THEORETICAL CALCULATION ON THE MAGNETOCRYSTALLINE ANISOTROPY OF NdFe$_{10.5}$V$_{1.5}$N$_x$

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The NdFe$_{10.5}$V$_{1.5}$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 $K_1$ and $K_2$, as well as the anisotropy field $H_K$ in the NdFe$_{10.5}$V$_{1.5}$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 RFe$_{12-y}$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 NdFe$_{12-y}$M$_y$N$_x$ nitrides with $\alpha_f < 0$ 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 NdFe$_{10.5}$V$_{1.5}$N$_x$. A quantitative comparison will be made for NdFe$_{10.5}$V$_{1.5}$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 1 atm. 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 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
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:

\[ E(\theta) = K_0 + K_1 \sin^2 \theta + K_2 \sin^4 \theta + \ldots. \]  

(1)

where \( \theta \) 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

\[ H_{4f} = H_{cf} + H_{ex} \]  

(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

\[ H_{ex} = g_J \mu_B H_m \cdot J \]  

(3)

where \( H_m \) is molecular field and \( g_J \) is Lande factor.

The crystal-field Hamiltonian at the rare earth site is

\[ H_{cf} = B_{20} O_{20} + B_{40} O_{40} + B_{44} O_{44} + B_{50} O_{50} + B_{64} O_{64} \]  

(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 \( (\alpha_{2,4,6}) \) are introduced to represent this effect.

Finally, the perturbation Hamiltonian is

\[ H_{4f} = (1 - \alpha_2) B_{20} O_{20} + (1 - \alpha_4) (B_{40} O_{40} + B_{44} O_{44}) + (1 - \alpha_6) (B_{50} O_{50} + B_{64} O_{64}) + g_J \mu_B H_m (J_x \sin \theta + J_z \cos \theta). \]  

(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)_{12}N_x and Y(Fe,V)_{12}N_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

\[ E(\theta) = -NKT \ln (2 \pi e^{E_i/KT}) \]  

(6)

where \( N \) is the density of Nd\(^{3+}\) ions, \( T=295K \) and \( E_i \) is the eigenvalues of \( H_{4f} \) and can be obtained by solving the following secular equation:

\[ | <LSJM'|H_{4f}|LSJM > - E_i \delta_{M',M} | = 0 \]  

(7)

where \( L=3, S=\frac{3}{2}, J=\frac{9}{2}, \) and \( M',M=\pm \frac{9}{2}, \pm \frac{7}{2}, \ldots, \pm \frac{9}{2} \).

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}N_2, and, \( x \) is proportional to \( 6V/V \), 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 \( H_A=10.3T \) 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 Nd\(^{3+}\) 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 500K\(^{2}\) 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 Sm\(_2\)Fe_{17}N_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.

Fig. 3. The anisotropy constant of Nd$^{3+}$ ions in NdFe$_{10.5}$V$_{1.5}$N$_x$.

\[
K_1 = -\left(\frac{3}{2} B_{20} < O_{20} > + 5 B_{40} < O_{40} > \right) + \frac{21}{2} B_{60} < O_{60} > \\
K_2 = -\left(\frac{35}{8} B_{40} < O_{40} > + \frac{189}{8} B_{60} < O_{60} > \right)
\]

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 cannot 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
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 $K_I$ 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 $H_{cj}=4.5kOe$, $B_s=10.5kG$ and $(BH)_{max}=16.1MGOe$ has already been obtained.

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REFERENCES