Magnetism, the Kondo Effect and Spin Correlations in $TbFe_2(Si_{1-x}Ge_x)_2$

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A series of intermetallic compounds $TbFe_2(Si_{1-x}Ge_x)_2$ with $0 \le x \le 1$ and $\Delta x = 0.1$ was prepared, and x-ray diffraction, electric resistivity and magnetic susceptibility measurements were performed. For all concentrations $0 \le x \le 1$, besides the low temperature Neél point T_N and the Kondo temperature T_K, the high temperature characteristic points T_{SC} were observed, where spin fluctuations start to influence the transport and magnetic properties of the material. The values of T_N and T_{SC}, obtained for different x, have a direct relationship with the behavior of the c-axis, and all these quantities have a minimum at x = 0.4. The decrease of T_N with the crystal lattice condensation is rather unusual and can be related to the Kondo mechanism. The $TbFe_2Ge_2$ compound can be characterized as an antiferromagnetic Kondo lattice. Some other mechanisms of the T_N and T_{SC} behavior are also discussed.

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I. Introduction

The rare earth ternary intermetallic compounds $TbFe_2X_2$(X=Si, Ge) have a $ThCr_2Si_2$ type crystal structure with a space group of $I4/mmm$ [1]. The dimension of the tetragonal unit cell is approximately $4 \times 4 \times 10$ Å^3. The neutron diffraction study [1] revealed that at low temperatures $TbFe_2X_2$ transform from a paramagnetic (PM) state into an antiferromagnetic (AF) state. Only Tb atoms possess a magnetic moment and the magnetic structure is incommensurate with the crystallographic unit cell. The ^{57}Fe Mössbauer spectroscopy measurements by Noakes *et al.* [2] have proved that Fe atoms in $TbFe_2Si_2$ possess no magnetic moments, and the Fe atoms occupy only one type of local site, i.e., there is no site exchange of the Fe and Si atoms. Duh *et al.* [3, 4] reported the magnetic and electric properties of $TbFe_2X_2$ (X = Si, Ge). The obtained Neél temperature T_N is 6.5 K in $TbFe_2Si_2$ [3] and 8.5 K in $TbFe_2Ge_2$ [4]. Besides the antiferromagnetic transition appearing at low temperature, they found another anomaly at high temperature where the resistivity and inverse magnetic susceptibility deviate from a linear law. It was suggested [3, 4] that the observed anomaly may be due to a spin correlation effect, and two mechanisms were discussed to explain the observed deviation from the linear law. One of them is related to the spin fluctuations of localized electrons and the other one is due to gap formation in the spin-excitation spectrum of itinerant electrons (the spin-gap effect). It is not yet clear, which mechanism of spin fluctuations is the proper one. In this paper we present x-ray diffraction, resistivity and magnetic susceptibility data for the mixture series of polycrystalline $TbFe_2(Si_{1-x}Ge_x)_2$.

II. Experimental

Eleven samples of polycrystalline $TbFe_2(Si_{1-x}Ge_x)_2$ with $0 \le x \le 1$ and $\Delta x = 0.1$ were prepared by the melting of stoichiometric amounts of the constituent materials in an argon arc furnace. The purities of the raw materials were Tb:3N5, Fe:6N, Si:6N and Ge:6N. To improve the homogeneity, the metallic buttons were remelted several times, and the buttons were placed upside down during each melting. After melting the overall weight loss was less than 1%. Then the samples were sealed in a quartz tube and annealed at 800 C for seven days.

The x-ray measurements were performed with a MAC MXP3 x-ray diffractometer. For all concentrations x, the x-ray diffraction spectra of $TbFe_2(Si_{1-x}Ge_x)_2$ can be indexed well to a body-center tetragonal crystal structure of the $ThCr_2Si_2$ type with space group $I4/mmm$.

The magnetic susceptibility measurements were performed using the Physical Property Measurement System (PPMS) (Quantum Design Co.) in the temperature range 2-300 K, and in an applied magnetic field of H = 2 kOe. In all of the measurements, the sample was first cooled down to a specified temperature in zero field, then an external magnetic field was applied, and all of the data were taken at each step of the temperature and field variations. The resistivity measurements were also performed using the PPMS with a standard four-probe technique.

III. Results and discussion

The room temperature values of the lattice parameter c determined from x-rays in $TbFe_2(Si_{1-x}Ge_x)_2$ as a function of x are given in Fig. 1. According to the Vegard law, a lattice parameter of substitutional solid solutions is a linear function of the atomic composition. It is clear from Fig. 1 that the parameter c does not obey the Vegard law, and a sharp bend appears in the lattice spacing curve with a minimum at x = 0.4. Usually the existence of sharp bends is attributed to an electron density variation resulting in Brillouin zone overlaps.

Figure 2 shows the temperature dependence of the dc magnetic susceptibility of $TbFe_2(Si_{1-x}Ge_x)_2$ measured in the field H = 2 kOe. At low temperatures, an antiferromagnetic transition is observed in all of the samples; the T_N value as a function of x are given in Fig. 3. We found that the behavior of T_N is very unusual. With increasing x, the T_N value first decreases, attains the minimum value of 4.6 ± 0.5 K at x = 0.4, and then increases up to the maximum value of 8.1 ± 0.5 K in $TbFe_2Ge_2$. Comparing Figures 1 and 3, one can see that T_N and c-axis values have similar dependence on x, and they both pass the minimum at x = 0.4.

Normally, T_N behaves in an opposite way, i.e., it increases when lattice parameters decrease and vice versa. An exception is known for the rare-earth orthoferrites $RFeO_3$ [5], which are antiferromagnetic insulators with a strong superexchange Fe-O-Fe coupling. When R in $RFeO_3$ changes from La to Lu, the lattice parameters decrease due to the decreasing of the ionic radius of R. However, the T_N values decrease too because the angle of the chemical bond Fe-O-Fe decreases from 180-degrees, thus diminishing the exchange interaction [5].

In intermetallic systems like $TbFe_2(Si_{1-x}Ge_x)_2$, the exchange interaction is mediated by conduction electrons, and the behavior of T_N is mainly determined by the band structure. It must be noted that the behavior of T_N in our $TbFe_2(Si_{1-x}Ge_x)_2$ system is different from that in the $CePd_2(Si_{1-x}Ge_x)_2$ system, where the lattice expansion depresses T_N [6]. However a similar behavior had been observed recently in the $U(Pd_{1-x}Fe_x)_2Ge_2$ system [7], where T_N decreased with changing x along with decreasing of the c axis and interatomic U-U distance values. The

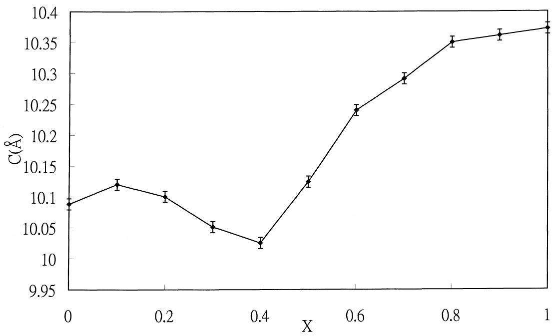

FIG. 1. Lattice parameter c in the $TbFe_2(Si_{1-x}Ge_x)_2$ system as a function of x.

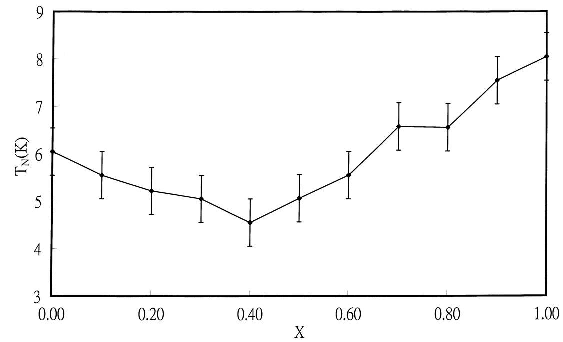

FIG. 3. Neél temperatures T_N as a function of x for $TbFe_2(Si_{1-x}Ge_x)_2$ system.

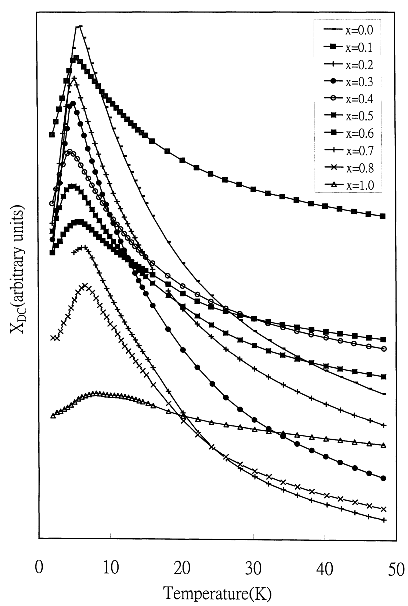

FIG. 2. Temperature dependencies of the dc magnetic susceptibility in $TbFe_2(Si_{1-x}Ge_x)_2$ for $x = 0.0 \sim 1.0$ (from top to bottom) measured in an applied magnetic field of 2 kOe.

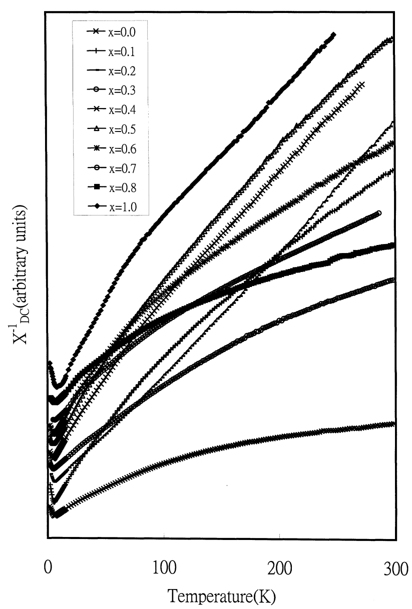

FIG. 4. Temperature dependences of the inverse magnetic susceptibility for $TbFe_2(Si_{1-x}Ge_x)_2$ in an applied field of 2 kOe.

crystal structure of $TbFe_2(Si_{1-x}Ge_x)_2$ and $U(Pd_{1-x}Fe_x)_2Ge_2$ is the same, but the substitution is taking place on different local sites, so the mechanisms of T_N suppression may be somewhat different.

Endstra *et al.* [8] suggested the "f-d hybridization model" to account for the systematic in the magnetic-ordering temperatures of the MT_2X_2 compounds (M = U, RE; T = 3d, 4d, or 5d transition metal; and X = Ge, Si). In this model, an ordering of f spins of M appears as a result of competition between an indirect f-d-f magnetic interaction of the local M moments (a conduction-electron-mediated RKKY-type interaction) and a Kondo-type spin-compensating mechanism. Both interactions depend on the exchange-coupling parameter J_{df}, which is proportional to the f-d hybridization strength and depends both on filling the d band and on the distance between the d and f atoms in the crystal structure. As a result of the competition of two contributions, a maximum of the magnetic ordering temperature T_N is expected at $J_{df} = J_c$ on the T-J phase diagram for the Kondo lattice. The theory predicts a decrease of T_N as J_{df} is increased above its critical value. Brandt and Moshchalkov [9] suggested a similar behavior in the "concentrated Kondo systems". Taking into account the above ideas, we can conclude from the T_N behavior in $TbFe_2(Si_{1-x}Ge_x)_2$ that the Kondo regime prevails at $x < 0.4$.

Figure 4 shows the temperature dependence of the inverse magnetic susceptibility. For all concentrations x, two anomalies are observed in the $1/\chi = f(T)$ curves. The anomalies at low temperatures are typical of the magnetic phase transition from a paramagnetic into an antiferromagnetic state. The second anomaly appears at higher temperature, where the inverse susceptibility deviates from linearity, i.e. it does not obey the Curie-Weiss law. We found that in the high-temperature range, where the contribution from the Tb crystal-field splitting of the ground state may be neglected, the susceptibility can be fitted to the law: $\chi = [\chi_0 + C/(T - \theta)]$, where χ_0 is the temperature-independent contribution due mainly to itinerant-electron Pauli paramagnetism. The fit shows that in the series $TbFe_2(Si_{1-x}Ge_x)_2$, the Pauli term χ_0 is rather high at all x values, and for the end members $TbFe_2Si_2$ and $TbFe_2Ge_2$ it is in the range (2.1-2.4) $\times 10^{-4}$ and (3.4-4.1) $\times 10^{-5}$ emu g^{-1} Oe^{-1}, respectively.

The characteristic temperature of deviation of the $1/\chi = f(T)$ curves from the Curie-Weiss law we denote by T_{SC}. The plot of T_{SC} as a function of x is given in Fig. 5. It appeared that the $T_{SC} = f(x)$ behavior has the same tendency as the c-axis behavior (see Fig. 1), and it shows a minimum at $x = 0.4$.

As was discussed in [3, 4], the observed anomaly at T_{SC} may be related to a spin correlation effect. To get more information, we have investigated the temperature dependence of resistivity (ρ) in these materials, the data for $TbFe_2Si_2$ and $TbFe_2Ge_2$ are shown in Fig. 6. It was found that the resistivity of $TbFe_2Ge_2$ is about ten times higher than that of $TbFe_2Si_2$ (the resistivity data of $TbFe_2Si_2$ are multiplied by 10). In the low temperature region one can observe three anomalies in the $\rho(T)$ curve of $TbFe_2Ge_2$ (Fig. 6). There is a first upward bend at about 8 K, a downward bend at about 35 K, followed by a second upward bend at about 130 K. This is reminiscent of a

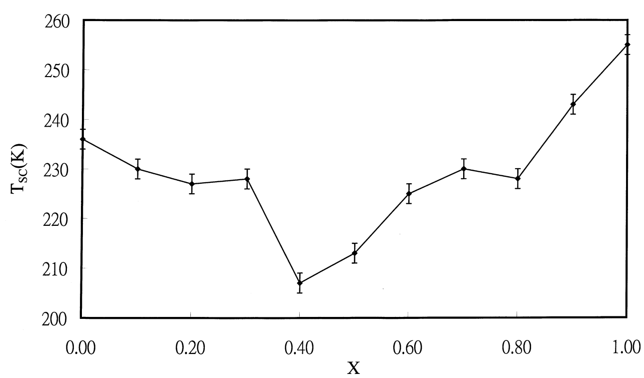

FIG. 5. The T_{SC} values as a function of x for the $TbFe_2(Si_{1-x}Ge_x)_2$ system.

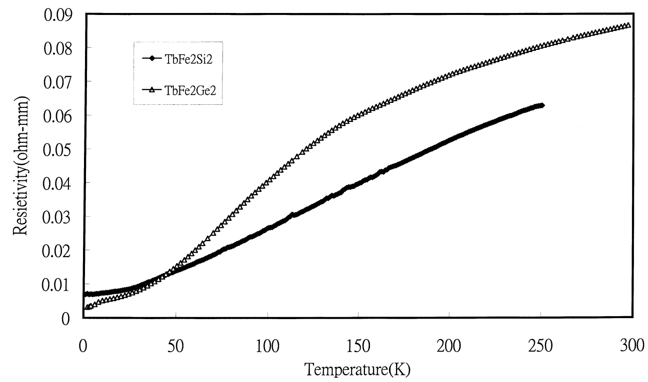

FIG. 6. The temperature dependence of resistivity for $TbFe_2Si_2$ and $TbFe_2Ge_2$. The resistivity data of $TbFe_2Si_2$ are multiplied by 10.

characteristic Kondo-lattice "double bump" structure due to the combined effect of a crystalline-electric field and the Kondo effect [6]. The temperature-dependent behavior of resistivity in $TbFe_2Ge_2$ is qualitatively similar to that observed in $CePd_2Ge_2$ [6], showing thereby the presence of crystal-field and Kondo effects. Thus for $TbFe_2Ge_2$, the temperatures of about 8 K, 35 K and 130 K may be attributed to the Neél (T_N), Kondo (T_K) and crystal-field (T_{CF}) points, respectively. For $TbFe_2Si_2$ in the low temperature region, the resistivity shows an anomaly only at T_K, and no anomalies were observed at T_N and T_{CF} (see Fig. 6). Thus, the $TbFe_2Ge_2$ compound can be characterized as an antiferromagnetic Kondo lattice.

It was also found that in all compounds the ½(T) curves deviate from a linear law at the temperature, which coincides with the T_{SC} points, where $1=\hat{A} = f$(T) deviates from linearity. Recently, a correlation between the deviation of the resistivity from T-linearity and the change in the spectrum of spin fluctuations was found in the high temperature superconductors YBCO [10-12]. This deviation corresponds to gap formation in the spin-excitation spectrum (the "spin gap" effect), as suggested from neutron and NMR studies [13, 14]. It was shown [10, 12] that, if a spin gap exists, the ½(T) and $\hat{A}$(T) curves will deviate from linear behavior before the compound transforms from a paramagnetic to an antiferromagnetic state. Some other mechanisms of the deviation of the resistivity from T-linearity were discussed in [3].

In our $TbFe_2(Si_{1¡x}Ge_x)_2$ system, spin fluctuations appear at a relatively high temperature T_{SC}, i.e., the fluctuations exist in the region $T_N < T < T_{SC}$ before the compound transforms into the antiferromagnetic state. At these temperatures, charge transport may be influenced by the spin excitations. It is seen in Fig. 6 that at $T < T_{SC}$ the deviation from linearity is small in $TbFe_2Si_2$, whereas it is quite distinct in $TbFe_2Ge_2$. Therefore, we suggest that the spin correlations responsible for the change in transport properties at T_{SC} are much stronger in $TbFe_2Ge_2$ than in $TbFe_2Si_2$.

The correlation of $T_{SC} = f(x)$ behavior with the c-axis behavior in $TbFe_2(Si_{1¡x}Ge_x)_2$ is of special interest. The small substitution of Ge for Si causes a lattice condensation with minimum at $x = 0.4$. The effect of quantum fluctuations (the quantum effect of phonons on the energy spectrum of electrons) on the lattice condensation (or phonon order parameter m_p) has been considered theoretically for quasi-one-dimensional electron-phonon systems such as organic or high temperature superconductors [15-17]. Schmeltzer *et al.* [15] obtained that, at certain values of electron-phonon coupling parameter g, quantum fluctuations reduce m_p from the static mean-field value. Chu and Ye [16] have found that the lattice condensation due to quantum fluctuations is reduced in the strong electron-phonon coupling regime and it is enhanced in the small coupling regime. It was also shown in [17] that inclusion of fluctuations strongly modifies the superconducting gap equation in quasi-two-dimensional systems, and there is a possibility that fluctuations may increase the superconducting transition temperature. The $TbFe_2(Si_{1-x}Ge_x)_2$ compounds have a tetragonal structure with $c/a \approx 2.5$ and in a certain sense they may be considered as low-dimensional systems. So, it is interesting to apply the above ideas about lattice condensations to these materials in order to explain the observed anomalies by the quantum fluctuation effect. Then according to [16], it can be suggested that in the $TbFe_2(Si_{1-x}Ge_x)_2$ system the electron-phonon coupling first is weakening at small substitutions of Ge for Si as the lattice condensation enhances. The coupling reaches a minimum at $x = 0.4$, and then it increases with increasing x to obtain the maximum value in $TbFe_2Ge_2$ as the quantum fluctuations reduce the lattice condensation. It seems that the absolute values of resistivity (which in $TbFe_2Ge_2$ is ten times higher than in $TbFe_2Si_2$) as well as the temperature-dependent behavior of resistivity (Fig. 6) support this suggestion. Then we are able to observe the quantum fluctuations effect from a weak coupling regime to a strong coupling regime in one physical system $TbFe_2(Si_{1-x}Ge_x)_2$.

Acknowledgments

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