

Aspherical Spin Density in S-State Cations

T. A. KAPLAN

Lincoln Laboratory,* Massachusetts Institute of Technology, Lexington, Massachusetts

(Received 18 June 1964)

A calculation of the first-order effect of spin-orbit coupling on a $(3d)^5$ unperturbed S-state ion in a cubic crystal field has led to a new contribution $\sigma_1(\mathbf{r})$ to the ionic spin density. The integral over space of $\sigma_1(\mathbf{r})$ is zero and $\sigma_1(\mathbf{r})$ is perpendicular to the unperturbed spin density $\sigma_0(r)$; while $\sigma_0(r)$ is spherically symmetric about the nucleus, $\sigma_1(\mathbf{r})$ is highly aspherical. In $\alpha\text{-Fe}_2\text{O}_3$ at room temperature, the spin density consists of the large "antiferromagnetic" component σ_0 , plus the new term σ_1 , plus the weak ferromagnetic or Dzialoshinsky term σ_D , which is spherical. In neutron scattering, it is found that σ_1 contributes to the same "ferromagnetic" Bragg peaks as does σ_D , and in the same order of magnitude. Hence the new term is probably important for understanding the surprising, highly aspherical ferromagnetic spin-density distribution recently observed in $\alpha\text{-Fe}_2\text{O}_3$ by Pickart, Nathans, and Halperin. In general, $\sigma_1(\mathbf{r})$ will be nonzero under much less restrictive symmetry requirements than those needed for the nonvanishing of σ_D . In the course of discussion, it is pointed out that the Dzialoshinsky-Moriya theory of the weak ferromagnetism in $\alpha\text{-Fe}_2\text{O}_3$, for example, implies that the application of a spatially uniform magnetic field should influence the distribution of domains of antiferromagnetic spin components. This effect was observed by Pickart *et al.*

I. INTRODUCTION

THE weak ferromagnetism existing in the high-temperature phase of $\alpha\text{-Fe}_2\text{O}_3$ has been attributed by Dzialoshinsky¹ and Moriya² to a small canting of the antiferromagnetic sublattices. These sublattices are of course those containing Fe^{3+} which has the ground configuration $(3d)^5$ (6S). Hence, it was surprising when Pickart, Nathans, and Alperin³ found, in their recent polarized neutron experiment, that the weak component of the spin is spatially distributed in a highly aspherical way around an iron site, in direct contrast to the distribution of the strong "antiferromagnetic" component.

The evidence for this asphericity comes from the pair of outer Bragg reflections (330) and (114). In the experimental geometry, the corresponding reciprocal vectors \mathbf{K}_{330} , \mathbf{K}_{114} lie in the y - z plane of Fig. 1 and these are related by the reflection \mathcal{R} in the x - z plane, i.e., $\mathbf{K}_{114} = \mathcal{R}\mathbf{K}_{330}$. Also, the neutrons are polarized along the Dzialoshinsky moment, i.e., the x direction; because of this, as well as the experimental geometry, only the x component $\sigma_x(\mathbf{r})$ of the spin density is seen.^{3,4} If within a unit cell $\sigma_x(\mathcal{R}\mathbf{r}) = \sigma_x(\mathbf{r})$, then the magnetic structure factors for (330) and (114) would have to be the same. This would be true if, as in the simple canting picture, $\sigma_x(\mathbf{r})$ were a sum of localized atomic functions each spherically symmetric about the associated nucleus. However, these structure factors are found³ to be very different.

So for a calculation to be relevant to the neutron results,³ it must give an x component of spin density which is not invariant under \mathcal{R} . Furthermore, it must contribute to the "ferromagnetic" Bragg peaks, i.e., the same ones expected from the Dzialoshinsky moment,

this contribution to the (330) and (114) being of the same order as the latter. The purpose of this note is to suggest that intra-atomic spin-orbit coupling gives a spin density with these properties, and to discuss the result in a more general context.⁵

This mechanism is contained implicitly in Moriya's formalism.² He uses as one-electron basis functions $\psi_{\uparrow}(\mathbf{r}-\mathbf{R})$ and $\psi_{\downarrow}(\mathbf{r}-\mathbf{R})$ which he describes as having spin almost up and almost down. The modifier "almost" is needed because of intraatomic spin-orbit coupling. This means that the spin operators $\mathbf{S}(\mathbf{R})$ are not the true spins, but refer rather to these "almost" states. So let us call Moriya's "spin" operators $\mathbf{T}(\mathbf{R})$, reserving \mathbf{S} for true spin. To calculate the spin density, we would

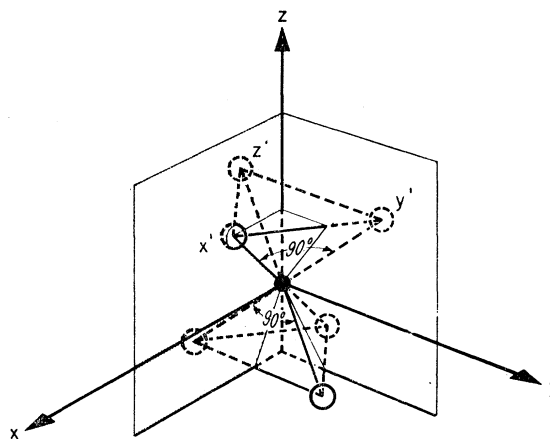


FIG. 1. Cation site \bullet , anion site \circ . In the corundum structure, z is the c axis, x is parallel to a 2-fold axis; the actual anion sites are distorted from the perfect octahedral coordination shown. In the high-temperature phase of $\alpha\text{-Fe}_2\text{O}_3$, the large antiferromagnetic moments point along $\pm y$, the Dzialoshinsky moment along x . x', y', z' are Cartesian coordinates with 3-fold symmetry around z , x' lying in the x - z plane.

* Operated with support from the U. S. Air Force.

¹ I. Dzialoshinsky, Phys. Chem. Solids 4, 241 (1958).

² T. Moriya, Phys. Rev. 120, 91 (1960).

³ R. Nathans, S. J. Pickart, and H. A. Alperin, International Colloquium on Scattering and Diffraction of Neutrons, Grenoble, 1963 (unpublished); following paper, Phys. Rev. 136, A1641 (1964).

⁴ M. Blume, Phys. Rev. 130, 1670 (1963).

⁵ In Ref. 3 it is shown that obvious covalence effects involving nearest neighbor Fe-O bonds cannot account for the difference between the (330) and (114) structure factors.

first find, from Moriya's "spin" Hamiltonian in the Hartree or internal-field approximation, the proper single-atom functions of the form $\Psi(\mathbf{R}) = a\psi_{\uparrow}(\mathbf{r}-\mathbf{R}) + b\psi_{\downarrow}(\mathbf{r}-\mathbf{R})$. A small "canting," in Moriya's sense, occurs here if, say, $(\psi_{\uparrow}(\mathbf{r}-\mathbf{R}), \mathbf{T}(\mathbf{R})\psi_{\uparrow}(\mathbf{r}-\mathbf{R})) = \frac{1}{2}\hat{y}$ and $|b/a|$ is small but nonzero (\hat{y} is a unit vector in the y direction); then $(\Psi(\mathbf{R}), \mathbf{T}(\mathbf{R})\Psi(\mathbf{R}))$ is a vector canted slightly from \hat{y} ; this canting is caused^{1,2} by the $\mathbf{D} \cdot \mathbf{T}(\mathbf{R}) \times \mathbf{T}(\mathbf{R}')$ terms in the "spin" Hamiltonian. To find the true physical spin density we must now express the $\psi_{\uparrow}, \Psi_{\uparrow}$ in terms of Moriya's orbital functions $\phi_{n'}(\mathbf{r}-\mathbf{R})$ (n' includes n , the ground function), and the true spin functions α, β , quantized along \hat{y} , say. It is easy to see that one obtains for the spin density, to first order in the spin-orbit coupling,

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_0 + \boldsymbol{\sigma}_D + \boldsymbol{\sigma}_1, \quad (1)$$

where $\boldsymbol{\sigma}_0 = \frac{1}{2}\hat{y}|\phi_n(\mathbf{r}-\mathbf{R})|^2$ (this is called the antiferromagnetic component in $\alpha\text{-Fe}_2\text{O}_3$); $\boldsymbol{\sigma}_D = |\phi_n(\mathbf{r}-\mathbf{R})|^2 \times [b(\alpha, \mathbf{S}\beta) + b^*(\alpha, \mathbf{S}\beta)^*]$, the Dzialoshinsky spin density; and $\boldsymbol{\sigma}_1$ is the extra term due to the deviation of $\Psi_{\uparrow}(\mathbf{r}-\mathbf{R})$ from $\phi_n(\mathbf{r}-\mathbf{R})\alpha$. Note that $\boldsymbol{\sigma}_D$ has the same \mathbf{r} dependence as the leading term, as expected on the simple canting model^{1,2}; in hematite $\boldsymbol{\sigma}_D$ is along \hat{x} , so that $b = -b^*$ for $(\alpha, \mathbf{S}\beta) = \frac{1}{2}(\hat{z} - i\hat{x})$.

If we continue with Moriya's formalism, in which there is one electron per atom, and we try to make it a model for hematite, we might take the ground orbital $\phi_n(\mathbf{r}-\mathbf{R})$ to be an S state. Then $\boldsymbol{\sigma}_0$ and $\boldsymbol{\sigma}_D$ would both be spherically symmetric, i.e., they would depend on \mathbf{r} only through $|\mathbf{r}-\mathbf{R}|$. Furthermore, $\boldsymbol{\sigma}_1$ would be zero, so that the effect in which we are interested would be lost. Much closer to reality, the unperturbed ground state for the Fe^{3+} ion is 6S , configuration $(3d)^5$. Furthermore, since the spin-orbit coupling is of the form $\sum \lambda(r_i)l_i \cdot s_i \equiv V$, rather than the function $\mathbf{L} \cdot \mathbf{S}$ of the total angular momenta, there will be nonzero matrix elements connecting 6S to other states (quartets), as is well known. Hence we can expect a nonzero $\boldsymbol{\sigma}_1$, and it is to the calculation of this quantity that we now address ourselves.

II. FIRST-ORDER CALCULATION

We consider a $(3d)^5$ configuration of electrons moving in an octahedral field with splitting parameter $10Dq \equiv \Delta$, indicated symbolically by the anion sites in Fig. 1. Because the field W (symmetry C_3) resulting in the corundum structure from the distortion of the anion sites and from the other cations produces splittings much less than Δ ,⁶ we treat it along with the spin-orbit interaction V as a perturbation. Then W does not enter in first order. We take as the unperturbed ground state 6S with $S_z = \frac{5}{2}$, $\zeta = y$ for the high- T phase of hematite,⁷ and other directions considered below. We have found

⁶ D. S. McClure, *J. Chem. Phys.* **36**, 2757 (1962).

⁷ Since the experiment was performed at room temperature which is $\sim \frac{1}{4}T_N$, considering only the state with maximum S_z is reasonable within our "single-cation" model.

that, to first order, the Hartree-Fock (H-F) approximation gives a spin density $\boldsymbol{\sigma}_1$ which deviates by only about 20% from the result of the calculation taking correlation into account within $(3d)^5$. Hence, for our order-of-magnitude purposes, we may discuss the calculation in terms of the simpler and intuitively more transparent H-F approximation. So we are concerned with the familiar one-electron orbitals $f_{i\uparrow} = f_i(\mathbf{r})\alpha$, $f_{i\downarrow} = f_i(\mathbf{r})\beta$, where the five functions f_i consist of e_g 's (e 's) and t_{2g} 's (t 's) referred to $x'y'z'$ of Fig. 1, and α, β are the usual spin functions referred to the quantization axis ζ . The e 's lie above the t 's of the same spin by the energy Δ , and $f_{i\downarrow}$ lies above $f_{i\uparrow}$ by the intra-atomic exchange energy J . By a straightforward application of first-order perturbation theory, one finds the perturbed one-electron states $\Psi_{i\uparrow}$ (corresponding, respectively, to $f_{i\uparrow}$), calculates the spin density in $\Psi_{i\uparrow}$ and adds up the contributions from the occupied orbitals. The result (valid only for $J/\Delta > 1$) may be summarized by the formula

$$\boldsymbol{\sigma}_1 = 2 \frac{(\lambda/\Delta)}{(J/\Delta)^2 - 1} \frac{5}{4\pi} u^2(r) \mathbf{g}(\hat{r}) \equiv c \times \frac{5u^2(r)}{4\pi} \mathbf{g}(\hat{r}). \quad (2)$$

The coefficient c is

$$(\lambda/\Delta) \{ [(J/\Delta) - 1]^{-1} - [(J/\Delta) + 1]^{-1} \};$$

the first term comes from the mixing of t_4 into e_4 functions, the second from mixing of e_4 into t_4 (there is no contribution from mixing t 's into t 's or e 's into e 's). $u(r)$ is the radial part of the $3d$ orbitals, with $\int_0^\infty r^2 u^2 dr = 1$. The function \mathbf{g} , which depends on the unperturbed spin direction ζ , is (for $\zeta = x, y, \text{ or } z$)

$$\begin{aligned} \mathbf{g} = & \hat{y}\rho_2 + \hat{z}\rho_3, & \zeta = x \\ = & -\hat{x}\rho_2 & -\hat{z}\rho_1, & \zeta = y \\ = & -\hat{x}\rho_3 + \hat{y}\rho_1 & , & \zeta = z \end{aligned} \quad (3)$$

where

$$\begin{aligned} \rho_1 &= (24)^{-1/2} [\sqrt{3}\theta(2\xi + \eta) + \epsilon(2\xi - \eta + 2\zeta)], \\ \rho_2 &= (12)^{-1/2} [\sqrt{3}\theta(\eta - \xi) + \epsilon(2\zeta - \xi - \eta)], \\ \rho_3 &= (8)^{-1/2} [-\sqrt{3}\theta\eta + \epsilon(\eta + 2\zeta)]. \end{aligned} \quad (4)$$

Here $\theta, \epsilon, \xi, \eta, \zeta$ are the d orbitals in Griffith's notation⁸ (p. 226) divided by r^2 , and referred to the primed axes of Fig. 1. For example, $\xi = \sqrt{3}y'z'/r^2$. The functions ρ_i can be seen to be linear combinations of the spherical harmonics Y_{4m} ,⁹ and so are highly aspherical. It should be noted that the charge density remains spherical in this order (since the spin quantum numbers of the

⁸ J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge University Press, New York, 1961), cf. pp. 226, 311, 425, 437.

⁹ The symmetry "reason" why these turn out to be Y_{4m} is that the spin-orbit operator transforms like the vector representation T_1 (or Γ_4 in Bethe's notation) under cubic spatial operations. Hence the first-order addition to the atomic wave function and therefore also $\boldsymbol{\sigma}_1(\mathbf{r})$ must transform like T_1 . But since we are considering only the configuration $(3d)^5$, $\boldsymbol{\sigma}_1(\mathbf{r})$ must be a linear combination of Y_{4m} with $l=0, 2$ or 4 , the only ones of which can transform like T_1 being the Y_{4m} .

first-order addition to the wave function differ from those of the unperturbed state).

For α -Fe₂O₃ in the high- T phase, the unperturbed and the Dzialoshinsky spin densities are

$$\boldsymbol{\sigma}_0 = \frac{5}{4\pi} \frac{u^2(r)}{2} \hat{y}, \quad \boldsymbol{\sigma}_D = \epsilon \frac{5}{4\pi} \frac{u^2(r)}{2} \hat{x}, \quad (5)$$

where³ $|\epsilon| \cong 1.0 \times 10^{-3}$. In the polarized neutron experiment,³ only the x component is seen, so that we need consider only σ_{1x} ; so we need g_x for $\zeta = y$ which is

$$g_x(\hat{r}) = -\rho_2 = (3\sqrt{2}/4r^4)(y^2 - 3x^2)y_z \propto \text{Im} Y_{43}(\theta, \phi), \quad (6)$$

where Y_{43} is the spherical harmonic referred to the xyz axes. We note here that

$$g_x(\mathcal{R}\hat{r}) = -g_x(\hat{r}), \quad (7)$$

since \mathcal{R} takes $x \rightarrow x$, $y \rightarrow -y$, $z \rightarrow z$, satisfying the condition (needed in order to correspond to experiment³) that $\sigma_{1x}(\mathbf{r})$ must not be invariant under \mathcal{R} . Also note that $g_x(\hat{r})$ is invariant under the threefold rotations about the c axis.

III. COMPARISON WITH EXPERIMENT

The magnetic structure factor M which enters into the neutron experiment³ is proportional to the Fourier transform of $\sum[\sigma_D^{(j)} + \sigma_{1x}^{(j)}]$ giving $M = M_D + M_1$ (\sum means to sum over the four cations j in a unit cell). $\sigma_D^{(j)}$ is the same for all sites, apart from translation. Noting that the nearest-neighbor sites with *antiparallel* $\boldsymbol{\sigma}_0$ are related (in their unperturbed state) by a twofold axis ($x \rightarrow x$, $y \rightarrow -y$, $z \rightarrow -z$), Eq. (6) shows that in our present crystal-field calculation σ_{1x} will be the *same* for these two sites (apart from translation). Also the two sites with parallel $\boldsymbol{\sigma}_0$ are connected by a center of inversion (remembering that spins are pseudovectors), showing again that σ_{1x} is the same for these two sites. Hence $M = F(\mathbf{K}) \int \exp(i\mathbf{K} \cdot \mathbf{r}) \times (\sigma_D + \sigma_{1x}) d\mathbf{r}$ where $F(\mathbf{K}) = \sum \exp(i\mathbf{K} \cdot \mathbf{R}_j)$, and σ_D , σ_{1x} are given by (5) and (2). \mathbf{K} is the neutron scattering vector. The fact that $\sigma_D^{(j)}$ and $\sigma_{1x}^{(j)}$ both simply translate from site to site, giving the common factor $F(\mathbf{K})$, shows that σ_D and σ_{1x} contribute to the same "ferromagnetic" Bragg peaks.

To compare orders of magnitude, we find with the help of (2), (5), and (6), that

$$M_1/M_D = (2c/\epsilon) [f_4(K)/f_0(K)] g_x(\hat{K}), \quad (8)$$

where $f_n(K) = \int_0^\infty u^2(r) j_n(Kr) r^2 dr$, and $j_n(x)$ is the spherical Bessel function. $g_x(\hat{K})$ can be computed from (6); for the (114) and (330) reflections $|g_x| = 0.34$ (g_x being of opposite sign for these two reflections¹⁰).

¹⁰ Unique identification of the (114) and (330) reflections can be made if we know the coordinate system. We have used the following for the rhombohedral base vectors (the primitive translations): $\mathbf{a}_1 = -(\sqrt{3}a/2)\hat{x} - (a/2)\hat{y} + (c/3)\hat{z}$, $\mathbf{a}_2 = (\sqrt{3}a/2)\hat{x} - (a/2)\hat{y} + (c/3)\hat{z}$, $\mathbf{a}_3 = a\hat{y} + (c/3)\hat{z}$ with a and c positive; the reciprocal vectors \mathbf{b}_i are defined by $\mathbf{a}_i \cdot \mathbf{b}_j = \delta_{ij}$ and the Bragg scattering vectors are $\mathbf{K}_{hkl} = 2\pi(h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3)$. Note that with this choice, the cation

To obtain a rough estimate of c we take advantage of the close similarity between the optical spectra of hydrated salts of transition metal cations and of Cr₂O₃, Fe₂O₃, and NiO, as pointed out by Morin.¹¹ Then it is reasonable to assume that the values⁸ $\Delta/J \cong 0.51$, $\lambda/J \cong 0.013$, appropriate to Fe³⁺·6H₂O, are sufficiently close to those for Fe₂O₃ for our rough purposes. This gives $c = 0.018$. A crude estimate of f_4/f_0 may be obtained by approximating $r^2 u^2(r)$ as a δ function at the maximum, $r_0 \approx 0.5 \text{ \AA}$, in the radial distribution for iron, giving $f_n(K) \sim j_n(Kr_0)$. For the (114) or (330) reflections, $K = 5.1 \text{ \AA}^{-1}$, so that¹² $(f_4/f_0)_{114} \sim 0.16$. So we finally obtain $|M_1/M_D| \sim 1.9$. The *only* significance of this particular number is that it indicates that M_1 and M_D are of the same order of magnitude. Thus we have our main point, namely the structure factor pertinent to the polarized neutron experiment is, in our first order calculation,

$$M(\mathbf{K}) = M_D(\mathbf{K}) + M_1(\mathbf{K}), \quad (9)$$

where the Dzialoshinsky part satisfies $M_D(\mathbf{K}_{330}) = M_D(\mathbf{K}_{114})$, the new part $M_1(\mathbf{K}_{330}) = -M_1(\mathbf{K}_{114})$, and $|M_1| \approx |M_D|$ for these reflections. Hence it is not surprising that the values of M at these two reflections differ appreciably.

Now let us compare (9) with experiment in somewhat more detail. It is found³ that $M(114) = 0.005 \pm 0.008$, $M(330) = 0.082 \pm 0.007$ (in units of 10^{-14} cm). Also, Pickart *et al.* give the calculated value $M_D^{(\text{calc})} = 0.076$ appropriate to these two reflections; this value is uncertain to within roughly a factor of 2, however.¹³ For (9) to give the observed values one needs $|M_1(114)| \approx |M_D(114)|$, which, as we have shown, is not unreasonable. Furthermore, (9) with (7) predicts that

$$M_D(114) = \frac{1}{2} [M(114) + M(330)]. \quad (10)$$

(This is more general than would be indicated by the explicit derivation given, as discussed below.) Using the observed values of M at these two reflections then gives $M_D(114) \approx 0.044 \pm 0.008$ which is within the uncertainty in $M_D^{(\text{calc})}$, although only barely. Another reflection observed³ is the (222), for which $M(222) = 0.213 \pm 0.002$ and $M_D^{(\text{calc})}(222) = 0.210$. We have $M_1(222) = 0$, as follows from (7); hence, Eq. (9) agrees with this data. The other one of the four reflections observed is the (002), for which $M(002) = -0.011 \pm 0.004$, $M_D^{(\text{calc})}(002) = -0.064$ [the minus sign comes from $F(K)$]. If (9) is to agree with this, we would need

site of Fig. 1 is forced to be either type 1 or type 4 in Dzialoshinsky's notation (each of which sees identical octahedral fields).

¹¹ F. J. Morin, Bell System Tech. J. **37**, 1047 (1958).
¹² A rough check on this estimate was made by considering $u^2(r) \propto r^n e^{-\alpha r}$, choosing n and α to approximately fit the observed form factor $f_0(K)$, and then calculating $f_4(K)$. This gave somewhat larger values of $(f_4/f_0)_{114}$, but still of the same order of magnitude.

¹³ R. Nathans and S. J. Pickart (private communication). The uncertainty in $M_D^{(\text{calc})}(411)$ is due to the experimental uncertainty in the form factor f_0 (as measured on the large antiferromagnetic component) at this large scattering angle.

$M_1(002) \approx -M_D(002)$. However, we find $|M_1(002)| \approx (0.07)|M_D(002)|$. The large decrease in $|M_1(\mathbf{K})/M_D(\mathbf{K})|$ for \mathbf{K} changing from (114) to (002) (K changes from ≈ 5 to $\approx 3 \text{ \AA}^{-1}$) is due principally to the factor f_4/f_0 in (8). Thus our first-order calculation disagrees seriously with the results on this reflection.

IV. SUMMARY AND DISCUSSION

By investigating the first-order effect of spin-orbit coupling on a $(3d)^5$, unperturbed S -state ion in a cubic crystal field, we have found a new contribution $\sigma_1(\mathbf{r})$ to the ionic spin density. The integral of $\sigma_1(\mathbf{r})$ over space is zero and $\sigma_1(\mathbf{r})$ is perpendicular to the unperturbed spin density $\sigma_0(\mathbf{r})$. Whereas σ_0 is "spherically symmetric," depending only on the magnitude of \mathbf{r} measured from the nucleus, $\sigma_1(\mathbf{r})$ is highly aspherical, being a linear combination of Y_{4m} and hence depending sensitively on the direction of \mathbf{r} . We note that the charge density remains spherical to this order.

In $\alpha\text{-Fe}_2\text{O}_3$ at room temperature the total spin density consists of the large "antiferromagnetic" component σ_0 , the new term σ_1 , plus the Dzialoshinsky term σ_D , which is spherical about a cation nucleus for \mathbf{r} near that nucleus. Whereas σ_0 changes in translating from one cation to another within a unit cell, in accordance with the well-known antiferromagnetic ordering,¹⁴ σ_D does not change under such translations; we have found that the component of σ_1 parallel to σ_D also does not change under these translations, and therefore σ_1 and σ_D contribute to the same ferromagnetic peaks. In particular, the two contribute in the same order of magnitude to the (330) and (114) peaks, the contribution of σ_1 to (330) being minus that to (114) while σ_D contributes identically to these two peaks. Hence the magnetic scattering is expected to be different for these peaks (very much different if $|M_1| \gtrsim |M_0|$ at this scattering angle), so that the large difference observed³ for these peaks is no longer surprising.

To discuss the quantitative discrepancies let us first focus on the two outer reflections (330), (114). Because of the antisymmetry of M_1 under \mathcal{R} , reflection in the x - z plane, we obtained Eq. (10), with which the observations are considerably at variance, although not outside a large experimental uncertainty in the spherical form factor $f_0(k)$. Now it is easy to show that in general one must obtain this antisymmetry of M_1 as long as one considers interactions which are invariant under \mathcal{R} ; also in this case M_D must vanish.¹⁵ Although the crystal is *not* invariant under \mathcal{R} , the lack of invariance is usually thought to have only small effects. The non-invariance obviously affects M_D in an important way; to estimate its effect on M_1 we considered the term in

¹⁴ C. G. Shull, W. A. Strauser, and E. O. Wollan, Phys. Rev. **83**, 333 (1951).

¹⁵ The vanishing of M_D if \mathcal{R} is conserved is a special case of the symmetry conditions given in Ref. 2. The possibility that D can vanish because of symmetry properties of a pair of atoms shows that Moriya's formula $D/2J \sim \Delta g/g$ is incomplete (since Δg need not vanish when $D=0$).

second-order perturbation theory which is first order in spin-orbit times first order in the low-symmetry crystal-field W . On a point-charge model we found only a small change δM_1 in M_1 ($\approx 10\%$),¹⁶ δM_1 being invariant under \mathcal{R} . This would predict that Eq. (10) should be closely satisfied. It would be interesting to see if a more accurate measurement of f_0 at these reflections would indicate a value considerably smaller ($\sim \frac{1}{2}$) than the one used³ to obtain M_D (ca1e). This would be interesting since any violation of (10) must be traced directly to the nonconservation of \mathcal{R} , being independent of the detailed approximations that we have made within the single-cation model used.

Concerning the disagreement at the (002) peak, we frankly have no good idea about it. The agreement at the (222) peak (nearby in scattering angle) suggests that the trouble here does not lie with M_D (ca1e). Our estimate of $M_1(002)$, or more pertinently $M_1(002)/M_1(114)$, does depend on our approximation to the integrals over the radial function. In this connection, a more accurate measurement of f_0 at the outer reflections should permit a meaningful inversion of $f_0(k)$ to obtain the radial function and hence a better calculation of $f_4(k)$.

With a view towards testing further the presence of the effect calculated here, we note that the result requires the following predictions.

(a) Since the M_1 calculated here is essentially a single-ion effect, it should exist even in cases of high symmetry where the Dzialoshinsky moment is zero (like MnO, say). For example, in $\alpha\text{-Fe}_2\text{O}_3$ at low temperatures $\sigma_D=0$, σ_0 is parallel to the trigonal axis, and σ_1 contributes to the ferromagnetic Bragg peaks (as well as the antiferromagnetic peaks). For the x component we find from (3) and (4) that M_1 is as before, but now with¹⁷

$$g_x(\hat{r}) = (\sqrt{2}/4r^4)[3z^2(z^2-1) + x^2(3z^2+3-4x^2)].$$

For the experimental geometry with polarization and magnetic field along x , and \mathbf{K} in the y - z plane, this gives $g_x(\hat{K}) = -0.22$ for (114) or (330). That is, $|M_1|$ at low temperatures is only reduced by about $\frac{2}{3}$ from its value at room temperature (assuming saturation at the latter).

(b) Since $M_1 \propto f_4(k)$, $|M_1|$ initially increases¹⁸ with

¹⁶ A comparatively large contribution to this result enters as the spherical harmonic Y_{20} . To obtain it, it was necessary to consider correlation effects, since this contribution vanishes in the Hartree-Fock approximation.

¹⁷ We have omitted a term $(1/4r^4)xz(3r^2-7z^2)$ which is present in g_x , since this contributes only to the "antiferromagnetic" reflections.

¹⁸ This is reminiscent of the behavior found in Ti_2O_3 by S. C. Abrahams, Phys. Rev. **130**, 2230 (1963), and calculated by M. Blume (to be published) for configuration $(3d)^1$. In that case, it is apparently the orbital contribution to the magnetic moment density (the component parallel to the atomic moment) that gives rise to an effective form factor that initially increases with k , whereas in our calculation f_4 enters directly into the spin density. (To first order, there is no contribution either to the net orbital magnetic moment or to orbital scattering; this is because the atomic wave function to first order is $\psi = {}^6S + \lambda\phi$ where ϕ is a quartet state.)

k . Our crude approximation to $f_4(k)$ indicates that $f_4(k)$ is still rising at the (330) reflection, going through a broad maximum at $k \equiv 4\pi \sin\theta/\lambda$ between 10 and 14 \AA^{-1} . Furthermore the value of $f_4(k)$ at its maximum is much larger (by a factor of about 6) than at the (330) ($k \approx 5$).

(c) It should be possible in principle to experimentally check the sign of Eq. (6). The reason for this is as follows. The \mathbf{D}_{ij} in the Dzialoshinsky-Moriya theory are unique properties of a given structure, being independent of the "spins" \mathbf{T}_i as is evident from Moriya's expression² for the \mathbf{D}_{ij} . It follows from the energy expression $\sum \mathbf{D}_{ij} \cdot \mathbf{T}_i \times \mathbf{T}_j$ plus exchange that for a given antiferromagnetic arrangement with $\mathbf{D}_{ij} = 0$, say $\mathbf{T}_1^{(0)} = T\hat{y}$, $\mathbf{T}_2^{(0)} = -T\hat{y}$, the introduction of $\mathbf{D}_{ij} = D_{ij} \hat{z}$ will cause a *unique* canting $\delta\mathbf{T}_1 = \delta\mathbf{T}_2 = \epsilon\hat{x}$. That is, for given T there will be only one value ϵ , $-\epsilon$ being of higher energy. A degenerate state would be the *completely* spin-reversed state $T \rightarrow -T$ and $\epsilon \rightarrow -\epsilon$. The application of a magnetic field along $+x$ would clearly force a sign on ϵ and therefore a sign on T . In other words, the theory^{1,2} implies that the application of a *magnetic* field must influence the *antiferromagnetic* domain distribution. (Thermodynamic equilibrium is assumed, of course.) Such an effect was indeed observed.³ Hence, in principle, in the presence of a magnetic field, there is only one possible spin direction at any particular site. Now it appears to us that it should be possible to determine these directions from the polarized neutron experiments since one needs only the *relation* between the magnetic structure factor for the (222) (assumed to be due only to the Dzialoshinsky moment) and that for, say, the antiferromagnetic (210) peak.

For the reciprocal vectors defined in footnote 10, \mathbf{K}_{114} has positive y and z components so that $g_x(\mathbf{K}_{114}) > 0$. Let us suppose that the magnetic field points along the positive x axis; then $\epsilon < 0$ because the free-electron g factor is negative (this is not important here, but it is stated correctly to try to minimize confusion). If $\sigma_{0y} > 0$, as taken in (5), i.e., the antiferromagnetic spin components at either type 1 or type 4 sites point along the positive y axis as defined by Fig. 1 and footnote 10, then Eq. (9) with (8) and $(f_4/f_0)_{114} > 0$ would predict that $|M(114)| < |M(330)|$; if it turned out that $\sigma_{0y} < 0$, the inequality would be reversed. Although, as we have said, it should be possible to determine experimentally the sign of σ_{0y} , such a determination unfortunately will not be a convincing test of the mechanism discussed in this paper until one understands the mechanism for the difference between R_{210} and $R_{2\bar{1}0}$ in the notation of Pickart *et al.*³

It is perhaps worth pointing out that if one could be convinced that the main contribution to various neutron peaks were of the form (9) with M_1 coming from (2), the measurement of M_1 at these peaks would provide a quantitative check on the radial function determined in the usual way. [The latter, determined by inverting $f_0(k)$, will determine $f_4(k)$.]

It should also be noted that the effect calculated here should occur in ions other than those with unperturbed configuration $3d^5$. Although we have not tried to estimate it, we can see for example that for $3d^3$ (e.g., Cr^{3+}), the Hartree-Fock approximation (which would have to be justified again) would lead to Eq. (2) but with $c = -(\lambda/\Delta)[(J/\Delta)+1]^{-1}$, and the restriction $J/\Delta > 1$ removed. Estimating J as the energy for the ${}^4A_2 \rightarrow {}^2E$ transition, and using the numbers in Griffith⁸ pertinent to Cr^{3+} with octahedral H_2O coordination,¹¹ we find that c is reduced from its value calculated for Fe^{3+} by only about a factor of 2, suggesting that the effect might be observable in Cr_2O_3 for example.

We conclude with a qualitative remark about the *free* ion. As seen from Eq. (2), our new spin density σ_1 vanishes for a free ion ($\Delta=0$). Is it possible in the case of a free paramagnetic ion, in, say, an infinitesimal magnetic field which fixes the net moment in the z direction, to have a spin density $\sigma(\mathbf{r})$ which is not everywhere parallel to z ? If it were not possible, we would expect that symmetry considerations would tell us. We consider only the case where all the degeneracy in the ground state is due to the orientation of the magnetic moment; then the field removes the remaining degeneracy and so the physics must be invariant under the symmetry group of the Hamiltonian. This group G consists at least of C_z , the rotations about z ; I , the inversion through the origin; and Q , a 180° rotation about an axis in the x - y plane multiplied by time inversion. Let $\sigma_1(\mathbf{r})$ be the part of σ which is perpendicular to z . Application of I and C_z shows that $\sigma_1(x, y, -z) = -\sigma_1(x, y, z)$; subsequent application of Q shows that in cylindrical coordinates, $\sigma_1(xy, z)$ must have only a radial component. The latter of course must be cylindrically symmetric. Also $\sigma_z(x, y, -z) = \sigma_z(x, y, z)$ and σ_z must have cylindrical symmetry. $\sigma(\mathbf{r})$ having these properties satisfies all the requirements of G , and since there are no other pertinent operations as far as we can see, we conclude that $\sigma_1(r)$ need not be zero. Following these symmetry arguments slightly further shows easily that a free ion contribution to σ_1 could contribute only to the "antiferromagnetic" peaks in the neutron experiment.

Note added in proof. Our crude "delta-function" estimate of $(f_4/f_0)_{114} \sim 0.16$ for Fe^{3+} is probably very close to that obtainable from the Hartree-Fock atomic radial function of Watson and Freeman [Acta. Cryst. **14**, 27 (1961)], since their results give the values 0.18 and 0.12 for Fe^{2+} and Fe^{4+} , respectively. I thank M. Blume for pointing this out to me.

ACKNOWLEDGMENTS

I am indebted to R. Nathans, S. Pickart, and H. Alperin for communicating their experimental results to me and for providing the impetus behind the present work. I thank K. Dwight, N. Menyuk, and J. Dimmock for valuable discussions.