

# Orbital Contribution to the Magnetic Form Factor of $\text{Ni}^{++}$

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The effect of a residual orbital moment on the magnetic form factor of  $\text{Ni}^{++}$  is calculated. It is shown that the ordinary form factor is replaced by a tensor, and formulas are given for the slow-neutron magnetic-scattering cross sections of paramagnetic, ferromagnetic, and antiferromagnetic  $\text{Ni}^{++}$ . It is found that the unquenched orbital moment causes a 4% expansion of the form factor relative to the "spin-only" case, and that the anisotropic scattering is reduced by about ten percent.

## 1. INTRODUCTION

IN the theory of the magnetic scattering of neutrons by transition metal ions, as developed by Halpern and Johnson,<sup>1</sup> it is assumed that the orbital angular momentum is completely quenched by the crystalline field, and that its associated magnetic moment does not contribute to the scattering. An examination of the  $g$  factors for these ions shows, however, that there may be sizeable residual orbital moments present. For a substance with a completely quenched orbital moment we should expect a  $g$  factor of 2.00, and the deviation of the  $g$  factor from this value gives a measure of the orbital contribution to the total magnetic moment of the ion. Specifically,  $(1/g)(g-2)$  is the fraction of the total magnetic moment which is due to orbital motion. For the  $\text{Ni}^{++}$  ion, with a  $(3d)^8$  configuration, a number of measurements<sup>2,3</sup> of the  $g$  factor in different salts gives  $g \approx 2.2$ , so that about 10% of the  $\text{Ni}^{++}$  magnetic moment is due to orbital motion.

Recently Alperin<sup>4</sup> has measured the magnetic form factor for  $\text{Ni}^{++}$  in antiferromagnetic  $\text{NiO}$ . He found that the form factor was considerably expanded compared to that calculated for the free ion. In the interpretation of this experiment the contribution of the orbital moment was neglected. The present calculation was undertaken, apart from its general interest, to see to what extent this form factor expansion can be understood as due to the orbital contribution. We have found, in fact, that about 4% of the 17% expansion can be accounted for in this way.

Scattering by orbital moments has been considered previously by Trammell,<sup>5</sup> and in an elaboration of his work, by Odier and Saint-James.<sup>6</sup> They were concerned with rare-earth ions, in which the orbital moments are completely unquenched, and the effects of the crystalline field are secondary. In the case of transition metal ions, such as  $\text{Ni}^{++}$ , where the crystalline field nearly quenches the orbital angular momentum, the situation is reversed. In the following section the theory is de-

veloped for the  $\text{Ni}^{++}$  ion. This case is simple, because in  $\text{Ni}^{++}$  the orbital degeneracy is completely lifted by the cubic crystalline field (whereas in the  $\text{Fe}^{++}$  and  $\text{Co}^{++}$  ions the orbital degeneracy is not completely lifted,<sup>7</sup> and the discussion of the neutron scattering is more complicated). In  $\text{Ni}^{++}$  the crystalline field quenching is partially lifted by the spin-orbit coupling, which causes the admixture of a higher state into the ground state, giving rise to an orbital moment which influences the form factor in a way we wish to discuss.

## 2. THEORY

The differential cross section for the elastic magnetic scattering of unpolarized neutrons into solid angle  $d\Omega'$  is<sup>1</sup>

$$\frac{d\sigma}{d\Omega'} = (\gamma e^2/mc^2)^2 \sum_{q,q'} p_q \left| \sum_n \exp(i\mathbf{K} \cdot \mathbf{n}) \langle q' | \mathbf{T}_n | q \rangle \right|^2, \quad (1)$$

where  $|q\rangle$  and  $|q'\rangle$  are the initial and final states of the crystal (assumed to have the same energy),  $\mathbf{K} = \mathbf{k} - \mathbf{k}'$  is the difference between the initial and final wave vectors,  $\mathbf{k}$  and  $\mathbf{k}'$ , respectively, of the neutron ( $|\mathbf{k}| = |\mathbf{k}'|$ ),  $\mathbf{n}$  is a lattice vector,  $\gamma = -1.91$  is the gyromagnetic ratio of the neutron, and  $p_q$  is the probability that the state  $|q\rangle$  is occupied, usually given by the Boltzmann factor  $e^{-E_q/kT} (\sum_{q'} e^{-E_{q'}/kT})^{-1}$ . The operator  $\mathbf{T}_n$  represents the interaction of the neutron with the electrons of the ion at site  $\mathbf{n}$ , and is given by<sup>1</sup>

$$\mathbf{T}_n = \sum_j e^{i\mathbf{K} \cdot \mathbf{r}_j} \hat{\mathbf{K}} \times (\mathbf{s}_j \times \hat{\mathbf{K}}) - \frac{i}{\hbar K} \sum_j e^{i\mathbf{K} \cdot \mathbf{r}_j} (\hat{\mathbf{K}} \times \mathbf{p}_j), \quad (2)$$

where  $\mathbf{s}_j$  and  $\mathbf{p}_j$  are the spin and momentum of the  $j$ th electron,  $\mathbf{r}_j$  is the position of the electron relative to the lattice point  $\mathbf{n}$ ,  $\hat{\mathbf{K}}$  is a unit vector in the direction of  $\mathbf{K}$ , and the summation is over all electrons of the ion at lattice site  $\mathbf{n}$ . The angular momentum operators will be taken to be in units of  $\hbar$  throughout the paper.

The second term in Eq. (2), which represents the orbital contribution to the interaction, can be put in a simpler form, first derived by Trammell.<sup>5</sup> He showed that by expanding  $e^{i\mathbf{K} \cdot \mathbf{r}_j}$  in a power series and using the relation  $\mathbf{p}_j = (im/\hbar)[\mathcal{H}, \mathbf{r}_j]$ ,  $\mathcal{H}$  being the Hamiltonian

<sup>7</sup> J. Kanamori, *Progr. Theoret. Phys. (Kyoto)* **17**, 177 (1957).

<sup>1</sup> O. Halpern and M. H. Johnson, *Phys. Rev.* **55**, 898 (1939).

<sup>2</sup> J. Owen, *Proc. Roy. Soc. (London)* **A237**, 183 (1955).

<sup>3</sup> W. Low, *Phys. Rev.* **109**, 247 (1958).

<sup>4</sup> H. Alperin, *Phys. Rev. Letters* **6**, 55 (1961).

<sup>5</sup> G. T. Trammell, *Phys. Rev.* **92**, 1387 (1953).

<sup>6</sup> S. Odier and D. Saint-James, *J. Phys. Chem. Solids* **17**, 117 (1960).

without spin-orbit coupling for the scattering system, this term could be written as

$$-(i/\hbar K) \sum_j e^{i\mathbf{K}\cdot\mathbf{r}_j} \mathbf{p}_j \\ = (m/\hbar^2 K) \sum_j [\mathcal{J}\mathcal{C}, \mathbf{r}_j(i\mathbf{K}\cdot\mathbf{r}_j)^{-1}(e^{i\mathbf{K}\cdot\mathbf{r}_j}-1)] \\ + \frac{1}{4} \sum_j [f(\mathbf{K}\cdot\mathbf{r}_j)\mathbf{l}_j + \mathbf{l}_j f(\mathbf{K}\cdot\mathbf{r}_j)] \times \hat{\mathbf{K}}, \quad (3)$$

where the function  $f(\mathbf{K}\cdot\mathbf{r}_j) = f_j$  is given by

$$f_j = 2 \sum_n \frac{(i\mathbf{K}\cdot\mathbf{r}_j)^n}{n!(n+2)} = 2 \left[ \frac{d}{dx} \left( \frac{e^x - 1}{x} \right) \right]_{x=i\mathbf{K}\cdot\mathbf{r}_j}. \quad (4)$$

Some of the properties of this function will be discussed later.

If we neglect a small term arising from spin-orbit coupling (which is of the order of the ratio of spin-orbit coupling energy to electronic kinetic energy) the matrix elements of the first term in (3) between states of equal energy vanish, for

$$\langle q' | \sum_j [\mathcal{J}\mathcal{C}, \mathbf{r}_j(i\mathbf{K}\cdot\mathbf{r}_j)^{-1}(e^{i\mathbf{K}\cdot\mathbf{r}_j}-1)] | q \rangle \\ \approx (E_{q'} - E_q) \langle q' | \sum_j \mathbf{r}_j(i\mathbf{K}\cdot\mathbf{r}_j)^{-1}(e^{i\mathbf{K}\cdot\mathbf{r}_j}-1) | q \rangle = 0. \quad (5)$$

Trammell also gives an argument indicating that this term can be neglected for inelastic scattering. Using (3), the cross section becomes

$$\frac{d\sigma}{d\Omega'} = \left( \frac{\gamma e^2}{mc^2} \right)^2 \sum_{q,q'} p_q \left| \sum_n e^{i\mathbf{K}\cdot\mathbf{n}} \langle q' | \hat{\mathbf{K}} \times \sum_j \{ e^{i\mathbf{K}\cdot\mathbf{r}_j} \mathbf{s}_j \times \hat{\mathbf{K}} \right. \\ \left. + \frac{1}{4} [(\mathbf{l}_j \times \hat{\mathbf{K}}) f_j + f_j (\mathbf{l}_j \times \hat{\mathbf{K}})] \} | q \rangle \right|^2 \\ = \left( \frac{\gamma e^2}{mc^2} \right)^2 \sum_{q,q'} p_q \sum_{\mathbf{m},\mathbf{n}} e^{i\mathbf{K}\cdot(\mathbf{m}-\mathbf{n})} (\delta^{\alpha\beta} - \hat{\mathbf{K}}^\alpha \hat{\mathbf{K}}^\beta) \\ \times \langle q | Q_n^{\alpha\dagger} | q' \rangle \langle q' | Q_m^\beta | q \rangle, \quad (6)$$

where  $Q_n = \sum_j [e^{i\mathbf{K}\cdot\mathbf{r}_j} \mathbf{s}_j + \frac{1}{4} (\mathbf{l}_j f_j + f_j \mathbf{l}_j)]$ ,  $Q_n^\alpha$  and  $\hat{\mathbf{K}}^\alpha$  are the  $\alpha$  components of the vectors  $Q_n$  and  $\hat{\mathbf{K}}$ , and the summation convention has been employed for Greek letter indices.

### 3. DERIVATION OF THE FORM FACTOR

Figure 1 shows the spectrum of  $\text{Ni}^{++} (3d)^8$  in a cubic field, neglecting spin-orbit coupling. This spectrum has been determined by optical absorption experiments for Ni in MgO by Low<sup>8</sup> and for NiO by Newman and Chrenko.<sup>8</sup> A complete theoretical calculation (including spin-orbit coupling) has also been done for this configuration by Liehr and Ballhausen.<sup>9</sup> All of the information about the wave functions which we need, however, can be obtained by simple symmetry arguments.

The ground state neglecting spin-orbit coupling  ${}^3T_2$  is an orbital singlet with  $S=1$  and therefore has no orbital moment. The spin-orbit coupling will, however, mix into this  ${}^3T_2$  state small amounts of higher states and the cross terms of the admixture will give nonzero matrix elements of orbital angular momentum. The calculation

<sup>8</sup> R. Newman and R. M. Chrenko, Phys. Rev. **114**, 1507 (1959).

<sup>9</sup> A. D. Liehr and C. J. Ballhausen, Ann. Phys. **6**, 134 (1959).

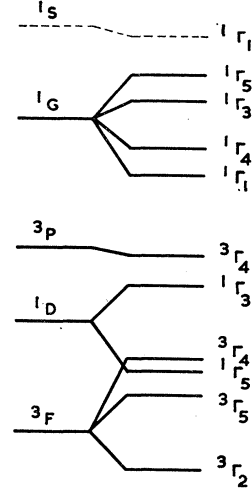


FIG. 1. Energy levels of  $\text{Ni}^{++}$  in a cubic field. Bethe's notation for the representations of the cubic group is used.

of this admixture is simplified in the case of  $\text{Ni}^{++}$  by a fortunate set of circumstances.

If we restrict ourselves to the configuration  $(3d)^8$ , there is no state other than the ground state which has the symmetry  ${}^3T_2$ . This means that the cubic field cannot cause any mixing into this state of spectroscopic states with different  $L$  or  $S$ , and it remains pure  ${}^3F$ :

$$|{}^3T_2\rangle = (1/\sqrt{2}) (|{}^3F M_L=2\rangle - |{}^3F M_L=-2\rangle), \quad (7)$$

where  $|{}^3F M_L=2\rangle$ , etc., are the wave functions of the  ${}^3F$  state. The same argument holds for the first-excited state  ${}^3T_5$  which also arises purely from the  ${}^3F$  state. This is mixed with the  ${}^3T_2$  ground state by spin-orbit coupling. Hence the calculations will all be done within the  ${}^3F$  manifold of state vectors. In these circumstances the spin-orbit coupling, which in general must be written  $\sum_i \zeta_i \mathbf{l}_i \cdot \mathbf{s}_i$ , can be expressed as  $\lambda \mathbf{L} \cdot \mathbf{S}$ , and the ground-state wave function (including spin-orbit coupling) can be written as

$$\left( 1 - \frac{\lambda}{\Delta} \mathbf{L} \cdot \mathbf{S} \right) |{}^3T_2 M_S\rangle \\ = \left( 1 - \frac{\lambda}{\Delta} \mathbf{L} \cdot \mathbf{S} \right) \frac{1}{\sqrt{2}} (|{}^3F M_L=2\rangle - |{}^3F M_L=-2\rangle) \\ + O(\lambda^2/\Delta^2). \quad (8)$$

Here  $\Delta$  is the energy of the  ${}^3T_5$  state relative to that of  ${}^3T_2$ . Spin-orbit coupling can also cause an admixture of the  ${}^1T_5(1D)$  states, but this cannot contribute to the orbital scattering and it makes only a small anisotropic contribution to the spin scattering, so we neglect it in the following discussion.

To evaluate the matrix elements in Eq. (6), we now assume that the state vectors  $|q\rangle$  can be written as a product of state vectors referring to the individual ions (Heitler-London model). Using the ground-state func-

tion (8) for  $\text{Ni}^{++}$  we must calculate

$$\langle {}^3\Gamma_2 M_S | (1 - (\lambda/\Delta) \mathbf{L}_n \cdot \mathbf{S}_n) \times Q_n^\alpha (1 - (\lambda/\Delta) \mathbf{L}_n \cdot \mathbf{S}_n) | {}^3\Gamma_2 M_S' \rangle. \quad (9)$$

In the absence of spin-orbit coupling (where the orbital moment is quenched) these matrix elements can be split into two parts, one referring to the space coordinates and the other to the spin coordinates, the spatial part being the magnetic form factor. We will now show that such a separation can still be accomplished, but the form factor now becomes a tensor. Writing  $Q_n^\alpha$  in full in (9), this becomes

$$\begin{aligned} & \langle {}^3\Gamma_2 M_S | \sum_j e^{i\mathbf{K} \cdot \mathbf{r}_{jS}^\alpha} | {}^3\Gamma_2 M_S' \rangle \\ & - (\lambda/\Delta) \langle {}^3\Gamma_2 M_S | L_n^\beta S_n^\beta \sum_j e^{i\mathbf{K} \cdot \mathbf{r}_{jS}^\alpha} \\ & + \sum_j e^{i\mathbf{K} \cdot \mathbf{r}_{jS}^\alpha} L_n^\beta S_n^\beta | {}^3\Gamma_2 M_S' \rangle \\ & - (\lambda/\Delta) \langle {}^3\Gamma_2 M_S | L_n^\beta S_n^{\beta \frac{1}{4}} \sum_j (l_j^\alpha f_j + f_j l_j^\alpha) \\ & + \frac{1}{4} \sum_j (l_j^\alpha f_j + f_j l_j^\alpha) L_n^\beta S_n^\beta | {}^3\Gamma_2 M_S' \rangle + O(\lambda^2/\Delta^2). \end{aligned} \quad (10)$$

The term  $\langle {}^3\Gamma_2 M_S | \frac{1}{4} \sum_j (l_j^\alpha f_j + f_j l_j^\alpha) | {}^3\Gamma_2 M_S' \rangle$  vanishes because the orbital moment is quenched in the unperturbed state  $| {}^3\Gamma_2 M_S \rangle$ . The first term in (10), which is the only one occurring in the absence of spin-orbit coupling, is equal to

$$\sum_j \langle \Gamma_2 | e^{i\mathbf{K} \cdot \mathbf{r}_j} | \Gamma_2 \rangle \langle SM_S | s_j^\alpha | SM_S' \rangle. \quad (11)$$

Using the algebra of vector coupling,<sup>10</sup> the spin matrix element can be written as

$$\langle SM_S | s_j^\alpha | SM_S' \rangle = \langle SM_S | \mathbf{s}_j \cdot \mathbf{S}_n / S(S+1) | SM_S \rangle \times \langle SM_S | S_n^\alpha | SM_S' \rangle, \quad (12)$$

where  $\mathbf{S}_n$  is the total spin of the ion at lattice site  $\mathbf{n}$ . Equation (11) then becomes

$$\begin{aligned} & \sum_j \langle \Gamma_2 | e^{i\mathbf{K} \cdot \mathbf{r}_j} | \Gamma_2 \rangle \langle SM_S | \mathbf{s}_j \cdot \mathbf{S}_n / S(S+1) | SM_S \rangle \\ & \times \langle SM_S | S_n^\alpha | SM_S' \rangle = f(\mathbf{K}) \langle SM_S | S_n^\alpha | SM_S' \rangle, \end{aligned} \quad (13)$$

where  $f(\mathbf{K})$  is the usual form factor obtained in the absence of the orbital moment.<sup>1</sup> For electrons with paired spins,  $\mathbf{s}_j \cdot \mathbf{S}_n$  will have opposite signs, and the contribution of these electrons will cancel, provided they have the same orbital wave function (this amounts to neglecting spin polarization effects). For the two unpaired electrons in  $\text{Ni}^{++}$ ,

$$\langle SM_S | \mathbf{s}_j \cdot \mathbf{S}_n / S(S+1) | SM_S \rangle = \frac{1}{2}, \quad (14)$$

and  $f(\mathbf{K})$  becomes

$$\begin{aligned} f(\mathbf{K}) &= \frac{1}{2} \langle \Gamma_2 | e^{i\mathbf{K} \cdot \mathbf{r}_1} + e^{i\mathbf{K} \cdot \mathbf{r}_2} | \Gamma_2 \rangle \\ &= \langle \Gamma_2 | e^{i\mathbf{K} \cdot \mathbf{r}_1} | \Gamma_2 \rangle, \end{aligned} \quad (15)$$

where  $\mathbf{r}_1$  and  $\mathbf{r}_2$  are the coordinates of the unpaired electrons.

Let us now consider the second term in (10). Separating the spin and orbital terms this is

rating the spin and orbital terms this is

$$\begin{aligned} & - (\lambda/\Delta) \sum_j \{ \langle \Gamma_2 | L_n^\beta e^{i\mathbf{K} \cdot \mathbf{r}_j} | \Gamma_2 \rangle \langle SM_S | S_n^\beta s_j^\alpha | SM_S' \rangle \\ & + \langle \Gamma_2 | e^{i\mathbf{K} \cdot \mathbf{r}_j} L_n^\beta | \Gamma_2 \rangle \langle SM_S | s_j^\alpha S_n^\beta | SM_S' \rangle \}. \end{aligned} \quad (16)$$

But

$$\begin{aligned} \langle \Gamma_2 | L_n^\beta e^{i\mathbf{K} \cdot \mathbf{r}_j} | \Gamma_2 \rangle &= \langle \Gamma_2 | (L_n^\beta e^{i\mathbf{K} \cdot \mathbf{r}_j})^\dagger | \Gamma_2 \rangle^* \\ &= \langle \Gamma_2 | e^{-i\mathbf{K} \cdot \mathbf{r}_j} L_n^\beta | \Gamma_2 \rangle^* = - \langle \Gamma_2 | e^{i\mathbf{K} \cdot \mathbf{r}_j} L_n^\beta | \Gamma_2 \rangle, \end{aligned}$$

since  $L_n^{\beta*} = -L_n^\beta$ , and  $|\Gamma_2\rangle$ , being nondegenerate, can be chosen to be real. Equation (16) then becomes

$$\begin{aligned} & - (\lambda/\Delta) \sum_j \langle \Gamma_2 | e^{i\mathbf{K} \cdot \mathbf{r}_j} L_n^\beta | \Gamma_2 \rangle \\ & \times \langle SM_S | s_j^\alpha S_n^\beta - S_n^\beta s_j^\alpha | SM_S' \rangle. \end{aligned} \quad (17)$$

In the commutator on the right we follow the procedure used in deriving (15) and replace  $s_j^\alpha$  by  $\frac{1}{2} S_n^\alpha$ , obtaining

$$\begin{aligned} & - (\lambda/\Delta) \langle \Gamma_2 | e^{i\mathbf{K} \cdot \mathbf{r}_1} L_n^\beta | \Gamma_2 \rangle \langle SM_S | [S_n^\alpha, S_n^\beta] | SM_S' \rangle \\ & = - (\lambda/\Delta) \langle \Gamma_2 | e^{i\mathbf{K} \cdot \mathbf{r}_1} L_n^\beta | \Gamma_2 \rangle \langle SM_S | i\epsilon^{\alpha\beta\gamma} S_n^\gamma | SM_S' \rangle \\ & = \varphi_S^{\alpha\gamma} \langle SM_S | S_n^\gamma | SM_S' \rangle, \end{aligned} \quad (18)$$

where

$$\varphi_S^{\alpha\gamma} = - (\lambda/\Delta) i\epsilon^{\alpha\beta\gamma} \langle \Gamma_2 | e^{i\mathbf{K} \cdot \mathbf{r}_1} L_n^\beta | \Gamma_2 \rangle, \quad (19)$$

and  $\epsilon^{\alpha\beta\gamma}$  is the unit antisymmetric tensor of third rank.

The orbital term in (10) can be transformed similarly, and we find

$$\begin{aligned} & - (\lambda/\Delta) \langle {}^3\Gamma_2 M_S | L_n^\beta S_n^{\beta \frac{1}{4}} \sum_j (l_j^\alpha f_j + f_j l_j^\alpha) \\ & + \frac{1}{4} \sum_j (l_j^\alpha f_j + f_j l_j^\alpha) L_n^\beta S_n^\beta | {}^3\Gamma_2 M_S' \rangle \\ & = \varphi_o^{\alpha\beta} \langle SM_S | S_n^\beta | SM_S' \rangle, \end{aligned} \quad (20)$$

where

$$\varphi_o^{\alpha\beta} = - (\lambda/\Delta) \langle \Gamma_2 | \frac{1}{2} \sum_j (l_j^\alpha f_j + f_j l_j^\alpha) L_n^\beta | \Gamma_2 \rangle. \quad (21)$$

Using the results of (15), (19), and (21), the matrix element (10) becomes

$$\begin{aligned} & \langle {}^3\Gamma_2 M_S | (1 - (\lambda/\Delta) \mathbf{L}_n \cdot \mathbf{S}_n) Q_n^\alpha (1 - (\lambda/\Delta) \mathbf{L}_n \cdot \mathbf{S}_n) | {}^3\Gamma_2 M_S' \rangle \\ & = F^{\alpha\gamma} \langle SM_S | S_n^\gamma | SM_S' \rangle, \end{aligned} \quad (22)$$

where

$$F^{\alpha\gamma} = f(\mathbf{K}) \delta^{\alpha\gamma} + \varphi_S^{\alpha\gamma} + \varphi_o^{\alpha\gamma}. \quad (23)$$

The tensor  $F^{\alpha\gamma}$  thus replaces the form factor of the "spin-only" case. It is easy to see that  $F^{\alpha\gamma}$  is real if there is a center of inversion in the crystal. This follows from the facts that the state  $|\Gamma_2\rangle$  is real and that  $e^{i\mathbf{K} \cdot \mathbf{r}_j}$  and  $f(\mathbf{K} \cdot \mathbf{r}_j)$ , although both complex, have nonvanishing matrix elements only for their real parts, the imaginary parts changing sign under inversion of the coordinates.

The scattering cross section, Eq. (6), can now be written as

$$\begin{aligned} d\sigma/d\Omega' &= \left( \frac{\gamma e^2}{mc^2} \right)^2 \sum_{MM'} p_{M'} \sum_{\mathbf{m}\mathbf{n}} e^{i\mathbf{K} \cdot (\mathbf{m}-\mathbf{n})} (\delta^{\alpha\beta} - \hat{K}^\alpha \hat{K}^\beta) \\ & \times F^{\alpha\mu} F^{\beta\nu} \langle M | S_n^\nu | M' \rangle \langle M' | S_m^\mu | M \rangle, \end{aligned} \quad (24)$$

where  $|M\rangle$  and  $|M'\rangle$  are magnetic state vectors for the entire crystal, assumed to be products of the state vectors for the individual ions,

<sup>10</sup> E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1935).

#### 4. CROSS SECTIONS FOR PARAMAGNETIC, FERROMAGNETIC, AND ANTIFERROMAGNETIC CRYSTALS

From Eq. (24) we can derive expressions for the elastic scattering cross sections for paramagnetic, ferromagnetic, and antiferromagnetic crystals.<sup>11</sup> For a paramagnetic substance in the absence of a magnetic field, the energy is independent of the quantum number  $M'$  and we can sum over these states by closure:

$$\sum_{MM'} p_M \langle M | S_n^\nu | M' \rangle \langle M' | S_m^\mu | M \rangle = \sum_M p_M \langle M | S_n^\nu S_m^\mu | M \rangle. \quad (25)$$

But this is simply the thermal average of  $S_n^\nu S_m^\mu$  at temperature  $T$ :

$$\sum_M p_M \langle M | S_n^\nu S_m^\mu | M \rangle = \langle S_n^\nu S_m^\mu \rangle_T. \quad (26)$$

Because different spins are uncorrelated in a paramagnet this can be expressed as

$$\langle S_n^\nu S_m^\mu \rangle_T = \frac{1}{3} S(S+1) \delta_{m,n} \delta^{\mu\nu}. \quad (27)$$

Substituting these relations in Eq. (22) we get the cross section for paramagnetic elastic scattering:

$$(d\sigma/d\Omega')_{\text{para}} = \frac{2}{3} N \left( \frac{\gamma e^2}{mc^2} \right)^2 S(S+1) \frac{1}{4} g^2 |\Phi(\mathbf{K})|^2, \quad (28)$$

where  $N$  is the number of unit cells in the crystal, and  $\frac{1}{4} g^2 |\Phi(\mathbf{K})|^2$

$$\begin{aligned} &= F^{\alpha\beta} F^{\alpha\beta} - \hat{K}^\alpha \hat{K}^\beta F^{\alpha\mu} F^{\beta\mu} \\ &= 2f^2 + 2f(\varphi_s^{\alpha\alpha} + \varphi_o^{\alpha\alpha}) \\ &\quad - \hat{K}^\alpha \hat{K}^\beta (\varphi_o^{\alpha\beta} + \varphi_s^{\alpha\beta} + \varphi_o^{\beta\alpha} + \varphi_s^{\beta\alpha}) + O(\lambda^2/\Delta^2) \\ &= 2f^2 + 2f\varphi_o^{\alpha\alpha} - \hat{K}^\alpha \hat{K}^\beta (\varphi_o^{\alpha\beta} + \varphi_o^{\beta\alpha}), \end{aligned} \quad (29)$$

making use of the antisymmetry of  $\varphi_s^{\alpha\beta}$  [see Eq. (19)]. Taking the square root of Eq. (29), we get for  $\Phi(\mathbf{K})$  (apart from an unimportant phase factor)

$$\Phi(\mathbf{K}) = (2/g) [f(\mathbf{K}) + \frac{1}{2} \varphi_o^{\alpha\alpha} - \frac{1}{4} \hat{K}^\alpha \hat{K}^\beta (\varphi_o^{\alpha\beta} + \varphi_o^{\beta\alpha})] + O(\lambda^2/\Delta^2). \quad (30)$$

The factor  $2/g$  has been inserted to make  $\Phi(0)=1$ , so that  $\Phi(\mathbf{K})$  is a conventionally normalized form factor.

In the case of a ferromagnetic substance the energy  $E_M$  depends very strongly on  $M$ . If  $\boldsymbol{\eta}$  is a unit vector in the direction of the magnetization and if we choose  $\boldsymbol{\eta}$  to be the axis of quantization of the states  $|M\rangle$ , the ground state will be the state of maximum spin in the direction of  $\boldsymbol{\eta}$ . Restricting ourselves to temperatures well below the Curie point, so that the magnetization is saturated,

we have

$$\sum_{MM'} p_M \langle M | S_n^\nu | M' \rangle \langle M' | S_m^\mu | M \rangle = \langle NS\boldsymbol{\eta} | S_n^\nu | NS\boldsymbol{\eta} \rangle \langle NS\boldsymbol{\eta} | S_m^\mu | NS\boldsymbol{\eta} \rangle, \quad (31)$$

where  $|NS\boldsymbol{\eta}\rangle$  is the spin state of the entire crystal with component of spin in the direction  $\boldsymbol{\eta}$  having the value  $NS$ ,  $S$  being the spin of a single ion. But

$$\langle NS\boldsymbol{\eta} | S_n^\nu | NS\boldsymbol{\eta} \rangle = \eta^\nu S. \quad (32)$$

Substituting this in Eq. (24), we get

$$\begin{aligned} \left( \frac{d\sigma}{d\Omega'} \right)_{\text{ferro}} &= S^2 \left( \frac{\gamma e^2}{mc^2} \right)^2 (\delta^{\alpha\beta} - \hat{K}^\alpha \hat{K}^\beta) \\ &\quad \times F^{\alpha\mu} F^{\beta\nu} \eta^\mu \eta^\nu \sum_{mn} e^{i\mathbf{K} \cdot (\mathbf{m}-\mathbf{n})} \\ &= S^2 \left( \frac{\gamma e^2}{mc^2} \right)^2 \frac{(2\pi)^3 N}{V_0} \sum_{\boldsymbol{\tau}} \delta(\mathbf{K}-\boldsymbol{\tau}) \\ &\quad \times (F^{\alpha\mu} F^{\beta\nu} \eta^\mu \eta^\nu - \hat{K}^\alpha F^{\alpha\mu} \eta^\mu \hat{K}^\beta F^{\beta\nu} \eta^\nu), \end{aligned} \quad (33)$$

where  $V_0$  is the volume of the unit cell and  $\boldsymbol{\tau}$  is  $2\pi$  times a vector of the reciprocal lattice. For a multi-domain crystal we must average over all possible directions  $\boldsymbol{\eta}$  of the magnetization. For spherical or cubic symmetry we have

$$(\eta^\mu \eta^\nu)_{\text{av}} = \frac{1}{3} \delta^{\mu\nu},$$

so that (33) becomes

$$\begin{aligned} \left( \frac{d\sigma}{d\Omega'} \right)_{\text{ferro}} &= \frac{2}{3} \left( \frac{\gamma e^2}{mc^2} \right)^2 S^2 \frac{(2\pi)^3 N}{V_0} \\ &\quad \times \frac{g^2}{4} \sum_{\boldsymbol{\tau}} \delta(\mathbf{K}-\boldsymbol{\tau}) |\Phi(\mathbf{K})|^2, \end{aligned} \quad (34)$$

where  $\Phi(\mathbf{K})$  is the same form factor [Eq. (30)] that was found for paramagnetic scattering.

For a simple antiferromagnetic substance in which there are two sublattices with spins in opposite directions, the arguments for the ferromagnet can be taken over if we make allowances for the fact that the magnetic unit cell may differ from the chemical unit cell. The cross section for a multi-domain antiferromagnet is found to be

$$\begin{aligned} \left( \frac{d\sigma}{d\Omega'} \right)_{\text{antiferro}} &= \frac{2}{3} \left( \frac{\gamma e^2}{mc^2} \right)^2 S^2 \frac{(2\pi)^3 N^{(m)}}{V_0^{(m)}} \\ &\quad \times \frac{g^2}{4} \sum_{\boldsymbol{\tau}} \delta(\mathbf{K}-\boldsymbol{\tau}) |\Phi(\mathbf{K})|^2 |F_m(\mathbf{K})|^2, \end{aligned} \quad (35)$$

where  $V_0^{(m)}$  and  $N^{(m)}$  are the volume and number of magnetic unit cells, respectively, and  $F_m(\mathbf{K})$  is the structure factor for the magnetic unit cell, given by

$$F_m(\mathbf{K}) = \sum_j (\pm) \exp(i\mathbf{K} \cdot \boldsymbol{\rho}_j). \quad (36)$$

<sup>11</sup> In this section we follow the derivations given by W. Marshall, Harvard University, 1959 (unpublished notes).

TABLE I. The matrix elements  $\langle dm | \varphi(\mathbf{K} \cdot \mathbf{r}) | dm' \rangle = \int R Y(r)_{2m}(\hat{r}) \times \varphi(\mathbf{K} \cdot \mathbf{r}) R(r) Y_{2m'}(\hat{r}) d^3r$ ,  $\varphi(\mathbf{K} \cdot \mathbf{r}) = 4\pi \sum_{LM} i^L h_L(Kr) Y_{LM}^*(\hat{K}) \times Y_{LM}(\hat{r})$ . For  $\varphi(\mathbf{K} \cdot \mathbf{r}) = e^{i\mathbf{K} \cdot \mathbf{r}}$ ,  $h_L(Kr)$  is the spherical Bessel function  $j_L(Kr)$ , while for  $\varphi(\mathbf{K} \cdot \mathbf{r}) = f(\mathbf{K} \cdot \mathbf{r})$  [Eq. (4)],  $h_L(Kr) = g_L(Kr)$ . The average  $\langle h_L \rangle$  is defined by  $\langle h_L \rangle = \int_0^\infty R^2(r) h_L(Kr) r^2 dr$ .

$m$	$m'$	$\langle dm   \varphi(\mathbf{K} \cdot \mathbf{r})   dm' \rangle [Y_{LM} = Y_{LM}(\hat{K})]$
2	2	$2(\pi)^{1/2} \langle h_0 \rangle Y_{00} + (4/7)(5\pi)^{1/2} \langle h_2 \rangle Y_{20} + (2/7)(\pi)^{1/2} Y_{40}$
2	1	$(2/7)(30\pi)^{1/2} \langle h_2 \rangle Y_{2-1} + (2/7)(5\pi)^{1/2} \langle h_4 \rangle Y_{4-1}$
2	0	$(4/7)(5\pi)^{1/2} \langle h_2 \rangle Y_{2-2} + (2/7)(15\pi)^{1/2} \langle h_4 \rangle Y_{4-2}$
2	-1	$(2/7)(35\pi)^{1/2} \langle h_4 \rangle Y_{4-3}$
2	-2	$(2/7)(70\pi)^{1/2} \langle h_4 \rangle Y_{4-4}$
1	2	$-(2/7)(30\pi)^{1/2} \langle h_2 \rangle Y_{21} - (2/7)(5\pi)^{1/2} \langle h_4 \rangle Y_{41}$
1	1	$2(\pi)^{1/2} \langle h_0 \rangle Y_{00} - (2/7)(5\pi)^{1/2} \langle h_2 \rangle Y_{20} - (8/7)(\pi)^{1/2} \langle h_4 \rangle Y_{40}$
1	0	$(2/7)(5\pi)^{1/2} \langle h_2 \rangle Y_{2-1} - (2/7)(30\pi)^{1/2} \langle h_4 \rangle Y_{4-1}$
1	-1	$(2/7)(30\pi)^{1/2} \langle h_2 \rangle Y_{2-2} - (4/7)(10\pi)^{1/2} \langle h_4 \rangle Y_{4-2}$
1	-2	$-(2/7)(35\pi)^{1/2} \langle h_4 \rangle Y_{4-3}$
0	2	$(4/7)(5\pi)^{1/2} \langle h_2 \rangle Y_{22} + (2/7)(15\pi)^{1/2} \langle h_4 \rangle Y_{42}$
0	1	$-(2/7)(5\pi)^{1/2} \langle h_2 \rangle Y_{21} + (2/7)(30\pi)^{1/2} \langle h_4 \rangle Y_{41}$
0	0	$2(\pi)^{1/2} \langle h_0 \rangle Y_{00} - (4/7)(5\pi)^{1/2} \langle h_2 \rangle Y_{20} + (12/7)(\pi)^{1/2} \langle h_4 \rangle Y_{40}$
0	-1	$-(2/7)(5\pi)^{1/2} \langle h_2 \rangle Y_{2-1} + (2/7)(30\pi)^{1/2} \langle h_4 \rangle Y_{4-1}$
0	-2	$(4/7)(5\pi)^{1/2} \langle h_2 \rangle Y_{2-2} + (2/7)(15\pi)^{1/2} \langle h_4 \rangle Y_{4-2}$
-1	2	$-(2/7)(35\pi)^{1/2} \langle h_4 \rangle Y_{43}$
-1	1	$(2/7)(30\pi)^{1/2} \langle h_2 \rangle Y_{22} - (4/7)(10\pi)^{1/2} \langle h_4 \rangle Y_{42}$
-1	0	$(2/7)(5\pi)^{1/2} \langle h_2 \rangle Y_{21} - (2/7)(30\pi)^{1/2} \langle h_4 \rangle Y_{41}$
-1	-1	$2(\pi)^{1/2} \langle h_0 \rangle Y_{00} - (2/7)(5\pi)^{1/2} \langle h_2 \rangle Y_{20} - (8/7)(\pi)^{1/2} \langle h_4 \rangle Y_{40}$
-1	-2	$-(2/7)(30\pi)^{1/2} \langle h_2 \rangle Y_{2-1} - (2/7)(5\pi)^{1/2} \langle h_4 \rangle Y_{4-1}$
-2	2	$(2/7)(70\pi)^{1/2} \langle h_4 \rangle Y_{44}$
-2	1	$(2/7)(35\pi)^{1/2} \langle h_4 \rangle Y_{43}$
-2	0	$(4/7)(5\pi)^{1/2} \langle h_2 \rangle Y_{22} + (2/7)(15\pi)^{1/2} \langle h_4 \rangle Y_{42}$
-2	-1	$(2/7)(30\pi)^{1/2} \langle h_2 \rangle Y_{21} + (2/7)(5\pi)^{1/2} \langle h_4 \rangle Y_{41}$
-2	-2	$2(\pi)^{1/2} \langle h_0 \rangle Y_{00} + (4/7)(5\pi)^{1/2} \langle h_2 \rangle Y_{20} + (2/7)(\pi)^{1/2} \langle h_4 \rangle Y_{40}$

$\varrho_j$  is the vector from the origin to the  $j$ th ion in the magnetic unit cell, and the plus or minus sign is to be taken according to the direction of the spin of the ion at  $\varrho_j$ .

Except for the difference in the form factor, these formulas are the same as those derived by Halpern and Johnson for the case where the orbital moment is completely quenched, and require no further discussion. Because of this difference in the form factor, however, it is no longer possible to interpret this quantity as the Fourier transform of the charge density.

## 5. CALCULATION OF THE FORM FACTOR FOR $\text{Ni}^{++}$

For the simple case of  $\text{Ni}^{++}$ , where there are two holes in the  $d$  shell, it is easiest to follow the straightforward procedure of writing the state  $|\Gamma_2\rangle$  in terms of one-electron wave functions  $|d_1 m_{11}\rangle |d_2 m_{12}\rangle$ , where  $|d_1 m_{11}\rangle$  is an eigenfunction referring to electron 1. Using tables of Clebsch-Gordan coefficients,<sup>10</sup> we find

$$|F M_L = 2\rangle = (1/\sqrt{2})(|d_1 2\rangle |d_2 0\rangle - |d_1 0\rangle |d_2 2\rangle),$$

$$|F M_L = -2\rangle = (1/\sqrt{2})(|d_1 0\rangle |d_2 -2\rangle - |d_1 -2\rangle |d_2 0\rangle). \quad (37)$$

We want to calculate  $f(\mathbf{K})$  and  $\varphi_o^{\alpha\beta}$  using the expression (7) for  $|\Gamma_2\rangle$ .

Consider  $f(\mathbf{K})$  first. Substituting (7) and (37) in (15), and remembering that  $e^{i\mathbf{K} \cdot \mathbf{r}_1}$  refers only to electron 1, we

obtain

$$f(\mathbf{K}) = \frac{1}{2} \langle d0 | e^{i\mathbf{K} \cdot \mathbf{r}} | d0 \rangle + \frac{1}{2} \langle d2 | e^{i\mathbf{K} \cdot \mathbf{r}} | d2 \rangle + \frac{1}{2} \langle d-2 | e^{i\mathbf{K} \cdot \mathbf{r}} | d-2 \rangle + \frac{1}{2} \langle d-2 | e^{i\mathbf{K} \cdot \mathbf{r}} | d-2 \rangle. \quad (38)$$

The problem is then reduced to the evaluation of the one-electron matrix elements

$$\langle dm | e^{i\mathbf{K} \cdot \mathbf{r}} | dm' \rangle = \int R(r) Y_{2m}^*(\hat{r}) e^{i\mathbf{K} \cdot \mathbf{r}} R(r) Y_{2m'}(\hat{r}) d^3r, \quad (39)$$

where  $R(r)$  is the radial wave function for the  $d$  electron and  $Y_{2m}$  is a spherical harmonic. To calculate these integrals we follow Weiss and Freeman<sup>12</sup> and expand  $e^{i\mathbf{K} \cdot \mathbf{r}}$  in spherical harmonics:

$$e^{i\mathbf{K} \cdot \mathbf{r}} = 4\pi \sum_{LM} i^L j_L(Kr) Y_{LM}^*(\hat{K}) Y_{LM}(\hat{r}), \quad (40)$$

where

$$j_L(Kr) = \frac{1}{2} i^{-L} \int_{-1}^{+1} e^{iKr\mu} P_L(\mu) d\mu$$

are the spherical Bessel functions. This gives for (47)

$$\begin{aligned} \langle dm | e^{i\mathbf{K} \cdot \mathbf{r}} | dm' \rangle &= 4\pi \sum_{LM} i^L \langle j_L \rangle Y_{LM}^*(\hat{K}) \int Y_{2m}^*(\hat{r}) Y_{LM}(\hat{r}) Y_{2m'}(\hat{r}) d\Omega \\ &= \sum_L 2[(2L+1)\pi]^{1/2} \langle j_L \rangle \\ &\quad \times C^L(2, m; 2, m') Y_{L, m-m'}^*(\hat{K}), \end{aligned} \quad (41)$$

where  $\langle j_L \rangle = \int_0^\infty R^2(r) j_L(Kr) r^2 dr$ , and the coefficients  $C^L(l, m; l', m')$  are tabulated by Condon and Shortley.<sup>10</sup> A complete table of the matrix elements (41) is given in Table I. Using these we obtain

$$f(\mathbf{K}) = \langle j_0 \rangle + \langle j_4 \rangle \{ (\pi)^{1/2} Y_{40}(\hat{K}) + \frac{1}{2} (10\pi/7)^{1/2} [Y_{44}(\hat{K}) + Y_{4-4}(\hat{K})] \}, \quad (42)$$

the formula derived by Weiss and Freeman.

To illustrate the calculation of  $\varphi_o^{\alpha\beta}$  we derive  $\varphi_o^{zz}$  explicitly, but we simply quote the results for the other  $\varphi_o^{\alpha\beta}$ . We want

$$\begin{aligned} \varphi_o^{zz} &= -(\lambda/\Delta) \langle \Gamma_2 | (l_1^z f_1 + f_1 l_1^z) L^z | \Gamma_2 \rangle \\ &= -\frac{1}{2} (\lambda/\Delta) \Delta \{ \langle F2 | (l_1^z f_1 + f_1 l_1^z) L^z | F2 \rangle \\ &\quad + \langle F-2 | (l_1^z f_1 + f_1 l_1^z) L^z | F-2 \rangle \\ &\quad - \langle F-2 | (l_1^z f_1 + f_1 l_1^z) L^z | F2 \rangle \\ &\quad - \langle F2 | (l_1^z f_1 + f_1 l_1^z) L^z | F-2 \rangle \} \\ &= -(\lambda/\Delta) \{ \langle F2 | (l_1^z f_1 + f_1 l_1^z) | F2 \rangle \\ &\quad - \langle F-2 | (l_1^z f_1 + f_1 l_1^z) | F-2 \rangle \\ &\quad - \langle F-2 | (l_1^z f_1 + f_1 l_1^z) | F2 \rangle \\ &\quad + \langle F2 | (l_1^z f_1 + f_1 l_1^z) | F-2 \rangle \}. \end{aligned} \quad (43)$$

<sup>12</sup> R. J. Weiss and A. J. Freeman, J. Phys. Chem. Solids **10**, 147 (1959).

TABLE II. Elements of the tensor  $\varphi_o^{\alpha\beta}$  as defined by Eq. (21). Only the symmetric combinations  $\varphi_o^{\alpha\beta} + \varphi_o^{\beta\alpha}$  are given, as these are all that is required for the form factor. The argument of the spherical harmonics is  $\hat{K}$ .

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$$\begin{aligned} \varphi_o^{xx} = & \frac{g-2}{4} \left\{ 4(\pi)^{\frac{1}{2}} \langle g_0 \rangle Y_{00} - \frac{4}{7} (5\pi)^{\frac{1}{2}} \langle g_2 \rangle Y_{20} + \frac{3}{14} (\pi)^{\frac{1}{2}} \langle g_4 \rangle Y_{40} \right. \\ & \left. + \frac{5}{4} \left( \frac{2\pi}{35} \right)^{\frac{1}{2}} \langle g_4 \rangle (Y_{44} + Y_{4-4}) + \frac{2}{7} (30\pi)^{\frac{1}{2}} \langle g_2 \rangle (Y_{22} + Y_{2-2}) - \frac{5}{14} \left( \frac{2\pi}{5} \right)^{\frac{1}{2}} \langle g_4 \rangle (Y_{42} + Y_{4-2}) \right\} \\ \varphi_o^{yy} = & \frac{g-2}{4} \left\{ 4(\pi)^{\frac{1}{2}} \langle g_0 \rangle Y_{00} - \frac{4}{7} (5\pi)^{\frac{1}{2}} \langle g_2 \rangle Y_{20} + \frac{3}{14} (\pi)^{\frac{1}{2}} \langle g_4 \rangle Y_{40} \right. \\ & \left. + \frac{5}{4} \left( \frac{2\pi}{35} \right)^{\frac{1}{2}} \langle g_4 \rangle (Y_{44} + Y_{4-4}) - \frac{2}{7} (30\pi)^{\frac{1}{2}} \langle g_2 \rangle (Y_{22} + Y_{2-2}) + \frac{5}{14} \left( \frac{2\pi}{35} \right)^{\frac{1}{2}} \langle g_4 \rangle (Y_{42} + Y_{4-2}) \right\} \\ \varphi_o^{zz} = & \frac{g-2}{4} \left\{ 4(\pi)^{\frac{1}{2}} \langle g_0 \rangle Y_{00} + \frac{8}{7} (5\pi)^{\frac{1}{2}} \langle g_2 \rangle Y_{20} + \frac{4}{7} (\pi)^{\frac{1}{2}} \langle g_4 \rangle Y_{40} \right\} \\ \varphi_o^{xy} + \varphi_o^{yx} = & \frac{g-2}{4} \left\{ -\frac{2}{7i} (30\pi)^{\frac{1}{2}} \langle g_2 \rangle (Y_{22} - Y_{2-2}) - \frac{5}{14i} \left( \frac{2\pi}{5} \right)^{\frac{1}{2}} (Y_{42} - Y_{4-2}) \right\} \\ \varphi_o^{yz} + \varphi_o^{zy} = & \frac{g-2}{4} \left\{ -\frac{2}{7i} (30\pi)^{\frac{1}{2}} \langle g_2 \rangle (Y_{21} + Y_{2-1}) - \frac{5}{28i} \left( \frac{\pi}{5} \right)^{\frac{1}{2}} \langle g_4 \rangle (Y_{41} + Y_{4-1}) + \frac{5}{4i} \left( \frac{\pi}{35} \right)^{\frac{1}{2}} \langle g_4 \rangle (Y_{43} + Y_{4-3}) \right\} \\ \varphi_o^{xz} + \varphi_o^{zx} = & \frac{g-2}{4} \left\{ -\frac{2}{7} (30\pi)^{\frac{1}{2}} \langle g_2 \rangle (Y_{2-1} - Y_{21}) + \frac{5}{28} \left( \frac{\pi}{5} \right)^{\frac{1}{2}} \langle g_4 \rangle (Y_{4-1} - Y_{41}) + \frac{5}{4} \left( \frac{\pi}{35} \right)^{\frac{1}{2}} \langle g_4 \rangle (Y_{4-3} - Y_{43}) \right\} \end{aligned}$$


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Substituting the expressions for  $|F2\rangle$  and  $|F-2\rangle$  and operating on the one-electron functions with  $l_1^z$ , we obtain

$$\varphi_o^{zz} = - (2\lambda/\Delta) \{ \langle d2 | f(\mathbf{K} \cdot \mathbf{r}) | d2 \rangle + \langle d-2 | f(\mathbf{K} \cdot \mathbf{r}) | d-2 \rangle \}. \quad (44)$$

The orbital calculation therefore leads to one-electron matrix elements of the form

$$\begin{aligned} \langle dm | f(\mathbf{K} \cdot \mathbf{r}) | dm' \rangle \\ = \int R(r) Y_{2m}^*(\hat{r}) f(\mathbf{K} \cdot \mathbf{r}) R(r) Y_{2m'}(\hat{r}) d^3\mathbf{r}. \end{aligned} \quad (45)$$

To evaluate these we use a procedure analogous to that used for Eq. (39). The function  $f(\mathbf{K} \cdot \mathbf{r})$ , which is defined by Eq. (4), can be expanded in spherical harmonics, just as  $e^{i\mathbf{K} \cdot \mathbf{r}}$  was expanded in Eq. (40):

$$f(\mathbf{K} \cdot \mathbf{r}) = 4\pi \sum_{LM} i^L g_L(Kr) Y_{LM}^*(\hat{K}) Y_{LM}(\hat{r}), \quad (46)$$

where

$$g_L(Kr) = \frac{1}{2} i^{-L} \int_{-1}^{+1} f(Kr\mu) P_L(\mu) d\mu, \quad (47)$$

and  $\mu$  is the cosine of the angle between  $\mathbf{K}$  and  $\mathbf{r}$ . The functions  $g_L(Kr)$  are similar to the spherical Bessel functions  $j_L(Kr)$  which appear in the expansion of  $e^{i\mathbf{K} \cdot \mathbf{r}}$ . It is the difference between  $g_L(Kr)$  and  $j_L(Kr)$  which leads to different shapes for the orbital and spin form factors. Using Eq. (47) and the properties of the

Legendre polynomials  $P_L(\mu)$ , we find

$$\begin{aligned} g_0(x) &= 2(1 - \cos x)/x^2, \\ g_2(x) &= (2/x^2) \cos x - (6/x^2) \sin x + (4/x^2), \\ g_4(x) &= \left( \frac{70}{x^4} - \frac{2}{x^2} \right) \cos x + \left( -\frac{70}{x^5} + \frac{20}{x^3} \right) \sin x + \frac{16}{3x^2}. \end{aligned} \quad (48)$$

The first two have been given by Trammell. The evaluation of the matrix elements (45) now proceeds exactly as for Eq. (39) except that  $\langle j_L \rangle$  is replaced by

$$\langle g_L \rangle = \int_0^\infty R^2(r) g_L(r) r^2 dr.$$

Using Table I we find

$$\begin{aligned} \varphi_o^{zz} = & - (4\lambda/\Delta) [ \langle g_0 \rangle + (4/7) (5\pi)^{\frac{1}{2}} \langle g_2 \rangle Y_{20}(\hat{K}) \\ & + (2/7) (\pi)^{\frac{1}{2}} \langle g_4 \rangle Y_{40}(\hat{K}) ]. \end{aligned} \quad (49)$$

$\lambda/\Delta$  can be expressed in terms of the  $g$  factor. For  $\text{Ni}^{++}$  we have<sup>13</sup>

$$g = 2 - 8\lambda/\Delta; \quad -\lambda/\Delta = (g-2)/8. \quad (50)$$

This result has been incorporated in Table II, where the expressions for the components of the tensor  $\varphi_o^{\alpha\beta}$  are given. We now need only substitute these results in Eq. (30) for the form factor  $\Phi(\mathbf{K})$ . If we substitute for the spherical harmonics their explicit forms as functions

<sup>13</sup> W. Low, *Paramagnetic Resonance* (Academic Press, Inc., New York, 1960), p. 92.

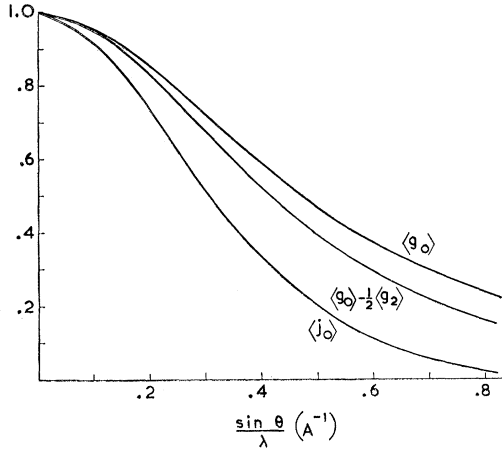


FIG. 2.  $\langle j_0 \rangle$ ,  $\langle g_0 \rangle$  and  $\langle g_0 \rangle - \frac{1}{2}\langle g_2 \rangle$  for  $\text{Ni}^{++}$ , calculated from Watson's wave function. The orbital magnetic form factor  $\langle g_0 \rangle$ ,  $\langle g_0 \rangle - \frac{1}{2}\langle g_2 \rangle$  is greatly expanded relative to the spin form factor  $\langle j_0 \rangle$ .

of  $\hat{K}_x$ ,  $\hat{K}_y$ ,  $\hat{K}_z$ , we obtain, after some straightforward algebra,

$$\Phi(\mathbf{K}) = \frac{2}{g} \left\{ \langle j_0 \rangle + \frac{(g-2)}{2} (\langle g_0 \rangle - \frac{1}{2}\langle g_2 \rangle) + \frac{15}{4} C_4(\hat{K}) \right. \\ \left. \times \left[ \langle j_4 \rangle + \frac{(g-2)}{2} \left( \frac{3}{14} \langle g_4 \rangle - \frac{1}{7} \langle g_2 \rangle \right) \right] \right\}, \quad (51)$$

where

$$C_4(\hat{K}) = \hat{K}_x^4 + \hat{K}_y^4 + \hat{K}_z^4 - \frac{3}{5} \quad (52)$$

is a cubic harmonic. This is to be compared with the "spin-only" form factor  $f(\mathbf{K})$ ,

$$f(\mathbf{K}) = \langle j_0 \rangle + (15/4) \langle j_4 \rangle C_4(\hat{K}). \quad (53)$$

The most important terms in Eqs. (51) and (53) are the spherical parts of the form factors, i.e., the parts not multiplied by the angular factor  $C_4(\hat{K})$ :

$$\Phi_S(K) = (2/g) [\langle j_0 \rangle + [(g-2)/2] (\langle g_0 \rangle - \frac{1}{2}\langle g_2 \rangle)], \\ f_S(K) = \langle j_0 \rangle. \quad (54)$$

The functions  $\langle j_L \rangle$  and  $\langle g_L \rangle$  for  $L=0, 2, 4$  have been evaluated for  $\text{Ni}^{++}$  using Watson's<sup>14</sup> analytic Hartree-Fock radial wave function. Since a table of  $\langle j_L \rangle$  has already been published by Watson and Freeman,<sup>15</sup> we give only the  $\langle g_L \rangle$  in Table III. In Fig. 2 we show the graphs of  $\langle j_0 \rangle$ ,  $\langle g_0 \rangle$ , and  $\langle g_0 \rangle - \frac{1}{2}\langle g_2 \rangle$  as functions of  $(\sin \theta)/\lambda$ . The "orbital" curves  $\langle g_0 \rangle$  and  $\langle g_0 \rangle - \frac{1}{2}\langle g_2 \rangle$  lie outside that of  $\langle j_0 \rangle$ , so that if we ignored the presence of an unquenched orbital moment and tried to interpret this as due to spin scattering, the form factor would appear to be expanded. This means that the presence

of an orbital moment simulates a contraction of the wave function. That this is true in general can be seen by comparing the behavior of  $j_L(x)$  and  $g_L(x)$  for small  $x$ . For  $j_L(x)$  we have<sup>16</sup>

$$j_0(x) \approx 1 - \frac{1}{6}x^2, \\ j_L(x) \approx \frac{x^L}{(2L+1)!!}, \quad (55)$$

where  $(2L+1)!! = 1 \times 3 \times 5 \times \cdots \times (2L+1)$ . Similar formulas can be derived for  $g_L(x)$  by using the relations<sup>17</sup>

$$\int_{-1}^{+1} \mu^n P_L(\mu) d\mu = \frac{2^{L+1} [\frac{1}{2}(n+L)]!}{[\frac{1}{2}(n-L)]! (n+L+1)!} \\ \text{if } n-L > 0, \quad n-L \text{ even,} \\ = 0 \quad \text{otherwise,}$$

and Eq. (46); we find

$$g_0(x) \approx 1 - \frac{1}{12}x^2, \\ g_L(x) \approx \frac{2}{L+2} \frac{x^L}{(2L+1)!!}. \quad (56)$$

Comparing (55) and (56) shows that for small  $K$ ,

$$\langle j_0 \rangle \approx 1 - \frac{1}{6}K^2 \langle r^2 \rangle, \\ \langle g_0 \rangle \approx 1 - \frac{1}{12}K^2 \langle r^2 \rangle, \\ \langle j_L \rangle \approx \frac{K^L}{(2L+1)!!} \langle r^L \rangle, \\ \langle g_L \rangle \approx \frac{2}{L+2} \frac{K^L}{(2L+1)!!} \langle r^L \rangle, \quad (57)$$

TABLE III. The functions  $\langle g_0 \rangle$ ,  $\langle g_2 \rangle$ , and  $\langle g_4 \rangle$  for  $\text{Ni}^{++}$ , calculated with Watson's<sup>15</sup> restricted Hartree-Fock wave function.

$\frac{\sin \theta}{\lambda} (\text{\AA}^{-1})$	$\langle g_0 \rangle$	$\langle g_2 \rangle$	$\langle g_4 \rangle$
0.0	1.0000	0.0000	0.0000
0.1	0.9599	0.0157	0.0000
0.2	0.8560	0.0540	0.0025
0.3	0.7229	0.0968	0.0093
0.4	0.5901	0.1311	0.0202
0.5	0.4729	0.1528	0.0329
0.6	0.3760	0.1629	0.0451
0.7	0.2987	0.1644	0.0555
0.8	0.2380	0.1599	0.0636
0.9	0.1909	0.1518	0.0692
1.0	0.1545	0.1418	0.0727

<sup>14</sup> R. E. Watson, "Iron Series Hartree-Fock Calculations," Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, 1959 (unpublished).

<sup>15</sup> R. E. Watson and A. J. Freeman, *Acta Cryst.* **14**, 27 (1961).

<sup>16</sup> P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York 1953).

<sup>17</sup> E. T. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge University Press, New York, 1927).

where

$$\langle r^L \rangle = \int_0^\infty R^2(r) r^{L+2} dr,$$

so that for small  $K$ ,  $\langle g_0 \rangle > \langle j_0 \rangle$  and  $\langle g_L \rangle < \langle j_L \rangle$  for  $L \neq 0$ .

## 6. DISCUSSION

Figure 3 shows the spherical parts of the form factors for Ni<sup>++</sup>,  $f_s(K)$  and  $\Phi_s(K)$ , taking  $g=2.2$ . The third curve is the spherical part of the form factor as determined experimentally by Alperin.<sup>4</sup> His results indicate that the radial 3d functions are greatly contracted in the solid as compared to the free ion (by about 17%), taking the latter to be given by Watson's unpolarized calculation for Ni.<sup>14</sup> This result is in disagreement with the fact that the  $g$ -factor measurements<sup>2</sup> indicate that  $\lambda_{\text{solid}} \approx \frac{3}{4} \lambda_{\text{free ion}}$ , where the  $\lambda$ 's are the spin-orbit coupling constants for Ni<sup>++</sup>. This indicates an expansion of the Ni<sup>++</sup> wave function in the solid, since  $\lambda$  is roughly determined by  $\langle 1/r^3 \rangle$ .

We have found that the orbital contribution to the form factor does not resolve this difficulty since it accounts for only about 4% of the 17% expansion of the form factor (see Fig. 2).

It should be emphasized that we have used Watson's "restricted" Hartree-Fock wave functions in this calculation. A "spin-polarized" calculation has also been carried out for Ni<sup>++</sup> by Watson and Freeman.<sup>18</sup> The "spin-only" form factor for this case is also expanded relative to the restricted solution by about 4%. If we were to replace our  $\langle j_0 \rangle$  by this spin-polarized form factor the result would still not be sufficiently expanded to explain Alperin's form factor on the basis of an expanded charge distribution in the solid but together the two effects account for an 8% expansion of the form factor.

One further interesting effect of the orbital contribution concerns the anisotropic terms in the form factor.

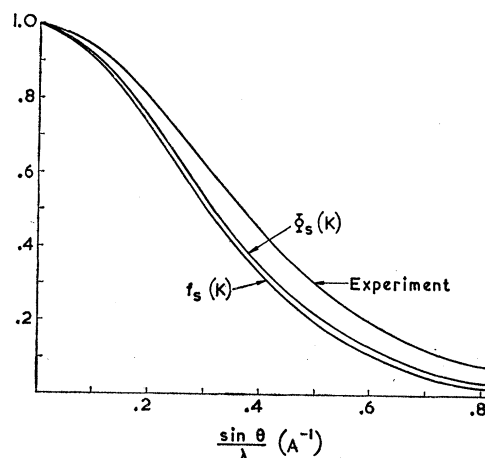


FIG. 3. The spherical part of the form factor for Ni<sup>++</sup>. The spin-only form factor [ $f_s(K)$ ], spin and orbit form factor [ $\Phi_s(K)$ ,  $g=2.2$ ], and Alperin's experimental form factor are shown.

Of the terms multiplying  $C_4(\hat{K})$  in Eq. (51), the orbital contribution is completely negligible compared to the  $\langle j_4 \rangle$  spin contribution. The orbital moment nevertheless affects this anisotropy strongly through the normalization factor  $2/g$ . The effect in Ni<sup>++</sup> is to reduce the anisotropy by 10%.

It is clear that the orbital scattering cannot always be ignored in an accurate interpretation of the experiments, but that it is not sufficient by itself to account for Alperin's results on NiO.

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<sup>18</sup> R. E. Watson and A. J. Freeman, Phys. Rev. 120, 1125 (1960).