Magnetic phase transitions in the intermetallic compound Tb_6Al_3Si

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The magnetic properties of a new intermetallic compound Tb_6Al_3Si have been investigated at temperatures in the range 4.2–300 K using magnetic fields up to 240 kOe. The compound was found to be a ferromagnet with $T_N = 89$ K and its magnetic structure exhibited a series of consecutive transformations when the temperature and magnetic field were varied. At low temperatures the compound Tb_6Al_3Si was a metamagnet and the metamagnetic transition in single crystals exhibited an anomalously large hysteresis $\Delta H \to 65$ kOe in the limit $T \to 0$ K. The T–H diagram of Tb_6Al_3Si was plotted. A composition with the formula $Tb_6(Al_{1.23}Si_{0.61})_2$ from the homogeneity range of the Tb_6Al_3Si phase exhibited three magnetic transitions detected by neutron diffraction. The magnetic phase transitions occurring in Tb_6Al_3Si were described assuming independent transitions from the antiferromagnetic to the ferromagnetic phase in the terbium sublattices formed by the atoms in different crystallographic positions.

INTRODUCTION

The majority of ternary intermetallics have crystal structures with several inequivalent positions of the rare-earth ions and, because of the different local magnetocrystalline anisotropies of these positions, the magnetic behavior of the 4f electrons can be quite complex. Investigations of ternary rare-earth compounds with the 3*d* metals[1–3] have shown that in the case of magnetic ordering of the *d*-electron subsystem it is not always possible to reveal the role of each subsystem in the determination of the magnetic properties of such intermetallics. Therefore, it would be desirable to investigate new ternary R–A–B compounds (where R is a rare-earth element) with nonmagnetic A and B ions in order to determine the properties of the 4*f*-electron subsystem.

The Tb–Al–Si system is interesting, because over ten ternary compounds belong to it, but little work has been done on it.[4] Our earlier study[5] of the phase diagram of the system revealed a new ternary intermetallic compound with a stoichiometric composition corresponding to Tb_6Al_3Si. An x-ray structure analysis carried out on Tb_6Al_3Si single crystals established that this phase crystallizes in the tetragonal symmetry (space group $I/4mcm$) with the unit cell parameters $a = 11.581(6)$ Å, $c = 15.039(3)$ Å, and $Z = 8$ (Z is the number of formula units). Moreover, the Tb_6Al_3Si phase of the Tb–Al–Si system has a wide homogeneity region which is basically limited by $Tb_6(Al_{2-x}Si_x)_2$ and $Tb_6(Al_{2-4/3x}Si_x)_2$ solid solutions in the range $x = 0.45$–0.9 (Refs. 5–6). A preliminary investigation[7] of the magnetic properties of Tb_6Al_3Si single crystals showed that at temperatures $T < 100$ K this compound is magnetically ordered and its magnetic structure varies in a complicated manner with the sample temperature.

The aim of the investigation reported below was to study the magnetic state of the ternary intermetallic Tb_6Al_3Si as a function of temperature and magnetic field. The investigation was carried out on polycrystalline and single-crystal samples synthesized as described in Refs. 5 and 6. Our single crystals were platelets with the maximum dimensions $3 \times 2 \times 0.2$ mm and the direction of the tetragonal (C_4) axis coincided with the direction of the normal to the platelet plane. We determined the magnetization in the temperature range 4.2–300 K using static (up to 50 kOe) and pulsed (up to 240 kOe) magnetic fields; the methods were the same as those described in Refs. 8 and 9. The magnetic susceptibility was investigated in the temperature range 4.2–300 K in fields up to 10 kOe employing a PAR M-155 vibrating magnetometer with a low-temperature attachment. Neutron diffraction measurements were carried out using a D1B diffractometer at the Laue–Langevin Institute in Grenoble and a multicounter diffractometer at the Institute of Nuclear Physics, Gatchina.

EXPERIMENTAL RESULTS

Figure 1 shows the temperature dependences of the magnetic susceptibility and its reciprocal [$\chi(T)$, $\chi^{-1}(T)$]

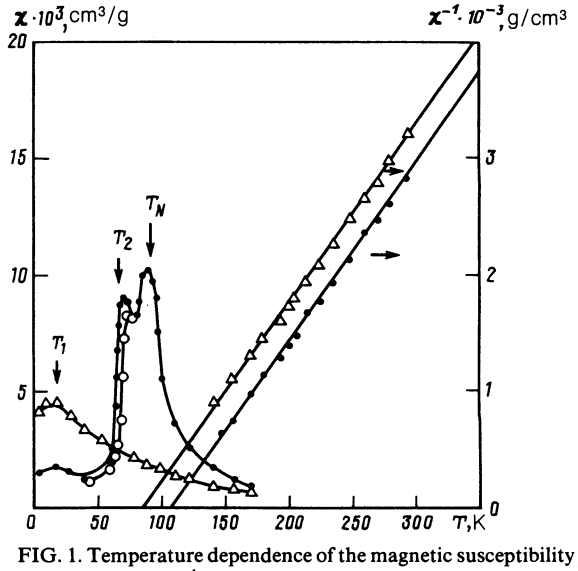

FIG. 1. Temperature dependence of the magnetic susceptibility $\chi(T)$ and of its reciprocal $\chi^{-1}(T)$, obtained in magnetic fields oriented along (●—cooling, ○—heating) and at right-angles (△) to the tetragonal axis of a Tb_6Al_3Si single crystal.

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recorded in a magnetic field 310 Oe oriented parallel ($H_\parallel$) and perpendicular ($H_\perp$) to the tetragonal axis of a Tb_6Al_3Si single crystal. At high temperatures ($T = 120$–300 K) the magnetic susceptibility along either direction was described well by the Curie–Weiss law with an effective magnetic moment $\mu_{eff} = 10 \pm 0.2\mu_B$, which was close to the theoretical value $\mu_{eff} = 9.7\mu_B$ for a free Tb^{3+} ion. The values of the paramagnetic Curie temperature were $\Theta_\parallel = 100 \pm 5$ K and $\Theta_\perp = 61 \pm 5$ K, respectively. At low temperatures in the magnetic field $H_\parallel$ the dependence $\chi_\parallel(T)$ exhibited several maxima at $T_N = 89$ K, $T_2 = 65$–69 K, and $T_1 = 25$ K. Below the temperature of the second maximum, at $T = T_2$ the susceptibility fell strongly, accompanied by a hysteresis ($T_2 = 65$ K during cooling and $T_2 = 69$ K during heating). In the perpendicular direction the susceptibility rose gradually as a result of cooling and exhibited just one maximum in the region of $T = T_1$; moreover, the magnetic susceptibility recorded in the range 4.2–300 K was independent of the direction of the magnetic field in the basal plane of the single crystal. Such behavior of $\chi(T)$ in a weak field suggested a uniaxial anisotropy of Tb_6Al_3Si.

The nature of the magnetization of the intermetallic Tb_6Al_3Si in the magnetically ordered state varied strongly with temperature. Figures 2 and 3 show $M(H)$ isotherms typical of different temperature ranges. We first consider the results of measurements obtained when the magnetic field was directed along the tetragonal axis of a single crystal (represented by continuous curves in Figs. 2 and 3). At low temperatures 4.2–25 K (Fig. 2) the $M(H)$ curves revealed two phase transitions. In low fields ($T = 4.2$ K, $H \approx 26$ kOe) a transition was accompanied by a smooth increase in the magnetization to values $\approx 8\mu_B$ per formula unit ($gJ = 9$ for Tb^{3+}).

A further increase in the magnetic field resulted in an abrupt change in the magnetization with hysteresis in $M(H)$ typical of first-order transitions. At temperatures $T < 8$ K after the first magnetization cycle the sample acquired a residual magnetic moment M_0. The value of M_0 decreased slowly with time (at $T = 4.2$ K after 30 min there was a 10% fall in M_0) and the rate of relaxation of this moment to zero increased rapidly with temperature in such a way that beginning from $T = 8$ K the residual moment was no longer observed. The critical first-order field fell monotonically with increasing temperature and approached zero at the end of the first temperature interval ($T_1 = 25$ K). In the interval 25–50 K the $M(H)$ curves (Fig. 3) exhibited one phase transition of the metamagnetic type. In the next interval 50–69 K there were again two phase transitions induced by the applied magnetic field. However, in this case the metamagnetic transition occurred in weaker magnetic fields and differed from the transition at $T < T_1$ by the size of the change in the magnetization. Finally, in the interval 69–89 K both these transitions became first-order. It should be stressed that although the $M(H)$ dependence obtained in fields $H < 5$ kOe had a positive curvature, at these temperatures there was no residual magnetic moment.

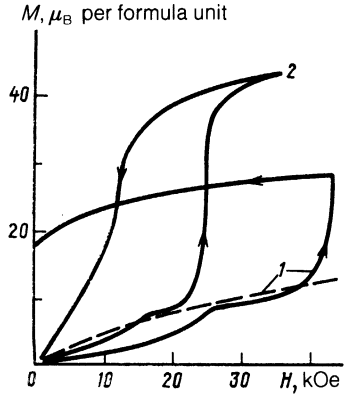

FIG. 2. Magnetization isotherms of a Tb_6Al_3Si single crystal obtained in a magnetic field H directed along (continuous curves) and at right-angles (dashed curve) to the tetragonal axis C_4 recorded in temperature intervals $T < T_1$: 1) $T = 4.2$ K; 2) $T = 16$ K.

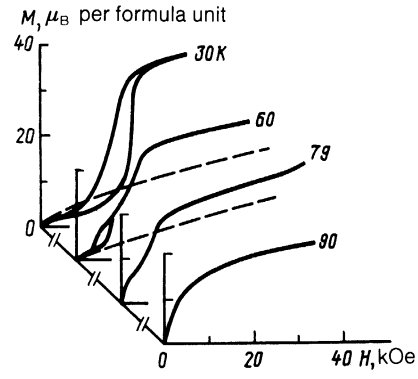

FIG. 3. Magnetization isotherms of a Tb_6Al_3Si single crystal obtained in a magnetic field H directed along (continuous curves) and at right-angles (dashed curves) to the tetragonal axis C_4 recorded in the interval $T_1 < T < T_N$.

The $M(H)$ dependence obtained in a field $H_\perp$ were monotonic (without any singularities) throughout the temperature range $T < T_N$ (dashed curves in Figs. 2 and 3). It should be noted that at $T = 4.2$ K the magnetization in a field $H_\perp \approx 25$ kOe had a tendency to saturation and was comparable in value with $M \approx 8\mu_B$ per formula unit in a field $H_\parallel \approx 25$ kOe. The magnetization in a field $H_\parallel = 40$ kOe at $T = 16$ K was $\approx 43\mu_B$ per formula unit, which corresponded to a parallel orientation of the magnetic moments of five terbium atoms. It should be mentioned also that at $T = 79$ K the dependence $M(H)$ recorded in a field $H_\parallel > 40$ kOe exhibited a nonmonotonic rise of the magnetization.

The number and nature of the phase transitions were determined more accurately by investigating polycrystalline samples in the region of homogeneity of Tb_6Al_3Si. It was found that a change of the relative content of silicon and aluminum in these intermetallics had no qualitative influence on the nature of the magnetic ordering and simply affected the values of the temperatures T_1, T_2, and T_N and the critical fields of the magnetic transitions. We selected a compound $Tb_6(Al_{1.23}Si_{0.61})_2$ for investigation because it showed no magnetic aftereffect; this enabled us to investigate the magnetization of this compound in pulsed magnetic fields. We obtained the results shown in Fig. 4. In fields $H < 100$ kOe the magnetization isotherms of $Tb_6(Al_{1.23}Si_{0.61})_2$ were qualitatively similar to the $M(H)$ dependence obtained for a single crystal in a field $H_\perp$ and they indicated the occurrence of two phase transitions, while

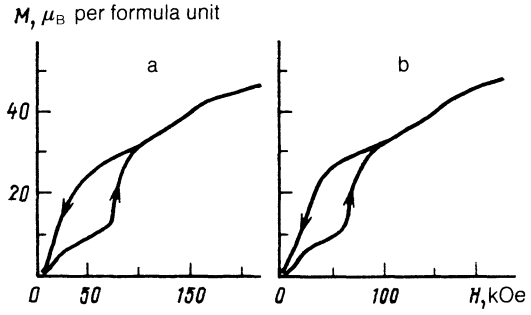

FIG. 4. Dependence $M(H)$ obtained for a polycrystalline sample of $Tb_6(Al_{1.23}Si_{0.61})_2$, recorded in pulsed magnetic fields: a) $T = 4.2$ K; b) $T = 11$ K.

in a field $H \approx 150$ kOe there was a third transition which seemed natural to attribute to the establishment of the parallel orientation of the magnetic moments of all the terbium atoms. We also found that the changes in the magnetization during the first and subsequent transitions were approximately the same. These results indicated that the application of a magnetic field to the compound Tb_6Al_3Si at temperatures $T < T_1$ induced consecutively a series of three phase transitions.

The magnetic state of Tb_6Al_3Si was determined more accurately in the absence of a field by neutron diffraction investigations of a polycrystalline sample of $Tb_6(Al_{1.23}Si_{0.61})_2$ at various temperature. We reproduced in Fig. 5 the neutron diffractograms of the difference spectra (entirely due to the magnetic scattering) of a polycrystalline same of $Tb_6(Al_{1.23}Si_{0.61})_2$, which were typical of three temperature intervals: $T < T_1$ (Fig. 5a), $T_1 < T < T_2$ (Fig. 5b), and $T_2 < T < T_N$ (Fig. 5c). In spite of the large neutron wavelength ($\lambda = 1.387$ Å), we were unable to identify completely these neutron diffractograms. Nevertheless, it was found from Fig. 5 that the magnetic structure of $Tb_6(Al_{1.23}Si_{0.61})_2$ was different in these temperature intervals. The position of the superstructure reflections at each

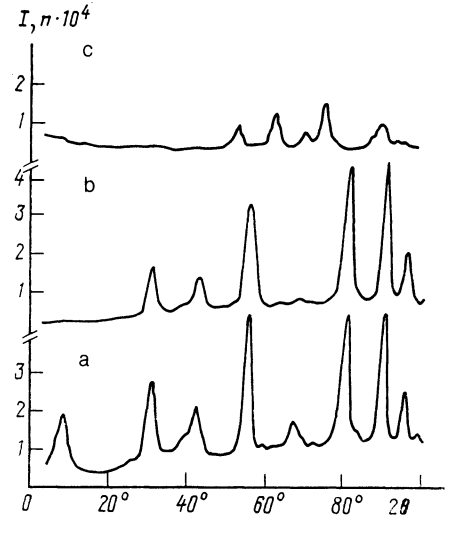

FIG. 5. Difference neutron diffractograms of Tb_6Al_3Si (only fragments are shown), recorded at temperatures 2 K (a), 35 K (b), and 75 K (c).

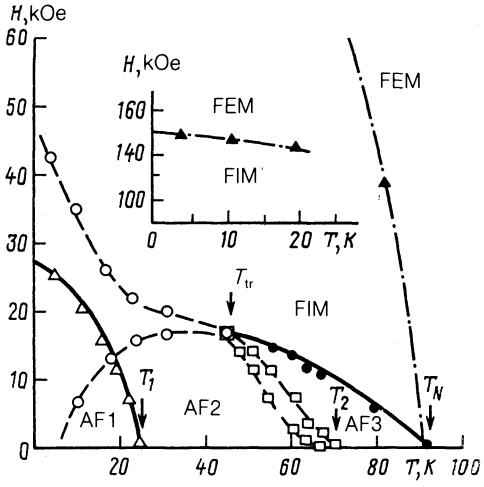

FIG. 6. Phase (H–T) diagram of a Tb_6Al_3Si single crystal recorded for a magnetic field applied along the tetragonal axis. The dashed curves represent the lines of loss of stability of the phases due to transitions of the first order. The chain curve is the tentative FIM–FEM transition line. The inset shows the line of the phase transition from the FIM to the FEM phase for a polycrystalline sample of $Tb_6(Al_{1.23}Si_{0.61})_2$.

temperature could not be described by a magnetic cell commensurate with the crystallographic cell. At 2 K the neutron diffraction patterns of $Tb_6(Al_{1.23}Si_{0.61})_2$ exhibited a system of reflections additional to those observed at 35 K, indicating a weak coupling between the magnetic sublattice formed by these components and the other magnetic subsystems.

DISCUSSION OF RESULTS

These results enabled us to plot the T–H phase diagram of the intermetallic compound Tb_6Al_3Si for a magnetic field directed along the tetragonal C_4 axis (Fig. 6). When temperature was varied in the range where a magnetic order existed in Tb_6Al_3Si, this compound exhibited three magnetic structures, which were incommensurate with the crystal structure. The absence of a spontaneous magnetization suggested that the phases observed in zero field were antiferromagnetic: AF1, AF2, and AF3. The boundaries of these phases in $H = 0$ ($T = 25$, 69, and 89 K) deduced from the magnetization measurements agreed with the temperatures of the phase transitions T_1, T_2, and T_N, respectively, which were deduced from the temperature dependences of the susceptibility $\chi(T)$.

The application of a magnetic field induced two new states: the ferrimagnetic (FIM) and ferromagnetic (FEM), shown in Fig. 6. The temperature dependence of the critical field for the transition from the FIM to the FEM phase for the composition $Tb_6(Al_{1.23}Si_{0.61})_2$, shown as an inset in Fig. 6, enabled us to estimate the magnitude and the change in this field in the case of a single crystal.[3)] The critical field for the FIM–FEM transition in the interval $T < T_1$ was practically independent of temperature and amounted to ≈ 150 kOe, which greatly exceeded both the field for the transition from the AF1 phase (< 25 kOe) and the field at which the stability of the AF2 phase was lost (< 46 kOe). At temperatures 80–89 K the field of the transition to the FEM phase fell strongly and at $T \approx 80$ K became less than 50 kOe. The tentative line of the transition to the FEM phase is represented by the chain curve in Fig. 6.

It is worth noting the unusual nature of the lines representing the loss of stability of the AF2 phase, i.e., the dependence $H_{c1}(T)$, and of the FIM phase, i.e., $H_{c2}(T)$, represented by the dashed curves in Fig. 6: cooling increased greatly the half-width of the hysteresis of the metamagnetic transition $\Delta H_c = (H_{c1} + H_{c2})/2$ and at $T < 8$ K it exceeded the transition field $H_c = (H_{c1} + H_{c2})/2$, which was the reason for the appearance of the residual magnetic moment in this temperature interval. This behavior of the boundaries of the stability of the phases in the case of the metamagnetic transition in the interval $T < T_1$ was in qualitative agreement with the results of theoretical investigations. Calculations of the T–H phase diagrams of a two-sublattice antiferromagnetic of the easy-axis type were reported in Refs. 10 and 11 for the case of a strong uniaxial anisotropy. It was shown there that in the case of such systems when the condition $2\lambda_{11}/(\lambda_{11} - \lambda_{12}) > 0$ is satisfied (λ_{11} and λ_{12} are the intrasublattice and intersublattice exchange interaction constants) we can expect a metastable state after the first magnetization cycle. Therefore, it is difficult to use the theoretical results of Refs. 10 and 11 to obtain any quantitative estimates in the case of Tb_6Al_3Si because of the complex magnetic structure of this compound.

One should mention also the presence of a triple point in the T–H phase diagram at $T_{tr} \approx 50$ K and $H_{tr} \approx 18$ kOe, where three phases (FIM, AF2, and AF3) coexisted. Above T_{tr} a first-order transition took place from the AF2 to the AF3 phase. The critical field of this transition fell rapidly with increasing temperature and vanished in the limit $T \to 69$ K.

In analyzing the properties of Tb_6Al_3Si we should bear in mind that the magnetic atoms in this compound occupy three crystallographically inequivalent positions (Tb1, Tb2, and Tb3) and have very different coordination polyhedra. A special feature of the crystal structure of Tb_6Al_3Si is also the fact that the Tb3 and Tb2 atoms are located in planes between which there are layers of nonmagnetic atoms, whereas the Tb1 atoms form pair clusters located between the magnetic atom planes. The shortest distances r_{Tb-Tb} of the Tb1–Tb1, Tb2–Tb2, and Tb3–Tb3 type obey the inequalities[6]

$$r_{Tb1-Tb1} < r_{Tb2-Tb2} < r_{Tb3-Tb3}.$$

A combined analysis of the dependences $M(H)$ for a Tb_6Al_3Si single crystal and a polycrystalline sample of $Tb_6(Al_{1.23}Si_{0.61})_2$ shows that in the case of Tb_6Al_3Si the AF1–AF2, AF2–FIM, and FIM–FEM phase transitions at $T = 4.2$ K the orientations (per one formula unit) of the magnetic moments of 1, 4, and 1 atoms of terbium, respectively, change. Since the number of the terbium atoms located at the inequivalent sites is also in the ratio 1:4:1, we can assume that Tb_6Al_3Si has three magnetic sublattices of the Tb1, Tb2, and Tb3 atoms, and that each of them has its own characteristic antiferromagnetic ordering, and the ratio of the critical fields at 4.2 K shows that the intrasublattice interactions in these structures are much stronger than the intersublattice interactions. The sequence of the magnetic phase transitions observed in Tb_6Al_3Si can therefore be regarded, in the first approximation, as a series of independent transitions from the AFM to the FEM phase of the terbium sublattices formed by atoms located in different crystallographic positions.

A change in the relative content of silicon and aluminum does not alter the nature of the magnetic ordering in intermetallics of the Tb_6Al_3Si phase, so that the T–H phase diagram shown in Fig. 6 is suitable for a quantitative description of the magnetic behavior of all compositions which have this structure (within the limits of the homogeneity region).

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