

Crystal fields in Nd₂Fe₁₄B

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The leading terms in the crystal field at both rare-earth sites in the new permanent magnet alloy Nd₂Fe₁₄B are B_{20} and B_{22}^2 . The sign of B_{20} explains the variation of the anisotropy constant K_1 reported by Sagawa *et al.* for the $R_2\text{Fe}_{14}\text{B}$ series. Noncollinear magnetic structures involving the rare-earth sublattices cannot be attributed to second-order crystal-field effects.

The identity of a new ternary iron-neodymium-boron phase which exhibits spectacular permanent-magnet properties¹⁻³ has recently been established as Nd₂Fe₁₄B. There have been several independent determinations of the structure.⁴⁻⁶ Herbst, Croat, Pinkerton, and Yelon⁴ solved the structure from powder neutron diffraction and further showed that the iron and neodymium moments are aligned in a parallel manner along the c axis of the tetragonal unit cell. Givord, Li, and Moreau⁵ used single-crystal x-ray methods to deduce a structure which is effectively identical to that of Herbst *et al.* According to both, the space group is $P4_2/mnm$ with unit-cell parameters $a = 8.79$ Å and $c = 12.19$ Å. Puckered double hexagonal nets of iron atoms lie perpendicular to the c axis and alternate with planes containing neodymium, boron, and the remainder of the iron. Boron atoms are at the centers of trigonal prisms of iron, the rectangular faces of which are capped by the neodymium atoms. Apart from a shift of the origin by $c/2$ and some minor differences in site nomenclature and atomic position parameters, the two structures are the same. Results similar to those of Givord *et al.* have also been obtained in another single-crystal x-ray structure determination by Shoemaker, Shoemaker, and Fruchart.⁶ Herein we will follow the nomenclature of Refs. 5 and 6 for the two inequivalent Nd sites.

$R_2\text{Fe}_{14}\text{B}$ alloys with the Nd₂Fe₁₄B structure have now been prepared for most of the rare earths from cerium to thulium, plus yttrium,^{7,8} and unit-cell parameters, Curie temperatures, and effective anisotropy fields were reported by Sagawa *et al.*⁷ These compounds all have easy c -axis anisotropy except $R = \text{Sm}, \text{Er}, \text{and Tm}$.

In order to help understand the magnetic anisotropy of Nd₂Fe₁₄B and the systematic variation of the anisotropy field down the series we calculated the crystal field at the rare-earth sites in Nd₂Fe₁₄B using the standard-point-charge approximation. Lattice sums were carried out making two extreme sets of assumptions. In the first, restricted, summation only the five Nd nearest neighbors in the plane were supposed to contribute with a charge of 3+ on each, following the approach of Sankar *et al.*⁹ for SmCo₅. In the second, extended, summation all three types of atoms were allowed to contribute to the crystal field, with charges of 3+, $\frac{9}{14}$ -, and 3+ for Nd, Fe, and B, respectively. Excellent convergence was achieved over a sphere of summation of radius 60 Å. The crystal-field parameters B_{nm} in the Hamiltonian

$$\mathcal{H}_{\text{CF}} = \sum_n \sum_m B_{nm} \hat{O}_{nm} \quad (1)$$

are listed in Table I for the 4*f* and 4*g* neodymium sites in both sums. No allowance is made at this stage for shielding effects. $B_{20}\hat{O}_{20}$ and $B_{22}^2\hat{O}_{22}^2$ are the dominant terms at both sites, all other terms being at least an order of magnitude smaller at 0 K. Although the point-charge model tends to underestimate B_{4m} and B_{6m} ,¹⁰ at room temperature and above, the fourth- and sixth-order terms in \mathcal{H}_{CF} should become insignificant due to the temperature variation of $\langle \hat{O}_{4m} \rangle$ and $\langle \hat{O}_{6m} \rangle$ as the 10th and 21st powers of the rare-earth magnetization, respectively.¹¹ The crystal-field results shown in Table I thus provide a ready explanation of the observed basal plane or c -axis anisotropy of the rare-earth series. The diagonal term in \mathcal{H}_{CF} , with $|J_z| = J$, is positive for Sm, Er, and Tm, and negative for Pr, Nd, Tb, Dy, and

TABLE I. Crystal-field parameters for Nd³⁺ in Nd₂Fe₁₄B (in K).

| Term | 4 <i>f</i> restricted | 4 <i>g</i> restricted | 4 <i>f</i> $r_{\text{max}} = 60$ Å | 4 <i>g</i> $r_{\text{max}} = 60$ Å |
|------------|--------------------------|--------------------------|---------------------------------------|---------------------------------------|
| B_{20} | -16.38 | -12.53 | -29.60 | -28.34 |
| B_{22}^2 | 4.99 | -13.76 | 32.61 | -40.96 |
| B_{40} | 6.18×10^{-3} | 4.11×10^{-3} | 1.85×10^{-2} | 1.72×10^{-2} |
| B_{42}^2 | -4.67×10^{-3} | 1.19×10^{-2} | -4.69×10^{-2} | 3.64×10^{-2} |
| B_{44}^2 | -7.79×10^{-3} | 1.64×10^{-2} | -9.09×10^{-2} | 6.20×10^{-2} |
| B_{60} | -2.59×10^{-4} | -1.54×10^{-4} | -1.05×10^{-3} | -9.23×10^{-4} |
| B_{64}^2 | 7.46×10^{-6} | -8.28×10^{-6} | 6.88×10^{-5} | -6.10×10^{-5} |

Ho in accord with the sign of α_J , the second-order Stevens' coefficient.¹²

While both Nd sites have easy directions of magnetization along the c axis, evaluation of the electric field gradient tensor at both sites indicates that the principal axis system for the $4g$ site is oriented with the z axis in the c plane at 45° to the a axis. The recently observed canted magnetic structure in Nd₂Fe₁₄B at low temperatures⁸ cannot be attributed to the second-order crystal field, but may possibly be due to anti-ferromagnetic Nd-Nd exchange coupling.

The measured anisotropy constant K_1 can be related to the difference in energy between easy-axis and basal-plane magnetization directions, ignoring higher-order anisotropy terms. As a first step, it is, therefore, reasonable to compare K_1 with the overall energy splitting of the rare earth's $4f$ shell.

The overall splittings of the $4f$ shell were calculated by computer diagonalization of the second-order crystal-field Hamiltonian using the restricted summation parameters. The second-order shielding factor σ_2 was taken as 0.5. The B_{nm} relevant to other rare earths were obtained from those of Nd (Table I) by scaling with the appropriate values of α_J and $\langle r^2 \rangle - a$ $4f$ electron radial average.¹³ The zero-temperature splittings thus obtained may be found in Table II. The actual energy splittings at room temperature will differ from those in Table II because of the action of temperature and exchange field, and the inadequacies of the point-charge model.¹⁴ Based on the reported Curie temperatures of Nd₂Fe₁₄B and Y₂Fe₁₄B,⁸ 593 and 575 K, respectively, we can estimate the Nd magnetization at room temperature using a two-sublattice molecular field model. The average iron moment was first deduced from our measurements of the ⁵⁷Fe average hyperfine field (29.5 T) to be $2.0\mu_B$ at room temperature, assuming $15 \text{ T } \mu_B^{-1}$ as derived from α -Fe. The molecular field coefficients ($\text{T}^2 \text{m}^3 \text{J}^{-1}$), λ_{NdFe} and λ_{FeFe} are calculated as 2.00×10^{-4} and 4.96×10^{-4} , respectively, assuming that λ_{NdNd} can be neglected. The reduced Nd magnetization is thence found to be 0.54 at 300 K, in accord with the observation of a greatly reduced Nd mo-

TABLE II. Zero-temperature crystal-field splittings in R₂Fe₁₄B (corrected for shielding).

| R | 4f | Splitting (K) | 4g |
|----|--------|---------------|--------|
| Pr | 1433 | | 1314 |
| Nd | 511 | | 411 |
| Sm | (-852) | | (-770) |
| Tb | 1099 | | 1025 |
| Dy | 1045 | | 980 |
| Ho | 401 | | 376 |
| Er | (-383) | | (-359) |
| Tm | (-929) | | (-866) |

ment by Herbst *et al.*⁴ It follows that the crystal-field splitting for Nd at the two sites at room temperature is reduced by a factor¹¹ of $(0.54)^{-3} = 6.25$ from the values in Table II. The measured value of K_1 , 3.5 MJ m^{-3} , would correspond to an average crystal-field splitting of 30 K if only the rare earth contributed to the anisotropy, which agrees within a factor of 2.6 with our calculations. Given the shortcomings of the point-charge approximation in metals, no better agreement could be expected.

Finally, we note that rare-earth single-ion anisotropy is *not* the only contribution to K_1 . Sagawa *et al.*⁷ report anisotropy fields (MA m^{-1}) of 3.1, 3.7, and 6.1 for $R = \text{Y, Ce, and Gd}$, respectively, and the anisotropic magnetization has been measured directly on crystals with $R = \text{Y}$,⁸ so there is clearly a significant anisotropy contribution from the iron sublattice.

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