

$$\Delta t'^{\alpha} = t'^{\alpha} - 1 = (S'^{\alpha} - S)/S.$$

These relations simplify the computation of the matrix elements in the primed frame. Beyond this we just grind it out by expanding S'^x and S'^y in terms of raising and lowering operators and using their known properties. One must consider many special cases, find a formula fitting all of them, put these results in (A2), and do the sums. We give here the results of this procedure up to $n=4$. The detailed calculations are found in Ref. 13.

Let $\delta_{\alpha\beta}$ be the Kronecker δ and $\epsilon_{\alpha\beta\gamma}$ the usual completely antisymmetric tensor. Then

$$(\theta, \phi | \Delta t^{\alpha} \Delta t^{\beta} | \theta, \phi) = \frac{1}{2S} (\delta_{\alpha\beta} - X^{\alpha} X^{\beta} + i \epsilon_{\alpha\beta\gamma} X^{\gamma}), \quad (\text{A3})$$

where \vec{X} is a unit vector in the direction (θ, ϕ) :

$$(\theta, \phi | \Delta t^{\alpha} \Delta t^{\beta} \Delta t^{\gamma} | \theta, \phi) = - (X^{\beta}/S) (\theta, \phi | \Delta S^{\alpha} \Delta S^{\gamma} | \theta, \phi), \quad (\text{A4})$$

$$\begin{aligned} & (\theta, \phi | \Delta t^{\alpha} \Delta t^{\beta} \Delta t^{\gamma} \Delta t^{\nu} | \theta, \phi) \\ &= (\theta, \phi | \Delta t^{\alpha} \Delta t^{\beta} | \theta, \phi) (\theta, \phi | \Delta t^{\gamma} \Delta t^{\nu} | \theta, \phi) \\ &+ 2(\theta, \phi | \Delta t^{\alpha} \Delta t^{\nu} | \theta, \phi) (\theta, \phi | \Delta t^{\beta} \Delta t^{\gamma} | \theta, \phi) \\ &+ (1/S) [(X^{\beta} X^{\gamma}/S) (\theta, \phi | \Delta t^{\alpha} \Delta t^{\nu} | \theta, \phi) \\ &- (\theta, \phi | \Delta t^{\alpha} \Delta t^{\nu} | \theta, \phi) (\theta, \phi | \Delta t^{\beta} \Delta t^{\gamma} | \theta, \phi)]. \quad (\text{A5}) \end{aligned}$$

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Conduction-Electron Contribution to Electric Field Gradients in Rare-Earth Metals

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The conduction-electron contribution to the electric field gradients in the heavy rare-earth metals has been calculated using a modified orthogonalized-plane-wave approach. Experimental results can be easily explained within the confines of the model and the amount of $5d$ character mixed into the conduction-electron wave function (characterized by a parameter ϵ_d) agrees well in both magnitude and sign with previous independent methods of determination. An attempt is made to correlate the magnitude of the $5d$ admixture with the d density of states in the conduction band.

INTRODUCTION

It is to be anticipated that the presence of conduction electrons in a metal may substantially modify the crystalline electric fields (CEF's) and electric field gradients (EFG's) from those which one might expect on the basis of insulator theory. One could envisage strong screening effects which

would reduce the effective fields to below the point-charge values. However, experimental evidence shows that the point-charge fields may be enhanced and even changed in sign.¹⁻³ It is therefore clear that conduction electrons must play an important role in this respect. A growing experimental interest in the determination of CEF's and EFG's by susceptibility, neutron-scattering, and Mössbauer-

effect measurements, as well as many other methods, has led to an increased theoretical effort to explain the results obtained. Two principal methods of describing the conduction electrons have been proposed, one using an augmented-plane-wave method⁴ and the other using a modified orthogonalised-plane-wave (OPW) technique.⁵ In the former case, which has been applied to both the calculation of CEF's and EFG's,⁴ agreement with experiment is apparently not yet satisfactory. The latter method has previously been applied only to the calculation of CEF's in heavy rare earths and their alloys with noble metals. Agreement with experiment is found to be reasonable although an adjustable parameter is contained in this approach which has not yet been given a clear physical interpretation. In the present paper we will apply this theory to the EFG problem in an effort to both understand more clearly the importance of the aforesaid parameter and to give a further test of the OPW technique in this application.

A comprehensive survey by Pelzl⁶ has concentrated on EFG's in heavy rare-earth metals. He has found that the experimentally measured field gradient originating from the lattice of point charges and the conduction electrons may be as much as 1000 times larger than that expected on the basis of calculation using a simple lattice-sum point-charge model. It is suggested that the origin of this large enhancement may be the combined effect of the lattice of point charges and the conduction electrons exterior to the atomic sphere together with the Sternheimer antishielding effect.⁷ Other workers, however, in discussing EFG's in metals and alloys⁸ propose that the dominant contribution may come from the electrons within the atomic sphere. In the following we shall essentially reconcile these two views and find that the magnitude of the EFG can be explained consistently within the OPW model. We shall first outline the method of calculation and then compare the theoretical results with those given by Pelzl for Gd, Tb, Dy, Ho, and Tm. Finally, we will discuss the necessity to admix the $5d$ character into the OPW used to represent the conduction electrons in terms of the d -band character in the heavy rare earths.

THEORY

Heavy rare-earth metals have an hexagonal closed-packed structure and the point symmetry of any one nucleus is D_{6h} . The nuclear-quadrupole interaction is found to be solely dependent on the z component of the EFG tensor where the z axis is defined to be the c axis. Inside the above metals the EFG q at a nuclear site assumed as the origin of a set of spherical polar coordinates is given by

$$q = \int 2[1 - \gamma(r)]\rho(r)r^{-3}P_2^0(\cos\theta) d\tau, \quad (1)$$

where $\rho(r)$ is the charge density at the point with position vector $\vec{r} = (r, \theta, \phi)$ which includes the density due to valence electrons, conduction electrons, and positive point charges which will describe the environment of the ion in question. P_2^0 is an associated Legendre polynomial of the first kind of degree 2. The integral in Eq. (1) is over all space and $\gamma(r)$ is the antishielding factor studied by Sternheimer⁷ and is a means of modifying the electric-quadrupole interaction to take into account the distortion of the closed shells in the presence of a source field. There are three main sources of the measured field gradient in a metal, namely, that from the valence electrons, the contribution from the CEF and the component from the conduction electrons so that the total gradient is often written

$$|e|q_{zz} = (1 - \gamma_\infty)|e|q_{zz}^{\text{lat}} - (1 - R_Q)|e|q_{zz}^A - |e|q_{zz}^{\text{ce}}. \quad (2)$$

In Eq. (2) the factors γ_∞ and R_Q describe the antishielding of the CEF by closed shells and the shielding of the partially filled $4f$ shells, respectively. The EFG's from the lattice, the valence electrons, and conduction electrons have been denoted in (2) by q_{zz}^{lat} , q_{zz}^A , and q_{zz}^{ce} , respectively.

The dominant contribution to the EFG for the rare earths comes from the term q_{zz}^A in Eq. (2) arising from the $4f$ electrons localized on the ions. This may be determined directly from Mössbauer-effect measurements or calculated in terms of the nuclear-quadrupole interaction (see Ref. 6). However, we shall in this paper be specifically interested in that part of Eq. (2) which arises from the conduction electrons and the lattice of point charges so that we take a simplified form:

$$|e|q'_{zz} = (1 - \gamma_\infty)|e|q_{zz}^{\text{lat}} - |e|q_{zz}^{\text{ce}}. \quad (3)$$

We examine the contribution from the conduction electrons, $|e|q_{zz}^{\text{ce}}$, first. To calculate the charge density of conduction electrons at a point \vec{r} we adopt a wave function ϕ_k developed in a previous theory⁵ and given by

$$\phi_k = \frac{N}{\sqrt{17Z}} \left(e^{i\vec{k}\cdot\vec{r}} - \sum_p b_{pk}\phi_p - \sum_t c_{tk}f_k - b_d\eta\epsilon_d\Psi_{5d} \right) |\beta\rangle, \quad (4)$$

where the conduction electrons have been assumed to be noninteracting with wave vectors \vec{k} on the Fermi surface. V is the volume bounded by a metal ion and its 12 nearest neighbors. N is a normalization constant given by

$$N^2 = \left[1 - \frac{1}{V} \left(\sum_p |b_{pk}|^2 + \sum_t |c_{tk}|^2 - b_d^2\eta(\epsilon_d^2 - 2\epsilon_d) \right) \right]^{-1} \quad (5)$$

and the coefficients b_{pk} , c_{tk} , and b_d are defined by

$$b_{pk} = \int e^{i\vec{k}\cdot\vec{r}} \phi_p^* d\tau; \quad c_{tk} = \int e^{i\vec{k}\cdot\vec{r}} f_t^* d\tau;$$

$$b_d = \int e^{i\vec{k}\cdot\vec{r}} \Psi_{5d}^* dr.$$

The sums over p and t are, respectively, over all $4f$ orbitals which are occupied in the ground term with spin down for one ion and over all core orbitals of any one rare-earth ion and its 12 neighbors. Strictly speaking the sum over p should be over all the $4f$ orbitals of a rare-earth ion and its neighbors but it can be shown that, at least for CEF's,⁹ the incomplete $4f$ shells of neighbors produce a negligible contribution to the CEF seen by the ion at the origin so we shall neglect these parts. In a similar way the term premultiplied by b_d is a component describing the $5d$ character of ϕ_k but only for the ion at the origin. The physical reason for the latter inclusion is that in the case of Gd^{3+} , the ion has a ground configuration of $4f^7 5d$ and a ground term 9D_2 which suggests that for this term the $5d$ orbital with angular dependence Y_2^2 is occupied.¹⁰ It is therefore possible that the other heavy rare-earth metals have conduction bands which contain $5d$ character. Indeed this is found to be the case from a number of band-structure calculations.^{11,12} b_d is defined to be the plane-wave overlap with the $5d$ orbital of the particular ion concerned (we have assumed the Gd $5d$ orbital tabulated by Herman and Skillman¹³ to be appropriate to all ions considered). For simplicity we have assumed that the $5d$ orbital with $m=2$ will have a dominant effect so that η is zero for all orbitals except the $5d$ orbital with angular dependence Y_2^2 . ϵ_d is a "mixing" parameter which in some way makes allowance for $5d$ character in the conduction-electron wave function; its physical significance will be discussed in more detail later.

It is well known that the normal electrostatic interaction between a conduction electron and a magnetic ion favors the conduction-electron spin parallel to the net spin of the ion.¹⁴ However, interband mixing sets up an effective exchange interaction which can dominate the purely electrostatic exchange¹⁵ so we have chosen to take ϕ_k with spin down, i. e., postmultiplying by the spin state $|\beta\rangle$.

From Eq. (3), we obtain the probability density $\phi_k \phi_k^*$ at the point \vec{r} and hence the charge density which is substituted into Eq. (2) to give the conduction-electron component of q'_{zz} , namely, q''_{zz} in the form

$$\begin{aligned} -|e| q''_{zz} = -n_0 |e| \frac{N^2}{V} \int_0^\infty 2[1 - \gamma(r)] \\ \times \left[16\pi^2 \left(a_{5d}^2 \epsilon_d^2 \frac{f_{5d}(r)}{r} - 2a_{5d} \epsilon_d \frac{f_{5d}(r) j_2(k_F r)}{r} \right) \right. \\ \times \int_0^{2\pi} \int_0^\pi |Y_2^2|^2 P_2^0(\cos\theta) \sin\theta d\theta d\phi \\ \left. + 16\pi^2 \left(\frac{a_p^2 f_{4f}^2(r)}{r} - 2a_p f_{4f}(r) j_3(k_F r) \right) \right. \end{aligned}$$

$$\left. \times \sum_p \int_0^{2\pi} \int_0^\pi |Y_3^m|^2 P_2^0(\cos\theta) \sin\theta d\theta d\phi \right] dr, \quad (6)$$

where a_{5d} and a_p are defined by the integrals

$$\begin{aligned} a_{5d} &= \int_0^\infty f_{5d}(r) j_2(k_F r) r^2 dr, \\ a_p &= \int_0^\infty f_{4f}(r) j_3(k_F r) r^2 dr, \end{aligned} \quad (7)$$

and n_0 is the number of conduction electrons in the volume V . The localized $4f$ and $5d$ wave functions have been assumed to take the form of products $f_{4f}(r) Y_3^m(\theta, \phi)$ and $f_{5d}(r) Y_2^m(\theta, \phi)$, where m is the component of orbital angular momentum $l_p = 3$ along the axis of quantization. j_3 and j_2 are spherical Bessel functions.

Within the atomic sphere one normally assumes, as, for example, in calculating the localized $4f$ -electron contribution q'_{zz} , that there is shielding of the $4f$ term which may be taken into account by using the shielding factor R_Q . Outside, we have the antishielding factor γ_∞ . In calculating a conduction-electron term involving $4f$ -electron character we must clearly take account of the fact that shielding and antishielding must also exist for the conduction electron. It seems more realistic physically, therefore, to assume a spatially dependent $\gamma(r)$ which varies from a value R_Q (representing shielding) to γ_∞ (representing antishielding) smoothly as a function of r . The radial integrals involved in Eq. (6) have therefore been performed using such a variation in $\gamma(r)$; we have not divided up the range of integration into parts inside and outside of the atomic sphere.

RESULTS

Using the Hartree-Fock self-consistent wave functions tabulated by Herman and Skillman¹³ we have computed the various contributions to the electric field gradient due to the conduction electrons given by Eqs. (4) to (7). The requisite values of k_F were determined using the formula given by Elliot¹⁶ for hexagonal close-packed lattices. Since the parameter ϵ_d is essentially unknown the results are best tabulated in the form of constants of a law of type:

$$-|e| q''_{zz} = (a\epsilon_d + b\epsilon_d^2 + c_{4f}) \times 10^{17} \text{ V cm}^{-2}, \quad (8)$$

where a and b are the calculated integrals from Eq. (6) which must be multiplied by ϵ_d and ϵ_d^2 and c_{4f} is the radial integral involving only the $4f$ radial wave-function terms in the same equation. The calculated values for a , b , and c_{4f} are given in Table I for each metal as a function of γ_∞ . Variation of γ_∞ was performed since this parameter is not well known for each of the metals considered, and furthermore, this enabled us to study the sensitivity of this part of the total field gradient

to γ_∞ . Changes in the shielding parameter R_Q were not taken into account since the contribution to the conduction-electron field gradient coming from this term was negligible with respect to the overall effect from terms involving γ_∞ .

Pelzl⁶ has given experimental values for the electric field gradient due to point charges and conduction electrons, obtained by subtracting the localized $4f$ -electron contribution from the total electric field gradient. The point-charge calculations he also presents show that the experimental EFG due to the conduction electrons and point charges must be dominated by the conduction-electron contribution, the ratio of experimental to point-charge-calculated EFG varying from 74 to nearly 500 for the metals we have considered. We therefore assume, for comparison with our own results, that the experimental EFG's quoted by Pelzl⁶ (referred to in his paper as V_{zz}^{exp}) arise solely from the conduction electrons. These values are also quoted in Table I. The result for Tm is changed in sign from that reported by Pelzl to allow for an apparent error made in interpreting the original results of Uhrich and Barnes.¹⁷

For Gd the situation is not complicated by the c_{4f} term arising from the $4f$ character in the conduction-electron wave function since the angular integral involved in calculating c_{4f} in Eq. (6) is zero. From comparison with experiment, therefore, one should be able to obtain some feeling for the magnitude and character of the ϵ_d parameter. In Table II we give the values for ϵ_d needed to fit with experiment as a function of γ_∞ . The value taken for R_Q in the calculations was 0.5. The values are clearly all of the same order of magnitude and negative sign and are consistent with the range of values found for other rare-earth metals from calculation of the CEF parameters.¹⁸ From Table I one can see that such small values of ϵ_d indicate that the $4f$ part of the conduction-electron wave function provides the dominant contribution to the EFG for the other heavy rare-earth metals considered.

For the remaining rare earths for which calculations were made, we are somewhat hampered by the fact that ϵ_d cannot be determined so directly as for Gd. Furthermore, γ_∞ is known accurately in only one case,⁷ Tm, so that a scheme for interpreting the theoretical results must be decided. To cover what we consider to be "all possibilities" and give a feeling for the sensitivity of the theoretical result to γ_∞ and ϵ_d we have used two techniques. First, we have assumed that γ_∞ decreases linearly in going from -20 for Tb to -80 for Tm. Coincidentally we have assumed that ϵ_d is a function of γ_∞ and that, irrespective of the metal, the given γ_∞ suggests a definite ϵ_d as given for Gd in Table II. Thus the value of γ_∞ chosen for a metal

TABLE I. Calculated parameters of Eq. (8) for the rare-earth ions considered as a function of the antishielding parameter γ_∞ .

γ	Gd			Tb			Dy			Ho			Tm		
	a	b	c_{4f}	a	b	c_{4f}	a	b	c_{4f}	a	b	c_{4f}	a	b	c_{4f}
-20	-30.98	579.1	0	-32.0	595.4	5.29	-31.43	582.3	4.93	-30.86	578.4	1.79	-31.07	567.3	-4.29
-40	-60.97	1111.5	0	-62.97	1142.9	10.29	-61.84	1117.7	9.58	-60.73	1110.2	3.49	-61.13	1089.0	-8.33
-60	-90.95	1644.0	0	-93.93	1690.3	15.29	-92.25	1653.1	14.24	-90.59	1642.0	5.19	-91.18	1610.5	-12.38
-80	-120.9	2176.4	0	-124.9	2237.8	20.29	-122.7	2188.5	18.90	-120.5	2173.8	6.89	-121.2	2132.1	-16.42
-100	-150.9	2708.9	0	-155.9	2785.3	25.29	-153.1	2723.9	23.55	-150.3	2705.6	8.59	-151.3	2653.7	-20.47
Expt.		1.50			4.6			5.0			9.0			-5.0	

TABLE II. The ϵ_d parameter required to reproduce the measured EFG in Gd as a function of antishielding parameter γ_∞ .

γ_∞	ϵ_d
-20	-2.4×10^{-2}
-40	-1.4×10^{-2}
-60	-1.0×10^{-2}
-80	-8.0×10^{-3}
-100	-6.3×10^{-3}

enables us to ascertain ϵ_d from Table II. Second, we have taken a value of -80 for γ_∞ for all of the metals considered (approximately that value known for Tm⁷) and a typical value for ϵ_d of -10^{-2} . Both sets of calculated EFG's are given in Table III together with their individual ratios with the experimental values tabulated in Table I. As can be seen, whichever method of assigning a γ_∞ or ϵ_d we use, the discrepancy between theory and experiment is never greater than a factor of 5.

DISCUSSION

As is seen from the results given in Table III, the agreement between theory and experiment for the conduction-electron contribution to the electric field gradient is satisfactory. The greatest uncertainty arises in lack of knowledge of the antishielding parameter, γ_∞ , and its possible spatial variation. The theoretical result is not very sensitive to the magnitude of the shielding parameter. We have used a linear-interpolation scheme, being the simplest possible, for the radial dependence of $\gamma(r)$ from R_0 to γ_∞ . It is not obvious that this is necessarily correct, however; in the worst case that one assumes $\gamma(r)$ equal to γ_∞ outside the atomic sphere, the theoretical result is increased by a factor of 10 which means in the worst case a discrepancy of a factor of 50 with experiment which is still much better than predicted with a pure-point-charge model.⁶ What seems more likely is that $\gamma(r)$ will not vary linearly with radius and if the initial slope is less than the linear-interpolation slope then the theoretical values will be brought into closer agreement with experiment than shown in Table III.

The results for Gd show that ϵ_d is both negative and of order of magnitude 10^{-2} , in agreement with that found by an independent calculation of the crystal-field parameters.¹⁸ It is clearly of interest, but somewhat difficult, to give a physical interpretation to this parameter. The parameter as used here mixes into the conduction-electron

TABLE III. The EFG's calculated theoretically and compared with experiment (q_T/q_{expt}) using two different schemes for the value of γ_∞ . q_{T_d} : γ_∞ varied from -20 for Tb to -80 for Tm. q_{T_b} : γ_∞ equal to -80 throughout. The units are 10^{17} V/cm².

	Tb	Dy	Ho	Tm
q_{T_d}	6.40	10.67	6.26	-15.3
q_{T_d}/q_{expt}	1.39	2.1	0.70	3.1
q_{T_b}	21.4	20.0	6.3	-15.3
q_{T_b}/q_{expt}	4.7	4.0	0.7	3.1

wave-function $5d$ character on the basis that the atomic configuration for atoms of Gd and Lu, at both ends of the heavy rare-earth-metal table, includes $5d$ electrons and these may lead, in a metal, to $5d$ character in the bands. Such an admixture effect has been suggested previously¹¹ in an explanation of the measured saturation magnetization in pure Gd. ϵ_d was found to decrease in going across the rare-earth table from Gd to Dy¹⁸ which is consistent with a decrease in the d -band density-of-states behavior calculated by Keeton and Loucks¹² based on a $4f^7 5d^1 6s^2$ ground configuration for Gd and $4f^{10} 6s^2$ configuration for Dy. ϵ_d is also calculated to increase again in going across the series from Dy to Lu where one might expect an increased d density of states arising from the $4f^{14} 5d^1 6s^2$ ground configuration. One is thus tempted to suggest that the ϵ_d parameter invoked here and previously¹⁸ is linked to the $5d$ contribution to the d density of states in rare-earth metals and perhaps ought to be directly correlated with the d -band structure.

We find that the experimental results can be explained using the method of calculation presented and that, except in the case of Gd, the $4f$ character in the conduction-electron wave function gives rise to the largest contribution in the conduction-electron EFG. The greatest indeterminacy arises from lack of precise knowledge of the Sternheimer antishielding factor. It appears not to be necessary to differentiate between the regimes inside and outside the atomic sphere as was done by Pelzl⁶ and Watson *et al.*,⁸ especially since although this may simplify the theoretical calculation it may lead to a less realistic physical interpretation and may underestimate the role of the conduction electrons. The apparent correlation between the ϵ_d parameter used here and the d density of states at the Fermi energy should be investigated further.

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Sublattice Magnetization of FeBO₃ Single Crystals by Mössbauer Effect

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Mössbauer-effect (ME) measurements of the hyperfine interaction of the iron nuclei in single crystals of FeBO₃ have been used to study the temperature dependence of the sublattice magnetization. The results are found to be consistent with previously published nuclear-magnetic-resonance results and agree quantitatively with simple noninteracting-spin-wave theory for $T \leq T_N/3$, where T_N is the Néel temperature. The exchange integral calculated from fitting ME data to spin-wave theory, $J = 27.3 \pm 0.5$ K, is in very good agreement with that calculated from the Rushbrooke and Wood T_N relation, indicating that FeBO₃ is very dominantly a nearest-neighbor-exchange system. We estimate that the upper spin-wave branch (out plane) has a gap of about 23 K, which is primarily due to dipolar anisotropy but partly to the Dzyaloshinskii-Moriya field.

I. INTRODUCTION

Recently, there has been a great deal of interest in iron borate, FeBO₃, a transparent, green, weak ferromagnet, due to its possible application for magneto-optical devices.¹ The successful growth of single crystals of FeBO₃ has led to studies of crystal structure,² magnetic properties,^{3,4} optical properties,⁴ ferromagnetic resonance,⁵ magnetic structure,⁶ nuclear magnetic resonance,⁷⁻⁹ acoustic resonance,¹⁰ and Mössbauer effect.¹¹

FeBO₃ was first prepared by Bernal *et al.*,² who found it to have the rhombohedral calcite structure, space group $R\bar{3}c$, with lattice constants $a = 5.496$ Å and $\alpha = 49^\circ 38'$ (see Fig. 1). The compound is a typical weak ferromagnet³ with a spontaneous magnetization⁴ $4\pi M_s$ at 300 °K of 115 G and a Néel temperature $T_N = 348.35$ °K.¹¹

Neutron diffraction⁶ shows that the spins are perpendicular to the rhombohedral axis, in agreement with Mössbauer studies and symmetry considerations for the calcite structure. The Fe³⁺ magnetic moment at 77 °K is $4.7\mu_B$. The threefold [111] axis is the hard axis and the (111) plane is the easy plane of magnetization. The hard-axis anisotropy field (made up of dipolar and Dzyaloshinskii contributions) is 62 500 Oe at 300 °K,

while the in-plane anisotropy field is less than 1 Oe, as measured by ferromagnetic resonance.^{1,10} All of the iron spins are in the (111) plane with a small canting away from antiparallel configuration. Symmetry considerations show that the canting must also be in the easy plane.

The ferric ions in FeBO₃ are arranged essentially in two sublattices which are strongly coupled antiferromagnetically. The sublattice moments are slightly canted with respect to the antiferromagnetic axis so that a small net ferromagnetic moment results in a direction perpendicular to this axis. The angle between sublattice magnetization and the antiferromagnetic axis at zero external field is the canting angle. Petrov *et al.*,⁸ from their ferromagnetic-moment and sublattice-moment measurements, deduced a canting angle $\varphi = 0.016$ rad, which is constant over a very large temperature range. This result indicates that antisymmetric exchange¹² is responsible for the canting and the weak ferromagnetism. The same conclusion has been obtained for other weak ferromagnets such as the orthoferrites.¹³

The sublattice magnetization is measured by Petrov *et al.*,^{7,8} in terms of the hyperfine field (hf) at the Fe⁵⁷ nucleus from nuclear-magnetic-resonance (NMR) measurements. The measurements