Antiferromagnetic Coupling of $Pr_{0.9}RE_{0.1}Ni$ (RE = Tb, Dy, Ho) Single Crystals

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Magnetization and specific heat measurements were carried out on $Pr_{0.9}RE_{0.1}Ni$ (RE = Tb, Dy, and Ho) single crystals. Spin rearrangements were observed along the *c*-axis of single crystals with relatively small critical fields, B_c = 6.8, 4.0 and 2.6 T for RE = Tb, Dy and Ho, respectively. The magnetic phase transition temperatures, T_M, were extracted from the specific heat data: T_M = 22.7, 19.6 and 18.3 K with RE = Tb, Dy and Ho, respectively. The observed B_c values were used to estimate the heterogeneous (Pr-RE) exchange strength, and then calculate expected T_M values, which were found to be close to the experimental ones. The present results of B_c and T_M, together with the previous ones of $Pr_{0.9}Gd_{0.1}Ni$, were found to be consistent with the de Gennes rule.

KEYWORDS: PrNi, spin rearrangement, antiferromagnetic coupling

1. Introduction

It is well known that the sign of the coupling of the rare earth (RE) magnetic moments with the transition metal (T) moments changes between light and heavy RE elements.[1-4] An illustrative example is the addition of Dy to $Nd_2Fe_{14}B$, resulting in increased coercivity, but decreased remanence and energy product due to the antiparallel coupling between the Dy and Nd magnetic moments.[5] The conduction electron polarization due to a RE ion is negative with respective to the spin moment at the ion site and therefore the coupling of the spins of a RE ion and the conduction electrons is antiferromagnetic (antiparallel). Consequently, it follows that there is an antiferromagnetic coupling of the total magnetic moments of heavy RE ions with transition metal ions, whereas the coupling is ferromagnetic for the light RE's with

transition metal ions. These observations reflect the Hunds rule that has $J = L+S$ and $J = L-S$ for the heavy and light rare earths, respectively, and are consistent almost universally with data for RE-T compounds in literature.[4-10] For intermetallic compounds that mix light and heavy REs, the arrangement of the magnetic moments of the heterogeneous RE ions is also antiferromagnetic (leading to a ferrimagnetic structure). This antiferromagnetism, originating from the opposite sense of the spin-orbit interactions of heavy and light rare earths, is illustrated by a number of experimental studies.[1-4] Our recent reports on the magnetic properties of $Pr_{1-x}Gd_xNi$[11,12], $Nd_{1-x}Gd_xNi$[13], $Pr_{1-x}Tb_xNi$ and $Nd_{1-x}Tb_xNi$[14], using single crystals, all documented this type of behavior. Amongst these mixed compounds, those containing Pr also showed evidence of a field dependence of the magnetic structure that has not been reported in the literature previously. The magnetization data along the *c*-axis (easy-axis of PrNi), indicates a critical field (B_c) for a transition from a ferrimagnetic to ferromagnetic state. The variations of the B_c with x in $Pr_{1-x}Gd_xNi$ were found to correlate well with a simple model whereby the Zeeman term becomes equal to the heterogeneous exchange at B_c.[12] One could ask whether this model remains valid when the total spin and orbital angular moments of the substitute rare earth elements change. PrNi is appropriate system in which to test this since the spin rearrangement is expected to occur at only small applied field due to the relatively weak exchange interactions within this rare earth-nickel system. In this work, studies where by 10 atm% of Tb, Dy or Ho has been substituted at the Pr ion-site in the PrNi system have been carried out. Both the critical field B_c and the ordering temperature T_M are found to scale according to the de Gennes factor for all the compounds with substitutions at 10 atm% (from Gd to Ho) into PrNi. Since here we are primarily

interested in the antiferromagnetic coupling of the light and heavy RE moments, and the crystal structures of heavy RENi are different from that of PrNi[15-17], the amount of heavy RE substitution for Pr was confined to a small range to avoid the complication of structural (crystallographic) changes within the analysis.

2. Experimental

The single crystal samples of $Pr_{0.9}RE_{0.1}Ni$ (RE = Tb, Dy, and Ho) were grown using the Bridgeman method. Polycrystalline starting material was prepared by argon arc melting, then packed in an alumina crucible and vacuum-encapsulated in a quartz tube before it was passed through a Bridgeman furnace over a week. The crystallographic orientations of the single crystals were determined by the Laue x-ray back reflection method, with the observed Laue patterns consistent with the samples being single phase of the CrB-type (Cmcm) orthorhombic crystal structure.[15] The crystal structures of TbNi, DyNi and HoNi are different from that of PrNi (and GdNi), which is CrB-type, being TbNi-type[16] for TbNi, and FeB-type for DyNi[17] and HoNi.[16] From the x-ray powder diffraction investigations, however, it was found that the substitution of a small amount of Tb, Dy or Ho for Pr did not effect the crystal structure, with it remaining CrB-type. Small samples, cubic in shape, were cut from the crystal boles for use in the various measurements. DC magnetization data (M) were measured using a SQUID magnetometer (MPMS) with external fields (B) up to 7 T in the temperature range from 2 to 300 K. The specific heat measurements for the samples were made using a PPMS, nominally in the same temperature range.

3. Results and Discussions

Magnetization data for $Pr_{0.9}RE_{0.1}Ni$ (RE = Tb, Dy, Ho) at a temperature of 2 K along the c-axis are shown in Fig. 1. The magnetic behaviour of $Pr_{0.9}Tb_{0.1}Ni$ has been discussed previously,[13] while that of Dy or Ho in $Pr_{0.9}RE_{0.1}Ni$ is new. A critical field

value (B_c) is estimated from the point maximum slope (dM/dB_{max}) for each data set. The estimates of B_c are listed in Table 1, together with that of $Pr_{0.9}Gd_{0.1}Ni$.[12] Since in contrast to the Gd case, magnetic anisotropy due to the crystal electric field (CEF) effect is expected for Tb, Dy, and Ho substituting Pr in PrNi, this potentially complicates the magnetic structures at low applied field. The magnetic structure of TbNi is reported to be ferromagnetic with the saturation moment (M_S) of 6.49 μ_B.[18] Those of DyNi[17] and HoNi[19] are, however, non-collinear; both have ferromagnetic components along the *a*-axis and antiferromagnetic components along the *c*-axis. The reported M_S values are 8.8 μ_B /DyNi[17] and 9.8 μ_B /HoNi.[19]

The *M* values for the ferromagnetic (M_S) and antiferromagnetic (M_{AF}) arrangements of Pr and RE can be calculated using the relations $M_S = (1-x)M_S(PrNi) + xM_S(RENi)$, and $M_{AF} = |(1-x)M_S(PrNi) - xM_S(RENi)|$, taking $M_S(PrNi) = 2.35$ μ_B[20] and $M_S(RENi)$. Estimates for M_{AF} and M_S yield M_{AF} = 1.42, 1.19, 1.09 μ_B, and M_S = 2.72, 2.95, 3.05 μ_B for RE = Tb, Dy, Ho, respectively. The calculated value of M_{AF} for $Pr_{0.9}Tb_{0.1}Ni$ matches observation reasonably well, but those for $Pr_{0.9}Dy_{0.1}Ni$ and $Pr_{0.9}Ho_{0.1}Ni$ do not match for the reasons discussed, indeed the experimental M_{AF} show an opposite trend to the experimental ones with respect to the RE. The M_S values on the other hand, all agree well with the observed ones.

Temperature dependent magnetization data collected in an applied field of 1 T are shown in Fig. 2. The *M* vs. *T* curves (left) for RE = Tb and Dy indicate net ferromagnetism at the *c*-axis, while that of $Pr_{0.9}Ho_{0.1}Ni$ shows some evidence of antiferromagnetism, with a maximum around 10 K. The $1/\chi$ vs. *T* data (right in Fig. 2) is used to estimate values of the effective magnetic moments (M_{eff}) of 4.55, 4.76 and 4.74 μ_B for RE = Tb, Dy, and Ho, which agree well with the estimates of 4.61, 4.78,

and 4.78 μ_B, respectively, using a simple relation:

$$M_{\text{eff}} = \sqrt{0.9 \times M_{\text{eff}}(\text{Pr}^{3+})^2 + 0.1 \times M_{\text{eff}}(\text{RE}^{3+})^2} ,$$

in which M_{eff} (Pr^{3+}) and M_{eff} (RE^{3+}) are the free ion values.

Specific heat measurements for $Pr_{0.9}RE_{0.1}Ni$ were undertaken in zero applied field to determine the magnetic phase transition temperatures (T_M). The magnetic contributions ($C_M = C_{tot} - C_{lat}$) to the specific heat of the samples with PrNi are shown in Fig. 3(a). The C_M curves were estimated from the total measured specific heat (C_{tot}) by subtracting the lattice contribution (C_{lat}), which includes the conduction electron part (C_{el}) and the phonon part (C_{ph}), deduced from an additional measurement of the isomorphous nonmagnetic compound, LaNi, following the same scaling procedure described in our previous work.[14] The specific heat data indicate that the magnetic transition temperature of $Pr_{0.9}Tb_{0.1}Ni$ is marginally higher compared with T_M for PrNi, but those of $Pr_{0.9}Dy_{0.1}Ni$ and $Pr_{0.9}Ho_{0.1}Ni$ have decreased. The temperature variations of derivative dC_M/dT of the data shown in Fig. 3(b) provided the T_M values listed in Table 1.

Often magnetic transition temperatures follow the de Gennes rule where the de Gennes factor is given as $(g_J - 1)^2 J(J+1)$. This is true in the current case, as illustrated in Fig. 4, with B_c and T_M increasing monotonically against de Gennes factor for the $Pr_{0.9}RE_{0.1}Ni$ samples. This result also suggests that B_c for the magnetic rearrangement of $Pr_{0.9}RE_{0.1}Ni$ can be treated as a result of competition between a molecular field (exchange interactions) and an external field (Zeeman interactions).

The estimations of M_S and M_{eff} model the experimentally observed values along the *c*-axis very well, and thus support a simple picture that the Pr and RE moments are aligned anti-parallel below B_c. Adopting this model for the structures at the extremes,

estimates of T_M for $Pr_{1-x}RE_xNi$ can be made following the same procedure used for $Pr_{1-x}Gd_xNi$ system.[12] Explicitly we apply a molecular field approach, defining average fields at the Pr and RE sites as $H_e(RE) = \alpha m_{RE} - \beta m_{Pr}$ and $H_e(Pr) = \gamma m_{Pr} - \beta m_{RE}$, where α, β, γ are positive constants reflecting the interaction strength RE-RE, Pr-RE and Pr-Pr, respectively. Here $m_{RE} = xNM_{RE}$ and $m_{Pr} = (1-x)NM_{Pr}$ are the sublattice magnetizations, N is the number of RE spins per unit volume, and M_{RE} and M_{Pr} are the RE moments (expressed in SI units). In the paramagnetic phase, we define separate Curie constants C_{RE} and C_{Pr} for the RE and Pr sublattices respectively, then for an applied field H_a, we have

$$m_{RE}T = C_{RE}\left(H_a + \alpha m_{RE} - \beta m_{Pr}\right)$$
$$m_{Pr}T = C_{Pr}\left(H_a + \gamma m_{Pr} - \beta m_{RE}\right)$$

For the case $H_a = 0$, these equations can be solved to give an expression for T_M in terms of $\alpha, \beta, \gamma, C_{RE}$ and C_{Pr}:

$$T^2 - \left(\alpha C_{RE} + \gamma C_{Pr}\right)T + \left(\alpha\gamma - \beta^2\right)C_{RE}C_{Pr} = 0 .$$

All these parameters except for β can be evaluated from susceptibility data for the end point compounds PrNi and RENi. For example, we set $\gamma C_{Pr} = T_M = 19.8$ K and $\gamma = 25.45$, $\alpha C_{Gd} = T_M = 72.8$ K, $\alpha = 18.8$. The heterogeneous exchange strength β can be estimated assuming that B_c is the point at which the average Zeeman energy generated by the field on the antiparallel sublattice exceeds that due to the heterogeneous (Pr-RE) exchange, e.g. using the equations in the previous work,[12]

$$\Delta E_{ex}(x) = 2\mu_0 N^2 \beta x(1-x)M_{RE}M_{Pr} = \Delta E_{Zeeman} = 2xNM_{RE}B_c \ .$$

Thus $\beta = B_c / \mu_0 N(1-x)M_{Pr}$, for which we use the observed B_c values. The evaluated parameters of $\alpha, \beta, \gamma, C_{RE}$ and C_{Pr} listed in Table 1 enable us to calculate the magnetic transition temperature for the $Pr_{0.9}RE_{0.1}Ni$ samples. The calculation reproduces the

observed T_M quite well and the estimations indicate that the heterogeneous exchange strength is found to be similar in magnitude to the homogeneous one. Overall these findings indicate that the simple picture of the realignment of the minority RE spins occur at the critical field B_c, corresponding to a structural change from ferrimagnetism to ferromagnetism.

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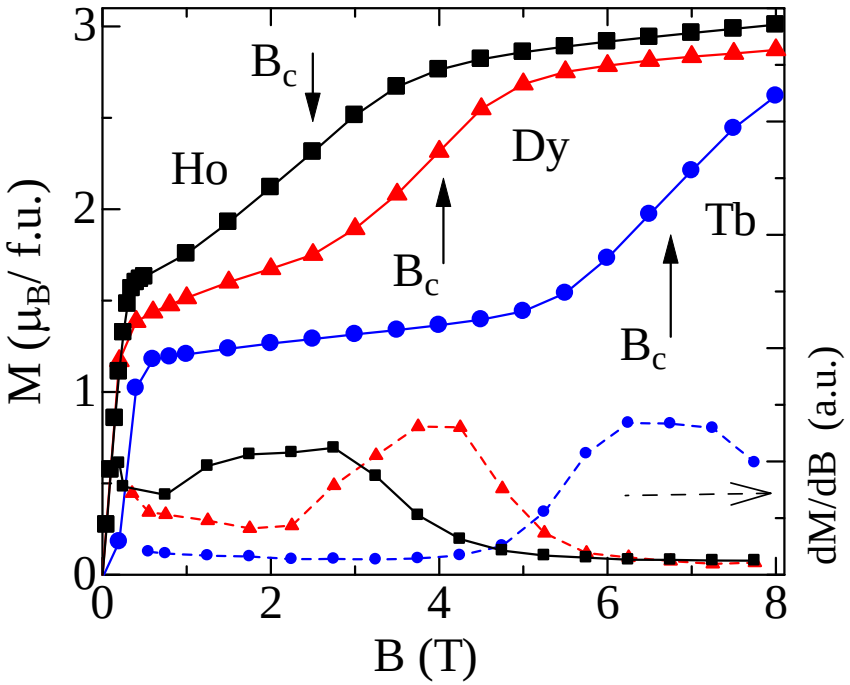

Fig. 1 (Color online) Magnetization of $Pr_{0.9}Tb_{0.1}Ni$, $Pr_{0.9}Dy_{0.1}Ni$, and $Pr_{0.9}Ho_{0.1}Ni$ observed at 2 K in an applied field along the *c*-axis. Arrows indicate critical fields B_c.

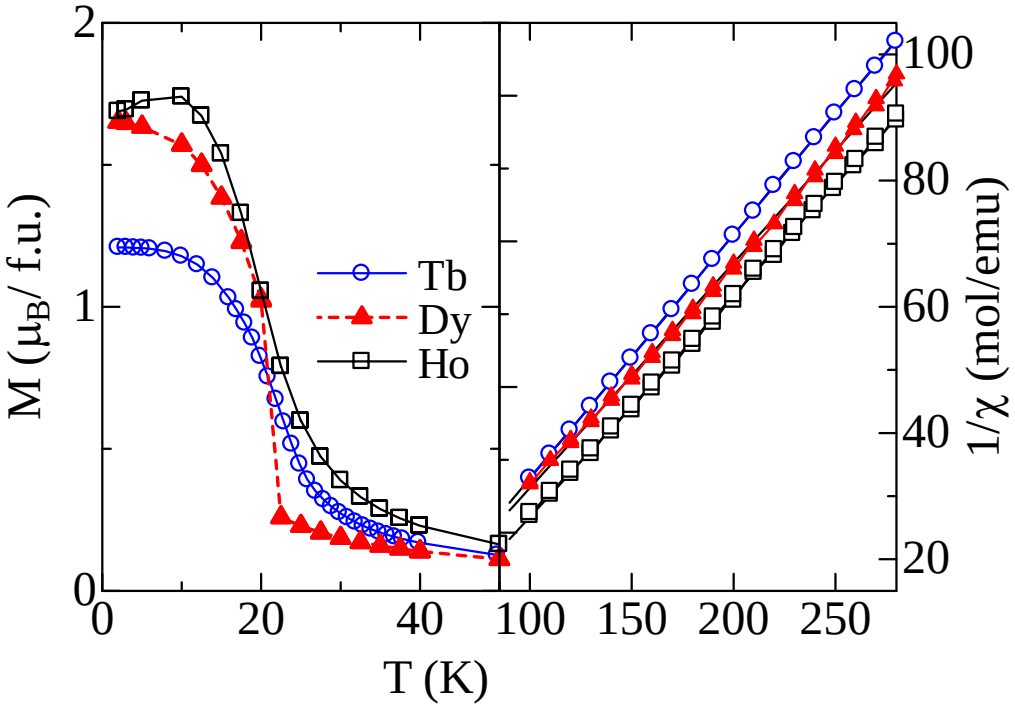

Fig. 2 (Color online) Temperature dependences of magnetization for $Pr_{0.9}Tb_{0.1}Ni$, $Pr_{0.9}Dy_{0.1}Ni$, and $Pr_{0.9}Ho_{0.1}Ni$ in an applied field of 1 T (left). Reciprocal susceptibility observed at the *c*-axis in a field of 1 T (right).

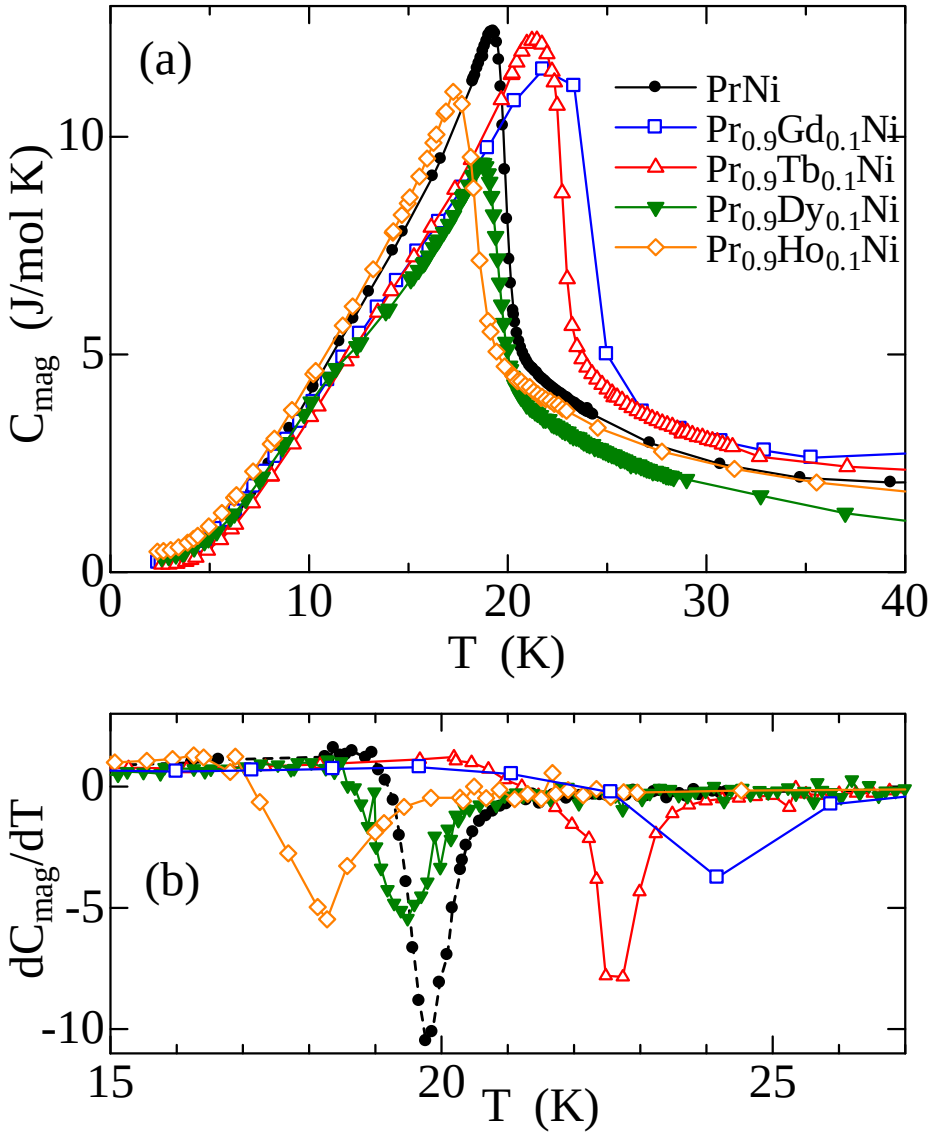

Fig. 3 (Color online) (a) Magnetic contribution to the specific heat of $Pr_{0.9}RE_{0.1}Ni$ (RE = Gd, Tb, Dy and Ho) and PrNi in zero applied field (See text for detail of derivation). (b) Temperature variations of derivative dC_M/dT.

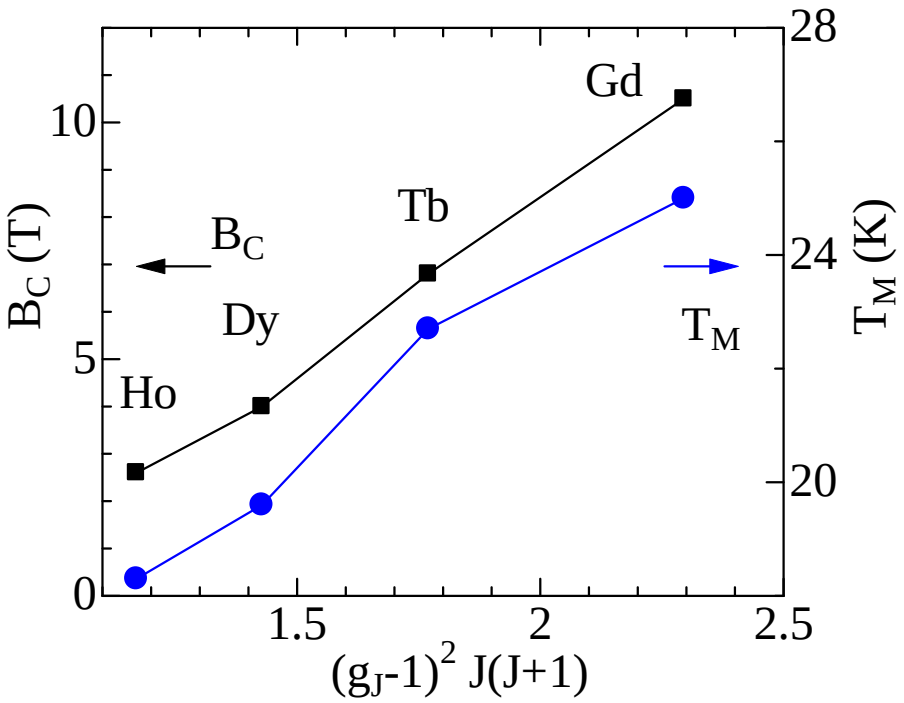

Fig. 4 (Color online) Magnetic transition temperature T_M (right scale), and critical field B_c (left scale) for the $Pr_{0.9}RE_{0.1}Ni$ (RE = Gd, Tb, Dy and Ho) against de Gennes factor.

Table 1 Parameters of RENi and $Pr_{0.9}RE_{0.1}Ni$ used for the calculation of magnetic transition temperature T_M-cal.

RE	T_M (RENi) [K]	Bc [T]	M_{eff}(RE) [μ_B]	C(RE)	α(RE)	β(RE)	T_M-cal. [K]	T_M-obs. [K]
Gd	72.8	10.5[a)]	7.94	3.86	18.84	18.13	23.4	24.7
Tb	52	6.8	9.72	5.80	8.97	11.74	21.3	22.7
Dy	62	4.0	10.65	6.95	8.92	6.91	19.6	19.6
Ho	32	2.6	10.61	6.90	4.64	4.49	18.5	18.3

a) reference[12)]