

tively. The analysis leading to the  $\langle r^{-3} \rangle_{\text{exp}}$  was based on the assumption of a restricted Hartree-Fock function. Inspection of the spin density in Fig. 1 suggests that there are additional sources to this hyperfine term and that we should not expect detailed agreement in  $\langle r^{-3} \rangle$ 's. We have not investigated this particular aspect of the problem.

## VI. CONCLUSION

We have been investigating the effect of relaxing one of the restrictions associated with the conventional restricted Hartree-Fock formalism. The particular restriction in question, (iii), requires common  $U_i(r)$ 's for electrons of differing  $m_s$  value. Relaxation of this constraint in a calculation for  $\text{Ni}^{+2}$  has led to measurable effects in the electron spin distribution of that ion. A Fermi contact hyperfine parameter was obtained which, in common with earlier calculations, is in fair agreement with experiment. Of perhaps greater importance is the

effect on the magnetic form factor which represents an electronic spin distribution measurably different from that of either of the  $3d$  electron types. This suggests that experimentally determined magnetic form factors for an ion like  $\text{Ni}^{+2}$ , can perhaps be misleading if interpreted as arising directly from a single  $3d$  charge distribution. This difficulty is most likely to occur for an ion with an almost filled shell, where the "paired" electrons of that shell can be spin polarized so as to make a contribution to the magnetic scattering.

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# Crystalline Field and Spin Polarization Effects on Electron Densities and Magnetic Form Factors

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The combined effects of spin (or exchange) polarization and an external crystalline field on charge densities, x-ray and magnetic form factors, and hyperfine parameters are investigated following the analytic Hartree-Fock self-consistent field approach. The crystalline field was represented by a crude cubic field arising from an octahedral array of point charges surrounding the central ion—in this case  $\text{Ni}^{+2}$ . In the strong field approximation the atomic  $3d$  electrons are "split" by the crystalline field and the spinpolarization effect, resulting in a description of these electrons by a set of three distinct orbitals (each having different radial distributions and called  $t_{2g}\uparrow$ ,  $t_{2g}\downarrow$  and  $e_g\uparrow$ ). The ion's spin density leads to a Fermi contact hyperfine term in better agreement with experiment than the value reported in an earlier spin polarized calculation for the free  $\text{Ni}^{+2}$  ion and a magnetic form factor whose Fourier transform resembles none of the individual  $3d$  charge distributions.

## I. INTRODUCTION

IN earlier investigations we have considered several factors affecting charge densities and measured magnetic form factors<sup>1-3</sup> of iron series ions. An external

crystalline field was shown to produce two effects on the  $3d$  charge density for an ion like  $\text{Mn}^{++}$  and hence on its magnetic form factor as well: (1) an expansion of the  $3d$  charge density from its free ion value and (2) a "splitting" of the doubly degenerate ( $e_g$ ) and triply degenerate ( $t_{2g}$ ) cubic functions from their common free ion value, resulting in two different radial charge densities. The expansion effect, as suggested by experimental  $F^k(3d,3d)$  integrals was shown<sup>2</sup> to be compatible with neutron diffraction data.<sup>4</sup> The splitting effect led to the prediction that a half-closed shell ion, like  $\text{Mn}^{++}$

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<sup>1</sup> R. E. Watson, Phys. Rev. **117**, 742 (1960). There is an error associated with this calculation; an erratum is available from the author.

<sup>2</sup> A. J. Freeman and R. E. Watson, Phys. Rev. **118**, 1168 (1960), and J. Appl. Phys. **31**, 374S (1960).

<sup>3</sup> R. E. Watson and A. J. Freeman, preceding paper [Phys. Rev. **120**, 1125 (1960)], henceforth denoted as I.

<sup>4</sup> J. M. Hastings, N. Elliot, and L. M. Corliss, Phys. Rev. **115**, 13 (1959).

or  $\text{Fe}^{+3}$ , would show asymmetries in the form factor of the form suggested by Weiss and Freeman<sup>5</sup> arising from the resultant nonspherical charge distribution. It was suggested<sup>2</sup> that the  $\text{Mn}^{++}$  data of Hastings, Elliott, and Corliss<sup>4</sup> did in fact show such asymmetries. Recently, Nathans, Pickart, and Alperin<sup>6</sup> reported a careful polarized neutron study of  $\text{Fe}_3\text{O}_4$  which showed a distinct asymmetry in the  $\text{Fe}^{+3}$  form factor. This appeared as a splitting of the form factor (from its spherically symmetric value) for two reflections which occurred at the same  $\sin\theta/\lambda$  value and was interpreted by them as arising from our proposed splitting effect on the otherwise spherically symmetric  $\text{Fe}^{+3}$  ion. This evidence may be taken as confirming that such an effect is observable.

Since  $\text{Mn}^{+2}$  was a rather special case of a half-closed shell, with its  $3d$  electrons having all their spins aligned, we later investigated the effect of *exchange* or *spin* polarization on a more general transition metal ion having a net spin density and  $3d$  electrons of both spins. This was reported<sup>8</sup> as a spin polarized Hartree-Fock calculation for the free  $\text{Ni}^{++}$  ion. The results and discussion associated with that calculation will be referred to frequently (as I) in this paper. A spin polarized calculation simply consists of letting the atomic one-electron wave functions of differing spin have different radial dependence. Due to exchange terms, a Hartree-Fock many-electron function with a net spin will, in the spin-polarized formalism, yield differences in radial functions for electrons differing only in the  $m_s$  quantum number. The results showed  $3d$  scattering factors for x-ray and neutron diffraction which, due to spin polarization, were measurably different. These results suggested that, for an ion like  $\text{Ni}^{++}$ , measured absolute  $3d$  neutron (i.e., magnetic) form factors could not be relied on to give direct and detailed information concerning  $3d$  electron distributions. The free ion calculation yielded additional results of interest. Among these was a Fermi contact hyperfine parameter<sup>7</sup> ( $\chi$ ) which was in rough agreement with experiment as were calculations<sup>8,9</sup> using similar approaches.

We are here reporting on an investigation of the combined effects due to spin polarization and an external crude cubic field on charge densities, magnetic form factors, and hyperfine parameters. The external field was treated in a manner similar to that reported in an earlier calculation<sup>1</sup> for  $\text{Mn}^{+2}$ , namely a cubic field due to an octahedral array of six point charges. This and other details of our model were in large part determined by computational considerations. We have stayed within the single configuration Hartree-Fock

formalism. The resultant model of a  $\text{Ni}^{++}$  ion in a crystalline environment is *exceedingly crude*. Elsewhere<sup>2,10</sup> we have discussed some of the shortcomings of the model we use here and some of the difficulties associated with "improving" it.

In the section which follows we briefly describe the calculation and discuss some of the shortcomings of the model. The interested reader will find further discussion pertinent to the calculation in I. The third section reports and discusses the computational results with emphasis on  $\chi$  and the  $3d$  scattering factors and frequent comparison with spin-polarized (I) and conventional<sup>11,12</sup> Hartree-Fock calculations for the free  $\text{Ni}^{++}$  ion.

Before describing our calculation we must emphasize the crudity of our model. Because of this crudity, we cannot claim to predict experimental observables but must be content with observing only the effects predicted by the model assuming that these effects have some reasonable relationship to reality.

## II. DESCRIPTION OF CALCULATION

In the present version of the Hartree-Fock formalism we will deal with orthonormal one-electron wave functions of the form,

$$\phi_i = [U_i(r)/r] S_i(\theta, \phi) \mathcal{S}_i(\sigma), \quad (1)$$

where  $\mathcal{S}_i(\sigma)$  is a spin function (with a spin quantum number  $m_s = \pm \frac{1}{2}$ ) and  $S_i(\theta, \phi)$  is an angular function. The  $\mathcal{S}_i(\sigma)$ 's and  $S_i(\theta, \phi)$ 's are assigned to the  $\phi_i$ 's and the radial functions,  $U_i(r)$ 's, are solved for variationally. The normalization condition of the  $U_i(r)$ 's is:

$$\int_0^\infty [U_i(r)]^2 dr = 1. \quad (2)$$

The  $U_i(r)$ 's are to be analytic, i.e.:

$$U_i(r) = \sum_j C_{ij} R_j(r), \quad (3)$$

where the basis functions [ $R_j(r)$ 's] are:

$$R_j(r) = N_j r^{A_j+1} e^{-Z_j r}. \quad (4)$$

$l$  is the one-electron orbital angular momentum appropriate for the one-electron function of which  $U_i(r)$  is the radial part and  $N_j$  is a normalization constant. A set of  $R_j$ 's is supplied for each  $l$  value for which Hartree-Fock solutions are to be obtained.  $U_i(r)$ 's of common  $l$  value are constructed from a common set of  $R_j$ 's. The set of  $N_j$ 's,  $A_j$ 's, and  $Z_j$ 's, defining the  $R_j$ 's used in this calculation appears in Table I. This set was used in previous conventional (or restricted<sup>11</sup>) and spin polar-

<sup>5</sup> R. J. Weiss and A. J. Freeman, J. Phys. Chem. Solids **10**, 147 (1959).

<sup>6</sup> R. Nathans, S. Pickart, and J. Alperin, Conference on Neutron Diffraction in Relation to Magnetism and Chemical Bonding, Gatlinburg, Tennessee, April, 1960 (to be published).

<sup>7</sup> See A. Abragam, J. Horowitz, and M. H. L. Pryce, Proc. Roy. Soc. (London) **A230**, 169 (1955).

<sup>8</sup> J. H. Wood and G. W. Pratt, Jr., Phys. Rev. **107**, 995 (1957).

<sup>9</sup> V. Heine, Phys. Rev. **107**, 1002 (1957).

<sup>10</sup> A. J. Freeman and R. E. Watson, Phys. Rev. **120**, 1254 (1960).

<sup>11</sup> R. E. Watson, Technical Report No. 12, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, June, 1959 (unpublished); scattering factors based on this calculation appear in reference 12.

<sup>12</sup> Appearing in part in R. E. Watson and A. J. Freeman, Acta Cryst. (to be published).

TABLE I. Parameters ( $A_i$ ,  $Z_i$ , and  $N_i$ ) which define the basis set ( $R_i$ 's).

	$j$	$A_i$	$Z_i$	$N_i$
$R_i$ 's used for the construction of $s$ functions ( $l=0$ )	1	0	29.2991	317.18411
	2	1	25.9035	3943.3516
	3	1	13.3851	756.87370
	4	2	12.4174	2844.7630
	5	2	7.4187	468.90632
	6	2	4.4208	76.593477
$p$ functions ( $l=1$ )	7	0	18.2297	1638.3933
	8	0	11.0602	469.76085
	9	1	10.1407	1400.1563
	10	1	6.1124	238.05644
	11	1	3.7142	41.635831
$d$ functions ( $l=2$ )	12	0	2.3154	7.9639743
	13	0	4.5232	82.984888
	14	0	8.5025	755.70446
	15	0	15.0077	5521.2606

ized (see I) Hartree-Fock calculations for the free  $\text{Ni}^{++}$  ion. Further discussion of the analytic Hartree-Fock approach and of the  $\text{Ni}^{++}$  basis set may be found in I.

This calculation differs with the restricted Hartree-Fock formalism in several ways. First,  $\phi_i$ 's differing only in  $m_s$  values are allowed different  $U_i(r)$ 's. This is the spin polarized Hartree-Fock formalism. Secondly, we are placing the ion into an external cubic potential and we will also allow those  $\phi_i$ 's of the same  $l$  which interact differently with the cubic potential to have differing  $U_i(r)$ 's. This approach was used in the earlier  $\text{Mn}^{++}$  calculation.<sup>1</sup> In the restricted Hartree-Fock formalism  $\phi_i$ 's of the same shell ( $n$  and  $l$  value) are constrained to have the same  $U_i(r)$ .

The cubic potential used is that due to an octahedral array of six point charges, each at a distance of 3.949 a.u. from the  $\text{Ni}^{++}$  nucleus. This distance is appropriate for the  $\text{NiO}$  crystal. A charge of  $-2$  a.u. is associated with each point charge. This is an extremely crude approximation to a crystalline environment.<sup>10</sup> It will not, for example, produce the well-known expansion of iron series ion  $U_i(r)$ 's.<sup>13</sup>

We use the strong field description of the  $\phi_i$ 's. In other words,  $\phi_i$ 's belong to irreducible representations of the cubic group. This description affects only the  $3d$  shell ( $l=2$ ) where the fivefold spacial degeneracy ( $m_l=2, 1, 0, -1, -2$ ) of a spherical environment is broken into a double ( $e_g$ ) and triple ( $t_{2g}$ ) degeneracy. The angular dependencies and their transformation properties are:

$$\begin{aligned}
 e_g \left\{ \begin{array}{l} Y_2^0(\theta, \phi) \quad \text{which transforms as } 3z^2 - r^2/r^2, \\ 2^{-1/2}[Y_2^2(\theta, \phi) + Y_2^{-2}(\theta, \phi)] \quad \text{which transforms as } x^2 - y^2/r^2 \end{array} \right. \\
 t_{2g} \left\{ \begin{array}{l} 2^{-1/2}[Y_2^2(\theta, \phi) - Y_2^{-2}(\theta, \phi)] \quad \text{which transforms as } xy/r^2 \\ 2^{-1/2}[Y_2^1(\theta, \phi) - Y_2^{-1}(\theta, \phi)] \quad \text{which transforms as } yz/r^2 \\ 2^{-1/2}[Y_2^1(\theta, \phi) + Y_2^{-1}(\theta, \phi)] \quad \text{which transforms as } xz/r^2 \end{array} \right. \quad (5)
 \end{aligned}$$

<sup>13</sup> For a recent discussion of this see Freeman and Watson reference 2.

where the  $Y_{l=2}^m$ 's are spherical harmonics.<sup>14</sup> The argon core wave functions have zero valued matrix elements with the cubic field and the  $t_{2g}$  and  $e_g$  interact differently with it. Defining a radial cubic potential integral;

$$V^4(i) = \int_0^\infty [U_i(r)]^2 V_4(r) dr, \quad (6)$$

where

$$\begin{aligned}
 V_4(r) &\equiv r^4/r_0^5 \quad \text{for } r > r_0 = 3.949 \text{ a.u.} \\
 &\equiv r_0^4/r^5 \quad \text{for } r < r_0 = 3.949 \text{ a.u.} \quad (7)
 \end{aligned}$$

The cubic potential energy of a  $t_{2g}$  orbital is  $-4/3 V^4(t_{2g})$  a.u. and for an  $e_g$  orbital it is  $2 V^4(e_g)$  a.u.

The Hartree-Fock equations are obtained by applying the variational principle to a single configuration single determinant  $[1s\uparrow 1s\downarrow 2s\uparrow 2s\downarrow (2p\uparrow)^3 (2p\downarrow)^3 3s\uparrow 3s\downarrow (3p\uparrow)^3 (3p\downarrow)^3 (t_{2g}\uparrow)^3 (t_{2g}\downarrow)^3 (e_g\uparrow)^2]$ , the arrows denote the spin direction, i.e., the  $m_s$  value. A separate Hartree-Fock equation (but with the cubic potential included in the  $3d$  equations) is solved for each of the above listed electron types.<sup>15</sup>

There are several objections which can be raised against the computational model sketched above. There are the serious questions of (1) to what extent should one rely on the ionic model of a localized ion in an external "crystalline" potential and in turn (2) how appropriate is a point charge potential. We are not optimistic<sup>10</sup> about either the potential or "improvements" on it, e.g., by including potential contributions from ligand overlap and metal ion-ligand orthogonalization in the manner of Kleiner<sup>16</sup> and Phillips.<sup>17</sup> Perhaps a scheme, such as Jarrett's,<sup>18</sup> which includes covalent bonding effects (i.e., abandons the strict ionic crystalline field model) would be more appropriate (but then this scheme represents an almost impossibly complex starting point for the sort of calculation we are doing).

Accepting the point charge crystalline field description, there are objections which can be raised against our model of the  $\text{Ni}^{++}$  ion. If we consider the case where  $U_i(r)$ 's within each electron shell are constrained to be identical, we do not obtain the free ion  ${}^3F$  ground-state symmetry,<sup>19</sup> but due to invoking the strong field approximation we obtain a *prescribed* admixture of  $(3d)^8 {}^3F$  and  ${}^3P$  states. This illustrates that the strong field wave function will not behave properly for the case of weak cubic

<sup>14</sup> See E. U. Condon and G. H. Shortley, *The Theory on Atomic Spectra* (Cambridge University Press, Cambridge, 1953), for definition of phase conventions.

<sup>15</sup> Since each of the occupied  $3d$  spacially degenerate sets is completely filled, the only nonspherical contributions to the Hartree-Fock equation potentials are purely cubic. As a result, the sets of  $p$ ,  $t_{2g}$ , or  $e_g U_i(r)$ 's for electrons of one spin automatically have common radial dependence. This contrasts with the  $\text{Ni}^{++}$  spin polarized calculation (I) where due to the nonspherical charge distribution of the  $3d$  shell, it required, for example, a restriction to make the three  $U_{3p}(r)$ 's identical.

<sup>16</sup> W. H. Kleiner, J. Chem. Phys. **20**, 1784 (1952).

<sup>17</sup> J. C. Phillips, J. Phys. Chem. Solids **11**, 226 (1959).

<sup>18</sup> H. S. Jarrett, J. Chem. Phys. **31**, 1579 (1959).

<sup>19</sup> This contrasts with the earlier case<sup>1</sup> of  $\text{Mn}^{++}$  which does go to a free ion ground-state  ${}^6S$  symmetry.

TABLE II. The eigenvectors ( $C_{ij}$ 's) defining the radial functions ( $U_i$ 's) in terms of the basis functions ( $R_j$ 's). Arrows denote spin values ( $m_s = \pm \frac{1}{2}$ ).

$j =$	1	2	3	4	5	6
$i = 1s\uparrow$	0.91714942	0.10098380	-0.00162160	0.00128385	-0.00023285	-0.00000113
$1s\downarrow$	0.91715293	0.10098603	-0.00162883	0.00127384	-0.00023173	-0.00000222
$2s\uparrow$	-0.28035290	-0.16393688	0.68521182	0.45151615	0.03657875	-0.00119248
$2s\downarrow$	-0.28071085	-0.16433037	0.68673570	0.45230167	0.03388275	-0.00124178
$3s\uparrow$	0.10590205	0.05057639	-0.22336352	-0.41218570	0.39933836	0.82553764
$3s\downarrow$	0.10522826	0.05117850	-0.22509773	-0.40528274	0.39236458	0.82943944
$j =$	7	8	9	10	11	
$i = 2p\uparrow$	0.14686590	0.84369677	0.02086910	0.02115013	-0.00276999	
$2p\downarrow$	0.14662750	0.84683372	0.01868763	0.01911908	-0.00294307	
$3p\uparrow$	-0.04786085	-0.33669583	-0.05462141	0.57945798	0.57552605	
$3p\downarrow$	-0.04523677	-0.33945116	-0.04339378	0.56101911	0.58787476	
$j =$	12	13	14	15		
$i = 3d_{2g}\uparrow$	0.42869748	0.54437294	0.17218644	0.00423051		
$3d_{2g}\downarrow$	0.45161927	0.52353308	0.17334109	0.00352357		
$3d_{e_g}\uparrow$	0.39813342	0.57281534	0.16893942	0.00537533		

fields where a slightly perturbed free ion  $^3F$  function is very appropriate. The results, reported in the following section, will indicate that our cubic field is not of sufficient strength to really justify the use of the strong field approximation. "Intermediate" crystalline field wave functions are normally written as multiconfiguration wave functions. While one could obtain a variationally determined best set of one-electron functions for the construction of a multiconfiguration wave function, this is much more complicated than the Hartree-Fock formalism where one applies the variational principle to a single configuration. We have thus restricted ourselves to the strong field, single configuration case. The single determinant function (note that not all single configuration functions are single determinants) used by us is also desirable because of the particularly simple form taken by the results.

Additional comparatively minor objections can be raised against our model. For example, while wave function separability [see Eq. (1)] is rigorously correct for spherical environments, this is not so for cubic environments (as is discussed by Koster<sup>20</sup>).

We have seen that computational considerations have played a major role in the choice of our model. Heavy reliance was placed on using programs previously written for the IBM 704. Most of the machine computation was done on the IBM 704 computer at AVCO.

### III. RESULTS

The eigenvectors ( $C_{ij}$ 's), which define the one-electron radial functions ( $U_i$ 's) in terms of the basis functions ( $R_j$ 's), appear in Table II. Table III contains the one-electron energies ( $\epsilon_i$ 's), the one-electron nuclear potential +kinetic energies ( $K_i$ 's), the radial  $3d$  cubic field integrals [ $V^4(i)$ 's], the Slater  $F^k(3d,3d)$  integral and the

total energy of the ion both with and without the cubic field. These quantities are accurately evaluated for the functions defined in Table II. For definitions and comparison with calculated free ion results (see I).

Comparison with the calculated free ion  $^3F$  state total energy of  $-3012.04$  ry indicates that the present admixture of  $^3F$  and  $^3P$  character has led to a total energy for the ion in the cubic field which is higher by  $0.09$  ry. The cubic field has stabilized the ion by  $0.028$  ry, while invoking the strong field configuration has introduced an energy loss which is approximately four times this size. This suggests, as discussed earlier, that

TABLE III. The one-electron energies ( $\epsilon_i$ 's), one-electron nuclear potential +kinetic energies ( $K_i$ 's), cubic  $V^4(3d)$  integrals  $F^k(3d,3d)$ 's and total energy for  $Ni^{+2}$ .

	Spin $\uparrow$	Spin $\downarrow$
$\epsilon_{1s}$	-612.6610 ry	-612.6615 ry
$\epsilon_{2s}$	-77.3125	-77.1590
$\epsilon_{3s}$	-11.3667	-10.9695
$\epsilon_{2p}$	-67.3657	-67.2179
$\epsilon_{3p}$	-8.2127	-7.7290
$\epsilon_{t_{2g}}$	-2.8026	-2.6421
$\epsilon_{e_g}$	-3.0722	...
$K_{1s}$	-783.7034	-783.7037
$K_{2s}$	-192.2279	-192.2922
$K_{3s}$	-74.4763	-74.3795
$K_{2p}$	-190.8907	-190.9860
$K_{3p}$	-70.7004	-70.4597
$K_{t_{2g}}$	-59.7699	-59.1443
$K_{e_g}$	-60.5416	...
$V^4(t_{2g})$	0.00612	0.00655
$V^4(e_g)$	0.00558	...
$F^0(t_{2g},t_{2g})$	1.9695	1.9358
$F^2(t_{2g},t_{2g})$	0.9086	0.8887
$F^4(t_{2g},t_{2g})$	0.5647	0.5515
$F^0(e_g,e_g)$	2.0128	...
$F^2(e_g,e_g)$	0.9352	...
$F^4(e_g,e_g)$	0.5826	...
Total energy with cubic field terms =		-3011.9518 ry
Total energy without cubic field terms =		-3011.9234 ry

<sup>20</sup> G. F. Koster, Quarterly Progress Report, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, January, 1960 (unpublished), Vol. 35, p. 3, and to be published.

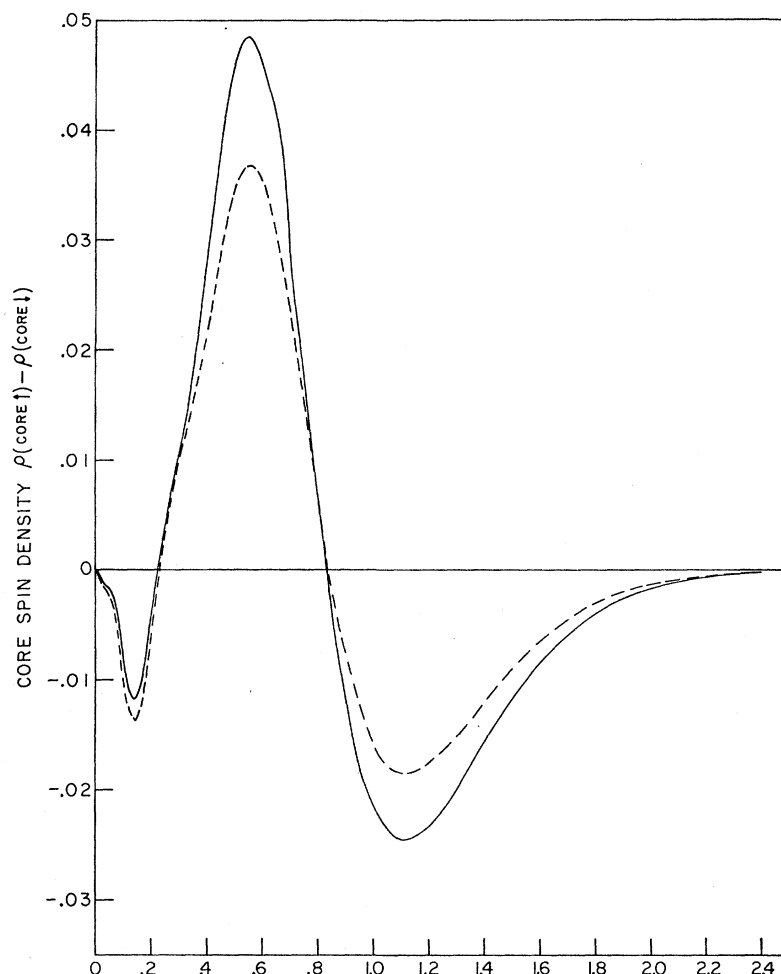


FIG. 1. The net radial spin density of the argon-like core for spin polarized (free ion)  $\text{Ni}^{2+}$  (dashed curve) and spin polarized  $\text{Ni}^{2+}$  in a cubic field (solid curve).

the choice of the strong field configuration was not entirely appropriate.

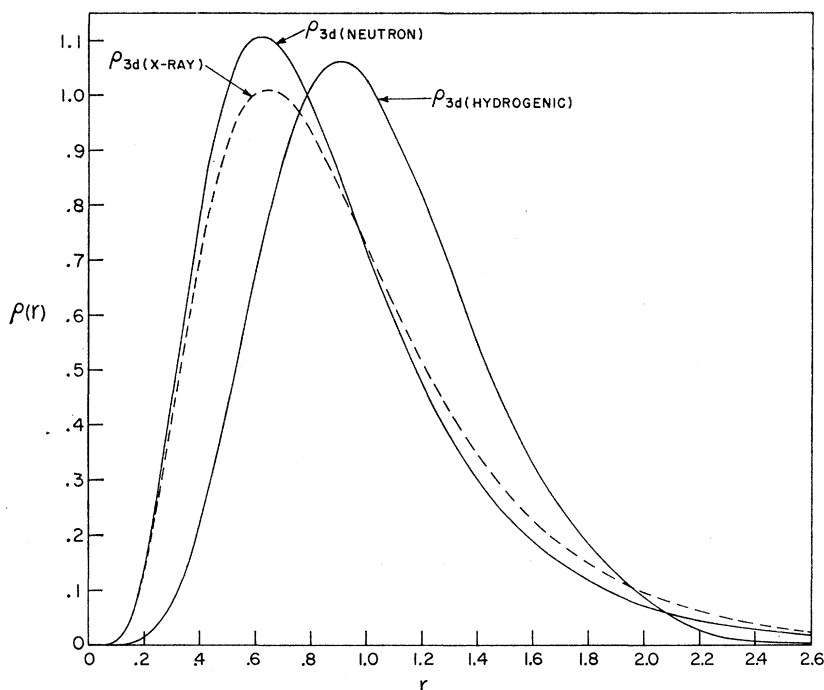
In standard crystal field theory, a single  $U_{3d}(r)$  is relied on and this function is assumed to be common to ion states with differing numbers of  $t_{2g}$  and  $e_g$  electrons. This leads to a crystalline field splitting parameter  $Dq$  which equals  $\frac{1}{3}V^4(3d)$  when we approximate the crystalline environment by the point charge potential.  $Dq$  is simply one-tenth of the energy contributed by the crystalline field when a  $t_{2g}$  electron is replaced by an  $e_g$  electron. From Table III we see a 15% variation in  $V^4(3d)$  integrals; in other words, reliance on a single  $U_{3d}(r)$ , and in turn on its  $V^4(3d)$ , is not fully justified. We should add that it is even worse to assume common  $U_{3d}(r)$ 's for two different multielectron states where one state has one more  $t_{2g}$  (and one fewer  $e_g$ ) orbital than the other. (This observation is based on our experience with Hartree-Fock solutions and not on a second calculation.)

The differences in  $\epsilon_i$ 's and  $K_i$ 's for electrons of differing spin are greater than in the free  $\text{Ni}^{++}$  case (I). The cubic field has expanded the six "paired"  $t_{2g}$  electrons

and has compressed the two unpaired  $e_g$  electrons. These two electrons are then better able to produce spin polarization effects via the exchange interaction with electrons of parallel spin. Noting that  $K_i$ 's of larger magnitude indicate relatively contracted  $U_i(r)$ 's, we see that the  $U_{1s\uparrow}$ ,  $U_{2s\uparrow}$  and  $U_{2p\uparrow}$  are expanded and the  $U_{3s\uparrow}$ ,  $U_{3p\uparrow}$ , and  $U_{t_{2g}\uparrow}$  are contracted relative to their counterparts of opposite spin. In other words, the  $U_i(r)$ 's of majority spin have converged on one another; this is as one would expect since the exchange interaction is attractive. This convergence is similar to that observed in the spin polarized free ion calculation (I) and is *not* in toward the nucleus. This produces a region with a net spin opposite to that of the whole ion in the immediate vicinity of the nucleus. This is indicated by Fig. 1 which shows the net radial spin density of the argon-like core, i.e.,;

$$\begin{aligned} \rho_A(r) &= \sum_{i=\text{argon core}} 2(m_s)_i [U_i(r)]^2 \\ &= \sum_{\text{spin}\uparrow} [U_i(r)]^2 - \sum_{\text{spin}\downarrow} [U_i(r)]^2. \quad (8) \end{aligned}$$

FIG. 2. Spin polarized 3d charge density,  $\rho_{3d}(\text{x ray})$ ; spin density,  $\rho_{3d}(\text{neutron})$ ; and a hydrogenic 3d charge density,  $\rho_{3d}(\text{hydrogenic})$  for  $\text{Ni}^{+2}$ .



Negative values indicate regions where a negative spin is associated with the electron distribution. Included in Fig. 1 is the  $\rho_A$  of the free ion calculation reported in I. We see that the polarization is greater in the case of the present calculation.

Form factor measurements provide us with direct information about electron densities. We will now discuss the 3d electron densities appropriate for the calculation of one-electron scattering factors for x-ray and neutron diffraction, i.e., the appropriate  $\rho_{3d}$ 's appearing in the spherical part of the form factor, given by

$$f_{3d}(k) = \int_0^\infty \rho_{3d}(r) \frac{\sin kr}{kr} dr, \quad (9)$$

where the  $k$  is  $4\pi \sin\theta/\lambda$ . The total ion coherent x-ray scattering factor consists of an argon core contribution [put a plus sign in the right-hand side of Eq. (8) and insert the resultant into Eq. (9)] plus a 3d shell contribution. The 3d contribution can be described in terms of an average one-electron 3d charge density, i.e.;

$$\rho_{3d}(\text{x ray}) = \frac{1}{8} (3[U_{t_{2g}\uparrow}]^2 + 3[U_{t_{2g}\downarrow}]^2 + 2[U_{e_g\uparrow}]^2). \quad (10)$$

Neutrons, on the other hand, interact only with the ion's spin density and dividing this density by the number of unpaired spins of the ion, we can define;

$$\rho_{3d}(\text{neutron}) = [U_{e_g\uparrow}]^2 + \frac{1}{2} \{3[U_{t_{2g}\uparrow}]^2 - 3[U_{t_{2g}\downarrow}]^2\} + \frac{1}{2}\rho_A. \quad (11)$$

The two densities are identical in the conventional Hartree-Fock description where the three  $U_{3d}$ 's are identical and  $\rho_A$  equals zero. The present calculated

values for these appear in Fig. 2. Included is the charge density for a hydrogenic function that would yield an almost identical multiplet spectrum (i.e., its  $F^2(3d,3d)$  integral matches the average of those in Table III). Note that  $\rho_{3d}(\text{x ray})$  and  $\rho_{3d}(\text{neutron})$  can neither be well approximated by a hydrogenic  $\rho$  nor brought into each other simply by scaling.<sup>21</sup>

Various relevant 3d scattering factors and the argon core and total ion coherent x-rays scattering factors appear in Table IV. Figure 3 depicts  $f_{3d}(\text{neutron})$ ,  $f_{3d}(\text{x ray})$  and a form factor for the hydrogenic density of Fig. 2. Comparison with form factors<sup>12</sup> obtained from a restricted Hartree-Fock  $\text{Ni}^{++}$  function<sup>11</sup> shows that the two argon core scattering factors agree closely, with the result for the present calculation lying higher by as much as 0.005 electron unit (e. u.), (indicating a slight argon core charge density contraction). The  $f_{3d}(\text{x ray})$  and the restricted  $f_{3d}$  also agree closely with the former lying lower by as much as 0.0008 e. u. This differs with the free ion spin polarized  $f_{3d}(\text{x ray})$  which lay higher than the restricted  $f_{3d}$ . This is due to the cubic field which acted to expand the  $t_{2g}$  functions and contract the  $e_g$ 's. This coupled with the greater occupancy of the  $t_{2g}$  type caused a slightly expanded  $\rho_{3d}(\text{x ray})$  and in turn a lower  $f_{3d}(\text{x ray})$ .

Of greater interest is the substantial difference between  $f_{3d}(\text{neutron})$  and  $f_{3d}(\text{x ray})$ . This is twice the effect observed for the spin polarized free ion calculation and

<sup>21</sup> In I,<sup>3</sup> the inability to use scaling and the poor approximation of using hydrogenic 3d functions was discussed. See Freeman and Watson<sup>10</sup> for an indication of the effect of using a hydrogenic 3d function in a calculation for the well-known crystalline field splitting parameter  $Dq$ .

TABLE IV. Form factors for spin polarized  $\text{Ni}^{++}$  in a cubic field, in c.u.

$\sin\theta/\lambda$	$f_{t_{2g}\uparrow}$	$f_{t_{2g}\downarrow}$	$f_{e\uparrow}$	$f_{3d(\text{x ray})}$	$f_{3d(\text{neut.})}$	$f_{\text{argon core}}$	$f_{\text{total}}$
0.00	1.0000	1.0000	1.0000	1.0000	1.0000	18.00	26.00
0.05	0.9795	0.9787	0.9804	0.9794	0.9818	17.83	25.67
0.10	0.9213	0.9186	0.9248	0.9212	0.9298	17.56	24.93
0.15	0.8347	0.8292	0.8416	0.8344	0.8514	17.04	23.72
0.20	0.7314	0.7234	0.7416	0.7309	0.7562	16.36	22.21
0.25	0.6228	0.6128	0.6355	0.6222	0.6540	15.56	20.54
0.30	0.5177	0.5066	0.5316	0.5170	0.5525	14.70	18.84
0.4	0.3372	0.3267	0.3503	0.3366	0.3712	12.92	15.61
0.5	0.2051	0.1973	0.2148	0.2046	0.2313	11.28	12.92
0.6	0.1160	0.1111	0.1219	0.1156	0.1328	9.92	10.84
0.7	0.0592	0.0566	0.0621	0.0589	0.0679	8.85	9.32
0.8	0.0248	0.0238	0.0257	0.0246	0.0277	8.05	8.25
0.9	0.0050	0.0050	0.0049	0.0050	0.0044	7.44	7.48
1.0	-0.0055	-0.0052	-0.0062	-0.0056	-0.0080	6.95	6.99
1.1	-0.0106	-0.0100	-0.0114	-0.0106	-0.0138	6.55	6.47
1.2	-0.0124	-0.0119	-0.0132	-0.0124	-0.0156	6.19	6.09
1.3	-0.0125	-0.0120	-0.0132	-0.0125	-0.0154	5.84	5.74
1.4	-0.0117	-0.0113	-0.0122	-0.0117	-0.0141	5.51	5.42
1.5	-0.0104	-0.0101	-0.0109	-0.0104	-0.0123	5.17	5.09

an order of magnitude greater than current neutron diffraction experimental accuracy. Three-eighths of this difference is due to the difference between  $f_{e_g}$  and  $f_{3d(\text{x ray})}$ ; a similar fraction is due to the spin polarized  $t_{2g}$  electrons and the remaining quarter is due to the argon core contribution. In other words, spin polarization of "paired" electrons is the larger source of the difference and the charge density associated with the magnetic form factor ( $\rho_{3d(\text{neutron})}$  of Fig. 2) does not closely resemble that of any of the  $3d$  orbitals. At this point we must stress a point made earlier, namely that the results of this section are not to be interpreted as a prediction of experimental results, but rather as an

indication of some effects related to experiment. In the case of form factors, our very crude model does not produce the expansion of  $U_{3d}(r)$ 's for iron series ions in salts which are suggested by experimental  $F^k(3d,3d)$  integrals and spin-orbit coupling parameters and which have been observed in absolute  $f_{3d(\text{neutron})}$  measurements<sup>4</sup> for  $\text{Mn}^{++}$ . The effect on the magnetic form factor predicted by our calculation is of the same order of magnitude as the effect of function expansion, but of opposite direction. This is seen by an analysis (using optical absorption data) similar to that carried out earlier<sup>2</sup> for  $\text{Mn}^{++}$ . The principle conclusion to be drawn from Table IV is that for an ion with paired  $3d$  electrons, such as  $\text{Ni}^{++}$ , it is dangerous to interpret experimentally observed magnetic form factors as direct Fourier transforms of  $3d$  charge densities.

We have only had occasion to discuss the spherical part of the form factor [see Eq. (9)], whereas we should emphasize that the actual form factor will not be a smooth curve but will show "bumps," as was discussed by Weiss and Freeman.<sup>5</sup> These can be calculated according to the prescription of these authors.

Let us now consider the Fermi contact hyperfine parameter<sup>8</sup> ( $\chi$ ) which occurs in an  $\mathbf{S} \cdot \mathbf{I}$  hyperfine interaction ( $\mathbf{I}$  being the nuclear spin). For a Hartree-Fock function it takes the form;

$$\chi = \frac{1}{S} \left\{ \sum_{\text{spin}\uparrow} \left[ \frac{U_i(r)}{r} \right]^2 - \sum_{\text{spin}\downarrow} \left[ \frac{U_i(r)}{r} \right]^2 \right\}_{r=0}, \quad (12)$$

where the subscript  $r=0$  denotes that the term is to be evaluated for that value of  $r$ . Only  $s$  functions contribute to  $\chi$ . While the common isotopes of Ni have no nuclear spin, we can rely on the observation of Abragam, Horowitz, and Pryce that  $\chi$ , for the doubly ionized iron series ions in salts, has a roughly constant value of  $\sim 3.0$  a.u. Table V lists the contributions to  $\chi$  from the  $1s$ ,  $2s$ , and  $3s$  shells and the total  $\chi$ 's for the present

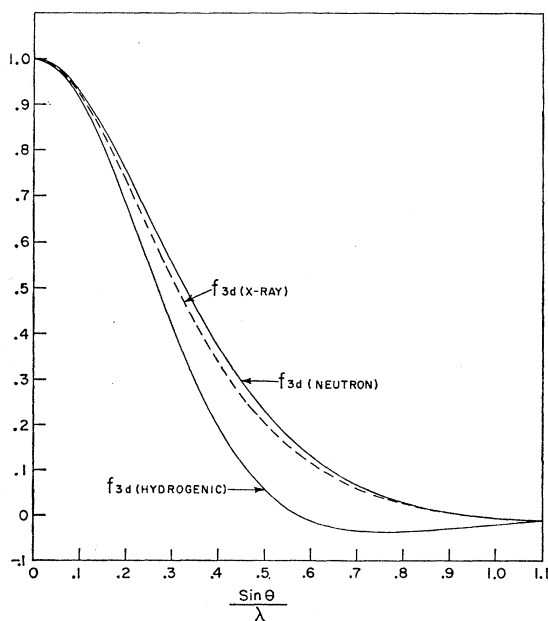


FIG. 3. Magnetic form factor,  $f_{3d(\text{neutron})}$ ;  $3d$  x-ray form factor,  $f_{3d(\text{x ray})}$ ; and a  $3d$  hydrogenic form factor,  $f_{3d(\text{hydrogenic})}$  for the corresponding electron densities of Fig. 2.

calculation and the earlier free ion spin polarized calculation (I). Again we see that the spin polarization is generally greater in the present calculation. Despite this we obtain a *smaller*  $\chi$ , (note the reversal of core spin densities near the nucleus in Fig. 1) which is in better agreement with experiment than the free ion value by about 20%. This is due to the comparatively large change in the 3s shell contribution. Because of the competition between terms of differing sign, the value of  $\chi$  is quite sensitive to 3s function behavior which is in turn comparatively sensitive to 3d behavior. Marshall<sup>22</sup> has made similar observations. Effects beyond the Hartree-Fock formalism may also be expected to appreciably perturb the value of  $\chi$ . Therefore, we would not be surprised if the good value of  $\chi$  was accidental rather than due to some fundamental "rightness" of the calculation.

In concluding the discussion of  $\chi$  we should note that the calculation relied on a rather limited basis set (the  $R_j$ 's) which was chosen for its ability to describe the over-all properties of the ion wave function and not details of the function near the nucleus. We are investigating the possible effect of the limited basis set on the computed value of  $\chi$ .

Another hyperfine parameter is  $\langle r^{-3} \rangle$  which is the expectation value of  $r^{-3}$  for the 3d functions. This parameter is normally related to the spectra by assuming a restricted Hartree-Fock description of the ion. The calculated values of  $\langle r^{-3} \rangle$  are 7.10, 6.91, and 7.32 a.u. for the  $t_{2g\uparrow}$ ,  $t_{2g\downarrow}$ , and  $e_{g\uparrow}$  orbitals, respectively. These have little relation to experimental values because of the failure of our model to produce the earlier mentioned 3d expansion. Interpolating from Abragam, Horowitz, and Pryce's tables we obtain experimental  $\langle r^{-3} \rangle$ 's of 6.3 a.u. for a neutral  $(3d)^8(4s)^2$  Ni atom and 5.8 a.u. for  $\text{Ni}^{++}$  in a salt. Due to the absence of the 3d expansion one would expect better agreement of our values with the neutral Ni value (which represents a smaller perturbation on the  $\text{Ni}^{++}$  3d functions than does the crystalline environment of the salt).

<sup>22</sup> W. Marshall (private communication), and also see W. Marshall, Phys. Rev. **110**, 1280 (1958).

TABLE V. Calculated Fermi contact term parameters ( $\chi$ 's) for the free  $\text{Ni}^{++}$  ion and  $\text{Ni}^{++}$  in cubic field spin polarized Hartree-Fock calculations. Individual s-shell contributions are listed.

Contribution to $\chi$ from	Free $\text{Ni}^{++}$ (from I)	$\text{Ni}^{++}$ in cubic field (present calculation)
the 1s shell	-0.27 a.u.	- 0.32 a.u.
2s shell	-9.62	-10.10
3s shell	5.95	7.15
Total $\chi$	-3.94	- 3.27

#### IV. CONCLUSIONS

We have been investigating the effects predicted by a spin-polarized Hartree-Fock calculation for  $\text{Ni}^{++}$  in a crude cubic field. We made use of the strong field description of the ion, and the results suggest that such a description is not appropriate. The results of greatest interest have been those dependent on the ion's spin distribution. Those discussed were the Fermi contact hyperfine term and the magnetic form factor. The contact term  $\chi$  was smaller in magnitude than the calculated free ion result despite greater spin polarization. It was also in substantially better agreement with experiment.

Perhaps of greater interest is the 3d magnetic form factor,  $f^{3d(\text{neutron})}$ , which has a Fourier transform which resembles none of the 3d charge densities but instead represents a comparatively contracted electron distribution. The same effect was observed for the earlier spin polarized free ion calculation (I) but here it is a factor of two greater. This result suggests that for an ion like  $\text{Ni}^{++}$ , an absolute measurement of a  $f^{3d(\text{neutron})}$  cannot be directly related to a Fourier transform of a 3d orbital density.

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