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Magnetic phase transitions in $Nd_{1-x}Pr_xFe_{11}Ti$ compounds

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Abstract. Spin-reorientation transitions in $Nd_{1-x}Pr_xFe_{11}Ti$ compounds have been studied by measuring the temperature dependence of the a.c. susceptibility and the magnetization. The angular dependence of the magnetization on the applied field was measured on magnetically aligned samples in a SQUID magnetometer. In $NdFe_{11}Ti$, the easy magnetization direction at room temperature was determined by x-ray diffraction to be the *c*-axis; at low temperatures, the SQUID measurements show a cone to be stable. At temperatures between 170 and 250 K, the SQUID measurements display more complex behaviour, which is attributed to the occurrence of a first-order magnetization process in this compound. The easy magnetization direction of $Nd_{1-x}Pr_xFe_{11}Ti$ compounds with $0.2 \leqslant x \leqslant 0.4$ changes from easy *c*-axis at high temperatures via a basal plane to easy cone at low temperatures. The magnetic phase diagram of the $Nd_{1-x}Pr_xFe_{11}Ti$ system is given. For $PrFe_{11}Ti$, the critical field of the FOMP transition below 230 K, which corresponds to the critical temperature of the first-order transition, and the anisotropy fields at temperatures ranging from 240 to 300 K have been further investigated by means of the SPD technique.

1. Introduction

It is well known that the Nd- and Pr-containing nitride counterparts of $R(Fe, Ti)_{12}$ (R denotes a rare-earth element) compounds exhibit intrinsic properties comparable with those of $Nd_2Fe_{14}B$ [1–3] and that they may be considered as candidates for permanent-magnet applications. Recently, the structure and magnetic properties of $R(Fe, Ti)_{12}$ compounds have intensively been studied [4–6]. Generally, in $RFe_{11}Ti$ compounds, the R ion occupies a single 2a thorium site in the tetragonal $ThMn_{12}$ structure while the Fe and Ti ions preferentially occupy the three manganese sites, 8f, 8i and 8j. Fe has been found to occupy 8f and 8j sites fully in $Y(Fe_{11}Ti)$ [7]. Pareti *et al* [8] have reported that in $Nd(Fe, Ti)_{12}$, besides the spin-reorientation (SR) transition from easy *c*-axis to easy cone which takes place at $T_{sr} = 163$ K, two kinds of first-order magnetization process, including FOMPs of type A1C and P2, are present at low and high temperatures. The former is a discontinuous rotation of M_s from an intermediate position to the saturation when the field is applied

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along the *c*-axis in an easy-cone sample, and the magnetic transition has been identified as a type-2 (P2) FOMP, when the applied field is perpendicular to the *c*-axis and the final state after the transition is not the saturated state, and the onset temperature of the P2 type FOMP in $NdFe_{11}Ti$ is very close to room temperature. In contrast with this, in $PrFe_{11}Ti$ no SR has been found from 4.2 K to 800 K [3]. In addition, no FOMP has been found in $PrFe_{11}Ti$ at low temperatures. The spin reorientations in the $Nd_{1-x}Y_xFe_{11}Ti$ system have been studied by Luong *et al* [9]. Kou *et al* [10] reported that spin reorientations are present in $Pr_{1-x}Y_xFe_{11}Ti$ compounds with $0.6 \leqslant x \leqslant 0.8$.

In the present work, the magnetic anisotropy and the magnetic transitions in $(Nd_{1-x}Pr_x)Fe_{11}Ti$ compounds are reported.

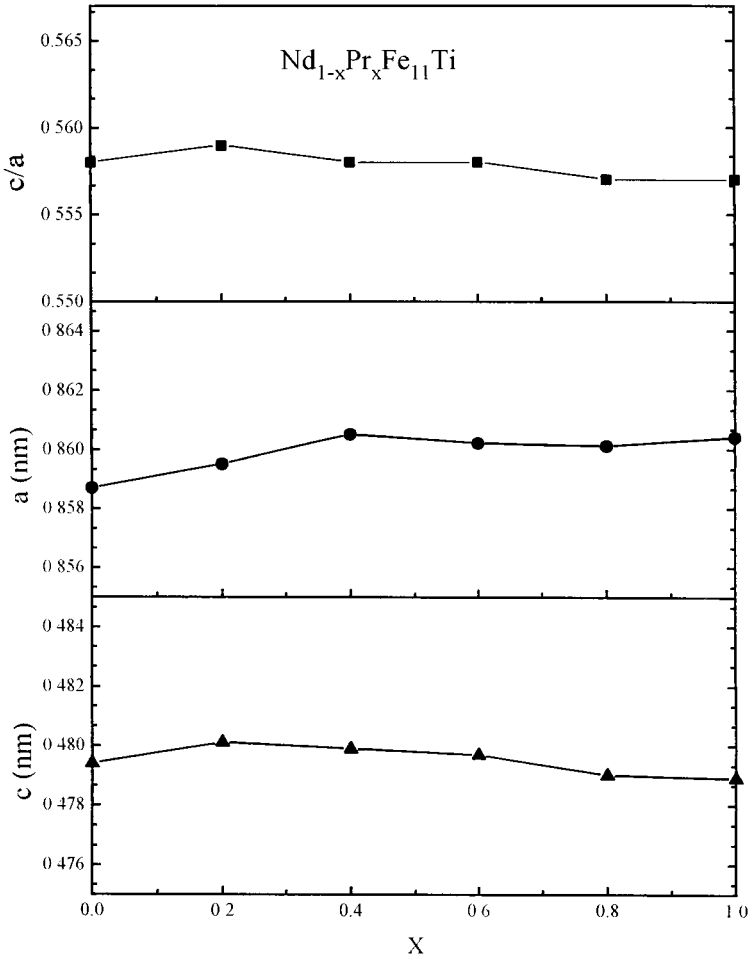


Figure 1. Lattice constants *a*, *c* and *c*/*a* of $Nd_{1-x}Pr_xFe_{11}Ti$ compounds.

2. Experimental details

Polycrystalline samples of $(Nd_{1-x}Pr_x)Fe_{11}Ti$ with $x = 0.0$, 0.2, 0.4, 0.6, 0.8 and 1.0 were prepared by arc melting under purified argon with appropriate excess amounts of

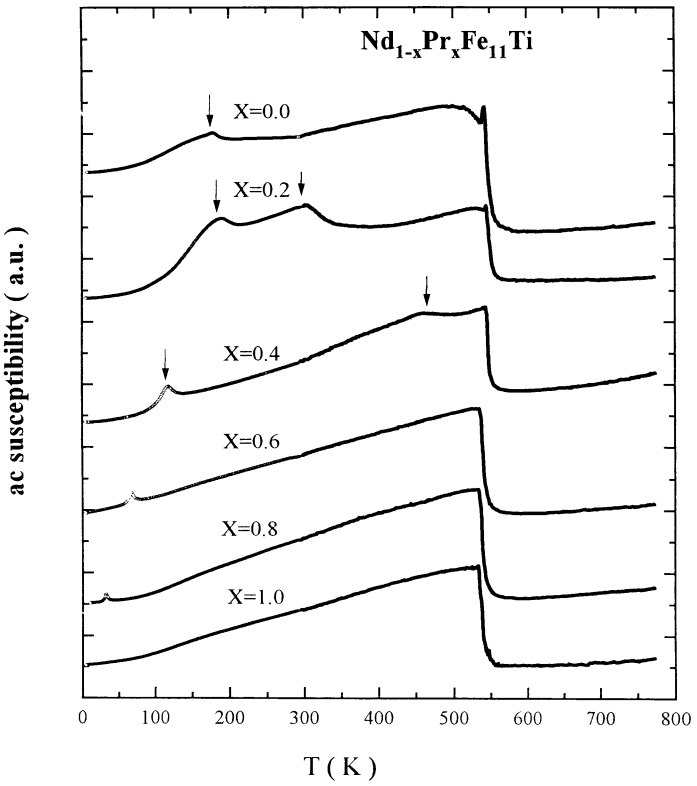


Figure 2. Temperature dependence of the a.c. susceptibility of $Nd_{1-x}Pr_xFe_{11}Ti$ compounds.

the pure starting materials in comparison with the stoichiometric compositions. Ingots were subsequently heat treated at 1100 °C for 3 to 15 days under purified argon. X-ray diffraction checks showed that all the homogenized samples are essentially of single phase with the expected tetragonal structure except for some samples in which less than 3 wt% of Fe_2Ti or α-(Fe, Ti) impurity phases were found as estimated from x-ray diffraction and the additional EDX analyses. The lattice constants of the tetragonal compounds were determined from x-ray diffraction patterns (figure 1). To determine the easy magnetization direction (EMD) of the compounds at room temperature, x-ray diffraction experiments were carried out on either magnetically aligned (with the incident x-ray beam parallel to the alignment direction) or randomly oriented powders. For a reason that will be made clear later in this paper, the sample with $x = 0.2$ was aligned at a temperature of about 100 °C. Cylindrical samples for magnetic measurements were prepared by aligning powders in a field of 1 T and fixing them in epoxy resin. The rotation-alignment method was used for the preparation of the samples with easy-plane magnetization at room temperature [11]. A SQUID magnetometer with a maximum field of 5 T was applied to measure the easy- and hard-magnetization curves of magnetically aligned samples in the temperature range from 5 to 350 K. By using a goniometer on the SQUID magnetometer, the temperature dependence of the easy magnetization direction was studied by measuring the magnetization of aligned samples as a function of the angle between the alignment direction of the sample and the applied field of 1 T. Spin reorientations and Curie temperatures were detected for bulk samples by a.c.

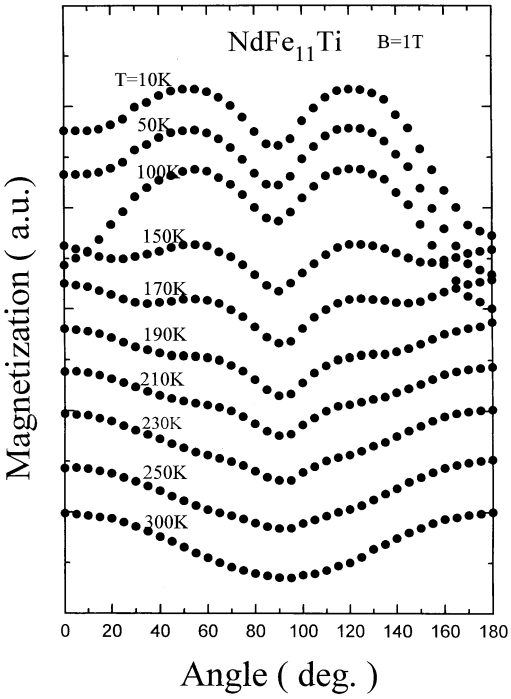


Figure 3. Dependence of the magnetization of $NdFe_{11}Ti$ on the angle between the direction of the magnetic alignment and the external field of 1 T at various temperatures.

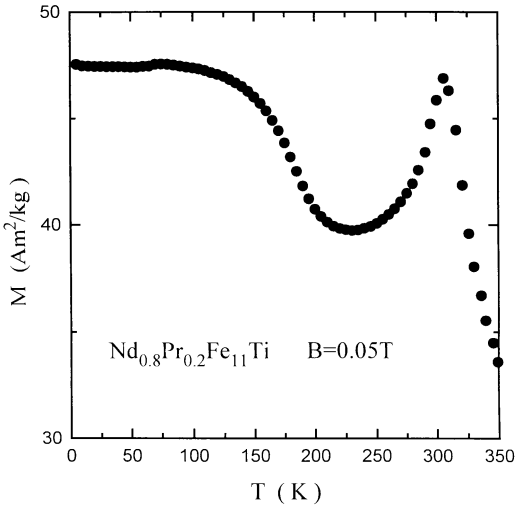


Figure 4. Temperature dependence of the magnetization of $Nd_{0.8}Pr_{0.2}Fe_{11}Ti$ in a field of 0.05 T.

initial susceptibility measurements in the temperature range from 4.2 to 300 K with an a.c. field of 48 A m^{-1} and frequency of 109 Hz at the University of Amsterdam, and from 300 to 773 K with an a.c. field of 16 A m^{-1} and frequency of 1.13 kHz in the Institute of

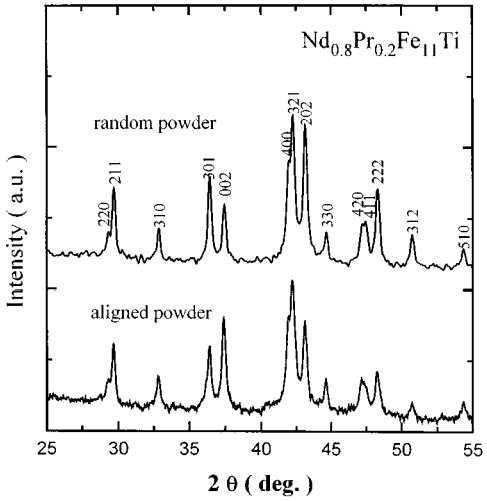
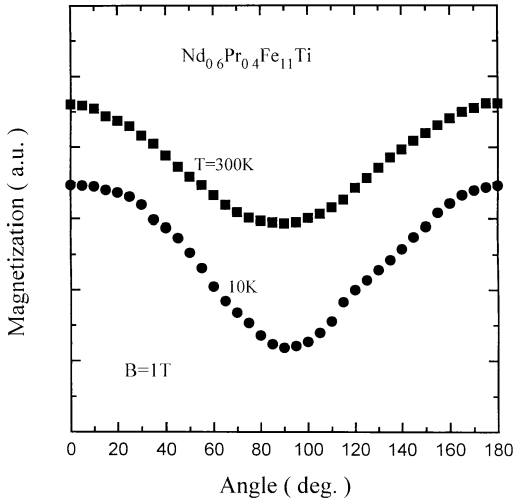


Figure 5. X-ray diffraction patterns of the magnetically aligned (at ≈100 °C) and randomly oriented powders of $Nd_{0.8}Pr_{0.2}Fe_{11}Ti$.

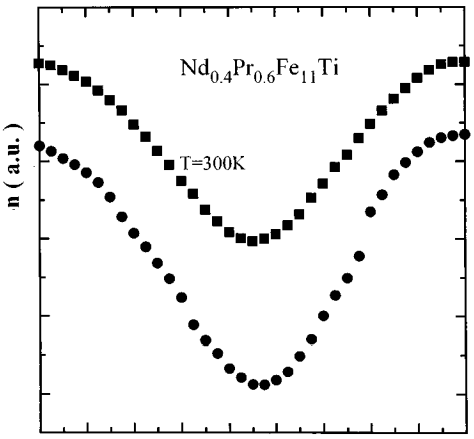
Metal Research (IMR). Measurements of the anisotropy field B_a and the critical field B_{cr} of FOMPs for the aligned sample of $PrFe_{11}Ti$ were carried out by means of the singular-point detection (SPD) technique in the pulsed-field facility at the Institute for Experimental Physics of the Technical University, Vienna, which is operated from 4.2 to 300 K with a maximum field of 30 T. The SPD technique developed by Asti *et al* [12, 13] can be efficiently used to be determine directly the anisotropy field B_a of polycrystalline samples. In a uniaxial magnetic compound, according to SPD theory, a singularity in the second derivative of the magnetization (dM^2/dB^2) versus the external field occurs at $B = B_a$ with the external field perpendicular to the alignment direction of the sample. In recent years, the anisotropy field B_a of samples with easy-plane magnetization, like $PrFe_{11}Ti$, can be successfully measured by this method through a rotation-alignment preparation of samples [11]. The same method can be also used to detect an FOMP if it is present [14], and these techniques have been effectively used in the present work.

3. Results and discussion

The temperature dependence of the a.c. susceptibility of $Nd_{1-x}Pr_xFe_{11}Ti$ compounds is displayed in figure 2. The values for Curie temperature of compounds of this series, which have been derived from figure 2, are listed in table 1. It is found that the Curie temperature of the compounds slightly decreases with increasing Pr content. The tendency of the change is in good agreement with the result reported in [4], although the Curie temperature of $PrFe_{11}Ti$ has not been given in [4]. The peaks (one or two) below the Curie temperature in the temperature dependence of the a.c. susceptibility correspond to spin-reorientation transitions. The spin-reorientation temperatures for the different compositions are also summarized in table 1. X-ray diffraction shows that when $x = 0$, the c axis is the easy magnetization direction at room temperature, whereas the compounds for $0.4 \leqslant x \leqslant 1$ have an easy-plane type of magnetization. The magnetization of $NdFe_{11}Ti$ as a function of the angle between the alignment direction and the external field of 1 T is given in figure 3



(a)



(b)

Figure 6. (a) Dependence of the magnetization of $Nd_{0.6}Pr_{0.4}Fe_{11}Ti$ on the angle between the direction of the magnetic alignment and of the external field of 1 T at 10 and 300 K. (b) Dependence of the magnetization of $Nd_{0.4}Pr_{0.6}Fe_{11}Ti$ on the angle between the direction of the magnetic alignment and of the external field of 1 T at 10 and 300 K.

for various temperatures ranging from 10 to 300 K. This method can be used efficiently to detect the type of easy magnetization direction and the temperature of a spin-reorientation transition [15, 16]. From x-ray diffraction, we can conclude that the *c*-axis is the EMD at room temperature. The magnetization of the $NdFe_{11}Ti$ sample is shown in figure 3 to have a maximum value in the direction 0° at 300 K. After the sample is rotated through 90°, the magnetization measured along the external field direction reaches a relative minimum. The magnetization at 10 K shows a maximum at about 53°, which shows that the anisotropy of the sample has changed from easy *c*-axis at 300 K to easy cone at 10 K. The cone angle, which amounts to 53°, is nearly constant from 10 to 150 K, which is in good agreement with the results in [3] and [8]. It can be seen, from figure 3, that at 150 K the minimum

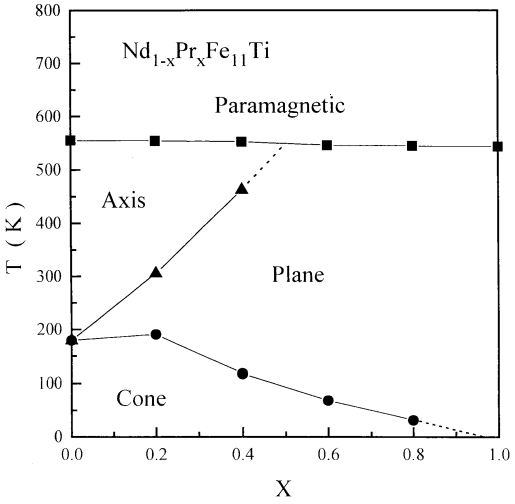


Figure 7. Magnetic phase diagram of $Nd_{1-x}Pr_xFe_{11}Ti$.

of magnetization at the angle 0° has changed into a maximum, and thus, two maxima of magnetization exist. With further increasing temperature, the maximum of the magnetization at 0° becomes the highest one at about 170 K, which means that the magnetization direction changes from the easy cone to the easy axis. The observation that the angle of the maximum at non-zero angle, which at higher temperatures becomes a shoulder, does not gradually shift to 0° as the temperature increases, indicates that the SR transition is first order [17]. Between 170 and 250 K, the minimum of the free energy corresponding to the maximum of the magnetization at non-zero angle is a relative minimum. According to the theory of Asti and Bolzoni [18], the external magnetic field can change the free energy by a different amount for various angles so as to induce an FOMP from one minimum of energy to another inequivalent one. We attribute the maximum at non-zero angle to the occurrence of an FOMP.

Table 1. Magnetic data of $Nd_{1-x}Pr_xFe_{11}Ti$ compounds.

x	T_c (K)	EMD 300 K	B_{cr} (T) 5 K	T_{sr1} (K)	T_{sr2} (K)
0.0	555	*c*-axis	3.2	178	
0.2	554	*c*-axis[a]		190	305
0.4	553	*ab*-plane	3.5	117	462
0.6	545	*ab*-plane	4.4	68	
0.8	544	*ab*-plane		31	
1.0	543	*ab*-plane	7.4		

[a] This result was obtained at 373 K.

In figure 2, two peaklike anomalies are clearly visible for the sample of $x = 0.2$, possibly related to two SR transitions T_{sr1} and T_{sr2}. To find out whether the anomalies originate from SR transitions, the temperature dependence of the magnetization of a powder sample with $x = 0.2$ has been measured in a field of 0.05 T (figure 4). The two different anomalies which correspond to SR transitions are found at temperatures which are in good

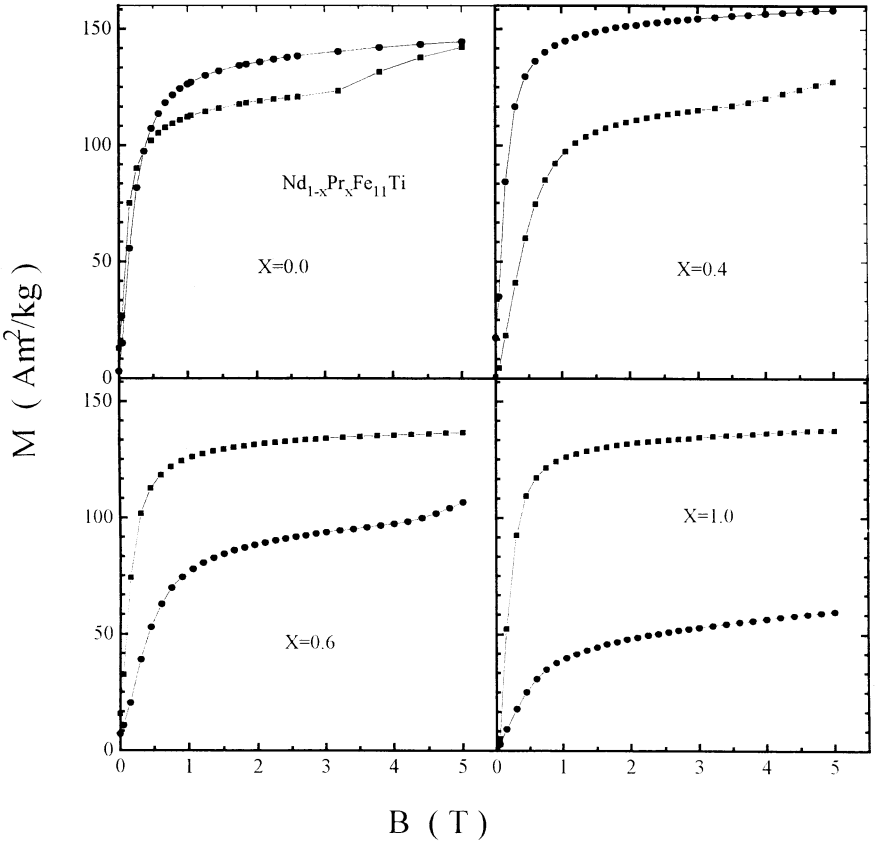


Figure 8. Easy- and hard-magnetization curves at 5 K of $Nd_{1-x}Pr_xFe_{11}Ti$ for $x = 0.0$, 0.4, 0.6 and 1.0, measured on magnetically aligned powders.

agreement with the results in figure 2. In order to determine the EMD of the sample well above the SR at about 300 K, x-ray diffraction was carried out on a magnetically aligned sample which was fixed at ≈100 °C by epoxy resin. The result is shown in figure 5 together with the result on randomly oriented powder. Although the other reflections hardly change, it is evident that the intensity of the (002) reflection is enhanced. This indicates the EMD is easy-*c*-axis type above $T_{sr1} = 305$ K.

The results on samples with $x \geqslant 0.2$, to be discussed below, present evidence that the anisotropy is of easy in-plane type in the temperature interval $T_{sr2} < T < T_{sr1}$, whereas it is easy-cone type below T_{sr2}. To determine the EMD of the samples for $0.4 \leqslant x \leqslant 0.8$ below T_{sr1}, the magnetization of the compounds with $x = 0.4$ and $x = 0.6$ as a function of angle between the alignment direction and the external field direction was measured at 300 and 10 K (figures 6(a) and (b)). In comparison with the results at 300 K, a similar magnetic behaviour is found at 10 K. Detailed inspection of the results at 10 K reveals rather indistinct maxima of the magnetization at about 50° and 120° in figure 6(a) and at about 60° and 125° in figure 6(b), respectively. These rather blurred peaks look not really symmetric with respect to 90°. From the results of figure 3, it seems reasonable to conjecture that they may be also related to FOMP phenomena. In figure 2 anomalies corresponding to SR transitions are clearly observed. On the basis of the result in the compound with $x = 0$,

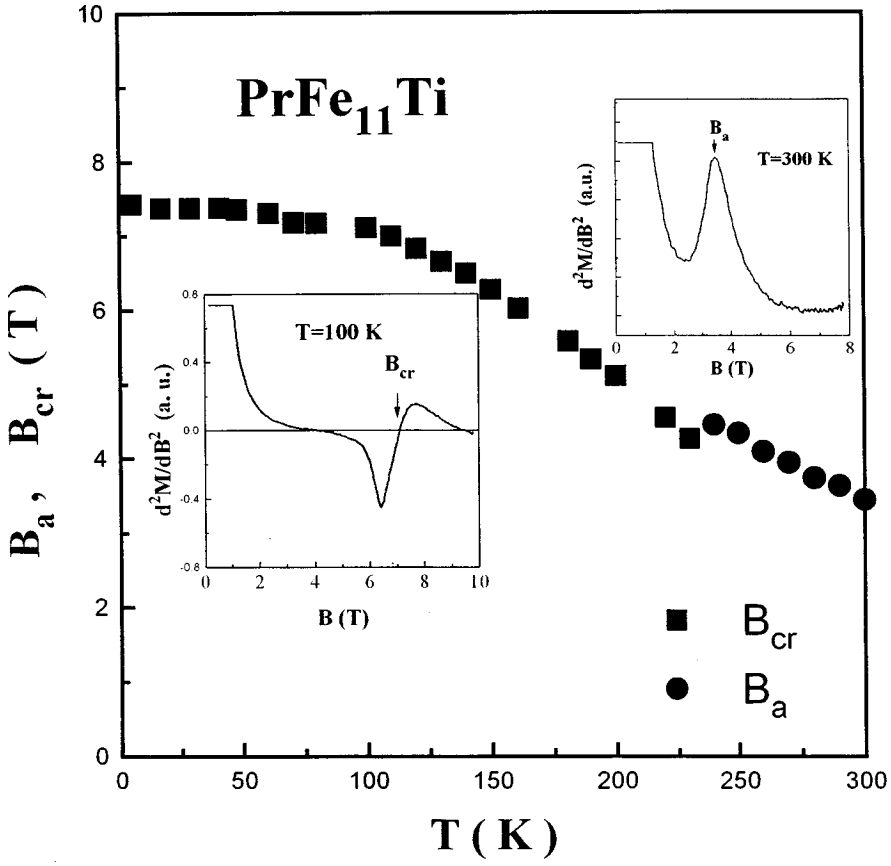


Figure 9. Dependence of B_{cr} (black squares) and B_a (black circles) on temperature in $PrFe_{11}Ti$. The insets are d^2M/dH^2–B curves at 100 and 300 K of magnetically aligned $PrFe_{11}Ti$ powders, respectively.

the EMD of the samples with $0.4 \leqslant x \leqslant 0.8$ below T_{sr} can be assumed to be easy cone. The angle of the cone apparently is so close to 90° that the angle cannot be easily detected by this method. The EMDs of the samples with $0.2 \leqslant x \leqslant 0.4$ change from c-axis at high temperatures via basal plane to a cone at low temperatures. According to the above results, a magnetic phase diagram of $Nd_{1-x}Pr_xFe_{11}Ti$ is proposed as shown in figure 7. This diagram indicates that with increasing Pr content the easy in-plane anisotropy of the rare-earth sublattice enhances. The easy-axis and easy-cone zones are gradually contracted, making room for easy plane. Finally, the easy-plane anisotropy of the Pr sublattice in $PrFe_{11}Ti$ dominates the c-axis Fe-sublattice anisotropy up to Curie temperature.

Figure 8 shows the easy- and hard-magnetization curves of $Nd_{1-x}Pr_xFe_{11}Ti$ for $x = 0.0$, 0.4, 0.6 and 1.0, measured at 5 K. FOMPs are observed for the samples with $x = 0.0$, 0.4 and 0.6. The values of the critical field of the FOMP are listed in table 1. From figure 8, it is concluded that the anisotropy of the compounds increases with increasing Pr content. This conclusion can also be drawn from the change of the ratio c/a in the compounds (figure 1). Particularly in $PrFe_{11}Ti$, through a direct extrapolation it may be inferred from figure 8 that the anisotropy field must be higher than 10 T. However, it has been reported [3] that the crystalline-electric-field (CEF) parameter A_0^2 of $PrFe_{11}Ti$ is close to that of $NdFe_{11}Ti$. Thus,

it is expected that the FOMP may exist in $PrFe_{11}Ti$ above 5 T at about 5 K. Therefore, measurements of the anisotropy field B_a and the critical field B_{cr} of the FOMP have been carried out on an aligned sample of $PrFe_{11}Ti$ by means of the SPD technique from 4.2 to 300 K (figure 9). In order to exhibit the dependence of the second field derivative of the magnetization dM^2/dB^2 on the applied field B at different temperature and understand how to determine the anisotropy field B_a and the critical field B_{cr} of the FOMP by the SPD technique, two typical SPD patterns of the dM^2/dB^2 against B corresponding to the anisotropy field B_a and the critical field of the FOMP transition for $PrFe_{11}Ti$ are given in figure 9, as the insets at 300 K and 100 K, respectively. It is clear that the FOMP indeed exist in $PrFe_{11}Ti$, the value of B_{cr} being 7.4 T at 5 K. With increasing temperature, B_{cr} decreases to 4.3 T at 230 K. The temperature dependence of B_a from 240 to 300 K is also given in figure 9. Thus, it is important indeed to consider the contribution of higher-order CEF terms to the magnetocrystalline anisotropy in $PrFe_{11}Ti$.

Acknowledgments

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