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Neutron diffraction studies of $\text{Pr}(\text{Fe}, \text{V})_{12}$ and $\text{Pr}(\text{Fe}, \text{V})_{12}\text{N}_x$

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Abstract. The structural and magnetic properties of the compounds $\text{Pr}(\text{Fe}, \text{V})_{12}$ and their nitrides have been studied by means of neutron diffraction and crystal-field calculation. Neutron diffraction studies show that the compounds $\text{Pr}(\text{Fe}, \text{V})_{12}$ and their nitrides exhibit ThMn_{12} -type structure, the vanadium atoms occupy 8i sites, and the nitrogen atoms occupy the 2b sites. It is also found that the direction of the magnetic moments changes from that of the ab -plane to that of the c -axis upon nitrogenation, which is consistent with the results of calculations based on crystal-field theory and the single-ion model.

1. Introduction

Generally, the compounds $\text{RFe}_{12-x}\text{M}_x$ are stabilized in the ThMn_{12} -type structure, where R stands for the rare-earth elements except La, Ce, Pr, and $\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Mo}, \text{W}, \text{Si}$, or Al. Since the discovery of the effects of interstitial nitrogen atoms on the $\text{RFe}_{12-x}\text{M}_x$ compounds [1], the compounds $\text{NdFe}_{12-x}\text{M}_x\text{N}_y$ have been considered as good candidates for permanent-magnet applications. The interstitial nitrogen atoms not only have a sensitive effect of increasing the Curie temperature T_c and saturation magnetization σ_s , but also give rise to profound changes in the magnetocrystalline anisotropy [2–6].

The physical and chemical properties of Pr are similar to those of Nd, so $\text{Pr}(\text{Fe}, \text{M})_{12}\text{N}_x$ is expected to have good permanent-magnetic properties. In addition, up to now, rare-earth magnets have mostly been prepared from Nd, which makes Pr, the associate mineral of Nd, surplus to requirements to a greater and greater extent, which leads to a much lower cost of Pr compared to that of Nd.

In 1992, the first successful synthesis of the compounds $\text{Pr}(\text{Fe}, \text{Mo})_{12}$ and their nitrides was reported [7]; since then, much attention has been focused on the compounds $\text{Pr}(\text{Fe}, \text{Mo})_{12}$ and their nitrides [8, 9]. Recently, we have synthesized the compounds $\text{Pr}(\text{Fe}, \text{V})_{12}$ and their nitrides [10]. The Curie temperature of $\text{PrFe}_{10.5}\text{V}_{1.5}\text{N}_x$ takes values up to 820 K, its saturation magnetization is about 143 emu g^{-1} , and its magnetic anisotropy field is 108 kOe at room temperature [10]. It appears that the nitrides of $\text{Pr}(\text{Fe}, \text{V})_{12}$ hold significant promise as competitors to $\text{Nd}_2\text{Fe}_{14}\text{B}$.

In this paper, the structural and magnetic properties of the compounds $\text{Pr}(\text{Fe}, \text{V})_{12}$ and their nitrides are reported.

2. Experiment method

The samples were prepared by arc melting 99.5% pure materials in a purified argon atmosphere, and then heat treating them at 800–1000 °C for about a week. The nitrides were prepared by passing purified nitrogen gas at atmospheric pressure over finely ground powder samples (about 10–30 μm) at 500–550 °C for 4–8 h, then rapidly cooling them to room temperature. The neutron scattering investigations were carried out at the China Institute of Atomic Energy. The data were collected by scanning the samples from 8° to 75.2° in steps of 0.15° at room temperature, with a neutron wavelength of 1.159 Å. The diffraction patterns were analysed by means of the Rietveld profile technique.

3. Results and discussion

3.1. Crystallographic structure

Figure 1 shows the neutron diffraction pattern of $\text{PrFe}_{10.5}\text{V}_{1.5}$. There is a little bit of α -Fe. The neutron diffraction pattern of the nitrides is shown in figure 2, and is similar to that of $\text{PrFe}_{10.5}\text{V}_{1.5}$. The results of the refinement show that $\text{PrFe}_{10.5}\text{V}_{1.5}$ and its nitrides crystallize in the ThMn_{12} -type tetragonal structure with the space group $I4/mmm$. The lattice parameters (a , c) and unit-cell volume (V) are listed in table 1. The expansion of the unit-cell volume is 1.68%. It is less than that found in previous work (3.3%) [10]. The volume fractions of α -Fe for the present alloys and nitrides are 2.13% and 6.67%, respectively. These are too small to affect the refinement.

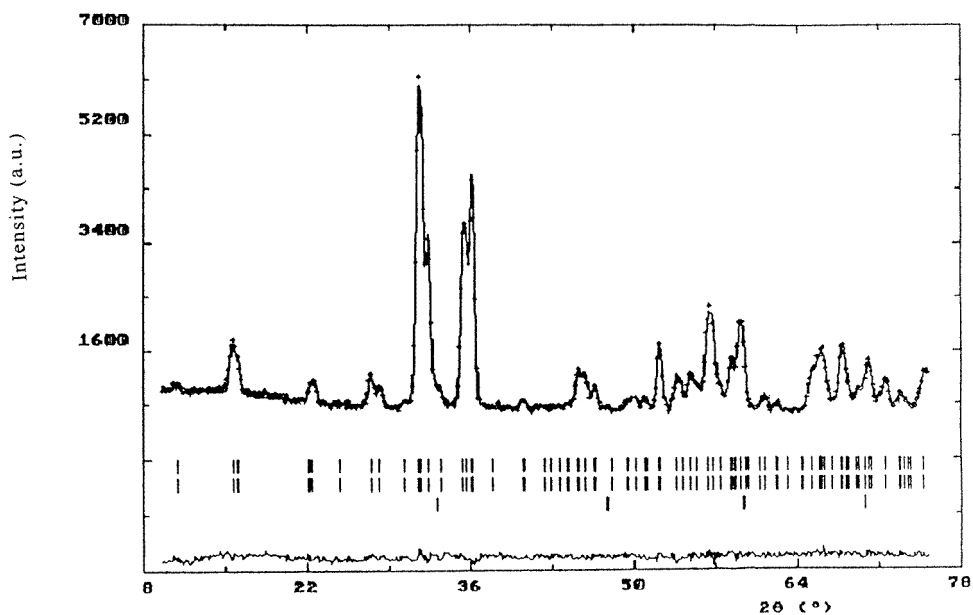


Figure 1. The neutron diffraction pattern of $\text{PrFe}_{10.5}\text{V}_{1.5}$ at room temperature.

Yelon and Hadjipanayis reported that vanadium was located at the 8j site ($x, 1/2, 0$) in $\text{YFe}_{10}\text{V}_2\text{N}_x$ [11]. The former and latter investigations of the location of vanadium in ThMn_{12} -type compounds both found that V occupied the 8i site [12, 13]. Our results indicate that Pr

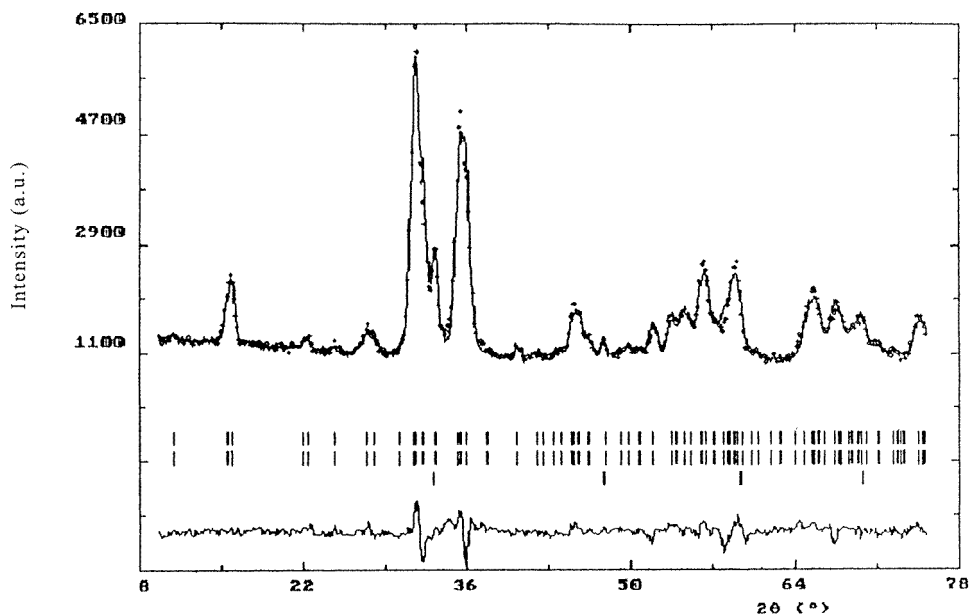


Figure 2. The neutron diffraction pattern of $\text{PrFe}_{10.5}\text{V}_{1.5}\text{N}_x$ at room temperature.

Table 1. The lattice parameters a and c , unit-cell volumes V , and relative change in unit-cell volume upon nitrogenation $\Delta V/V$ of $\text{PrFe}_{10.5}\text{V}_{1.5}\text{N}_x$ in comparison with $\text{PrFe}_{10.5}\text{V}_{1.5}$.

| | a (Å) | c (Å) | V (Å ³) | $\Delta V/V$ |
|--|------------|------------|--------------------------|--------------|
| $\text{PrFe}_{10.5}\text{V}_{1.5}$ | 8.556 | 4.773 | 349.4 | |
| $\text{PrFe}_{10.5}\text{V}_{1.5}\text{N}_x$ | 8.638 | 4.837 | 360.9 | 3.29% |

atoms occupy 2a sites, V atoms occupy 8i sites, Fe atoms occupy 8f, 8j, and other 8i sites, and N atoms enter interstitial 2b sites. The parameters of the crystallographic structure are listed in table 2. The content of V is less than the nominal stoichiometry, which is due to the vaporization during the melting. The nitrogen content is only 0.43, and it is less than that of our previous sample studied in reference [10], which is why the unit-cell-volume expansion of these samples is small.

3.2. Magnetic anisotropy

The interstitial nitrogen atoms have the effect of increasing the Curie temperature T_c and saturation magnetization σ_s . Upon nitrogenation, T_c for $\text{PrFe}_{10.5}\text{V}_{1.5}$ increases to about 200 K and σ_s increases from 121.4 emu g⁻¹ to 142.8 emu g⁻¹ at room temperature, while it increases from 131.4 emu g⁻¹ to 157.5 emu g⁻¹ at 1.5 K [10]. Moreover, the interstitial nitrogen atoms give rise to a significant change in the magnetocrystalline anisotropy.

It was found that the easy-magnetization direction of $\text{PrFe}_{10.5}\text{V}_{1.5}$ lies in the basal plane from 0 K to T_c . A dramatic change in magnetocrystalline anisotropy occurs upon nitrogenation. For $\text{PrFe}_{10.5}\text{V}_{1.5}\text{N}_x$, the c -axis becomes the easy-magnetization direction [10].

The neutron diffraction refinements also give magnetic moments (see table 3), and they indicate the change in magnetocrystalline anisotropy upon nitrogenation. Before nitrogenation,

Table 2. Neutron diffraction refinement results for PrFe_{10.5}V_{1.5} and PrFe_{10.5}V_{1.5}N_x.

| Atoms | Site | x | y | z | Occupancy |
|------------------------------|------|-------------|--------|--------|-----------|
| Pr | (2a) | 0 | 0 | 0 | 2 |
| Fe | (8i) | 0.35951(49) | 0 | 0 | 5.639(56) |
| Fe | (8j) | 0.27436(41) | 0.5000 | 0 | 8 |
| Fe | (8f) | 0.2500 | 0.2500 | 0.2500 | 8 |
| V | (8i) | 0.35951(49) | 0 | 0 | 2.361(56) |
| $R_p = 8.43\%, R_B = 3.85\%$ | | | | | |
| Pr | (2a) | 0 | 0 | 0 | 2 |
| Fe | (8i) | 0.36005(76) | 0 | 0 | 5.692(97) |
| Fe | (8j) | 0.27137(76) | 0.5000 | 0 | 8 |
| Fe | (8f) | 0.2500 | 0.2500 | 0.2500 | 8 |
| V | (8i) | 0.36005(76) | 0 | 0 | 2.308(97) |
| N | (2b) | 0 | 0 | 0.5000 | 0.855(63) |
| $R_p = 12.8\%, R_B = 5.62\%$ | | | | | |

Table 3. Magnetic moment parameters of PrFe_{10.5}V_{1.5} and PrFe_{10.5}V_{1.5}N_x.

| Atoms | Site | μ_x (μ_B) | μ_y (μ_B) | μ_z (μ_B) | μ (μ_B) |
|----------------|------|---------------------|---------------------|---------------------|-------------------|
| Pr | (2a) | 1.44(30) | 0 | 0 | 1.44(30) |
| Fe | (8i) | 1.76(17) | 0 | 0 | 1.76(17) |
| Fe | (8j) | 1.73(17) | 0 | 0 | 1.73(17) |
| Fe | (8f) | 1.71(17) | 0 | 0 | 1.71(17) |
| V | (8i) | 0 | 0 | 0 | 0 |
| $R_m = 6.48\%$ | | | | | |
| Pr | (2a) | 0 | 0 | 1.50(30) | 1.50(30) |
| Fe | (8i) | 0 | 0 | 1.76(17) | 1.76(17) |
| Fe | (8j) | 0 | 0 | 1.79(17) | 1.79(17) |
| Fe | (8f) | 0 | 0 | 1.78(17) | 1.78(17) |
| V | (8i) | 0 | 0 | 0 | 0 |
| N | (2b) | 0 | 0 | 0 | 0 |
| $R_m = 6.85\%$ | | | | | |

the magnetic moments of Pr and Fe atoms lie in the *ab*-plane, but they ‘prefer’ the *c*-axis after nitrogenation. The total magnetic moment also increases upon nitrogenation.

Using the crystallographic parameters that have been established, the crystal-field coefficients, the magnetic anisotropy constants, and the magnetic anisotropy field of Pr³⁺ in the PrFe_{10.5}V_{1.5} compounds and their nitrides are calculated by means of the single-ion model [2, 10]. A comparison of the crystal-field coefficients before and after nitrogenation is given in table 4. The interstitial nitrogen atoms make the value of A_{20} for the Pr³⁺ ions change from $-29.6 \text{ K } a_0^{-2}$ to $203.9 \text{ K } a_0^{-2}$ (a_0 is the Bohr radius). Compared to the higher-order crystal-field coefficients, the second-order crystal-field coefficients A_{20} are dominant in determining the magnetocrystalline anisotropy behaviour. Since α_J for Pr is negative, the easy-magnetization direction of PrFe_{10.5}V_{1.5}N_x ‘prefers’ an easy axis, whereas that of PrFe_{10.5}V_{1.5} lies in the basal plane.

Table 5 lists the calculation results for the magnetic anisotropic constants and magnetic

Table 4. Crystal-field coefficients of the rare-earth sublattices of the compounds $PrFe_{10.5}V_{1.5}$ and $PrFe_{10.5}V_{1.5}N$. (a_0 is the Bohr radius.)

| | A_{20} ($K a_0^{-2}$) | A_{40} ($K a_0^{-4}$) | A_{44} ($K a_0^{-4}$) | A_{60} ($K a_0^{-6}$) | A_{64} ($K a_0^{-6}$) |
|-----------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|
| $PrFe_{10.5}V_{1.5}$ | -29.59 | -1.692 | 4.527 | -0.0298 | -0.0480 |
| $PrFe_{10.5}V_{1.5}N$ | 203.85 | 40.14 | 1.270 | 1.952 | 0.0257 |

Table 5. Magnetic anisotropy constants and the magnetic anisotropy fields of $PrFe_{10.5}V_{1.5}$ and $PrFe_{10.5}V_{1.5}N$ at 1.5 K and 300 K.

| | 1.5 K | | | 300 K | | |
|--|--------------------------|--------------------------|------------------|--------------------------|--------------------------|------------------|
| | K_1 ($J cm^{-3}$) | K_2 ($J cm^{-3}$) | B_A (T) | K_1 ($J cm^{-3}$) | K_2 ($J cm^{-3}$) | B_A (T) |
| $PrFe_{10.5}V_{1.5}$ (calculated) | -4.77 | 1.54 | <i>ab</i> -plane | -1.28 | 0.107 | <i>ab</i> -plane |
| $PrFe_{10.5}V_{1.5}$ (experimental) | — | — | <i>ab</i> -plane | — | — | <i>ab</i> -plane |
| $PrFe_{10.5}V_{1.5}N$ (calculated) | 3.22 | 1.51 | 10.0 | 5.23 | 0.012 | 9.18 |
| $PrFe_{10.5}V_{1.5}N_x$ (experimental) | 4.24 | 1.32 | 11.0 | 3.92 | 0.608 | 8.98 |

anisotropic fields of $PrFe_{10.5}V_{1.5}$ and $PrFe_{10.5}V_{1.5}N$. For comparison, the magnetic measurement results are also listed in table 5. The calculation results are consistent with the experiment results.

It is easy to understand the calculation results. The nitrogen atoms occupy the 2b sites and possess the same $I4/mmm$ point symmetry as the rare-earth sites; however, their electronic charge is opposite to that of the rare-earth ions. In addition, the nitrogen atoms are the nearest ligands of the rare-earth ions. Thus, the contribution from neighbouring nitrogen ions to the crystal field is positive and large, while that from neighbouring rare-earth ions is negative but small.

4. Conclusions

It is concluded that nitrogen atoms occupy interstitial 2b sites in $PrFe_{10.5}Mo_{1.5}N_x$, and that they make the second-order crystal-field parameter (A_{20}) change from negative to positive upon nitrogenation, which results in the change of the easy-magnetization direction of $PrFe_{10.5}V_{1.5}$ from an easy plane to an easy axis. This is consistent with the results of a calculation based on crystal-field theory and the single-ion model.

Acknowledgments

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