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Theoretical construction of the magnetic Hamiltonian and zero-temperature anisotropic energy in $Nd_2Fe_{14}B$

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The magnetic Hamiltonian of $Nd_2Fe_{14}B$ at the Nd site has been constructed using a first-principles approach based on the energy-band results. The crystal-field parameters are evaluated using the real-space charge-density distribution and the exchange field is obtained by applying an approximate Stoner model to the spin-polarized density of states. The calculated stabilization energy is in good agreement with the experimental measurement. It is also shown that the exchange field predominates in the magnetic Hamiltonian but the fourth-order and second-order off-diagonal crystal-field terms are not entirely negligible.

The magnetic behavior of the rare-earth–transition-metal–boron compound $Nd_2Fe_{14}B$ has received considerable attention in recent years due to its high performance as a permanent magnet. Both theoretical and experimental investigations[1,2] indicate that the anisotropy in magnetization is mainly from the rare-earth ions and the source of this anisotropy is attributed to the combined effect of the crystal field and the exchange field, such that the basic magnetic Hamiltonian can be written as

$$H = H_{\rm CF} + H_{\rm ex} . \tag{1}$$

The crystal field $H_{\rm CF}$ and the exchange field $H_{\rm ex}$ are given by

$$H_{\rm CF} = \sum B_{nm} O_n^m , \tag{2}$$

$$H_{\rm ex} = g_B \mu_B \mathbf{J} \times H_m , \tag{3}$$

where B_{nm} are the crystal-field parameters (CFP), O_n^m the Stevens operators, and H_m the molecular-field parameter all taken at the Nd sites. Up to now, all the analyses with regard to the magnetic anisotropic energy in $Nd_2Fe_{14}B$ are semiempirical in nature because of the difficulties involved in constructing a reliable Hamiltonian. Some researchers obtained CFP from magnetization curve analysis,[3,4] while others treated them as fitting parameters.[1] The point-charge model (PCM) has been routinely used[5-8] to calculate the CFP which gives unrealistic results because the model is obviously oversimplified. As for the exchange field, the situation is even worse. There is not even a simple theoretical estimate of H_m for $Nd_2Fe_{14}B$ and one has to rely entirely on the experimentalists to determine H_m. Unfortunately, there are too many parameters involved in the crystal-field part of H and this complicates the experimental data analysis. Although the higher-order field terms are generally believed to be less important, especially at high temperatures, it is undesirable to discard some of them without any compelling justification. As a matter of fact, in the extreme case,[1] only one term B_{20} is kept in $H_{\rm CF}$. Thus, the Hamiltonians used in these analyses are arbitrary empirical model Hamiltonians, and the conclusions obtained from such analyses could be misleading. It is highly desirable that an alternative scheme based on a more fundamental approach be developed.

In this paper, we show that the basic Hamiltonian (1) can be constructed based only on the spin-polarized band-structure results without using any empirical data from experimental measurements. In order to check the validity of such a Hamiltonian, we have calculated the stabilization energy of $Nd_2Fe_{14}B$ at zero temperature and compare it with experimental measurement. The relative importance of $H_{\rm CF}$ and $H_{\rm ex}$ is clarified. We also test explicitly the influence of neglecting some of the CFP, thereby providing necessary insight important to the correct interpretation of magnetic measurements. The present work is therefore a good attempt to connect the fundamental aspect of the electronic structure with the magnetic and other measurable properties for $Nd_2Fe_{14}B$.

Based on the spin-polarized band structure of $Nd_2Fe_{14}B$ calculated by Gu and Ching,[9] we have recently devised[10] a numerical procedure for the calculation of CFP of $Nd_2Fe_{14}B$ using the real-space charge-density distribution. The method consists of using a PCM for the contribution from the charge density on other sites away from Nd and numerical integration for contribution from the charge density in the vicinity of the Nd on site. The effective ionic charges in the PCM calculation were obtained from the site decomposition of Mulliken charges given by the band-structure calculation.[9] For the on-site contribution, a tesseral harmonic expansion of charge density by successive least-squares fitting plays a central role in reducing the dimension of integration from three to one. The final CFP are the sum of these two contributions. The distinctive feature of this method is that no arbitrary fitting parameters or data of empirical origin were used and the calculation is therefore of first principles in nature.

The calculated CFP up to fourth order for the f and g sites of Nd ion are listed in Table I. From these results the following circumstances are apparent. (i) The CFP of the same order are of the same magnitude. Hence, there is no justification in neglecting the off-diagonal terms such as B_{22}, B_{24}, B_{44} and keeping only the diagonal ones of the same order as B_{20} (Ref. 1) or B_{20} and B_{40} (Ref. 11). (ii) The signs for B_{22} on f and g sites are opposite and their

TABLE I. Crystal-field parameters in K at Nd sites in $Nd_2Fe_{14}B$ from Ref. 8.

Site	B_{20}	B_{22}	B_{40}	B_{42}	B_{44}
f	-3.77	-1.45	0.022	0.050	0.014
g	-2.85	1.26	0.018	0.063	-0.019

magnitudes close. One tends to believe that the effects of B_{22} from different sites will cancel each other if the total Hamiltonian of the system is a summation over all sites in the crystal. This may not be true because for a single-ion anisotropy, the basic Hamiltonian must be diagonalized separately. (iii) The differences in CFP between f and g sites are appreciable. In a pure PCM calculation, the leading terms of the second-order CFP on f and g sites are very close.[5-7] This is because the PCM takes into account only the effect of environmental charges at a distance and a single effective ionic charge is assigned for all ions of the same element regardless of whether they are crystallographically equivalent or not. This leads to a false impression that the difference in the crystal fields between f and g sites is not important. From the band-structure calculation,[9] it is clear that the crystallographically inequivalent ions have different effective ionic charges. This results in a difference in the charge-density distributions around the f and g sites.[9] Our calculated values for B_{20} on the f and g sites are -3.77 and -2.85 K, respectively. The difference is not negligible and may have important implications in relation to the local level splitting which have not yet been studied experimentally. Diagonalization of H_{CF} led to local moments of $4.47\mu_B$ and $4.22\mu_B$ for f and g sites, respectively, which are very close to $J=4.5$ for the ground state of the Nd ion, a condition necessary for the usual magnetization analysis.

The first-principles calculation of CFP has provided the first part of the basic Hamiltonian (1). For the second part, there has been no previous effort to evaluate the exchange field in $Nd_2Fe_{14}B$, mainly because of the complexity of its structure. In simple metals and alloys, the Stoner model[12] has been routinely applied to the band structure to obtain the phenomenological molecular field. Although the model can be criticized as being oversimplified since it neglects the gain in the exchange energy due to spin fluctuation,[13] it is still a good approximation at low temperature. The local magnetic moments on different Fe sites obtained from band calculation[9] were in good agreement with experiment, thus indicating the applicability of the Stoner model in this system. It is also well known that the Stoner model is based on a rigid-band approximation. In $Nd_2Fe_{14}B$, the total density of states (DOS) of $Nd_2Fe_{14}B$ for spin-up and spin-down bands are not of the same shape and use of the Stoner model may be questionable. Fortunately, a careful examination of the DOS diagram which is reproduced in Fig. 1 clearly reveals that all the partial DOS (PDOS) for spin-up and spin-down bands are close to a rigid shift in the energy scale. We may apply the Stoner model to each PDOS separately and determine an approximate exchange splitting for each case. The total exchange splitting Δ is assumed to be an average over all those PDOS which can be expressed as

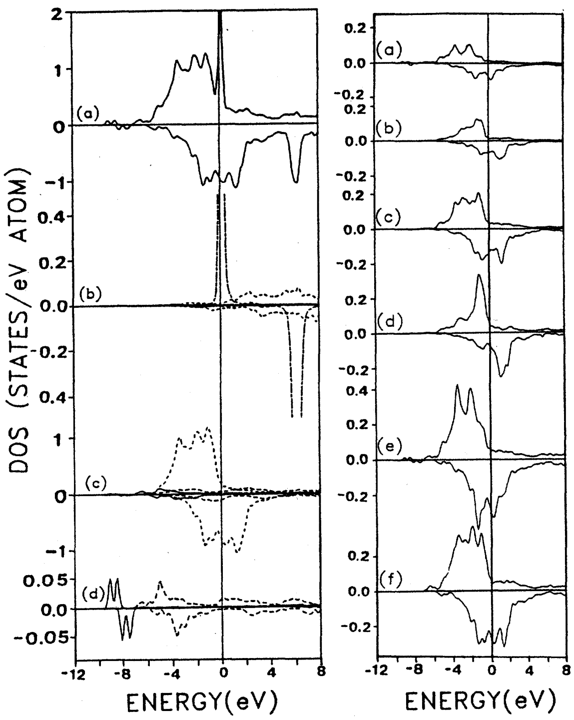

FIG. 1. DOS and PDOS of $Nd_2Fe_{14}B$ from Ref. 9 for the spin-up (above zero) and spin-down (below zero) bands. Left-hand panel: (a) Total DOS; (b) solid line, Nd $6s$; dashed line, Nd $4f$; (c) solid line, Fe $4s$; dashed line, Fe $4p$; dotted line, Fe $3d$; (d) solid line, B $2s$; dashed line, B $2p$. Right-hand panel: PDOS at different Fe sites: (a) $4e$, (b) $4c$, (c) $8j_1$, (d) $8j_2$, (e) $16k_1$, (f) $16k_2$.

$$\overline{\varepsilon_{k\uparrow}-\varepsilon_{k\downarrow}}=\Delta=IM/\mu_B\ , \tag{4}$$

where I is the Stoner parameter, M the total magnetic moment of the unit cell, and the average is taken over all pairs of spin-up and spin-down bands at all **k** points where the bands were calculated. In this way, we obtained a Stoner parameter of 71.4 K in $Nd_2Fe_{14}B$. The average root-mean-square deviation is 22.6 K, which is an indication of how far the approximate Stoner model deviates from an ideal one. The molecular field H_m for the whole unit cell is obtained through the Stoner parameter by the relation[12]

$$H_m=\frac{I}{2\mu_B^2}M=\frac{\Delta}{2\mu_B}\ . \tag{5}$$

To obtain the molecular field on the Nd site for H_{ex}, we assume that magnetic ions in a unit cell share the field in proportion to their contribution to the total magnetic moment. In $Nd_2Fe_{14}B$, the local magnetic moments on f and g sites of Nd are $3.04\mu_B$ and $3.01\mu_B$, while the total moment is $163.4\mu_B$ (Ref. 9). We thus obtain H_m of 216.9 and 214.8 K for f and g sites, respectively. It should also be pointed out that the application of the Stoner model based on the spin-polarized band structure implies that the effects of the conduction electrons, which are mainly from the Fe sites, are properly taken into account.

H_{ex} and H_{CF} constitute a complete Hamiltonian for the magnetic structure. Both are obtained from the results of the energy-band calculation. To test the validity of this Hamiltonian, we have calculated the zero-temperature stabilization energy at the Nd site in $Nd_2Fe_{14}B$. This concept was introduced by Greendan and Rao.[14] The stabilization energy is the difference between the ground-state magnetic energies, with the molecular field H_{ex} being parallel or perpendicular to the tetragonal axis. The anisotropy energy can be written as

$$E_A(0)=K_1\sin^2\theta+K_2\sin^4\theta\,, \tag{6}$$

where θ is the angle between the magnetization direction and the **c** axis, and the stabilization energy is interpreted as a simple effective anisotropic coefficient:

$$E_{stab}=|K_1+K_2|\,. \tag{7}$$

The magnetic Hamiltonian is diagonalized within the ground-state multiplet $^4I_{9/2}$ of the Nd^{3+} ion, which has the multiplet wave function

$$|J,M_J\rangle=|\tfrac{9}{2},\tfrac{9}{2}\rangle,|\tfrac{9}{2},\tfrac{7}{2}\rangle,\ldots,|\tfrac{9}{2},-\tfrac{9}{2}\rangle\,.$$

The matrix elements of the Stevens operators can be easily calculated in this basis since they are expressed in terms of the total angular momentum operators. For example, $O_2=3J_z-J(J+1)$; $O_2^z=(J_+^z+J_-^z)/2$, etc. The exchange field is also expressed in terms of the total angular momentum operator **J**. The matrix is 10×10 in size. To obtain the stabilization energy, we diagonalize the Hamiltonian twice, one with the molecular field being parallel to the **c** axis, the other perpendicular to the **c** axis. The difference between the lowest energy levels in these two cases gives E_{stab}.

It is instructive to check the effects of ignoring specific crystal-field terms as was done in some experimental analysis of the magnetic data. To this effect, we have calculated the E_{stab} for three different choices of H_{CF} in (3): (a) H_1: keeping only B_{20} and neglecting B_{22} and all higher-order terms; (b) H_2: keeping B_{20} and B_{40}, while neglecting B_{22} and all other fourth-order terms; (c) H_3: keeping all second- and fourth-order field terms. Although the sixth-order CFP have also been calculated by us[10] using the first-principles approach, we do not include them in H_{CF} because they are less reliable. In our calculation of CFP, a PCM with effective charges obtained from band structure was used to evaluate the contribution from the charge density at distant sites. For the sixth-order terms, one cannot take enough sites to reflect the true angular dependence of the sixth-order tesseral harmonics because of the rapid convergence. As pointed out by Schmidt,[15] it is impossible for PCM to give an accurate estimation for the sixth-order field term. The neglect of the sixth-order term in H_{CF} may, to certain extent, affect the accuracy of the magnetic Hamiltonian. Nevertheless, the sixth-order term was found to be much smaller than the second- and the fourth-order terms.[10]

The calculated stabilization energies for $Nd_2Fe_{14}B$ for the three different Hamiltonians are listed in Table II. It is clear that when we keep only the lower order or only the diagonal terms, the difference in the stabilization energies of the f and g sites is large. However, if all the second- and fourth-order field terms are included (H_3), this difference tends to diminish. This behavior is not surprising because the lower-order field terms are far from being spherically symmetric. With additional higher-order components added, the crystal field tends to be more spherically symmetric, thus bringing the anisotropy between f and g sites closer. From our calculation, it is also clear that at the low temperature, the crystal-field part of the anisotropy energy is due to a combined effect of both the lower- and higher-order terms. Therefore, in analyzing experimental data, it is unrealistic to neglect fourth-order terms while making no distinction between f and g sites.

TABLE II. The stabilization energy in K for Hamiltonians H_1, H_2, and H_3.

Site	H_1	H_2	H_3
f	93.63	118.82	155.20
g	138.99	159.38	139.28

The calculated effective anisotropy coefficient values of 18.1 (16.4) $\times10^7$ erg/cm^3 on the f (g) site are listed in Table III together with those from experiments.[16–18] The calculated result corresponds to the Hamiltonian H_3 in which all the crystal-field terms up to the fourth order are included. The agreement with the available experimental data is quite satisfactory. Sinnema *et al.*[16] obtained an averaged value of 21.9×10^7 erg/cm^3 which is considered to be more reliable since the experiment was carried out in a higher magnetic field of up to 35 T. The data of 12.0×10^7 erg/cm^3 by Yamauchi *et al.*[17] was obtained from the measurement with a magnetic field of only 2 T. Using only a single CFP B_2^0 for H_{CF} and molecular-field values based on a $3d$-$4f$ spin-coupling parameter deduced from high magnetic field studies,[19] Radwanski and Franse[1] calculated the rare-earth contribution to the anisotropy energy in $R_2Fe_{14}B$ where R is a rare-earth element. The value of R=Nd is 12.3×10^7 erg/cm^3. Our present approach is quite different from that of Ref. 1 since no arbitrary parameters are used in the calculation.

The relative importance of H_{CF} and H_{ex} in the total Hamiltonian can be estimated by calculating the overall splittings using only part of the total Hamiltonian. We have obtained an approximate ratio of 5.8 for H_{ex}/H_{CF}. This means the exchange field is much stronger in comparison to the crystal field. This preponderance in the strength of the exchange field in determining the anisotropic energy is consistent with the fact that the spin-

TABLE III. Anisotropy coefficient K_1 in 10^7 erg/cm^3 on Nd sites.

Calculated values (Present work)		Experimental values		
f site	g site	Ref. 16	Ref. 17	Ref. 18
18.1	16.4	21.9	12.0	11.0

density map of $Nd_2Fe_{14}B$ shows a network type of structure in the direction parallel to the c axis.[9] It is also interesting to note that Radwanski and Franse[1] had obtained the same ratio for H_{ex}/H_{CF}. However, they have used only one term, $B_{20} = -2.0$ K for H_{CF}, and a comparatively smaller value of the anisotropy coefficient was obtained.

The good agreement of our calculated stabilization energy with experimental measurements indicates that the Hamiltonian we constructed is basically sound. Since no arbitrary parameters or experimental information were used in the calculation, this first-principles approach to the magnetic properties of complex intermetallic compounds will have some predictive power. The accuracy of the calculation can be further improved as long as the accuracy of the band-structure calculation can be improved. Although the present calculation of anisotropy energy is limited to zero temperature, it is possible to extend to the case of nonzero temperature using the excited states of the Hamiltonian. The basic Hamiltonian obtained by us using the more fundamental approach can be coupled with several different theoretical formalisms[20,21] to study finite-temperature magnetism. However, the Stoner model may not be adequate for finite-temperature studies and a more realistic calculation of the exchange interaction will be needed.

In conclusion, we have succeeded in establishing a basic Hamiltonian for the magnetic structure for $Nd_2Fe_{14}B$ from first principles. The accuracy of such a theoretical calculation is at a level comparable with experimental measurements. It is expected that such a calculation will be extremely valuable in interpreting various magnetic measurements in similar hard magnets.

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