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The magnetic characteristics of the $Tb(Ni_{1-x}Co_x)_2Ge_2$ system

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Abstract

The compounds $TbNi_2Ge_2$ and $TbCo_2Ge_2$ both crystallize with the $ThCr_2Si_2$ structure. $TbNi_2Ge_2$ has a complex H–T phase diagram while $TbCo_2Ge_2$ has a much simpler, though disputed phase diagram. In order to investigate the effects on the magnetism of $TbNi_2Ge_2$ due to cobalt substitution, single crystals of $Tb(Ni_{1-x}Co_x)_2Ge_2$ with x ranging from 0 to 1 have been grown from a psuedoternary melt. We have traced the Néel and Weiss temperatures as a function of cobalt concentration, x. Close to $x=0.5$, the Weiss temperature is positive, indicating predominately ferromagnetic interactions (in contrast to $x<0.4$ and $x>0.6$ for which the Weiss temperatures are negative), $\chi(T \approx T_N)$ is a maximum and the critical field for metamagnetism is a minimum. Nevertheless, the compound orders antiferromagnetically, similar to all other members of the dilution series. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Magnetically ordered materials; Crystal growth; Magnetisation

1. Introduction

For many years the family of compounds that crystallize with the $ThCr_2Si_2$ structure have prompted much interest by demonstrating many interesting physical phenomena. One such phenomenon, metamagnetism, is vividly manifested in the compound $TbNi_2Ge_2$. At low fields two antiferromagnetic transitions are observed, which have recently been characterized by neutron diffraction experiments [1,2]. The first transition occurs at 17 K between the paramagnetic state and an incommensurate AF state, and the second at 9 K from the incommensurate state to a commensurate AF state. A similar compound is $TbCo_2Ge_2$, that also crystallizes with the $ThCr_2Si_2$ structure. Recently there has been some controversy about its low field states. Ref. [3] reports only one transition at 32 K in a crystal grown by a tri-arc Czochralski method, while Ref. [4] reports two transitions observed on an arcmelted sample at 31 K and at 22 K.

In this paper we report the effects on the magnetic characteristics of $Tb(Ni_{1-x}Co_x)_2Ge_2$ crystals grown from a ternary melt as we gradually make the transition from nickel to cobalt on the transition metal site of the $ThCr_2Si_2$ structure.

2. Experimental methods

Single crystals of $TbTM_2Ge_2$ were grown from a ternary melt [5], where TM represents the transition metal component ($Ni_{1-x}Co_x$). Elemental components were combined in a ratio of $Tb_6TM_{47}Ge_{47}$ in an alumina crucible and sealed in a quartz ampoule with a partial pressure of argon. The ampoule was then heated to 1250°C and slowly cooled over a period of ~100 h to a temperature between 1000°C and 1100°C, at which point the remaining melt was decanted. As x increased, the necessary decanting temperature increased to 1100°C. The crystals grown in this manner have a plate-like morphology with the c-axis perpendicular to the plane of the plate [1] and typical dimensions of $6\times8\times1$ mm^3 and a mass of 200 mg.

Clean, single-grain samples with typical mass of 15 mg were chosen for measurement. DC magnetization data were obtained using a Quantum Design MPMS SQUID magnetometer. Measurements were made with fields applied parallel and perpendicular to the c-axis. Magnetization as a function of applied field at 2.0 K was measured for fields up to 55 kOe. Magnetization as a function of temperature was measured at a low field of 1 kOe from 2 K to 350 K. To avoid complications due to hysteresis, all measurements were performed with increasing field or temperature, respectively.

Transition temperatures were determined from the peaks in $d(\chi T)/dT$, where χ is the DC susceptibility, defined experimentally at low fields as $\chi = M/H$, which is thought to be proportional to the magnetic component of the specific heat capacity close to an antiferromagnetic transition [6]. The polycrystalline average of the DC magnetic susceptibility was calculated by $\chi_{poly} = (2\chi_\perp + \chi_\parallel)/3$,

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where $\chi_{\perp}$ is the DC susceptibility with the field applied perpendicular to the c axis and $\chi_{\parallel}$ is the same with the field applied parallel to the c axis. The high temperature susceptibility data were well fitted by $\chi = C/(T-\theta)$, where θ is the Weiss temperature and C is the Curie constant.

3. Results and discussion

In Fig. 1, the DC susceptibility is shown below 40 K for fields applied parallel to and perpendicular to the c axis for three samples of $Tb(Ni_{1-x}Co_x)_2Ge_2$, (a) $x=0.0$, (b) $x=0.5$, and (c) $x=1.0$. These three samples, along with all samples measured, display high anisotropy with an easy axis along [001] (i.e. for $H\|c$) caused by strong CEF anisotropy. All samples also show two transitions. For $TbNi_2Ge_2$, transitions occur at 16.6 K and 9.4 K, which is in good agreement with previous measurements [1,2]. Transitions in $TbCo_2Ge_2$ occur at 33.5 K and 29.1 K. The Néel temperature of 33.5 K is comparable to values reported elsewhere [3,4]. The second transition at 29.1 K is contradictory to Ref. [3] which does not report any second transition, and Ref. [4], which places it at 22 K. The Néel temperature for $TbNiCoGe_2$ (i.e. $x=0.5$) is 25.9 K and the second transition is located at about 9 K. This low temperature transition is weaker and broader than the similar transitions in the pure compounds. It should be noted that the magnitude of χ for this alloy is about six times greater than that of either pure compound.

The inverse magnetic susceptibility $(1/\chi)$ of $Tb(Ni_{1-x}Co_x)_2Ge_2$ is plotted in Fig. 2 for (a) $x=0.0$, (b) $x=0.5$, (c) $x=1.0$. Values of C determined from fits to the Curie–Weiss law at high temperatures were consistent with the effective moment of terbium of 9.72 μ_B, with no systematic deviations with change in the cobalt concentration. For the unalloyed compounds there is an upturn of the inverse susceptibilities away from a Curie–Weiss linear behavior below ~100 K. This indicates a tendency for antiferromagnetism. In the $x=0.5$ sample, there is a downturn in the polycrystalline average data. This would indicate a trend toward ferromagnetism for $T \geq T_N$ and is consistent with the observation of the large signal in the χ plot for this sample.

The Weiss temperature in both axial and planar directions as well as for the polycrystalline average for various values of x is shown in Fig. 3a. The positive values of the axial Weiss temperatures indicate ferromagnetic interactions are dominant between planes and the negative planar values indicate antiferromagnetism dominates within the plane. Although it should be noted that CEF corrections could change these values. Axial θs gently increase as x increases from 0.0 to about 0.75 then slightly decrease as x increases to 1.0. Planar θs remain fairly level as x increases to 0.6, after which values fall precipitously. The polycrystalline values are negative in the pure nickel and cobalt compounds, but as x is varied the values increase and become slightly positive near $x=0.5$ indicating predominately ferromagnetic interactions, though these compounds all order antiferromagnetically. Also plotted are the

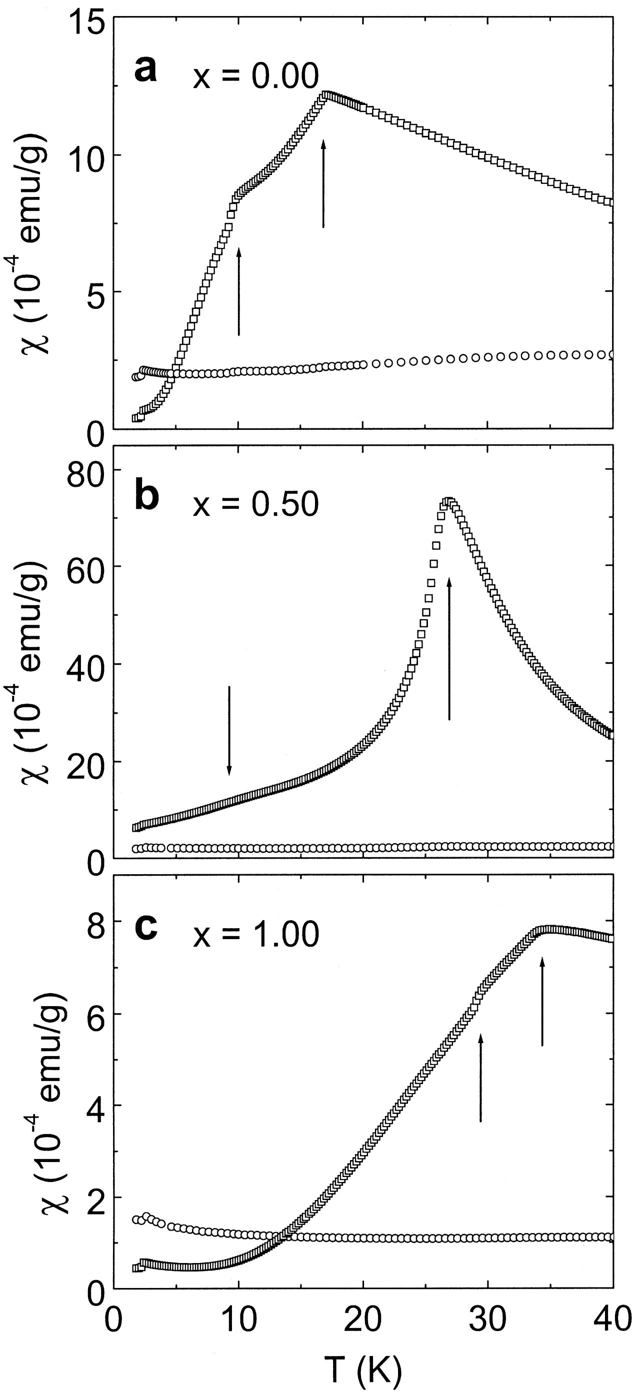

Fig. 1. The DC magnetic susceptibility of $TbTM_2Ge_2$ measured in 1 kOe, with applied field parallel (□) and perpendicular to the c-axis (○). The arrows indicate transitions as determined by peaks in $d(\chi T)/dT$. (a) $TbNi_2Ge_2$, (b) $Tb(NiCo)Ge_2$, (c) $TbCo_2Ge_2$.

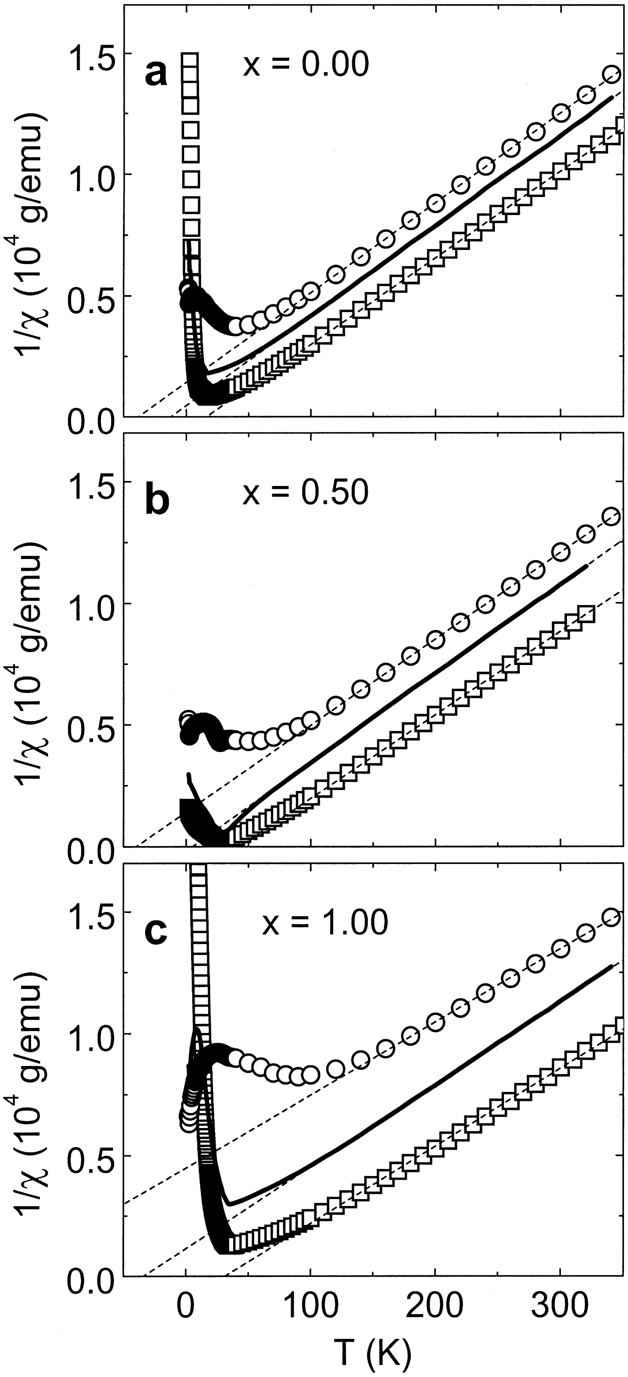

Fig. 2. The inverse DC magnetic susceptibility measured in 1000 Oe for applied fields parallel (□) and perpendicular to the *c*-axis (○) and the polycrystalline average (solid line). Dotted lines show extrapolation of high temperature ($T>200$ K) fits using the Curie–Weiss law. (a) $TbNi_2Ge_2$, (b) $Tb(NiCo)Ge_2$, (c) $TbCo_2Ge_2$.

values of T_N versus cobalt concentration (Fig. 3b). The error bars associated with lower transition temperature reflects that the associated peak in $d(\chi T)/dT$ becomes smaller and broader in the region $0.2<x<0.6$. The transition temperatures increase as x increases, plateaus between

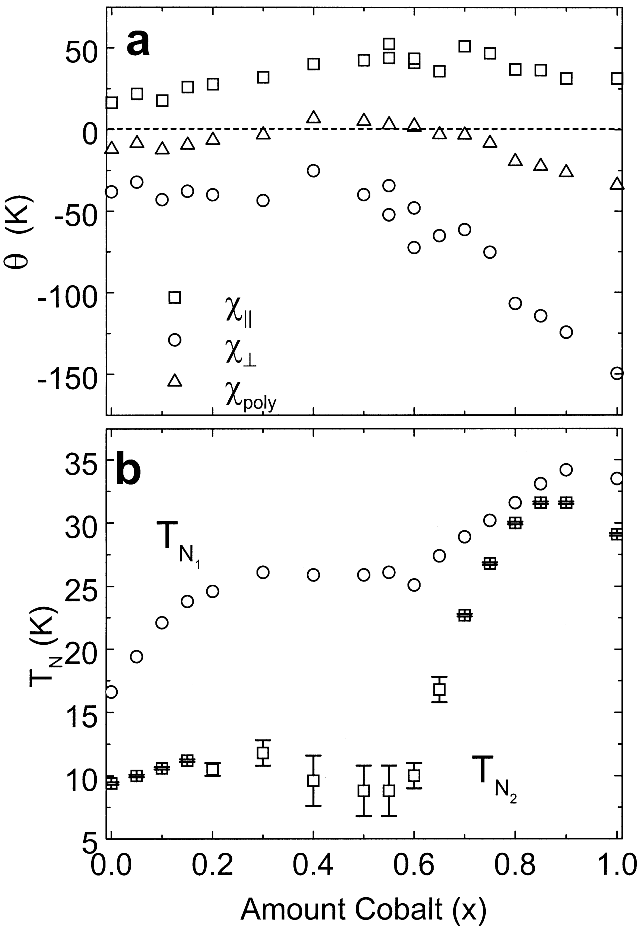

Fig. 3. (a) The Curie temperature (θ) derived from fits of the Curie–Weiss law as a function of cobalt concentration for applied fields parallel (□) and perpendicular to the *c*-axis (○) and the polycrystalline average (△). The line highlights $\theta=0$. Panel (b) shows Neel temperatures for transitions from paramagnetic to antiferromagnetic region (○) and between one antiferromagnetic region to another (□) as a function of cobalt concentration.

0.2 and 0.6, then climbs rapidly until $x=1.0$. It should be noted that for $x\geq 0.6$ both T_N and θ values change rapidly.

Fig. 4 displays the metamagnetic characteristics of this system. Whereas pure $TbNi_2Ge_2$ has a rich phase diagram [1,2], the primary features as cobalt is substituted are metamagnetic states with M_{sat} of 2 μ_B/Tb, 5 μ_B/Tb, 9 μ_B/Tb. As x is increased there is a *non-monotonic* change in the critical fields for these states. This is clearly seen in Fig. 5. As x increases the critical fields decrease, there is a minimum at $x\approx 0.5$, and then the critical fields increase as x continues to increase. This minimum in H_{crit} at $x\approx 0.5$ is consistent with the deviation in χ^{-1} data toward ferromagnetic interactions for this x value.

In conclusion, in the $Tb(Ni_{1-x}Co_x)_2Ge_2$ system, there are two low field antiferromagnetic states across the entire series, the transition temperatures tend to increase with x, with a sharp increase for $x>0.6$. In addition there is a

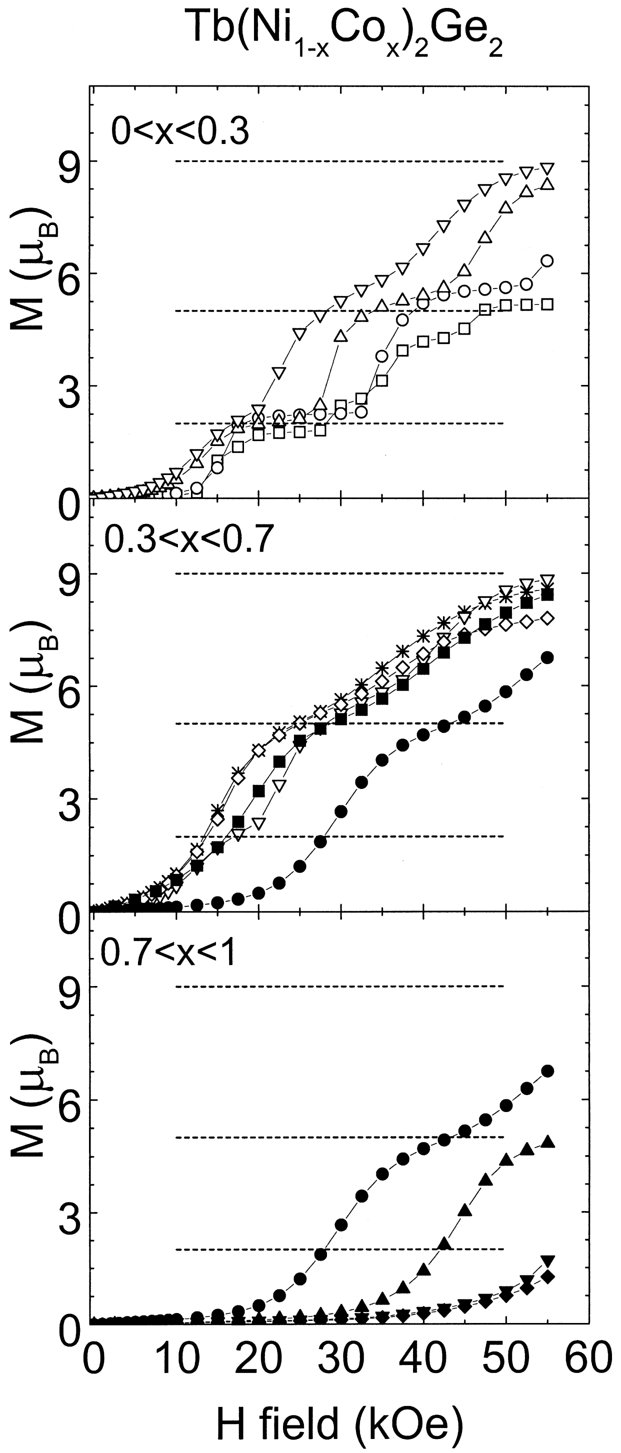

Fig. 4. Magnetization per Tb atom in Bohr magnetons as a function of field for selected cobalt concentration (x) measured at 2 K. Dotted lines highlight particular metamagnetic states. $x=0.0$ (□), $x=0.1$ (○), $x=0.2$ (△), $x=0.3$ (▽), $x=0.4$ (◇), $x=0.5$ (*), $x=0.6$ (■), $x=0.7$ (●), $x=0.8$ (▲), $x=0.9$ (▼), $x=1.0$ (♦).

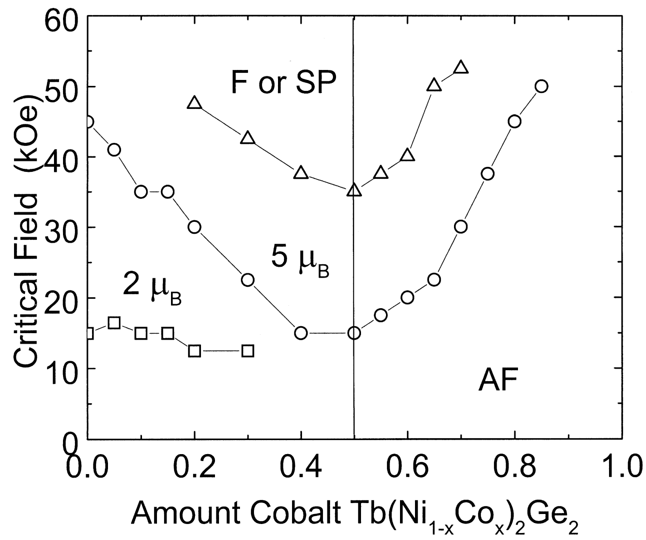

Fig. 5. Phase diagram showing critical applied fields for prominent metamagnetic states as a function of cobalt concentration measured at 2 K.

tendency toward ferromagnetism for $T > T_N$ at intermediate values of x.

Acknowledgements

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