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Journal of Alloys and Compounds 408–412 (2006) 58–61

Journal of ALLOYS AND COMPOUNDS

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Yttrium substitutional effects on geometrically frustrated system TbNiAl

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Available online 14 June 2005

Abstract

The magnetic properties of the ternary rare-earth compound TbNiAl with the hexagonal ZrNiAl crystal structure have been discussed in terms of a geometrically magnetic frustration. We have carried out measurements of magnetic susceptibility and magnetization of $Tb_{1-x}Y_xNiAl$ ($0 \leq x \leq 0.3$) polycrystalline samples to study the dilution effect on magnetic properties of TbNiAl. A small substitution of nonmagnetic ions of Y ($x \geq 0.1$) for magnetic ions of Tb stabilizes the ferromagnetic state. This finding suggests that the number of frustrated bonds is strongly reduced by introduction of nonmagnetic Y sites and a dominant ferromagnetic interaction appears instead.

PACS: 75.30.Kz; 75.30.−m; 75.30.Cr

Keywords: Frustration; Antiferromagnetism; $Tb_{1-x}Y_xNiAl$; Magnetic susceptibility; Magnetization

1. Introduction

The equoatomic ternary rare-earth and uranium intermetallic compounds RT_dX and UT_dX (R = rare-earth, T_d = transition metal, X = p-metal, U = uranium) are intensively investigated. Members of this family exhibit a variety of interesting phenomena, such as heavy fermion behavior and geometrical frustration. Especially geometrical frustration leads to a rich and complex behavior for the magnetic ordering. For example, heavy fermion compound CePdAl ($\gamma_0 = 270\,\mathrm{mJ\,mol^{-1}\,K^{-2}}$) with the hexagonal ZrNiAl-type structure as shown in Fig. 1 antiferromagnetically orders below Néel temperature $T_N = 2.7\,\mathrm{K}$ [1,2]. The ordered and disordered moments coexist down to 180 mK at least. The theoretical model including the Kondo screening and the first-nearest neighbor J_1 and second-nearest neighbor J_2 in-plane exchange interactions explained the anomalous magnetic ordering of CePdAl below T_N with $J_1 > 0$ and $J_2 < 0$ [3].

The compounds chosen for the present investigation are ternary rare-earth intermetallic compounds TbT_dAl (T_d = Ni and Pd) with the homologous crystal structure as CePdAl. Magnetic Tb ions are arranged in the basal plane with a triangular coordination symmetry similar to the kagomé lattice. Two of those layers are separated by a nonmagnetic layer, containing T_d and Al atoms. Each Tb ion is connected with four nearest Tb ions and two second-nearest Tb ions, which form a triangle in the basal plane. Both compounds display similar magnetic properties [4,5]. First, they show antiferromagnetically successive phase transitions at T_{N1} and T_{N2} ($T_{N1} = 47\,\mathrm{K}$ and $T_{N2} = 23\,\mathrm{K}$ in TbNiAl, $T_{N1} = 43\,\mathrm{K}$ and $T_{N2} = 22\,\mathrm{K}$ in TbPdAl). Secondly, a strong magnetocrystalline anisotropy along the *c*-axis leads to an Ising-like antiferromagnetic ordering. Thirdly, the amplitude of the ordered moment at some crystallographically equivalent sites is largely reduced between T_{N1} and T_{N2}.

Their peculiar magnetic properties in TbT_dAl have been discussed in terms of a geometrically magnetic frustration. Antiferromagnetic exchange couplings between Tb ions together with the strong magnetocrystalline anisotropy give rise to the formation of geometrical frustration of magnetic mo-

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doi:10.1016/j.jallcom.2005.04.096

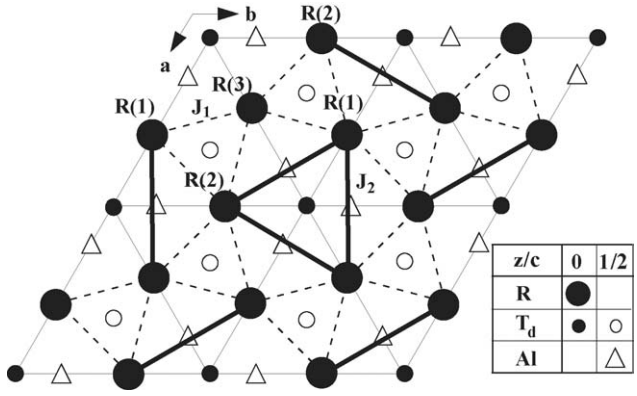

Fig. 1. Crystal structure of RT_dAl (R = rare-earth elements, T_d = Ni, Pd). The broken lines and thick lines represent the nearest neighbor and second-nearest couplings, J_1 and J_2 in the *ab* plane, respectively.

ments. The magnetic interactions to be considered in TbT_dAl are simpler than those in CePdAl because of lack of the Kondo screening effect. So understanding of magnetic properties in TbT_dAl should lead to one in CePdAl.

In order to study the yttrium substitutional effect on magnetic properties of geometrically frustrated system TbNiAl, we have carried out measurements of magnetic susceptibility and magnetization of $Tb_{1-x}Y_xNiAl$ ($0 \le x \le 0.3$) polycrystalline samples. In this paper, we focus on the phase transition from antiferromagnetism to ferromagnetism in $Tb_{1-x}Y_xNiAl$ polycrystalline samples. Surprisingly, a critical field H_c which shows the metamagnetic transition from the antiferromagnetic (AF) state to the field-induced ferromagnetic (FIF) state rapidly disappears in $x \ge 0.1$. A small substitution of nonmagnetic ions of Y for magnetic ions of Tb stabilizes the ferromagnetic (F) ground state instead of the AF ground state. A tentative magnetic phase diagram of $Tb_{1-x}Y_xNiAl$ ($0 \le x \le 0.3$) was described. We will discuss these anomalous magnetic properties by geometrical frustration and competition between AF and F interactions.

2. Experimental

Polycrystalline samples of $Tb_{1-x}Y_xNiAl$ ($0 \le x \le 0.9$) were synthesized by arc-melting stoichiometric mixtures of pure elements (Tb:3N, Y:3N, Ni:4N and Al:5N) in a pure Ar atmosphere. The experiments of X-ray diffraction on the powdered samples were performed by X-ray diffractometer (Rigaku Co. Ltd) at room temperature. Each as-cast sample shows almost a single phase with the hexagonal ZrNiAl-type structure except for a small amount of unknown phases. Annealing at 1000 °C for 72 h could reduce amount of unknown phases to some extent. The lattice constants for annealed samples were obtained from fitting X-ray powder patterns by the RIETAN Rietverd analysis program [6]. The dc magnetic susceptibility χ and isothermal magnetization M for as-cast samples were measured by a SQUID magnetometer (Quantum Design Ltd.) in the temperature of 1.9–300 K and under magnetic field up to 5 T. Since $Tb_{1-x}Y_xNiAl$ shows a large magneto-crystalline anisotropy along the *c*-axis, powdered samples which were sieved below 25 μm diameter were prepared as a free-powdered sample to avoid underestimation of magnetic moment along the easy direction.

3. Experimental results and discussion

3.1. Structural properties

Fig. 2 displays the lattice constants a and c, a unit cell volume V_{cell} of $Tb_{1-x}Y_xNiAl$ as a function of x. The value of a linearly increases with a slope da/dx of 0.31% and that of c linearly decreases with a slope dc/dx of −0.42%. They follow the Vegard's law. The cell volume V_{cell} and the average lattice constant $V_{cell}^{1/3}$, which is defined as the cubic root of the cell volume, linearly decrease with negative slopes dV_{cell}/dx and $dV_{cell}^{1/3}/dx$ of −0.034 and −0.038%, respectively. The values of V_{cell} and $V_{cell}^{1/3}$ in $TbPd_{1-y}Ni_yAl$ decreased with larger negative slopes dV_{cell}/dy and $dV_{cell}^{1/3}/dy$ of −1.4 and −1.5%, respectively [7], than those in $Tb_{1-x}Y_xNiAl$. It means that a chemical pressure effect by substitution is less crucial in $Tb_{1-x}Y_xNiAl$ than in $TbNi_{1-y}Pd_yAl$.

3.2. Magnetic properties

Fig. 3 shows the temperature T dependence of magnetic susceptibility $\chi(T)$ in $Tb_{1-x}Y_xNiAl$ ($0 \le x \le 0.3$) at low temperatures. Each $\chi(T)$ curve increases with decreasing

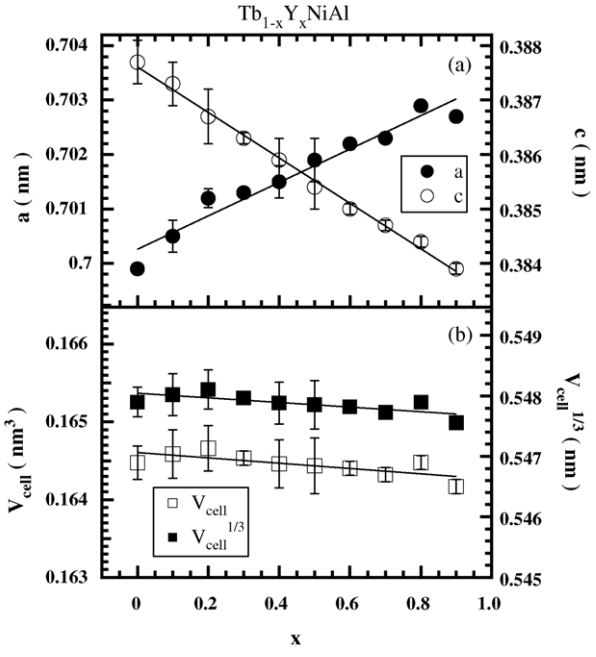

Fig. 2. Crystal structure parameters: (a) lattice constants and (b) a unit cell volume V_{cell} and the average lattice constant $V_{cell}^{1/3}$, as a function of Y concentration in $Tb_{1-x}Y_xNiAl$.

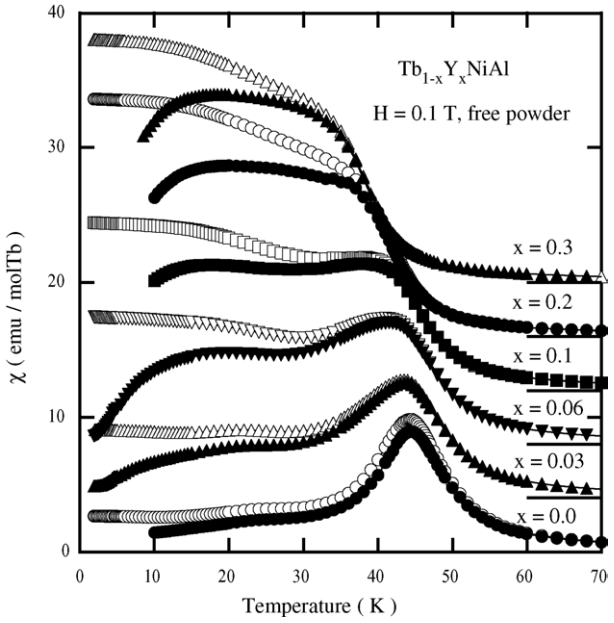

Fig. 3. Temperature dependence of the magnetic susceptibility under 0.1 T in free-powdered sample $Tb_{1-x}Y_xNiAl$. The data were collected for 0.1 T after cooling the sample from 80 to 1.9 K at zero field (solid symbols) or in the field of 0.1 T (open symbols). In order to avoid overlapping, each curve is vertically shifted by +4 emu/mol Tb.

temperature from room temperature and starts to deviate from a characteristic temperature T_{ord} in a zero-field cooling (ZFC) process and a field-cooling (FC) process. For example the $\chi(T)$ curve in TbNiAl has a peak at 45 K which is often shown in a typical AF transition. The actual Néel temperature T_{N1}, however, turned out to be 47 K which agrees with evolution of magnetic Bragg peaks in the neutron diffraction experiment [4]. As a fact, application of a smaller field like 0.01 T revealed a change of slope at 47 K. So we defined T_{ord} as a magnetic ordering temperature. On the other hand, a small hump at 23 K in $\chi(T)$ curves for $x = 0$ is attributed to ordering of disordered moment at T_{N2}. The $\chi(T)$ curve of the FC process for $x = 0.1$ increases with decreasing temperature, has a small hump at around 40 K and increases again to lower temperatures. The $\chi(T)$ curves of the FC process for $x = 0.2$ and 0.3 increase with decreasing temperature, largely bend at around T_{ord} and saturate below about 13 K. The $\chi(T)$ curves of the ZFC process for $x \geq 0.1$ start to decrease below about 13 K. The origin of these anomalies of $\chi(T)$ curves of FC and ZFC processes at around 13 K for $x \geq 0.1$ are not clear. They may have some relation to motion of ferromagnetic domains as mentioned after.

Fig. 4 shows T dependence of inverse magnetic susceptibility $1/\chi(T)$ in $Tb_{1-x}Y_xNiAl$ ($0 \leq x \leq 0.3$). The amplitude of $1/\chi(T)$ is proportional to T above about 100 K. The Curie–Weiss temperature θ_p and the effective magnetic moment μ_{eff} were determined from fitting to the Curie–Weiss law $\chi(T) = N_0\mu_{eff}^2\mu_B^2/(3k_B(T-\theta_p))$ in the temperature range of 100–300 K, where N_0, μ_B and k_B are a number of Tb ions in a mole, the Bohr magneton and the Boltzmann constant,

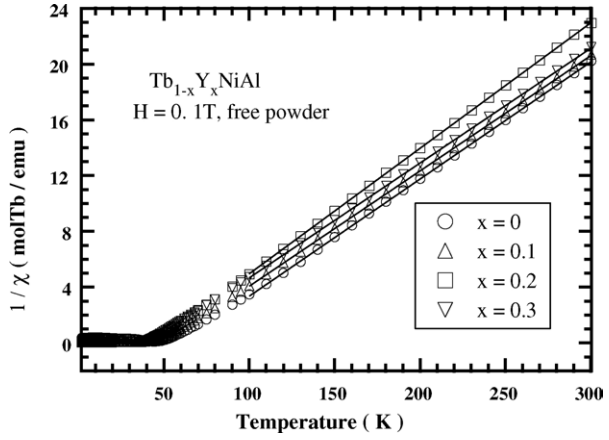

Fig. 4. Temperature dependence of the inverse magnetic susceptibility under 0.1 T in free-powdered sample $Tb_{1-x}Y_xNiAl$.

respectively. The magnetic parameters obtained from Figs. 3 and 4 are plotted in Fig. 5. The amplitude of μ_{eff} is estimated to be about $9.8\mu_B$/Tb which is close to that of $9.72\mu_B$ for a free Tb^{3+} ion.

Fig. 6 shows the isothermal magnetization $M(H)$ as a function of magnetic field H at 5 K in the free-powdered sample of $Tb_{1-x}Y_xNiAl$. All $M(H)$ curves demonstrate a tendency of saturation above 1 T. The saturation moment approaches to $8\mu_B$ which is less than an ordered moment of $9\mu_B$ for a free Tb^{3+} ion. This reduction must be mainly due to the crystalline-field effect. The $M(H)$ curves for $0.0 \leq x \leq 0.06$ exhibit a metamagnetic transition from the AF state to FIF state at a critical field H_c with a hysteresis. The amplitude of H_c was estimated from the mean value of field corresponding to an inflection point in increasing and decreasing field processes. It rapidly suppresses with increasing x as shown in the inset of Fig. 6. The $M(H)$ curves for $0.1 \leq x \leq 0.3$ agree with typical hysteresis ones as shown in ferromagnetism. Thus, the data of $\chi(T)$ and $M(H)$ indicate that magnetic ground sate in $Tb_{1-x}Y_xNiAl$ changes from the AF state to the F state at $x \approx 0.1$.

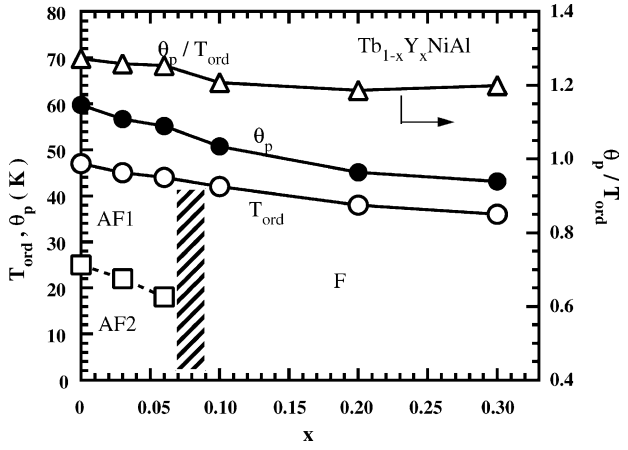

Fig. 5. Magnetic parameters and phase diagram in $Tb_{1-x}Y_xNiAl$.

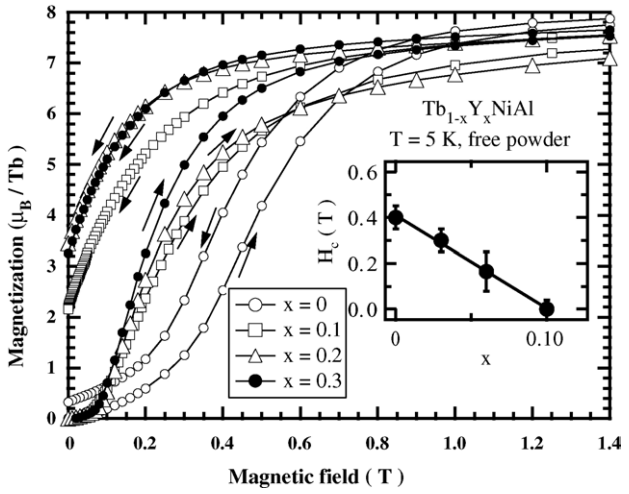

Fig. 6. Isothermal magnetization of the free-powdered sample $Tb_{1-x}Y_xNiAl$ at 5 K. Since the observed amplitude of magnetization along the field direction slightly deviates from a systematic change with increase of x due to incompleteness of alignment and powder size, all the data were normalized to fit the amplitude of magnetization at 5 T and 5 K along the c-axis in a single crystal TbNiAl [9]. The inset shows the metamagnetic transition field H_c as a function of x.

Let us compare the phase diagram in $Tb_{1-x}Y_xNiAl$ with those in other substitutional system, $TbPd_{1-y}Ni_yAl$ and $TbNi_{1-z}Cu_zAl$.

Very recently we have reported the results of magnetic measurements in $TbPd_{1-y}Ni_yAl$ ($0 \leq y \leq 1$) [7,8]. Since the crystal structures of both ternary compounds are identical and substituting Ni for Pd will not change a number of free electrons crucially, one can expect a chemical pressure effect and a random effect on the geometrically magnetic frustration. The paramagnetic Curie temperature θ_p and T_{N1} show minima at $y_c \approx 0.4$, whereas the lattice constant c shows a maximum at y_c. A small magnetic field H_c below 1.1 T at 5 K along the magnetically easy c-axis collapses the AF structure and induces the F structure. The y-dependence of H_c also shows a maximum at y_c. The common y-dependence of θ_p, T_{N1}, H_c and c indicates that substitutional effects on $TbPd_{1-y}Ni_yAl$ are mainly governed by the exchange interaction along the c-axis. A simple two sublattice model could explain the y-dependence of magnetic parameters H_c, T_{N1} and θ_p [8].

On the other hand, G. Ehlers et al. reported that substitution of a few percent Cu for Ni suppresses the AF ground state in $TbNi_{1-z}Cu_zAl$ [10]. The neutron diffraction experiment revealed that ferromagnetic domains increase with increase of Cu concentration in the transition range $0.01 \leq z \leq 0.1$ and the ground state for $z \geq 0.1$ changes to ferromagnetic one. It means that antiferromagnetism of TbNiAl is in the vicinity of the phase boundary between the AF and F states.

Hence, it is most likely that the number of frustrated bonds, which characterizes the AF state is strongly reduced by introduction of nonmagnetic Y site and a dominant ferromagnetic interaction easily recovers the ferromagnetic ordering instead.

4. Conclusions

We have prepared pseudoternary polycrystalline samples $Tb_{1-x}Y_xNiAl$ with an almost single phase by a conventional arc-melting method to study the dilution effect on magnetic properties of geometrically frustrated system TbNiAl. Measurements of magnetic susceptibility and magnetization of $Tb_{1-x}Y_xNiAl$ ($0 \leq x \leq 0.3$) polycrystalline samples were examined. Surprisingly, a critical field H_c which shows the metamagnetic transition from the AF state to the FIF state rapidly vanishes in $x \geq 0.1$. Namely, small substitution of nonmagnetic ions of Y for magnetic ions of Tb stabilizes the F state instead of the AF state. It suggests that the number of frustrated bonds, which characterizes the AF state is strongly reduced by introduction of nonmagnetic Y site and a primarily dominant ferromagnetic interaction destroys the AF ground state and the F ordering appears instead.

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