin^2\Theta_{Co}]|, \tag{4}$$

where p is the magnetization anisotropy of cobalt sublattice, the signs "+" and "–" refer to temperatures below and above T_{comp}, respectively. We assumed $M_{Co}(T)$ and $p(T)$ to have the same character as in $YCo_{3.5}Ni_{1.5}$ [12], taking into account the difference in stoichiometry. The calculated $M_{Ho}(T)$ dependence is presented in Fig. 4. The value of M_S extrapolated to $T = 0$ K is equal to 9.22 μ_B/ion.

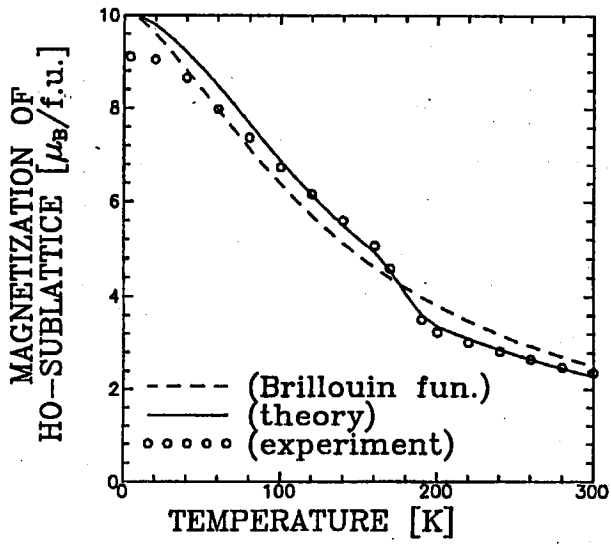

Fig. 4. Temperature dependence of the Ho-sublattice magnetization in $HoCo_3Ni_2$ single crystal. The circles represent experimental points, the solid line shows calculated dependence obtained from relation (3b) for $K_R = 1.5$ K. The dashed line is the Brillouin function.

This value is the same as reported in [6], but a little smaller than the single-ion value $gJ\mu_B = 10\mu_B$. This difference can be attributed to limited quenching of the magnetic moment of holmium by the crystal field.

In the second step the dependence $M_{Ho}(T)$ was calculated on the basis of formula (3b). The n_{HoCo} constant was taken from the spin-flop transition experiment, and the same Θ values as in Fig. 2 were used. Therefore, there was only

one free parameter K_{Ho}. The best fitting of $M_{Ho}(T)$ to the experimental data was assured by $K_{Ho} = 1.5$ K. This value of K_{Ho} is intermediate between those reported in [5] and [6]. For comparison, the experimental and calculated dependences $M_{Ho}(T)$ are shown in Fig. 4. To emphasize the influence of Ho-sublattice anisotropy on its magnetization dependence, the Brillouin function has been also added (dashed line). It is evident from Fig. 4 that the magnetization anisotropy cannot be neglected. The value of the $\Delta M(160\ \text{K}) = 0.85\ \mu_B$/f.u. determined directly from the experiment agrees quite well with $\Delta M_S(160\ \text{K}) = 0.94\ \mu_B$/f.u. obtained theoretically by above fitting procedure.

Subsequently, we used the determined values of intersublattice exchange field parameter n_{HoCo} and microscopic anisotropy constant K_{Ho} to evaluate the macroscopic intersublattice exchange and anisotropy constants I_{HoCo}, k_{Ho} at 0 K. The relationships between these parameters are as follows [6]:

$$I^0_{HoCo} = (z_1 + z_2)(1 - x)n_{HoCo}J, \tag{5a}$$

$$k^0_{Ho} = N_{Ho}K_{Ho}J(J - 1/2), \tag{5b}$$

where $z_1 = 6$, $z_2 = 12$ denote numbers of R-ion magnetic nearest neighbours in 2(c) and 3(g) sites, respectively; $x = 0.4$ is the concentration of nickel in investigated $Ho(Co_{1-x}Ni_x)_5$ compound. As could be expected from magnetic measurements described earlier, I^0_{HoCo} and k^0_{Ho} are of the same order of magnitude: 68.96×10^7 erg/cm^3 and 15.03×10^7 erg/cm^3, respectively. The agreement between above results and those reported earlier [5, 6] seems to be quite reasonable.

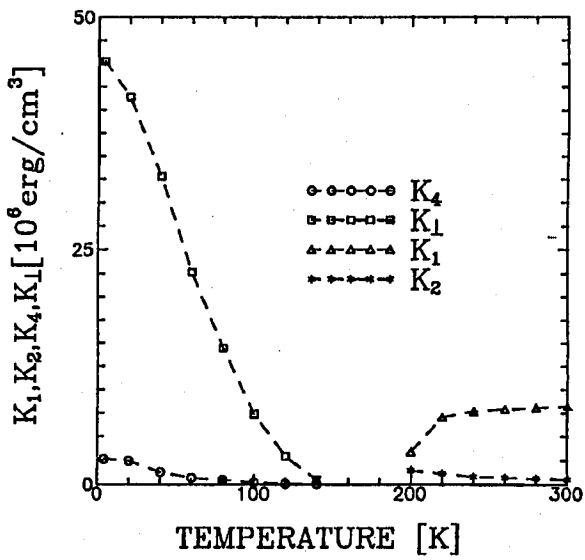

Fig. 5. Effective anisotropy constants K_1, K_2, $K_\perp$ and K_4 versus temperature.

Experimental magnetic isotherms made it also possible to evaluate the temperature dependence of anisotropy constants by minimizing the free energy of

ferrimagnetic structure in the external magnetic field $\boldsymbol{H}$:

$$E = E_A - \boldsymbol{M}_S \cdot \boldsymbol{H}. \tag{6}$$

where E_A denotes the anisotropy energy of hexagonal structure given by Eq. (1). This method, as applied to ferromagnetic systems in order to determine first and second anisotropy constants K_1, K_2, is often referred to as the Sucksmith–Thompson procedure [13]. The temperature dependencies of anisotropy constants, obtained with this method, are presented in Fig. 5. Because the canting of magnetic structure neglected in these calculations can lead to a remarkable reduction of magnetic anisotropy in the vicinity of the compensation point, the calculated anisotropy constants should be treated, near T_{comp}, rather as effective anisotropy constants. These anisotropy constants, similarly as those determined from torque measurements [5], are not related simply to the intrinsic magnetocrystalline anisotropy parameters [14].

4. Conclusions

The field and temperature induced phase transitions have been studied in detail for $HoCo_3Ni_2$ single crystal. The important role in these transitions is played by the magnetization anisotropy. The exact value of intersublattice exchange parameter $n_{HoCo} = 4.78\ \mathrm{K}/\mu_B^2$ was determined through analysis of in-plane first order moment reorientation (FOMR) transition. By fitting of temperature dependence of Ho-sublattice magnetization, the second-order microscopic anisotropy constant $K_{Ho} = 1.5$ K/Ho-ion was obtained. It allowed us to determine the macroscopic intersublattice exchange and the anisotropy of Ho sublattice. The thermal variations of effective anisotropy constants from 4.2 K to room temperature showed that values of K_2 and K_4 should not be neglected.

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