High-field magnetization study of a Tm_2Co_{17} single crystal

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Tm_2Co_{17} is a ferrimagnet with $T_C=1170$ K and, at 4.2 K, has a spontaneous magnetic moment $M_s=13.4\ \mu_B$/f.u. Magnetization curves were measured on a Tm_2Co_{17} single crystal along the principal axes in pulsed magnetic fields up to 70 T at 4.2 K. The curve along the easy [001] direction exhibits a distinct anomaly at $\mu_0 H_{cr}=39$ T, where the magnetization exhibits a stepwise rise from M_s to $M_{flip}=40.6\ \mu_B$/f.u. The observed transition from the ferrimagnetic ground state (with $M_s=17\mu_{Co}-2\mu_{Tm}$) to a saturated spin-flip state with parallel orientation of the sublattice moments and $M_{flip}=17\mu_{Co}+2\mu_{Tm}$ is unusual for 3*d*-4*f* intermetallics because it does not proceed via an intermediate angled-sublattice state. Rather, a collinear remagnetization of the Tm sublattice takes place: as the applied magnetic field grows, the Tm moments disorder at first, reaching a fully disordered paramagnetic state at $H=H_{cr}$, then they order magnetically in the opposite sense.

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I. INTRODUCTION

Tm_2Co_{17} belongs to the "2-17" series of *R*-*T* intermetallic compounds (*R* is a rare-earth and *T* is one of the late 3*d* transition metals Fe, Co, and Ni). The *R*-*T* intermetallics, especially the ones with high content of the *T* metal, have been extensively studied for several decades all over the world because of their practical importance as high-performance magnetic materials. The magnetic behavior of the *R* sublattice is determined by the 4*f* electrons whereas the 3*d* electrons are responsible for the *T*-sublattice magnetism. The strongest exchange interaction is the 3*d*-3*d* interaction, which determines the high Curie temperature T_C. The exchange interaction between 4*f* electrons is very weak and can be neglected compared to other interactions. The 4*f*-3*d* interaction, although much weaker than the 3*d*-3*d* interaction, is of special importance since by this interaction the strongly anisotropic *R*-sublattice magnetization is coupled to the much less anisotropic *T*-sublattice magnetization. In this way, some of the *R*-*T* compounds exhibit large anisotropy even at room temperature, one of the prerequisites for potential application of ferromagnetic *R*-*T* compounds (with light *R*) as permanent-magnet material.[1–3]

In R_2T_{17} with heavy *R* elements (Gd-Tm), the magnetic moments of the *R* and *T* sublattices are coupled ferrimagnetically. In high magnetic fields, this antiparallel structure will be broken and a forced-ferromagnetic state is expected. Since R_2T_{17} compounds exhibit large magnetic anisotropy, single crystals are strongly desirable for quantitative studies of their magnetism. Many compounds R_2T_{17} have been prepared in single-crystalline form and studied systematically in high magnetic fields, typically up to 35–40 T.[1,2,4] For the majority of these compounds, the preferred moment direction is located in the hexagonal basal plane of the hexagonal crystal structure of the Th_2Ni_{17} type. If a sufficiently large magnetic field is applied along one of the main crystallographic directions in the basal plane, field-induced transitions will occur before the forced-ferromagnetic state is reached. Observation of these transitions, which are primarily based on the interplay between the strength of the applied field and the strength of the *R*-*T* interaction, requires high magnetic fields, in the approximate field range of 20–250 T. Transitions of this type have been found in Ho_2Co_{17} (Ref. 5) and later in several other compounds. There are only three ferrimagnetic R_2T_{17} compounds, Er_2Co_{17}, Tm_2Co_{17}, and Tm_2Fe_{17}, in which the easy moment direction is along the hexagonal *c* axis. Field-induced phase transitions should occur in these compounds as well. Exceptionally, if the anisotropy proves stronger than the intersublattice exchange, an easy-axis ferrimagnet may go over directly to the forced-ferromagnetic state. Such a possibility is not realized in Er_2Co_{17}, where a field-induced transition from the collinear ferrimagnetic structure to an intermediate canted structure has been observed at about 40 T.[6] As the field is further increased, the forced-ferromagnetic state is approached gradually. Compounds with Tm still remain good candidates for finding metamagnetism. So far they have not been studied in sufficiently high fields to observe the transition.

Tm_2Co_{17} has a hexagonal crystal structure of the Th_2Ni_{17} type with two nonequivalent positions for the Tm atoms and four positions for the Co atoms. It is a ferrimagnet with Curie temperature $T_C=1170$ K and, at $T=4.2$ K, it has a spontaneous magnetic moment $M_s=13.4\ \mu_B$/f.u. as determined in measurements on single crystals in which the maximum applied field was 15 T and no field-induced transition was observed.[7] In this work, we present and discuss the magnetization curves at 4.2 K along the principal axes of a Tm_2Co_{17} single crystal in pulsed magnetic fields up to 70 T.

II. EXPERIMENTAL

An ingot of Tm_2Co_{17} was prepared by arc melting in Ar atmosphere. The purity of the constituting metals was

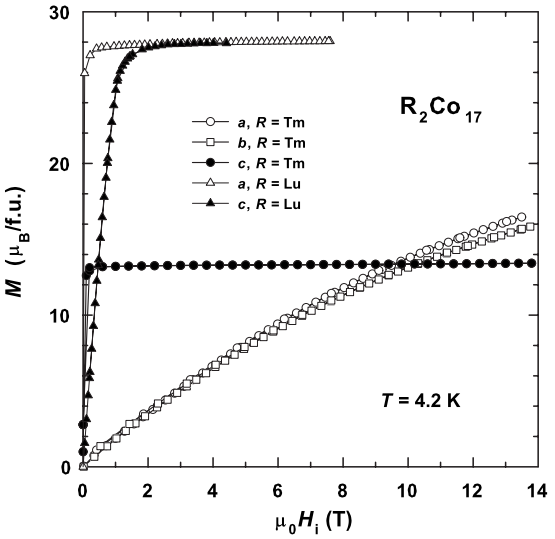

FIG. 1. Comparison of the magnetic isotherms of Tm_2Co_{17} and Lu_2Co_{17} single crystals, measured at $T=4.2$ K in steady magnetic fields applied along the principal axes.

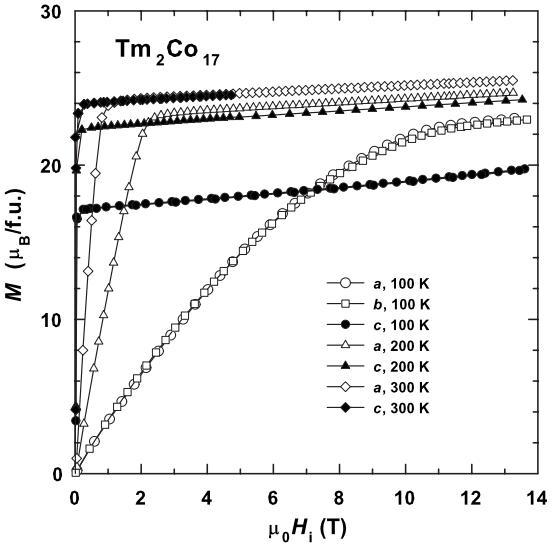

FIG. 2. Temperature evolution of the magnetic isotherms of a Tm_2Co_{17} single crystal, measured in steady fields applied along the principal axes.

99.99% for Co and 99.8% for Tm. Pieces of the ingot were remelted and slowly cooled in a resistance furnace with varying temperature gradient. For the extraction of a single crystal, grains larger than 2 mm were selected. Their single-crystalline state was checked and they were oriented for measurements by backscattering Laue patterns. The lattice parameters $a=828.1$ pm, $c=809.8$ pm agree with reported values.[8]

The magnetization curves were measured at $T=4.2-300$ K in fields up to 14 T along the principal axes of the single crystals using a PPMS-14 magnetometer (Quantum Design). All magnetization curves presented in this paper have been corrected for the demagnetization field. At 4.2 K, the magnetization measurements of Tm_2Co_{17} were extended up to 70 T using a nondestructive pulsed-field magnet with a pulse duration of 6 ms at the Megagauss Laboratory of the Institute for Solid State Physics of the University of Tokyo. The magnetization was detected by an induction method with a standard pick-up coil system. Additional measurements in a 20-ms-pulse field ranging up to 60 T and directed along the c axis of the crystal were performed at the Dresden-Rossendorf High-Field Laboratory at $T=4.2$ and 1.4 K.

III. RESULTS AND DISCUSSION

Figure 1 shows the magnetization curves of a Tm_2Co_{17} single crystal at 4.2 K in steady magnetic fields applied along the [100] (a axis), [120] (b axis), and [001] (c axis). One can see that the c axis is the easy-magnetization direction and that the spontaneous magnetization M_s amounts to 13.4 μ_B/f.u. For comparison, the corresponding magnetization curves for a Lu_2Co_{17} single crystal (taken from Ref. 9) are also shown. The b-axis curve of Lu_2Co_{17} coincides with the a-axis curve and is not shown in Fig. 1. Since Lu is a nonmagnetic R element, the magnetic properties of Lu_2Co_{17} can be considered to represent the Co-sublattice contribution to the magnetization of Tm_2Co_{17}.

The magnetic anisotropy of Lu_2Co_{17} is much weaker than that of Tm_2Co_{17}, and, also, the types of anisotropy are different. The easy-magnetization axes of Lu_2Co_{17} are located in the basal plane and the first anisotropy constant K_1 determined by the Sucksmith-Thompson method[10] equals -0.57 MJ m^{-3}. The K_1 value of Tm_2Co_{17} being determined by the same method is 2.6 MJ m^{-3}. This already clearly shows the dominating Tm-sublattice contribution to the total anisotropy. However, because the hard-direction magnetization curves of Tm_2Co_{17} do not saturate at the M_s value but intersect the easy-axis curve with increasing magnetization, the Sucksmith-Thompson method is evidently nonapplicable to this compound.

A small but visible difference in the magnetization curves of Tm_2Co_{17} along the a and b axes indicates that there is some anisotropy within the basal plane. In general, however, the hard-direction magnetization curves of highly anisotropic materials can be strongly influenced by a nonperfect quality of the crystal or by slight misorientation. The intrinsic character of the observed in-plane anisotropy in Tm_2Co_{17} is demonstrated by the fact that it disappears at elevated temperatures (Fig. 2). Already at 100 K, the a- and b-axes curves coincide (for this reason, the b curves at higher temperatures are not shown in Fig. 2).

The crossing of the magnetization curves along the easy axis and hard axis shows that the magnetization process along the hard axis is not a coherent rotation of both oppositely aligned sublattices but includes also a field-induced noncollinearity of the two sublattices. This means that the K_1 value determined by the Sucksmith-Thompson method is underestimated. Such a crossing, occurring at 4.2 K at 10 T, is seen at 100 K (at 7 T) and 200 K (2.3 T) as well (Fig. 2). At these temperatures, saturation of the magnetization along the hard direction is reached at fields above the crossing and, due to the field-induced noncollinearity of the sublattice mo-

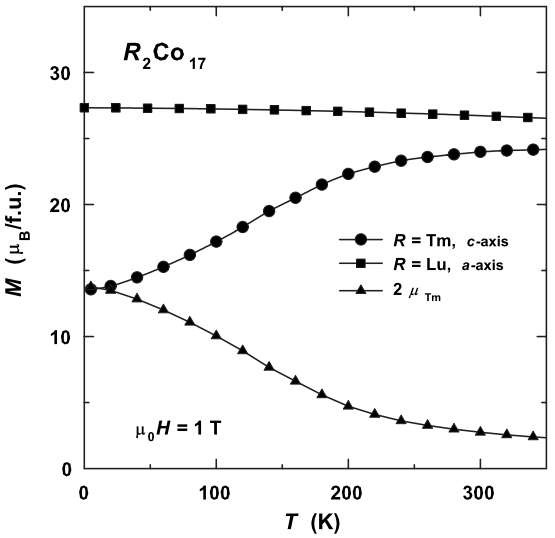

FIG. 3. Temperature dependence of the magnetization of Tm_2Co_{17} and Lu_2Co_{17} single crystals in a field of 1 T applied along the easy-magnetization axis. The contribution of the Tm sublattice is also shown.

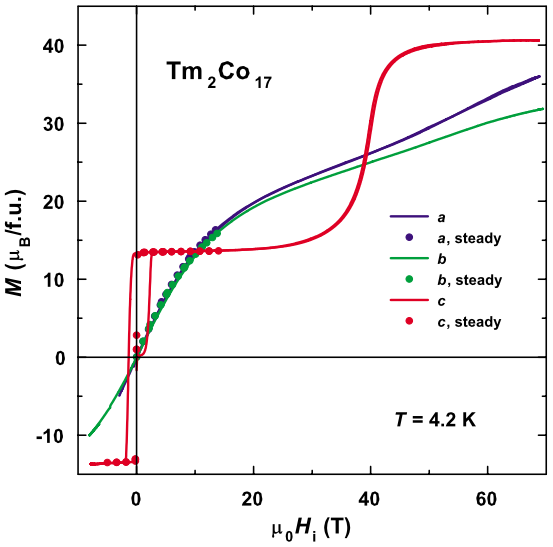

FIG. 4. (Color online) Magnetization curves of a Tm_2Co_{17} single crystal, measured at $T=4.2$ K in pulsed fields applied along the principal axes. Symbols represent the steady-field data.

ments, the saturation magnetization value is larger than along the easy axis where the sublattice moments remains collinear and antiparallel. At 300 K, this difference vanishes which means that the noncollinearity disappears. The low-temperature contribution of the Tm sublattice to K_1 has been calculated in framework of a single-ion model by extrapolation of high-temperature dependence (above 300 K, where the field-induced noncollinearity is assumed to be absent).[7] At 4.2 K, the K_1 value obtained by such extrapolation is equal to 9 MJ m^{-3}, i.e., more than three times larger than the Sucksmith-Thompson estimate. Therefore, the Co-sublattice contribution (−0.57 MJ m^{-3}) is only a few percent of the total anisotropy and can be neglected. This is not valid, however, at 300 K, where the values of K_1 of Tm_2Co_{17} and Lu_2Co_{17} are comparable (0.42 MJ m^{-3} and −0.15 MJ m^{-3}, respectively).

Figure 3 shows the temperature dependence of the magnetization of Tm_2Co_{17} and Lu_2Co_{17} measured in an applied field of 1 T along the easy axis of each compound. At lower temperatures (less than 0.3–0.4 T_C), the magnetization is practically equal to the spontaneous magnetization M_s. The difference of the spontaneous magnetizations of Lu_2Co_{17} and Tm_2Co_{17} can be assigned to the Tm-sublattice magnetization in the latter compound. This yields at $T=4.2$ K: $M_{Tm}=2\mu_{Tm}=13.8\mu_B$, which corresponds well to the magnetic moment of a free Tm^{3+} ion, $\mu_{Tm}=g_J J\ \mu_B=7\mu_B$ ($g_J=7/6$ is the Landé factor and $J=6$ is the total angular momentum). This is good evidence of a collinear antiparallel arrangement of the Tm- and Co-sublattice moments in Tm_2Co_{17}. However, one should keep in mind that the direction of the magnetic moment of the Co sublattice in Tm_2Co_{17} and Lu_2Co_{17} is different and an uncertainty of about $0.2\mu_B$ for the μ_{Tm} value may exist for this reason. The Tm moment decreases rapidly with increasing temperature but even $2\mu_{Tm}\approx 2\mu_B$ (at $T=300$ K) is enough to provide the uniaxial anisotropy which overcomes the easy-plane anisotropy of the Co sublattice with $M_{Co}=17\mu_{Co}\approx 26\mu_B$.

Figure 4 presents the magnetization curves along the principal axes measured at 4.2 K in pulsed fields up to 70 T. A large magnetization rise around a critical field $\mu_0 H_{cr}=39$ T (determined as the inflection point of the curve) is observed in fields applied along the c axis. The anomaly has wide "tails" before and after the steep part and practically lacks hysteresis. Figure 5 shows fits of the c-axis data the following expression,

$$M = M_{Co} + 2\mu_{Tm} B_6\left(\mu_{Tm}\mu_0 \frac{H - H_{cr}}{kT}\right), \qquad (1)$$

where $B_6(x)$ is the Brillouin function for $J=6$, $M_{Co}=27.0\ \mu_B$/f.u., $\mu_{Tm}=6.8\mu_B$, and $\mu_0 H_{cr}=39$ T. In Eq. (1) the Tm sublattice is regarded as a paramagnet experiencing an external magnetic field H and a molecular field H_{cr} from the Co sublattice, whose magnetization is parallel to $\boldsymbol{H}$ and fully saturated. The crystal field on Tm and any Tm-Tm exchange are neglected. Despite the simplifications, Eq. (1) is in no unreasonable agreement with experiment, even when $T=4.2$ K is used, which is the nominal starting temperature of the sample before the high-field pulse. [It should be noted that the pulsed-field magnetization process is not an isothermal one, as assumed in Eq. (1), but is rather akin to an adiabatic process.] The agreement is much better if the temperature in Eq. (1) is set to a higher value, $T=6$ K, see the dashed line in Fig. 5. It is not clear at present whether this is due to a real magnetocaloric effect or is a result of the approximations in Eq. (1). It is apparent though, that the shape of the central part of the curve—provided our interpretation of it is correct—should be sensitive to temperature. To verify this point, we remeasured the c-axis curve at $T=4.2$ and 1.4 K at the Dresden-Rossendorf High-Field Laboratory, where a maximum field of 60 T was available. The 60 T data at $T=4.2$ K coincide well with those taken in the 70 T field (see the upper panel in Fig. 5). A slightly sharper shape of the curve in the former case corresponds to the lower maximum

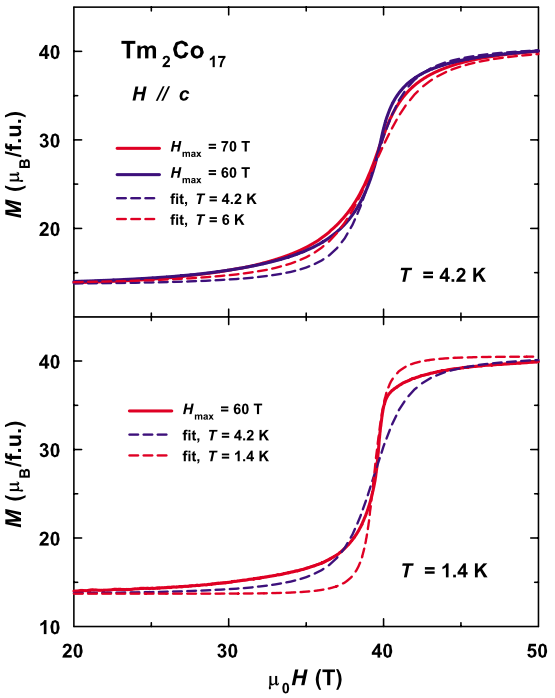

FIG. 5. (Color online) Magnetization curves along the c axis. Upper panel: solid lines are experimental data at $T=4.2$ K in pulses with a maximum field of 70 and 60 T, dashed lines are fits to Eq. (1). Lower panel: solid line is an experimental curve at $T=1.4$ K in a pulse with a maximum field of 60 T, dashed lines are fits to Eq. (1).

field with the longer pulse duration and therefore, to a smaller magnetocaloric effect. The curve at $T=1.4$ K (lower panel) is considerably sharper than the one at $T=4.2$ K and its maximum slope is well reproduced by Eq. (1) with $T=1.4$ K. The strong influence of temperature on the shape of the rising part of the curve confirms our supposition that the magnetization in the c direction proceeds via continuous paramagnetic remagnetization of the Tm sublattice. Coherent magnetization rotation can be ruled out; if it were the case, the broadening of the transition would have to be ascribed to other reasons, such as imperfection of the sample shape and/or composition. The latter mechanisms are (i) essentially independent of temperature and (ii) grossly insufficient to account for the observed transition width.

Thus, we associate the steep rise in the magnetization curve along the c axis with paramagnetic remagnetization of the Tm sublattice. In this process $\boldsymbol{M}_{\mathrm{Tm}}$ remains collinear with $\boldsymbol{M}_{\mathrm{Co}}$ and $\boldsymbol{H}$, which is a sign of strong single-ion anisotropy of Tm. Such a continuous transition between a ferrimagnetic ground state and a ferromagnetic high-field state—without any intermediate canted-sublattice phases or phase transitions—is rare in Co-rich intermetallics. Its most unusual aspect is the notion that an applied magnetic field of 39 T makes the initially saturated Tm sublattice fully disorder.

To verify our interpretation of the anomaly observed when $\boldsymbol{H}\|\boldsymbol{c}$, let us now estimate H_{cr} from the magnetization curves taken when $\boldsymbol{H}\perp\boldsymbol{c}$. Limiting ourselves to low temperatures, we regard the system as a conjunction of two exchange-coupled sublattices exposed to an applied magnetic field $\boldsymbol{H}$. The energy of the system is presented as follows:

$$E=\lambda\boldsymbol{M}_{\mathrm{Co}}\cdot\boldsymbol{M}_{\mathrm{Tm}}-\boldsymbol{M}_{\mathrm{Co}}\cdot\boldsymbol{H}-\boldsymbol{M}_{\mathrm{Tm}}\cdot\boldsymbol{H}+\text{anisotropy energy}. \tag{2}$$

Here λ is the Tm-Co exchange constant, $\lambda>0$.

According to the above, H_{cr} is just the molecular field on Tm in the absence of any Tm-Tm exchange,

$$H_{\mathrm{cr}}=\lambda M_{\mathrm{Co}}. \tag{3}$$

When $\boldsymbol{H}\perp\boldsymbol{c}$, the magnetization of the Co sublattice does not become parallel to the applied field $\boldsymbol{H}$ at least as long as $\mu_0 H<70$ T. Therefore, the total effective field on Tm, $\boldsymbol{H}-\lambda\boldsymbol{M}_{\mathrm{Co}}$, is never too small whereas, by assumption, the temperature is low. Consequently, M_{Tm} is Eq. (2) may be regarded as a constant, as well as M_{Co}.

According to Eq. (3), in order to evaluate H_{cr}, one needs to know the intersublattice exchange constant λ. This would be readily obtainable if the expression for the energy, Eq. (2), did not contain an unknown anisotropy energy. Then the magnetization curve could be calculated analytically for any direction of applied field, the slope of its middle part being exactly $1/\lambda$.[11] However, in Tm_2Co_{17} the anisotropy energy cannot be neglected, it is what makes the magnetization curve along the $\boldsymbol{c}$ axis step-wise rather than gently sloping. In particular, it is the strong anisotropy of the Tm sublattice that is important; the weaker Co anisotropy may be neglected. Finding λ is still possible because the condition $M=\lambda^{-1}H$ is fulfilled at least at one point of the magnetization curve, namely, where $\boldsymbol{M}_{\mathrm{Tm}}\perp\boldsymbol{H}\|\boldsymbol{c}$. At that point the anisotropy energy reaches its maximum, yet it does not manifest itself in any way because its angular derivative is nil. Therefore,

$$\lambda=\frac{H_{\perp}}{M_{\perp}}, \tag{4}$$

where $H_{\perp}$ and $M_{\perp}$ are the abscissa and the ordinate of the orthogonality point. Now by Eq. (3),

$$H_{\mathrm{cr}}=\frac{M_{\mathrm{Co}}}{M_{\perp}}H_{\perp} \tag{5}$$

and the problem is thus reduced to locating the orthogonality point in the magnetization curve. One of us has recently found the orthogonality magnetization to be the geometric mean of the spontaneous magnetization M_{s} and the magnetization of the forced ferromagnetic (or spin-flip) phase M_{flip},[12]

$$M_{\perp}=\sqrt{M_{\mathrm{s}}M_{\mathrm{flip}}}. \tag{6}$$

So from $M_{\mathrm{s}}=13.4$ μ_{B}/f.u. and $M_{\mathrm{flip}}=40.6$ μ_{B}/f.u., we find $M_{\perp}=23.3$ μ_{B}/f.u. The corresponding abscissa, $\mu_0 H_{\perp}=31.8\pm1.6$ T, is then determined from the experimental data of Fig. 4, as the average value for the two basal-plane curves (with $\boldsymbol{H}\|\boldsymbol{a}$ and $\boldsymbol{H}\|\boldsymbol{b}$). Finally, Eq. (5) yields $\mu_0 H_{\mathrm{cr}}=37\pm2$ T. This estimate agrees well with the value found directly from the experimental magnetization curve along the easy axis $\boldsymbol{c}$, $\mu_0 H_{\mathrm{cr}}=39$ T. The agreement corroborates our interpretation of the observed anomaly as a transition between the ferrimagnetic and ferromagnetic states. One should

note that earlier theoretical calculations yielded for H_{cr} in Tm_2Co_{17} an overestimated value, $\mu_0 H_{cr}=48$ T.[13]

Summarizing, we have studied high-field magnetization curves of an easy-axis ferrimagnet Tm_2Co_{17}. Our most interesting finding is a large rise of magnetization in a field directed along the sixfold axis c at about $\mu_0 H_{cr}=39$ T. It is attributed to a direct ferri-to-ferromagnetic transformation by way of paramagnetic remagnetization of the Tm sublattice. This is a continuous process—at least at the temperature of liquid He—no intermediate canted-spin phases or phase transitions occur and the sublattice moments remain collinear with the applied field. One striking feature of the remagnetization process is that during its first stage, when $H<H_{cr}$, the magnetic field acts against the magnetic order in the Tm sublattice, driving the latter into a fully disordered state at $H=H_{cr}$. It would be of interest to observe the magnetocaloric effect accompanying this process.

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