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THEORETICAL CALCULATION ON THE MAGNETOCRYSTALLINE ANISOTROPY OF
 $\text{NdFe}_{10.5}\text{V}_{1.5}\text{N}_x$ Jinbo Yang, Bo Cui, Weihua Mao, Xiedi Pei and Yingchang Yang
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The $\text{NdFe}_{10.5}\text{V}_{1.5}\text{N}_x$ compounds with different nitrogen content have been synthesized. The dependence of magnetic properties at room temperature on the nitrogen content was investigated in order to give evidence of the importance of the nitrogen content on the magnetic anisotropy of the rare earth sublattice. In the meantime, the theoretical calculations were performed to analyze the nitrogen content dependence of the magnetocrystalline anisotropy constants $K_{1,2}$, as well as the anisotropy field H_a in the $\text{NdFe}_{10.5}\text{V}_{1.5}\text{N}_x$. The results confirmed that the second-order crystal-field parameter A_{20} is dominant and, in the nitrides, the chief contribution to A_{20} comes from nitrogen located at 2b sites. Finally, the increase of nitrogen content will first turn the easy-plane magnetocrystalline anisotropy of the rare earth sublattice into easy-axis one and then enhance it linearly to a much larger value, which is in quite good agreement with experiment. © 1997 Elsevier Science Ltd

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INTRODUCTION

The ternary compounds $\text{RFe}_{12-y}\text{M}_y$ (R=rare earth, M=Ti, V, Cr, Mo, Si, Mn, W and Al) can absorb nitrogen atoms to a certain extent and as a result, leads to drastic changes in magnetic properties [1]. For instance, Curie temperature T_c and saturation magnetization M_s both increase by about 17% and 25%, respectively. And also important is the change of magnetocrystalline anisotropy upon nitrogenation. The previous calculation results [2] indicated that due to the introduction of interstitial N atom, the second-order crystal field coefficient A_{20} changes from small negative value to large positive value, which means that $\text{NdFe}_{12-y}\text{M}_y\text{N}_x$ nitrides with $\alpha_J < 0$ may be developed for permanent magnet applications [3]. Owing to the fact that the easy uniaxial anisotropy is a prerequisite for magnetic material with high coercivity, it is also of technical significance to study the mechanism of those anisotropy behaviors. In this work, base on the single-ion theory, we discuss the effect of the nitrogen content on the rare earth sublattice anisotropy

at room temperature in $\text{NdFe}_{10.5}\text{V}_{1.5}\text{N}_x$. A quantitative comparison will be made for $\text{NdFe}_{10.5}\text{V}_{1.5}\text{N}_x$ compounds between the theoretical anisotropy constants K_1 and K_2 and those of the experiments.

EXPERIMENTAL METHODS

Parent alloys were prepared by arc melting of 99.5% pure metals in an argon atmosphere, followed by a heat treatment at 900°C for one week. The nitrides were formed by passing purified nitrogen gas at 1atm. over fine powder samples at 480–600°C for 4–12 hours. The magnetization curves of aligned samples were measured using vibrating sample magnetometer (VSM) with a field of up to 20kOe at room temperature. Crystal phase was identified by X-ray diffraction analysis with $\text{Cu-K}\alpha$ radiation. The anisotropy constants K_1 and K_2 are deduced from the fitting of magnetization curves perpendicular to the alignment direction using Sucksmith–Thompson method [4]. A small calibration considering the demagnetization

field and non-collinearity due to the unperfection of samples were employed.

THEORETICAL CALCULATIONS

Since the aspherical orbital wavefunction of 4f electron interacts strongly with crystal field, the rare earth ions make a great contribution to the anisotropy of NdFe_{10.5}V_{1.5}N_x. The anisotropy energy of rare earth sublattice with tetragonal symmetry can be phenomenologically described as:

$$E(\theta) = K_0 + K_1 \sin^2 \theta + K_2 \sin^4 \theta + \dots \quad (1)$$

where θ is the angle between the c-axis and the magnetization vector. The contribution of the rare earth sublattice to the magnetocrystalline anisotropy can also be calculated using the single-ion theory. The perturbation Hamiltonian of the 4f electrons is

$$H_{4f} = H_{cf} + H_{ex} \quad (2)$$

where H_{cf} is the crystal-field Hamiltonian and H_{ex} represents the Nd-Fe exchange interaction in the molecular field approximation. H_{ex} can be written as

$$H_{ex} = g_J \mu_B \mathbf{H}_m \cdot \mathbf{J} \quad (3)$$

where H_m is molecular field and g_J is Lande factor.

The crystal-field Hamiltonian at the rare earth site is

$$H_{cf} = B_{20}O_{20} + B_{40}O_{40} + B_{44}O_{44} + B_{60}O_{60} + B_{64}O_{64} \quad (4)$$

where B_{nm} are crystal-field parameters depending on the specific rare earth ion and its neighbor environments, and O_{nm} are the Stevens equivalent operators. The 4f electrons lie within 5s and 5p orbits and are strongly screened from surrounding ions. Therefore, a set of screening factors ($\sigma_{2,4,6}$) are introduced to represent this effect.

Finally, the perturbation Hamiltonian is

$$H_{4f} = (1 - \sigma_2)B_{20}O_{20} + (1 - \sigma_4)(B_{40}O_{40} + B_{44}O_{44}) + (1 - \sigma_6)(B_{60}O_{60} + B_{64}O_{64}) + g_J \mu_B H_m (J_x \sin \theta + J_z \cos \theta). \quad (5)$$

To decide crystal-field parameters, 16 rare earth ions, 44 iron ions and 16 nitrogen ions are considered as ligands because the farther ions are shielded not only from the outer electrons of Nd but also by the "sea" of free electrons and nearer ions, therefore, their contribution is negligible. The effective charges of Nd and N ions are taken as +3e and -3e, respectively, and that of Fe (denoted as Z(Fe)) is an adjustable

parameter. Fitting to the temperature dependence of saturation magnetization of Nd(Fe,V)₁₂N_x and Y(Fe,V)₁₂N_x by using molecular field theory, we chose $g_J \mu_B H_m$ to vary between 60K and 90K. In addition, we included the effect of different nitrogen contents by multiplying its effective charge, -3e, with a factor x .

The free energy density is

$$E(\theta) = -NKT \ln(\sum_{i=1}^{10} e^{-E_i/KT}) \quad (6)$$

where N is the density of Nd³⁺ ions, $T=295$ K and E_i is the eigenvalues of H_{4f} and can be obtained by solving the following secular equation:

$$| \langle LSJM' | H_{4f} | LSJM \rangle - E_i \delta_{M'M} | = 0 \quad (7)$$

where $L=3$, $S=\frac{3}{2}$, $J=\frac{9}{2}$ and $M', M = -\frac{9}{2}, -\frac{7}{2}, \dots, \frac{9}{2}$

RESULTS AND DISCUSSIONS

The magnetization curves of NdFe_{10.5}V_{1.5}N_x with different nitrogen contents at 295K, parallel and perpendicular to the alignment direction, are plotted in Fig. 1. In order to compare the measured values with the calculation results, according to XRD patterns, it is assumed that $x=1$ corresponds to the sample with a nominal composition of NdFe_{10.5}V_{1.5}N₂, and, x is proportional to $\delta V/V$, the relative change in unit cell volume upon nitrogenation, for other samples. It is noticed that the anisotropy field increases steadily with increasing nitrogen content, and reaches a maximum value $H_A=10.3$ T at $x=1.0$. The magnetocrystalline anisotropy of NdFe_{10.5}V_{1.5}N_x compounds arises from the contribution of both rare earth sublattice and transition metal sublattice. The contribution from iron sublattice can be determined from measurements on YFe_{10.5}V_{1.5}N_x. Since the nitrogen content x can vary from 0 to 1.0, the corresponding effects of nitrogen content on rare earth sublattice anisotropy can be deduced experimentally.

A set of crystal-field parameters of Nd³⁺ are listed in Table 1, and corresponding second order crystal field coefficients A_{20} as a function of nitrogen content are summarized in Fig. 2. It is easy to see from Table 1. that the second order crystal-field parameter is dominant in determining the anisotropy of rare earth sublattice because the higher order items are so small in NdFe_{10.5}V_{1.5}N_x. The enhancement of the second-order crystal coefficient due to nitrogenation is substantially strong. The nitrogen-induced shift in A_{20} is about 500Ka^{-2} per neighboring nitrogen atom. As shown in Fig. 2, A_{20} increases linearly with nitrogen content. A similar results concerning the variation of A_{20} with x in Sm₂Fe₁₇N_x was also observed by Li *et*

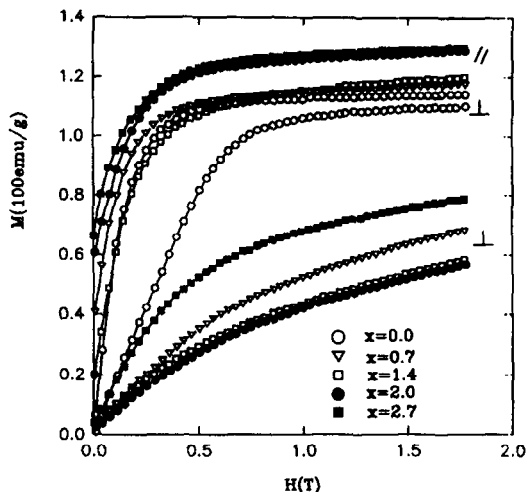


Fig. 1. The room temperature magnetization curves of the magnetically oriented powder samples NdFe_{10.5}V_{1.5}N_x.

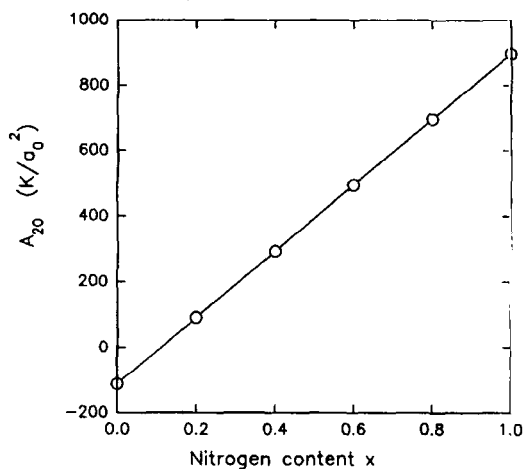


Fig. 2. The second order crystal field coefficients A_{20} as a function of nitrogen content.

al. [5] and Zhao *et al.* [6]. The sign change of A_{20} from negative to positive after nitrogenation is important because, as a result, the easy plane anisotropy in NdFe_{10.5}V_{1.5} gives way to easy c-axis anisotropy in NdFe_{10.5}V_{1.5}N_x. The increasing of nitrogen content will further enhance the c-axis anisotropy.

By solving equation (7) and then comparing equation (6) with equation (1), the anisotropy constants K_1 and K_2 of rare earth sublattice are obtained, and, together with the experimental value, are plotted in Fig. 3. The theoretical value of K_2 keeps almost unchanged as increasing nitrogen content, while K_1 increases linearly. Therefore the increase of the anisotropy of rare earth sublattice mainly comes from the increase of K_1 . The features of K_1 and K_2 can be understood by the relations between $K_{1,2}$ for rare earth sublattice and the

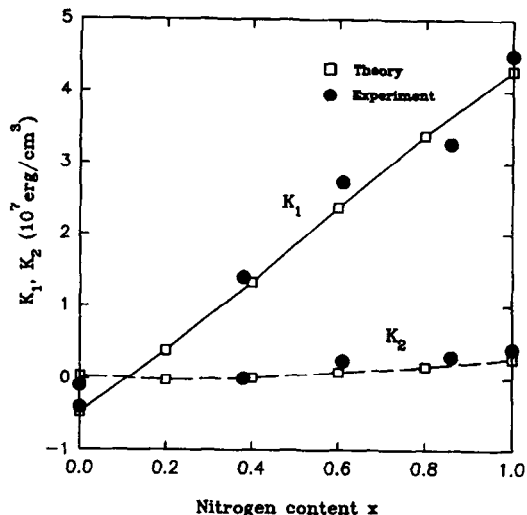


Fig. 3. The anisotropy constant of Nd³⁺ ions in NdFe_{10.5}V_{1.5}N_x.

crystal-field parameters [7]

$$K_1 = -\left[\frac{3}{2} B_{20} \langle O_{20} \rangle + 5 B_{40} \langle O_{40} \rangle + \frac{21}{2} B_{60} \langle O_{60} \rangle \right] \quad (8)$$

$$K_2 = -\left[\frac{35}{8} B_{40} \langle O_{40} \rangle + \frac{189}{8} B_{60} \langle O_{60} \rangle \right] \quad (9)$$

Since B_{20} is predominant and it decreases drastically with increasing nitrogen content, it has great influence on the anisotropy constant K_1 . This can also explain why K_1 is dominant compared to K_2 which mainly depends on B_{40} and B_{60} . The preferred magnetization direction will be along c-axis in the uniaxial system if K_1 is predominant and positive, as in the case of NdFe_{10.5}V_{1.5}N_x. The theoretical values of K_1 and K_2 are in good agreement with experiment except a small deviation in high nitrogen content region. This is partly because the nitrogen content of the sample can not be decided very accurately. We can conclude that with ideal crystal structure and full nitrogenated sample, a uniaxial anisotropy of 13T can be obtained as indicated in Fig. 2.

CONCLUSIONS

The experimental results showed that the increasing of nitrogen content in NdFe_{10.5}V_{1.5}N_x will enhance the magnetocrystalline anisotropy. Theoretical results based on single-ion theory are well consistent with experiment. It is shown that the contribution of neighbor

Table 1. Crystal-field parameters of rare earth sublattice $B_{nm}(K)$

x	B_{20}	$B_{40} \times 10^{-3}$	$B_{44} \times 10^{-3}$	$B_{60} \times 10^{-5}$	$B_{64} \times 10^{-5}$
0.0	0.80	0.43	-4.34	1.48	2.15
0.2	-0.64	-1.83	-3.73	-23.23	1.86
0.4	-2.09	-4.09	-3.12	-47.95	1.58
0.6	-3.54	-6.31	-2.51	-72.66	1.30
0.8	-4.99	-8.61	-1.89	-97.37	1.02
1.0	-6.43	-10.87	-1.28	-122.1	0.74

nitrogen ions to the second-order crystal-field coefficient A_{20} is positive and larger while the contribution of neighbor rare earth ions is negative and smaller. The former increases linearly and give rise to the linear increase of K_1 with increasing nitrogen content. For the fully nitrogenated samples, with strong uniaxial anisotropy field, high Curie temperature and saturation magnetization, NdFe_{10.5}V_{1.5}N_x is promising for permanent magnet applications. In fact, anisotropic magnetic powders with $H_{cJ}=4.5\text{kOe}$ $B_r=10.5\text{kG}$ and $(BH)_{\max}=16.1\text{MGoe}$ has already been obtained.

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