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Magnetocrystalline anisotropy of $R_2Fe_{14}BN_x$ ($R = Pr, Nd$)

X. C. Kou,* T. S. Zhao,[†] R. Grössinger, and H. R. Kirchmayr

Institute for Experimental Physics, Technical University of Vienna, A-1040 Wien, Austria

X. Li and F. R. de Boer

Van der Waals-Zeeman Laboratorium, University of Amsterdam, 1018 XE Amsterdam, The Netherlands

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The spin-reorientation transition, magnetic anisotropy, and first-order magnetization process (FOMP) of $R_2Fe_{14}BN_x$ compounds with $R = Pr$ or Nd have been investigated by ac-susceptibility measurements from 4.2 to 300 K, the singular-point-detection technique in a pulsed-field facility in fields up to 30 T between 4.2 and 500 K and magnetization measurements in the Amsterdam High-Field Installation in fields up to 35 T and 4.2 K. It is observed that, compared to the corresponding $R_2Fe_{14}B$ compounds, the anisotropy field, B_a , and the critical field of the FOMP, B_{cr} , of $R_2Fe_{14}BN_x$ are dramatically reduced, whereas the spin-reorientation temperature T_{SR} , of $Nd_2Fe_{14}BN_x$ is only slightly decreased. These experimental data are analyzed in terms of the crystalline-electric-field interaction combined with the R -Fe exchange interaction.

Recently, in the study of the magnetic properties of R - T intermetallic compounds, research interest has turned to the R -Fe nitrides.¹⁻³ These nitrides are generally obtained by a solid-gas reaction process at certain temperatures. It was shown that nitrogen atoms enter interstitially into the R_2Fe_{17} lattice. The magnetic properties of R_2Fe_{17} compounds are changed upon nitrogenation in a way that leads, e.g., for $Sm_2Fe_{17}N_x$ to the enhancement of the Curie temperature and the saturation magnetization and, particularly, to uniaxial magnetic anisotropy which is indispensable for materials used for permanent magnets. The magnetic properties of the $RFe_{11}TiN_x$ series also have been investigated.⁴ Among them $NdFe_{11}TiN_x$ has a high Curie temperature, high saturation magnetization, and also a high uniaxial anisotropy at room temperature. This all makes $NdFe_{11}TiN_x$, as well as $Sm_2Fe_{17}N_x$, promising candidates for permanent magnetic materials. Up to now, we know of no report concerning the intrinsic magnetic properties of $R_2Fe_{14}B$ compounds upon nitrogenation. A spin-reorientation transition has been observed in $Nd_2Fe_{14}B$ at 135 K.⁵ A first-order magnetization process (FOMP) has been detected in $Nd_2Fe_{14}B$ (Refs. 6 and 7) and $Pr_2Fe_{14}B$ (Refs. 7 and 8) below about 200 K. These observed magnetic properties has been analyzed by different groups⁹⁻¹¹ in terms of the crystalline electric-field interaction combined with the R -Fe exchange interaction. The purpose of the present paper is to investigate the magnetic properties of $Pr_2Fe_{14}B$ and $Nd_2Fe_{14}B$ after nitrogenation.

$Pr_2Fe_{14}B$ and $Nd_2Fe_{14}B$ were prepared by arc melting the pure starting materials of at least 99.9 wt% purity in an arc melting furnace under the protection of purified argon gas. The as-cast ingots were annealed at 900 °C for three weeks. $Pr_2Fe_{14}BN_x$ and $Nd_2Fe_{14}BN_x$ samples were obtained by nitrogenizing the finely powdered $R_2Fe_{14}B$ in a nitrogen-loading setup at 500 °C for two hours in nitrogen gas under a pressure of 50 bar. This nitrogen-loading

setup is equipped with a very sensitive balance. The amount of absorbed nitrogen can be directly obtained from the difference of the sample weight before and after nitrogenation. The nitrogen concentration in the nitrides $R_2Fe_{14}BN_x$ was determined to be $x \cong 1.0$. The phase purity of the resulting nitrides was checked by x-ray diffraction. The nitrides were found to be single phase with the tetragonal structure, except for a few percent of iron. Aligned samples were prepared by fixing powder magnetically aligned at room temperature at an external field of 1 T with resin-doped epoxy solution.

The temperature-induced change of the spin configuration of $Nd_2Fe_{14}BN_x$ was detected by measuring the temperature dependence of the components χ' (real component) and χ'' (imaginary component) of the ac susceptibility from 4.2 to 300 K in an ac field of 600 A/m with a frequency of 100 Hz. The value of the spin-reorientation temperature, T_{SR} , was defined as the temperature where $d\chi'/dT$ achieves a minimum. Figure 1 shows the temperature dependence of χ' and χ'' measured for $Nd_2Fe_{14}BN_x$. In $\chi''(T)$, a kink is clearly visible, located at exactly the same temperature where $d\chi'/dT$ reaches a minimum. Similarly, as for $Nd_2Fe_{14}B$,¹² it follows from this figure that the spin-reorientation temperature of $Nd_2Fe_{14}BN_x$ is 134 K.

At low temperatures, FOMP's are observed for $Nd_2Fe_{14}BN_x$ and $Pr_2Fe_{14}BN_x$, which in nature are similar to the FOMP's in the corresponding $R_2Fe_{14}B$ compounds, i.e., the FOMP observed in $Pr_2Fe_{14}BN_x$ is of type II, and in $Nd_2Fe_{14}BN_x$ is of type I. The type-I and type-II FOMP are characterized by whether after the FOMP transition the magnetization reaches the saturation state or not, respectively. The critical field of the FOMP, B_{cr} , is defined, in value, to be the minimum external field needed to induce the jump or discontinuity in the magnetization curve. The anisotropy field, B_a , and the critical field of the FOMP, B_{cr} , of $Pr_2Fe_{14}BN_x$ and

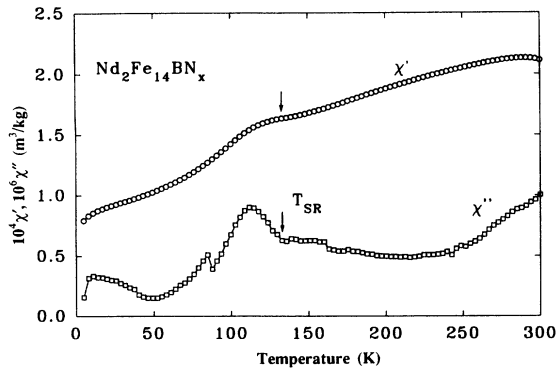


FIG. 1. Temperature dependence of the ac susceptibility, χ' and χ'' , of $\text{Nd}_2\text{Fe}_{14}\text{BN}_x$.

$\text{Nd}_2\text{Fe}_{14}\text{BN}_x$ have been studied in the temperature range from 4.2 to 500 K by the singular-point-detection (SPD) technique. Figures 2 and 3 show the temperature dependences of B_a and B_{cr} measured for $\text{Pr}_2\text{Fe}_{14}\text{BN}_x$ and $\text{Nd}_2\text{Fe}_{14}\text{BN}_x$, respectively. The data measured previously for $\text{Pr}_2\text{Fe}_{14}\text{B}$ and $\text{Nd}_2\text{Fe}_{14}\text{B}$ are also plotted for comparison.¹² The values of B_{cr} determined by the SPD technique at 4.2 K of $\text{Pr}_2\text{Fe}_{14}\text{BN}_x$ and $\text{Nd}_2\text{Fe}_{14}\text{BN}_x$ are 6.7 and 8.9 T, respectively. The values of B_a at 300 K of $\text{Pr}_2\text{Fe}_{14}\text{BN}_x$ and $\text{Nd}_2\text{Fe}_{14}\text{BN}_x$ are 4.7 and 4.6 T, respectively. Both B_{cr} and B_a of $\text{Pr}_2\text{Fe}_{14}\text{BN}_x$ and $\text{Nd}_2\text{Fe}_{14}\text{BN}_x$ are much lower than for $\text{Pr}_2\text{Fe}_{14}\text{B}$ and $\text{Nd}_2\text{Fe}_{14}\text{B}$. In contrast to the situation in $R_2\text{Fe}_{17}\text{N}_x$ compounds where the uniaxial anisotropy of the compounds is strongly enhanced upon nitrogenation,^{1,2} the values of B_a and B_{cr} of $R_2\text{Fe}_{14}\text{BN}_x$ are dramatically reduced after nitrogenation. Additionally, the onset temperatures of the FOMP transition in $\text{Pr}_2\text{Fe}_{14}\text{BN}_x$ and $\text{Nd}_2\text{Fe}_{14}\text{BN}_x$ are lower than that in the corresponding $R_2\text{Fe}_{14}\text{B}$ compounds.

Magnetization measurements have been done at 4.2 K on magnetically aligned $\text{Pr}_2\text{Fe}_{14}\text{BN}_x$ and $\text{Nd}_2\text{Fe}_{14}\text{BN}_x$ samples applying quasistatic fields up to 35 T in the High-Field Installation at the University of Amsterdam.

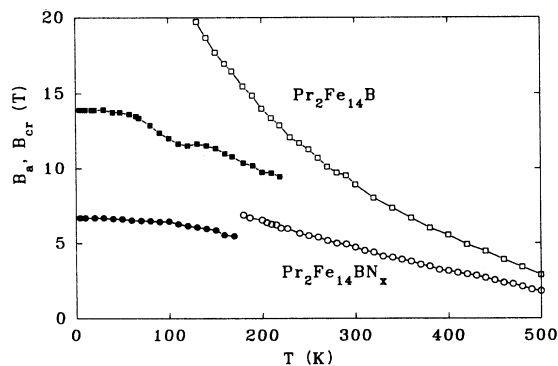


FIG. 2. Temperature dependence of the anisotropy field, B_a (○), and the critical field of the FOMP, B_{cr} (●), measured by the SPD technique for $\text{Pr}_2\text{Fe}_{14}\text{BN}_x$. The data of B_a (□) and B_{cr} (■) obtained previously for $\text{Pr}_2\text{Fe}_{14}\text{B}$ are presented for comparison (Ref. 12). The fact that the values of B_a and B_{cr} are not continuous is due to the occurrence of a type-II FOMP.

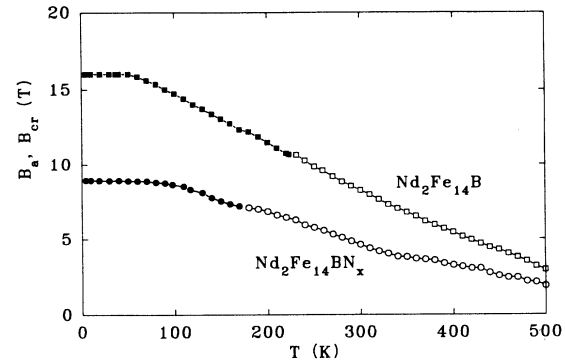


FIG. 3. Temperature dependence of the anisotropy field, B_a (○), and the critical field of the FOMP, B_{cr} (●), measured by the SPD technique for $\text{Nd}_2\text{Fe}_{14}\text{BN}_x$. The data of B_a (□) and B_{cr} (■) obtained previously for $\text{Nd}_2\text{Fe}_{14}\text{B}$ are presented for comparison (Ref. 12).

Two types of measurement procedures were employed. In the first type, the external field is programmed to change stepwise with time, decreasing from the maximum field value, and being constant during each step for about 20 ms. In this way, the field is constant during a time which is long compared with the decay time of the eddy currents induced during the pulse. Therefore this method is used in order to precisely determine the saturation magnetization. In the second type of measurement, the external field is programmed to change “linearly” with the time, again decreasing from the maximum field value. This method is used to precisely determine the critical field of the field-induced magnetization process. Of course, for this type of measurement a detailed comparison of these results with the results obtained by means of the stepwise pulse is necessary in order to check whether eddy currents have influenced the measurement. Figure 4 shows the field dependence of the magnetization at 4.2 K measured on a magnetically aligned $\text{Pr}_2\text{Fe}_{14}\text{BN}_x$ sample with the field applied parallel and perpendicular to the preferential direction. The FOMP transition is usually not very pronounced when the magnetization measurement is performed on magnetically aligned samples and an accurate determination of B_{cr} is difficult. Previously,¹² we deduced that a kink appears if dM/dB is plotted as function of the external field B . This kink is located exactly at the critical field where FOMP occurs. As shown in the inset in Fig. 4, such a kink is clearly seen for $\text{Pr}_2\text{Fe}_{14}\text{BN}_x$. The value for B_{cr} at 4.2 K, thus obtained, is 6.6 T for $\text{Pr}_2\text{Fe}_{14}\text{BN}_x$ and 8.7 T for $\text{Nd}_2\text{Fe}_{14}\text{BN}_x$. These values are in good agreement with the results obtained by the SPD technique (Table I). The reliability of this method is further corroborated by perfect agreement of the values for B_{cr} determined by this method at 4.2 K on aligned $\text{Pr}_2\text{Fe}_{14}\text{B}$ (13.9 T) and $\text{Nd}_2\text{Fe}_{14}\text{B}$ (16.2 T) samples and by measurements on $\text{Pr}_2\text{Fe}_{14}\text{B}$ (13.2 T) and $\text{Nd}_2\text{Fe}_{14}\text{B}$ (16.3 T) single crystals.⁷

The crystal structures of the $R_2\text{Fe}_{14}\text{BN}_x$ compounds and the corresponding $R_2\text{Fe}_{14}\text{B}$ compounds are the same. We assumed that the nitrogen atoms enter interstitially rather than substitutionally into the tetragonal $R_2\text{Fe}_{14}\text{B}$

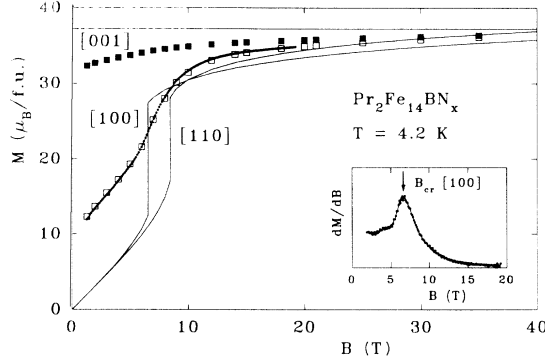


FIG. 4. Magnetic-field dependence of the magnetization at 4.2 K measured on the magnetically aligned $\text{Pr}_2\text{Fe}_{14}\text{BN}_x$ with the “stepwise” eternal field applied parallel (■) and perpendicular (□) to the alignment direction. The dotted line corresponds to data obtained with a pulse in which the field varies linearly with time. The solid lines represent the calculated magnetization curves along the [001], [100], and [110] direction at 0 K for $\text{Pr}_2\text{Fe}_{14}\text{BN}_x$, a single crystal. The inset shows field dependence of the first derivative of magnetization, dM/dB . The kink in the dM/dB vs B curve corresponds to the critical field of the FOMP.

lattice and that they occupy interstitial sites, which are near to the rare-earth ions. Therefore, the change of the magnetic properties of $R_2\text{Fe}_{14}\text{B}$ upon nitrogenation is mainly due to the rare-earth sublattice. This was found to be the case in $R_2\text{Fe}_{17}\text{N}_x$ (Refs. 1 and 3) and $R\text{Fe}_{11}\text{TiN}_x$ (Ref. 4) compounds. The first-order magnetization process and the spin reorientation phenomena observed at low temperatures in $R_2\text{Fe}_{14}\text{BN}_x$ compounds can be described in terms of the crystalline electric field (CEF) interaction combined with the R -Fe exchange interaction. Neglecting the difference between $4f$ and $4g$ sites in $R_2\text{Fe}_{14}\text{BN}_x$, there are two magnetically inequivalent rare-earth sites: $R(1)$ and $R(2)$. In the presence of an external magnetic field \mathbf{B} , the Hamiltonian of the $R(i)$ ion is given by

$$\mathcal{H}(i) = \lambda \mathbf{L} \cdot \mathbf{S} + \sum_{n,m} A_n^m(i) C_n^m + 2\mu_B \mathbf{S} \cdot \mathbf{B}_{\text{ex}} + \mu_B (\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{B},$$

$$A_n^m(1) = (-1)^{m/2} A_n^{-m}(1) = (-1)^{m/2} A_n^m(2),$$

$$(n = 2, 4, 6; |m| = 0, 2, 4, 6; |m| \leq |n|),$$

where λ is the spin-orbit coupling constant; \mathbf{L}, \mathbf{S} are the orbital and spin angular momenta, respectively; $A_n^m(i)$ are the CEF parameters of the $R(i)$ ion, and C_n^m the tensor operators, and \mathbf{B}_{ex} is the R -Fe exchange field acting on the $4f$ spin. The matrix elements of $\mathcal{H}(i)$ are calculated by using the irreducible tensor operator technique.¹³ The mixing of the first excited J multiplet of the Pr^{3+} ion ($\lambda = 620$ K) and the Nd^{3+} ion ($\lambda = 536$ K) is taken into account in the calculation. $\mathbf{B}_{\text{ex}}(T)$ is assumed to be proportional to and antiparallel to $\mathbf{M}_{\text{Fe}}(T)$, the magnetic moment of the Fe sublattice. The temperature dependences of the magnetic anisotropy constant of the Fe sublattice, $K_{\text{Fe}}^{\text{Fe}}(T)$, and $M_{\text{Fe}}(T)/M_{\text{Fe}}(0)$ are taken to be the same as those in $\text{Y}_2\text{Fe}_{14}\text{B}$ after scaling the different Curie temperatures.¹⁴ The value of $M_{\text{Fe}}(0)$ for $\text{Pr}_2\text{Fe}_{14}\text{BN}_x$ and for $\text{Nd}_2\text{Fe}_{14}\text{BN}_x$ is assumed to be the same as previously used for $\text{Pr}_2\text{Fe}_{14}\text{B}$ and $\text{Nd}_2\text{Fe}_{14}\text{B}$, i.e., $M_{\text{Fe}}(0) = 31 \mu_B/\text{f.u.}$ ¹⁵

The fact that the value of B_a at room temperature is much lower for $R_2\text{Fe}_{14}\text{BN}_x$ than that for $R_2\text{Fe}_{14}\text{B}$ gives direct evidence that the second-order CEF parameter of $R_2\text{Fe}_{14}\text{BN}_x$ is smaller. The value of A_2^0 is estimated by fitting the experimental B_a at 300 K under the assumption that the contributions to the anisotropy from the high-order CEF terms is negligible at 300 K.¹⁶ The simultaneous occurrence of a FOMP and a spin-reorientation phenomenon at low temperatures in $\text{Nd}_2\text{Fe}_{14}\text{BN}_x$ pose strict limitations on the estimated CEF parameters. Consequently, the most reliable CEF parameters can be obtained by fitting simultaneously the FOMP and the spin reorientation for one compound. The spin-reorientation transition in $\text{Nd}_2\text{Fe}_{14}\text{BN}_x$ is determined mainly by the temperature-induced competition between the diagonal second-order, fourth-order, and sixth-order CEF terms. Due to the large contribution from the sixth-order CEF term, the temperature-induced competition between the second-order and the sixth-order CEF terms plays an important role in determining the spin-reorientation temperature. The fact that the spin-reorientation temperature decreases only slightly upon nitrogenation suggests that the sixth-order CEF parameter, $|A_6^0|$, decreases nearly proportional to the second-order CEF parameter, A_2^0 . The fourth-order CEF parameter, A_4^0 , and the off-diagonal sixth-order CEF parameter, A_6^4 , can be estimated by fitting the FOMP transition. Table I lists the values of $2\mu_B B_{\text{ex}}$ and A_n^m at 0 K

TABLE I. The estimated parameters of $2\mu_B B_{\text{ex}}$ and A_n^m at 0 K for $R_2\text{Fe}_{14}\text{BN}_x$ and $R_2\text{Fe}_{14}\text{B}$ ($R = \text{Pr}, \text{Nd}$) (Ref. 15), the critical field of the FOMP, B_{cr} , at 4.2 K, and the anisotropy field, B_a , at 300 K determined by the SPD technique for $R_2\text{Fe}_{14}\text{BN}_x$ and $R_2\text{Fe}_{14}\text{B}$ ($R = \text{Pr}, \text{Nd}$) (Ref. 12), and the spin reorientation temperature, T_{SR} , for $\text{Nd}_2\text{Fe}_{14}\text{BN}_x$ and $\text{Nd}_2\text{Fe}_{14}\text{B}$ (Ref. 5). The symbol “ i ” represents $\sqrt{-1}$.

Compounds	$2\mu_B B_{\text{ex}}$	A_2^0	A_2^2/i	A_4^0	A_6^0	A_6^4	B_{cr}	B_a	T_{SR}
$\text{Pr}_2\text{Fe}_{14}\text{BN}_x$	780	240	± 130	-170	-600	-200	6.7	4.7	—
$\text{Pr}_2\text{Fe}_{14}\text{B}$	780	400	± 220	-100	-1100	-500	13.9	8.9	—
$\text{Nd}_2\text{Fe}_{14}\text{BN}_x$	630	320	± 170	-180	-300	-200	8.9	4.6	134
$\text{Nd}_2\text{Fe}_{14}\text{B}$	630	600	± 320	-260	-550	-400	16.2	8.3	135

used in the present calculation. The results obtained for $\text{Pr}_2\text{Fe}_{14}\text{B}$ and $\text{Nd}_2\text{Fe}_{14}\text{B}$ by fitting the magnetization curves of single crystals along different crystallographic directions at different temperatures are presented for comparison.¹⁵ This set of CEF and exchange-field parameters of $\text{Pr}_2\text{Fe}_{14}\text{B}$ and $\text{Nd}_2\text{Fe}_{14}\text{B}$, forming a part of our systematic investigation of the R - T compounds, is in general agreement with that obtained by Yamada *et al.*,⁹ Radwanski and Franse,¹⁰ and Cadogan *et al.*¹¹ Our work on heavy rare-earth $R_2\text{Fe}_{14}\text{B}$ compounds appeared in Ref. 17, where the comparison to the parameters obtained by Yamada *et al.*⁹ and Givord *et al.*¹⁸ was given, and fits well to the inelastic-neutron-scattering results by Loewenhaupt *et al.*¹⁹ Using the values for $2\mu_B B_{cx}$ and A_n^m listed in Table I, the spin-reorientation temperature

and the cone angle for $\text{Nd}_2\text{Fe}_{14}\text{BN}_x$ are calculated to be 132 K and 31.6° , respectively, whereas the critical field of the FOMP at 0 K are 6.6 and 8.5 T for $\text{Pr}_2\text{Fe}_{14}\text{BN}_x$ along the [100] and [110] directions, respectively, and 8.7 T for $\text{Nd}_2\text{Fe}_{14}\text{BN}_x$ along the [100] direction, which is in fair agreement with the experiments. The magnetization curves along different crystallographic directions for a $\text{Pr}_2\text{Fe}_{14}\text{BN}_x$ single crystal at 0 K have also been calculated and are shown in Fig. 4.

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*Present address: Laboratoire Louis Néel, Center National de la Recherche Scientifique, CNRS, 166X, 38042 Grenoble CEDEX, France. Permanent address: Institute of Metal Research, Academia Sinica, Shenyang 110015, People's Republic of China.

†Permanent address: Department of Physics, Jilin University, Changchun 130023, People's Republic of China.

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