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Origin of Effective Fields in Magnetic Materials*

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The origin of the effective magnetic fields at the nuclei of magnetic materials which have been determined by Mössbauer, nuclear magnetic resonance, electron paramagnetic resonance, specific heat, and nuclear polarization methods is investigated theoretically by means of the exchange polarization mechanism. Exchange-polarized iron series Hartree-Fock calculations were carried out for (a) free ions and neutral atoms, (b) ions in a (crude) crystalline field (as in a salt), and (c) spin densities and configurations which conform with energy band and neutron magnetic scattering observations for the ferromagnetic metals. The effective field data for metals, ferrites, rare-earth garnets, and salts are then discussed and it is shown that the dominant contribution to the effective field (in almost every case) arises from the (exchange) polarization of the core electrons by the spin density of the unpaired outer electrons. For the transition metals, the role of the conduction electrons is analyzed including some new contributions not previously considered. The data for ions like Fe^{3+} and Mn^{++} may be understood mainly on the basis of the core polarization term but such factors as covalent bonding, charge transfer, crystal field effects (such as distortions from cubic symmetry) must also be included. For ions like Fe^{++} and Co^{++} the (large) field due to unquenched orbital angular momentum must also be considered and several cases in which the orbital field dominates are discussed. The exchange polarization method and the accuracy of the analytic spin-polarized Hartree-Fock functions are discussed with regard to the sensitivity of the internal field to orbital descriptions, the effect of crystalline environments, and to expansion and contraction of the spin density. Each factor is investigated in detail by means of accurate exchange-polarized calculations. In conjunction with these studies a restricted Hartree-Fock calculation for Mn^{++} was carried out (and is reported as an Appendix) which is more accurate than existing calculations and indicates the accuracy of earlier analytic Hartree-Fock calculations.

I. INTRODUCTION

The Mössbauer,[1] specific heat,[2] electron paramagnetic resonance (EPR)[3–5] and nuclear magnetic resonance (NMR)[6–8] measurements have now been made on a great variety of magnetic solids, revealing the presence of large internal effective magnetic fields acting on the nuclei of these materials. These fields, when properly interpreted, can give important information about the distribution of the magnetic electrons and may yield valuable insights into the mechanism responsible for the magnetic behavior of solids.

In a large number of magnetic materials, the internal effective field is found to be negative, contrary to original expectations.[9] The origin of this negative field in ferromagnets is still not fully understood and it is the purpose of this paper to present some theoretical information and a description of some phenomena relating to this problem. Since the physical situation is less complex for free atoms and ions than for magnetic solids, we shall first discuss the former before the latter. We shall show that the overwhelming evidence indicates that the dominant term in all these cases is the contribution of the exchange polarization of the core electrons via the Fermi contact term.[10]

Fermi[10] and Fermi and Segrè[11] showed that atomic hyperfine fields could be understood to arise from the interaction of the magnetic moment of the nucleus with the electronic spin and orbital moments. Starting with the Dirac theory for the electron, Fermi found that the form of the Hamiltonian for the interaction of a nucleus with a single electron could be written as

$$H=-gg_I\mu_0\mu_N\{(8\pi/3)\delta(\mathbf{r})\mathbf{I}\cdot\mathbf{S}+r^{-3}\mathbf{I}\cdot(\mathbf{L}-\mathbf{S})+3r^{-5}(\mathbf{I}\cdot\mathbf{r})(\mathbf{S}\cdot\mathbf{r})\},\quad(1)$$

where **L**, **S**, and **I** represent, respectively, electron orbital, electron spin, and nuclear-spin angular momentum operators; μ_0 and μ_N are the Bohr and nuclear magnetons; and g and g_I are the electronic and nuclear

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[1] R. L. Mössbauer, Z. Physik **151**, 124 (1958); Naturwissenschaften **22**, 538 (1958); and Z. Naturforsch. **14a**, 211 (1959). It is almost impossible to list all the references to pertinent work in this fast developing field; only original references or those papers of immediate concern will be referred to when appropriate to the material in this paper.

[2] C. V. Heer and R. A. Erikson, Phys. Rev. **108**, 896 (1957); V. Arp, D. Edmunds, and R. Petersen, Phys. Rev. Letters **3**, 212 (1959).

[3] A. Abragam, J. Horowitz, and M. H. L. Pryce, Proc. Roy. Soc. (London) **A230**, 169 (1955); referred to hereafter as AHP.

[4] W. Low, *Paramagnetic Resonance in Solids* (Academic Press, Inc., New York, 1960).

[5] J. S. VanWieringen, Discussions Faraday Soc. **19**, 118 (1955).

[6] A. C. Gossard and A. M. Portis, Phys. Rev. Letters **3**, 164 (1959) and J. Appl. Phys. **31**, 205S (1960).

[7] C. Robert and J.-M. Winter, Compt. rend. **250**, 3831 (1960); J. I. Budnick, L. J. Brunner, E. L. Boyd, and R. J. Blume, Bull. Am. Phys. Soc. **5**, 491 (1960); A. C. Gossard, A. M. Portis, and W. J. Sandle, J. Phys. Chem Solids (to be published).

[8] Y. Kōi, A. Tsujimura and Y. Yukimoto, J. Phys. Soc. Japan **15**, 1342 (1960); Y. Kōi, A. Tsujimura and T. Kushida, *ibid.* **15**, 2100 (1960).

[9] W. Marshall, Phys. Rev. **110**, 1280 (1958).

[10] E. Fermi, Z. Phys. **60**, 320 (1930) and for a more recent coverage see H. Kopfermann, *Nuclear Moments* (Academic Press, Inc., New York, 1958).

[11] E. Fermi and E. Segrè, Rend. reale accad. nazl. Lincei **4**, 18 (1933); E. Fermi and E. Segrè, Z. Physik **82**, 729 (1933).

spectroscopic splitting factors. The delta-function term, which is called the Fermi contact term, is nonzero only for s electrons, for which case the last two terms, which are dipolar interaction terms, are zero.

The energy shift resulting from the hyperfine interaction Hamiltonian of Eq. (1) may be interpreted as arising from the interaction of an effective magnetic field, H_e, with the nuclear-spin magnetic moment. For the contact part of the Hamiltonian the field is of the form

$$\mathbf{H}_e = (8\pi/3) g\mu_0 \mathbf{S} |\psi(0)|^2, \tag{2}$$

where $\rho(0) = |\psi(0)|^2$ is the s electron's density at the nucleus.

Historically, the Fermi contact term has been generally accepted as providing the explanation of the origin of the hfs observed in free atom spectra and molecular beam measurements and more recently has been used to explain the observed Knight shifts in metals.[12] In all these systems the density at the nucleus of an outer *unpaired* s electron is considered to be responsible for the observed effective magnetic field. For systems such as those considered in this investigation (like Mn^{++} in the $3d^5$, ^6S configuration) with no unpaired s electrons but with a net spin, no hyperfine fields are expected to exist. The origin of the large hyperfine fields actually observed for these cases remained a puzzle until recently, when it was suggested by Sternheimer[13] that the polarization of the core electrons by the spin of the outer electrons would produce a net unpaired spin density at the nucleus and hence an H_e via the Fermi contact term. Wood and Pratt[14] and Heine,[14] in independent investigations, estimated the magnitude of the effect and showed that reasonable agreement with experiment could be achieved by this mechanism.

We have been investigating the contribution of "paired" electrons to the magnetic properties of solids utilizing the spin or exchange polarization mechanism in the Hartree-Fock (H-F) formalism.[15–17] Several effects have been studied. (1) Computations for the contribution of the "paired" electron spin density to an ion's neutron magnetic form factor suggest that the contribution is observable,[15] a suggestion which has been supported by a recent neutron diffraction investigation for NiO.[18] Further, in these calculations the H_e arising from the "paired" spin density of the core s electrons was found to be in good agreement with experiment but sensitive to the ion's environment.[17] These results confirmed, by means of accurate H-F calculations, the importance of the exchange polarization mechanism as the origin of the observed H_e. (2) The contribution of exchange polarization to an ion's magnetic interaction with neighboring ions and with its own conduction electrons in a solid was found to have important consequences for the magnetic behavior of rare-earth ions.[19] It was found that these ions carry a negative spin density in their outer reaches and it was shown that these rare-earth ions may appear to their neighbors as having *negative* spins (i.e., antiparallel to the $4f$-spin direction). (3) A preliminary report was given,[20] based on extensive exchange polarized Hartree-Fock calculations, which showed that the dominant contribution to the observed negative H_e in ferromagnets was due to the polarization of the core s electrons. In this paper we are reporting in detail our investigations of the effective fields for the iron transition elements and the role of this contribution in explaining H_e in a variety of materials.

In the sections which follow we will first discuss the spin or exchange polarized Hartree-Fock formalism, Sec. II, and the method of carrying out the calculations. Application is then made in Sec. III to the case of free divalent ions and the results of these calculations will be presented. Due to the lack of experimental data for the free ions we will make comparisons with some data for these ions in salts. Following the section on the divalent

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[12] See e.g. W. D. Knight, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1956), Vol. 2, p. 93.

[13] Fermi and Segrè[11] first considered the contact term associated with a closed s shell in their configuration-interaction estimate of H_c for the 6s shell of Tl. There have been other estimates of the H_c associated with an outermost s shell such as that of Koster [G. F. Koster, Phys. Rev. **86**, 148 (1952)] for Ga and of Abragam, Horowitz, and Pryce[3] for Mn^{++}. Sternheimer [R. M. Sternheimer, Phys. Rev. **86**, 316 (1952)] was the first to investigate the H_c associated with *all* core s shells in his perturbation treatment of Cl. Since that time there have been perturbation theory estimates of H_c for N by Das and Mukherjee [T. P. Das and A. Mukherjee, J. Chem. Phys. **33**, 1808 (1960)] and Blinder [S. M. Blinder, Bull. Am. Phys. Soc. **5**, 14 (1960)], and for Li and Na by Cohen, Goodings, and Heine [M. Cohen, D. A. Goodings, and V. Heine, Proc. Phys. Soc. (London) **73**, 811 (1959)]. Nesbet [R. K. Nesbet, Phys. Rev. **118**, 681 (1960)] has studied the Li hyperfine structure with an extensive configuration interaction investigation. By concentrating on improving the wave function in the immediate vicinity of the nucleus he obtained the best H_c (but not the best total energy) to date. As Nesbet has emphasized, "singly substituted" configuration interaction is just another way to build the same physical behavior into the wave function. Heine[14] and Wood and Pratt[14] made estimates of the effect of spin polarization in the Hartree-Fock formalism. Computational considerations kept them from rigorously solving the spin-polarized Hartree-Fock equations. The first spin-polarized Hartree-Fock solutions were those of Sachs [L. M. Sachs, Phys. Rev. **117**, 1504 (1960)] and Nesbet and Watson [R. K. Nesbet and R. E. Watson, Ann. Phys. **9**, 260 (1960); hyperfine effects were not considered in this paper] for Li. The subsequent spin-polarized Hartree-Fock investigations are listed, where appropriate, in what follows.

[14] J. H. Wood and G. W. Pratt, Jr., Phys. Rev. **107**, 995 (1957); V. Heine, *ibid.* **107**, 1002 (1957).

[15] R. E. Watson and A. J. Freeman, Phys. Rev. **120**, 1125 (1960).

[16] In addition to the discussion appearing in reference 15 various aspects of the problem are discussed in J. C. Slater, Phys. Rev. **82**, 538 (1951); P.-O. Löwdin, *ibid.* **97**, 1474, 1490, and 1509 (1955); R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 312 (1955); G. W. Pratt, Jr., Phys. Rev. **102**, 1303 (1956); B. H. Chirgwin, *ibid.* **107**, 1013 (1957); P.-O. Löwdin, Revs. Modern Phys. **32**, 328 (1960); R. McWeeny, *ibid.* **32**, 335 (1960); R. K. Nesbet, *ibid.* **33**, 28 (1961); W. Marshall (to be published); P.-O. Löwdin, Technical Note No. 48, Quantum Chemistry Group, Uppsala University, 1960 (unpublished).

[17] R. E. Watson and A. J. Freeman, Phys. Rev. **120**, 1134 (1960).

[18] H. Alperin, Phys. Rev. Letters **6**, 55 (1961).

[19] R. E. Watson and A. J. Freeman, Phys. Rev. Letters **6**, 277, 388(E) (1961).

[20] A. J. Freeman and R. E. Watson, Phys. Rev. Letters **5**, 498 (1960); R. E. Watson and A. J. Freeman, J. Appl. Phys. **32**, 118S (1961).

ions we will report, in Sec. IV, H_e, as calculated for the neutral iron series atoms, for which experimental data exist. From this section we go on in Sec. V to discuss in detail the case of an Fe atom in the metal, and considering the various sources to an effective magnetic field seen by the nucleus, we make comparisons with the results observed by NMR, Mössbauer, and other experiments for the ferromagnetic metals. In Sec. VI we analyze and discuss some of the remaining experimental data for magnetic atoms in salts in the light of an exchange-polarized H-F calculation for Fe^{3+} and the theoretical ideas reported in the earlier sections, and in Sec. VII we present some conclusions. In Appendix I we calculate the expectation value of S^2 (S= total spin angular momentum) for some of the single-determinant wave functions and discuss the dependence of the hyperfine fields on these quantities. The sensitivity of H_e to the accuracy of our solutions is discussed in Appendix II and we report in Appendix III the results of a conventional H-F calculation for Mn^{++} which is more accurate than any reported previously, and indicates the accuracy of an earlier series[21] of conventional Hartree-Fock calculations for the iron series ions.

II. EXCHANGE POLARIZATION IN THE HARTREE-FOCK METHOD

In the usual applications of the H-F method one assumes a single Slater determinant with one-electron functions which are solved for variationally by following a self-consistent field (SCF) procedure which minimizes the total energy of the system with respect to small variations of the one-electron functions.[22] There are several restrictions[23] which are associated with the conventional application of the method; the one that concerns us here involves the requirement that electrons in the same atomic shell but differing in spin (m_s quantum number) have the same radial wave functions. For systems with a net spin (say ↑) this restriction is no longer valid since the electrons of ↑ spin experience different exchange interactions than do the electrons of ↓ spin. Relaxing this restriction in the H-F calculations leads to different charge distributions for the orbitals in the same shell but differing in spin and hence to a spin density, $|\psi_\uparrow(0)|^2-|\psi_\downarrow(0)|^2$, for the closed s-electron shells which is now nonvanishing. This difference is the origin of the nonzero Fermi contact interaction for "paired" s-electron systems and a convenient measure of this is given by[3]

$$\chi=\frac{4\pi}{\mathcal{S}}\sum_{s\text{ shells}}\{\rho_\uparrow(0)-\rho_\downarrow(0)\},\tag{3}$$

where $\mathcal{S}$ denotes the number of unpaired electrons. With χ given in atomic units (a.u.), H_e is found in gauss by using the conversion factor 1 a.u. $=4.21\times10^4$ gauss.

The calculations which we are reporting have been done using SCF analytic techniques.[24] Normalized analytic radial functions, $U_i(r)$'s, are obtained as solutions of the Hartree-Fock radial equations. The $U_i(r)$'s have have the form:

$$U_i(r)=\sum\nolimits_j C_{ij}R_j(r).\tag{4}$$

Their normalization condition is

$$\int_0^\infty |U_i(r)|^2dr=1,\tag{5}$$

and the basis functions, R_j, are of the form:

$$R_j(r)=N_jr^{(l+A_j+1)}e^{-Z_jr},\tag{6}$$

where l is the one-electron angular momentum quantum number appropriate for the one-electron orbital of which $U_i(r)$ is the radial part. The N_j is a normalization constant and is expressible in terms of the other parameters, i.e.,

$$N_j=\left\{\frac{(2Z_j)^{2l+2A_j+3}}{(2l+2A_j+2)!}\right\}^{\frac{1}{2}}.\tag{7}$$

$U_j(r)$'s of common l value are constructed from a common set of $R_j(r)$'s. Except when otherwise noted, the basis sets [i.e., the $R_j(r)$'s] used here are those used in previous conventional Hartree-Fock calculations.[21] In the interest of conserving space we will, for the most part, supply neither the basis sets used nor the resultant eigenvectors (i.e., the C_{ij}'s).

Given the basis sets, i.e., the $R_j(r)$'s, the problem is reduced to solving the Hartree-Fock integro-differential equations for the eigenvectors (the C_{ij}'s) and their eigenvalues. This is done by straightforward matrix diagonalization and manipulation and avoids the problems of numerical accuracy inherent in the integrations of the numerical H-F method. The problem of basis sets is however always associated with the analytic Hartree-Fock method. First there is the question of the size of the

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[21] R. E. Watson, Phys. Rev. **118**, 1036 (1960); **119**, 1934 (1960); Technical Report No. 12, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, 1959 (unpublished).

[22] See, e.g., D. R. Hartree, *The Calculation of Atomic Structure* (John Wiley & Sons, Inc., New York, 1957).

[23] See our discussion in reference 15 and that of Löwdin, Nesbet, and Pratt, in reference 16.

[24] The analytic approach to solving Hartree-Fock equations has been developed by many workers. C. A. Coulson [Proc. Cambridge Phil. Soc. **34**, 204 (1938)] appears to have been the first to have used an expansion technique in a molecular problem, while C. C. J. Roothaan [Revs. Modern Phys. **23**, 69 (1951)] presented the approach in a particularly desirable form for closed-shell molecules. Nesbet, with his symmetry and equivalence restrictions, extended the method to nonclosed shells and emphasized its use for atomic cases [see reference 16 and also Quarterly Progress Reports No. 15, January, 1955, p. 10; No. 16, April, 1955, p. 38 and p. 41; No. 18, October, 1955, p. 4, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, Massachusetts (unpublished)]. Nesbet's approach was modified in the course of calculations by L. C. Allen, R. E. Watson, and R. K. Nesbet. Recently C. C. J. Roothaan [Revs. Modern Phys. **32**, 179 (1960)] has extended his formalism to cover the nonclosed shell case for the conventional restricted Hartree-Fock method where nonzero off-diagonal Lagrange multipliers occur. S. Huzinaga [Phys. Rev. **120**, 866 (1960); **122**, 131 (1961)] has extended Roothaan's formalism further.

set. A small set is desirable because of economy in computer time and retains the advantages of wave functions of analytic form. These advantages come from the ease, accuracy, and convenience with which matrix elements can be obtained if the functions are in analytic form. Large basis sets allow greater accuracy of solution (*providing* that we do not have too many basis functions which are too much alike, for then one finds it difficult to obtain accurate matrix diagonalization). With the basis sets used here we have a situation which is a compromise between the two extremes.

In practice, a spin or exchange polarized Hartree-Fock calculation consists of starting with a conventional (or restricted) single-determinant[25] H-F function and doing an SCF variational calculation in which the restraint, that one-electron orbitals differing only in m_s value be the same, has been relaxed. The resultant many-electron function is an approximate but *not* exact spin (S^2) eigenfunction, a matter which is discussed in Appendix I. This is so because the filled electron shells are no longer "closed," i.e., because of different one-electron radial functions for differing m_s values, the filled shells no longer make pure singlet contributions to the ion's spin behavior. Calculations for properly (spin) symmetrized, m_s unrestricted, H-F functions[26] for iron series atoms are well beyond current computational capabilities. An alternate, and inferior, procedure would be to symmetrize (e.g., through the use of projection operators[27]) the spin-polarized function *after* the SCF variational calculation. This also presents difficulties for many-electron systems the size of the iron series atoms and has therefore not been included here. Despite this, we should consider qualitatively what happens to χ when such symmetrization is done. The effect of applying a spin projection operator to our one-determinant wave function is to mix in determinants where one or more pairs of (opposing) orbital spins are flipped. Calculations for low-Z ions[28] show a reduction in $|\chi|$ with symmetrization and we would expect a similar reduction in the χ's given later in the paper.

Two other features of these calculations should be noted. (1) They are *nonrelativistic* Hartree-Fock calculations. Relativistic corrections to our wave functions would increase our χ by approximately 6 or 7%.[29] This is in the opposite direction to, and we believe smaller than, the above-mentioned symmetrization corrections. (2) It is well known that the Hartree-Fock formalism suffers from a serious imbalance. While it accurately treats the interelectronic interaction between electrons of parallel spin (via exchange), it inadequately handles "correlation" between electrons of antiparallel spin. Löwdin[30] and Herring [31] have stressed the importance of *including* correlation effects when treating the magnetic properties of many-electron systems. By virtue of having different orbitals for different spins some correlation has been built[32] into the spin-polarized functions but it is only a small fraction of the total effect. This lack may be serious when one uses the spin-polarized Hartree-Fock method to obtain effective fields and should be further investigated. It is perhaps the most important reason why detailed agreement between computation and experiment cannot be expected.

III. CONTACT TERM FOR DIVALENT IRON SERIES IONS

Before discussing the internal fields in magnetic solids, it is instructive to first discuss the available theoretical and experimental data for hyperfine fields in free atoms and ions since these offer a simpler system upon which to focus one's ideas and make comparisons. In this section we wish to compare the calculated spin-polarized Hartree-Fock χ's calculated for free divalent ions with experiment. Due to the lack of experimental data for the free ions, we will consider some of the data available for the ions in salts.

Abragam *et al.*,[3] reported values of χ for the divalent iron series ions based on an analysis of experimental hyperfine data for the ions in hydrated salts.[33] Their χ's are tabulated in Table I along with the contact term effective field, H_c, (where $H_c = \mathcal{S}\mu_0\chi$) and also $H_c/\mathcal{S}$ which is the field per unpaired spin. As suggested by AHP we see that χ has a roughly constant value of ~ -3 a.u., equivalent to an $H_c/\mathcal{S}$ of ~ -125 kgauss. The negative sign indicates that H_c is *antiparallel* to the net spin of the ion. The rough constancy of χ suggests that we are dealing with a polarizability which is linear in spin and this has important consequences in later discussions.[34]

Theoretical χ's resulting from our free-ion spin-polar-

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[25] On occasion the conventional Hartree-Fock function is constructed from a linear combination of several determinants in order to have a function which is an eigenfunction of L^2 and S^2. All the atomic states, for which calculations will be reported in this paper, are single-determinant cases.

[26] For an indication of what is involved for the much simpler case of atomic Li see Nesbet and Watson.[13]

[27] P.-O. Löwdin, Proceedings of the Paris Symposium on Molecular Quantum Mechanics 1958 (unpublished), p. 23. Technical Note No. 12, Quantum Chemistry Group, Uppsala University, 1958 (unpublished); Phys. Rev. **97**, 1509 (1955).

[28] This is based on Sach's experience[13] with Li and our own (to be published) with spin-polarized N.

[29] See Kopfermann, reference 10.

[30] P.-O. Löwdin (private communications and to be published).

[31] C. Herring (private discussion).

[32] The method of "different orbitals for different spins" [e.g., see P.-O. Löwdin, *Proceedings of the Nikko Symposium on Molecular Physics* (Maruzen, Tokyo, 1954), p. 13] when used with properly symmetrized many-electron wave functions has yielded as much as eighty-five percent of the "correlation energy" for simple applications (for example T. Itoh and H. Yoshizumi, J. Phys. Soc. Japan **10**, 201 (1955); J. Chem. Phys. **23**, 412 (1955)). Less than 1% of the "correlation energy" has been obtained for the larger (and unsymmetrized) systems considered in this paper.

[33] Paramagnetic resonance and optical absorption data of many workers (see AHP, reference 3, for these references). Some of these data are discussed in Sec. VI.

[34] The rough constancy of χ is based on a complicated theoretical analysis of the experimental data. For the present we accept this constancy but shall discuss it at length in Sec. VI where comparison with more recent data is made and correlated with theory.

Table I. Values of experimental hyperfine interaction χ, H_c, and $H_c/\mathcal{S}$ for the divalent iron series ions in hydrated salts.[a]

Ion	$V^{++}(3d^3)$	$Mn^{++}(3d^5)$	$Co^{++}(3d^7)$	$Cu^{++}(3d^9)$
χ (a.u.)	-2.8	-3.1	-2.5	-2.9
$H_c/\mathcal{S}$ (kgauss)	-118	-130	-105	-122
H_c (kgauss)	-354	-650	-315	-122

[a] Obtained from χ's reported by Abragam *et al.*[3]

ized Hartree-Fock calculations for Mn^{++}, Fe^{++}, and[35] Ni^{++} are listed in Table II. In addition, H_c's and individual shell contributions to the χ's are given. While being consistently more negative than the hydrated ion results of Table I, the computed χ's show the same degree of constancy as observed by AHP.

Inspection of the individual shell contributions to χ shows that the resultant H_c arises from a competition of terms of opposing sign. The 1*s* and 2*s* shells, which lie inside the 3*d*, have their majority spin electrons "attracted" outwards, leaving a region of negative spin density near the nucleus which in turn gives a negative contribution to H_c. Due to its close proximity to the 3*d* electrons one might expect the 3*s*-shell contribution to dominate, but this shell lies neither "inside" nor "outside" the 3*d*. The overlapping of the shells leads to competing tendencies and a contact contribution which is smaller than that of the 2*s* and is *positive*, i.e., the 3*s* shell acts as if it lies "outside" of the 3*d* insofar as χ is concerned. We also see that while the χ's may show a rough constancy, the individual shell contributions show a definite tendency to increase in magnitude with increasing *Z*. The fact that the individual electron shell contributions are not constant suggests that it is an oversimplification to describe the *s* electron polarizability as linear in the ion's spin. The makeup of the contact term is perhaps better seen in Table III where we list individual *s*-electron contributions to H_c for Mn^{++}. We see that an H_c of ~ -700 kgauss is made up of individual terms which are many times larger.

The competition of the terms contributing to χ and H_c suggests that these quantities are extremely sensitive to environment and over-all wave function behavior. Testing this we have obtained spin-polarized Hartree-Fock results for Ni^{++} in a crude cubic crystalline environment.[17] The environment produced a contraction in the unpaired 3*d* orbitals relative to free ion behavior. The results for the free and cubic field Ni^{++} ions are given in Table IV. We see that the individual shell contributions have increased for the cubic field case *but* that χ has decreased and that it is still larger in magnitude than the experimental value given by Abragam, Horowitz, and Pryce. These variations in total χ, as well as those in its separate contributions, are due to small variations in the 3*d* orbitals.

Table II. Theoretical contact-term χ's, H_c's, and individual *s*-shell contributions to χ as obtained for Mn^{++}, Fe^{++}, and Ni^{++}.

Ion	$Mn^{++}(3d^5)$	$Fe^{++}(3d^6)$	$Ni^{++}(3d^8)$
χ (a.u.)	-3.34	-3.29	-3.94
1*s*-shell contribution to χ	-0.16	-0.21	-0.27
2*s*-shell contribution to χ	-6.73	-7.80	-9.62
3*s*-shell contribution to χ	$+3.55$	$+4.72$	$+5.95$
H_c (kgauss)	-700	-550	-330

Table III. Individual *s*-electron contributions (in kgauss) to H_c as computed for Mn^{++}. ↑ will denote electrons with spin parallel (and ↓ antiparallel) to the 3*d*-shell spin.

		$ns\uparrow + ns\downarrow$
$1s\uparrow$	2 502 840	~ -30
$1s\downarrow$	-2 502 870	
$2s\uparrow$	226 670	-1400
$2s\downarrow$	-228 080	
$3s\uparrow$	31 210	$+740$
$3s\downarrow$	-30 470	
		Total ~ -690

We have just seen that H_c is sensitive to the ion's environment. Of equal interest is the question of sensitivity of χ to the accuracy of our Hartree-Fock solutions. Given our basis sets, our solutions are accurate to the digits reported here but there is the question of the limitations imposed by the basis sets. We have investigated this with a pair of spin polarized calculations for Mn^{++} where we have augmented the basis set (henceforth called set I) used in the computation reported above. These investigations, which are discussed in Appendix II, show that whereas the ion's total energy is insensitive, the contact field, H_c, is extremely sensitive (1) to greater variational freedom for the *s* functions near the nucleus *and* (2) to small improvements in the behavior of all the orbitals. This shows the importance of using a set of calculations of consistent accuracy so that comparisons will be meaningful. In the text we report results of calculations which consistently used basis sets equivalent to set I. In conjunction with these studies we did a conventional H-F calculation which is superior to existing calculations[36] for Mn^{++} and because of their usefulness the eigenvalues and eigenvectors are reported in Appendix III.

Table IV. Contact-term χ's (in a.u.) and individual *s*-shell contributions to χ as computed for the free Ni^{++} ion[a] and Ni^{++} in a cubic field.[b]

Contribution to χ	Free Ni^{++}	Ni^{++} in a cubic field
from the 1*s* shell	-0.27	-0.32
from the 2*s* shell	-9.62	-10.10
from the 3*s* shell	$+5.95$	$+7.15$
Total χ	-3.94	-3.27

[a] See reference 15.
[b] See reference 17.

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[35] The Ni^{++} results have appeared previously in reference 15.

[36] D. R. Hartree, Proc. Cambridge Phil. Soc. **51**, 126 (1955); R. E. Watson, reference 21; D. F. Mayers (unpublished).

TABLE V. Values of experimental hyperfine interaction χ, H_c, and $H_c/\mathcal{S}$ for the neutral iron series atoms.[a]

Atom	Sc($3d^14s^2$)	V($3d^34s^2$)	Mn($3d^54s^2$)	Co($3d^74s^2$)	Cu($3d^94s^2$)[b]
χ (a.u.)	0	−2.5	0	−1.8	−5.0
$H_c/\mathcal{S}$ (kgauss)	0	−105	0	−70	−210
H_c (kgauss)	0	−315	0	−210	−210

[a] Obtained from χ's reported by Abragam *et al.*[3]
[b] See reference 39a.

IV. CONTACT TERM FOR NEUTRAL IRON SERIES ATOMS

Abragam *et al.*,[3] have also extracted experimental contact terms for the $3d^n4s^2$ states of the free neutral iron series atoms. Their χ, H_c, and $H_c/\mathcal{S}$ values are given in Table V. We see that the χ's do not show the constancy (~ -3 a.u.) observed for the divalent ions but instead fluctuate with values ranging between zero and ~ -5 a.u. Spin-polarized Hartree-Fock calculations have been done for neutral Sc, V, Mn, Fe, Co, and Cu.[37] The resulting contact terms appear in Table VI. Included are the terms associated with the inner three s shells (called χ_3 and H_3) and with all four s shells (χ_4 and H_4) and this should be compared with Table V. The computed χ_4's do not show the fluctuations seen in experiment (Table V) but they, and the χ_3's, do show a tendency to increase with increasing Z. This will be discussed later.

Inspection of the neutral and divalent ion cases suggests that the experimentally observed fluctuations are associated with the $4s$ shells for which configuration interaction (i.e., wave-function descriptions beyond the one-electron Hartree-Fock formalism) is known to be important. Unfortunately, our spin-polarized Hartree-Fock functions are, for several reasons, inappropriate starting points for configuration interaction calculations. One reason is that erroneous and misleading results can be obtained from using improperly or inexactly symmetrized configurations (our functions are of course not exact spin states). While we are not prepared to do configuration interaction calculations, we can see under which conditions we would expect such calculations to be important. Listed in Table VII are those neutral and divalent ion "excited" configurations which differ by two one-electron orbitals from the "ground" configuration and hence are available[38] for configuration interaction. This list was obtained by inspection of Moore's[39] tables of atomic spectra. Note that no doubly substituted configurations occur for the divalent ions or for the two neutral atoms (Sc and Mn) which have zero valued experimental χ_4's. Sc and Mn are the two neutral atom cases where the computed χ_4's (of -0.5 a.u.) are roughly in agreement with experiment (allowing for the overestimation we have previously seen for χ_3's). For V and Co, for which there are one or two excited configurations, we see that the experimental χ's lie between the χ_3's and χ_4's. Configuration mixing would consist of replacing the $4s$ by other orbitals (hence reducing the $4s$ shell contribution), thus giving a χ which would be nearer to χ_3 the greater the configuration mixing. While the above effect of configuration mixing appears to cover V and Co it clearly does not cover the case of Cu where χ is larger[39a] (i.e., more negative) than the observed divalent ion value and our computed χ_3. Also, to obtain quantitative agreement with the observed V and Co χ's (using our χ_3's and χ_4's) one must demand that the excited configurations are as important as (or more than) the ground configuration. This requirement seems unreasonable. In the above discussion we have considered the effect of mixing "excited" configurations with a *given* "ground" configuration and have not considered the possibility of perturbations on the one-electron orbitals of the ground configuration. Investigations[40] of small ions, involving few configurations, have shown that the predictions of many observables are more profoundly affected by obtaining self-consistent solutions of the "ground" configuration one-electron orbitals when the orbitals "see" the presence of the "excited" configurations in the many-electron wave function than by the actual mixing (given the ground configuration) of excited configurations.[41]

The mixing of the V, Co, and Cu excited configurations will produce a radial expansion in the spin densities of the atoms. Now the spin densities are the source of the spin polarization (actually this is something of an oversimplification of the mechanism) and such expansions cause increases in χ_3's. We have observed this to be the case when comparing the free ion and cubic field results for Ni^{++} and we shall see it again in the next section. Necessary (and perhaps sufficient) to predicting the observed V, Co, and Cu hyperfine fields in terms of *limited* configuration interaction (i.e., to configurations listed in Table VII) is the inclusion of the repercussions of these excited configurations on the

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[37] Note that the $3d^94s^2$, ^2D state is not the neutral Cu ground state. Otherwise the calculations are for the ground states.

[38] In the case of configuration interaction where restricted Hartree-Fock functions are used, "excited" configurations have zero or small valued matrix elements with the "ground" configuration unless (1) they are of the same symmetry *and* (2) they differ in the assignment of two and only two one-electron orbitals [L. Brillouin, Actualités sci. industr. No. 71 (1933) and No. 159 (1934)]. We would expect this latter rule to hold, at least approximately, for the configuration interaction at hand and thus we have listed just doubly substituted configurations in Table VIII.

[39] *Atomic Energy Levels*, edited by C. E. Moore, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington D. C., 1949 and 1952), Vol. I and Vol. II.

[39a] *Note added in proof.* D. A. Goodings (private communication and to be published) has kindly informed us that the AHP value of χ for Cu has an error in sign. It is difficult to understand how such a large *positive* contact term can occur for such an atom. Perhaps further experimental work is called for to help resolve this anomaly.

[40] R. E. Watson, Ann. Phys. (to be published); R. E. Watson and A. J. Freeman (to be published).

[41] If one used a complete set of one-electron orbitals and a large scale configuration interaction investigation (which would involve substitution of inner shell orbitals) one could, of course, achieve the same effect as improving the ground configuration orbitals (i.e., letting them "see" the excited configurations).

TABLE VI. Computed neutral iron series atom contact term χ's and H's for the three inner s shells (χ_3 and H_3) and for all four s shells (χ_4 and H_4). Also included are individual s-shell contributions to χ and the $3d-ns$ radial exchange integrals[a] [$G^2(3d,ns)$]. χ's are in a.u., H's in kgauss, and $G^2(3d,ns)$'s in ry.

	Sc($3d4s^2$)	V($3d^34s^2$)	Mn($3d^54s^2$)	Fe($3d^64s^2$)	Co($3d^74s^2$)	Cu($3d^94s^2$)
χ_3	−2.90	−3.19	−3.43	−3.51	−3.62	−3.78
H_3	−119	−400	−715	−585	−453	−158
χ_4	−0.17	−0.45	−0.54	−0.59	−0.61	−0.69
H_4	−7	−57	−114	−96	−76	−29
contribution to χ from						
$1s$ shell	+0.17	+0.05	−0.03	−0.10	−0.15	−0.28
$2s$ shell	−3.01	−4.85	−6.63	−7.72	−8.77	−11.15
$3s$ shell	−0.06	+1.61	+3.23	+4.31	+3.30	+7.65
$4s$ shell	+2.73	+2.74	+2.89	+2.92	+3.01	+3.09
$G^2(3d,1s)$[a]	0.001	0.002	0.003	0.003	0.004	0.005
$G^2(3d,2s)$[a]	0.143	0.201	0.265	0.293	0.322	0.380
$G^2(3d,3s)$[a]	0.590	0.698	0.802	0.844	0.888	0.972
$G^2(3d,4s)$[a]	···	0.068	0.063	0.063	0.062	0.061

[a] Obtained from restricted Hartree-Fock calculations.[21]

ground configuration orbitals. The difficulties associated with accurate estimates of these repercussions provide a second good reason for not doing the configuration interaction computations.

Let us now consider the individual shell contributions to the neutral atom χ's. These have also been listed in Table VI. In addition we have listed the Slater exchange integrals[42] [$G^2(ns,3d)$] between the s and $3d$ orbitals which were obtained from restricted Hartree-Fock calculations.[21] The contribution from any one shell increases in magnitude with increasing Z. The $G^2(ns,3d)$'s show the same trend [except for the $4s$ shell where the $G^2(3d,4s)$ and χ contributions are roughly constant]. The trends in χ_3 and χ_4 seen in Table VI are due to a competition in effects, with the tendency of the $1s$ and $2s$ shells to become more negative (with increasing Z) dominating. Note that the $3s$ contribution in Sc is negative (and small). This is the only case in which this has been observed, whereas Marshall[43] suggested that in metals this would always be the case. The $1s$, $2s$, and $4s$ shell contributions are very roughly proportional in magnitude to the $G^2(ns,3d)$'s. Inspection of the $G^2(3s,3d)$'s would suggest that the $3s$ shell contribution should dominate. It does not. As discussed earlier this is due to the close overlapping of the $3s$ and $3d$ shells and the resulting competition between a negative and a positive contribution to χ.

The individual $4s$-electron contributions to H_c appear in Table VIII (along with the H_3's for comparison). These give some measure of the possible behavior of the $4s$ conduction bands in the metals and for this reason they have been tabulated. (The Fe data appearing here will be made use of in the next section.) It is generally thought that something under one electron (per atom) is associated with the $4s$ band in the metals. Most of this is in paired orbitals. With this in mind, the tabulated data suggest that the core electron's contact term will be very able to compete with that of the metal's $4s$ conduction band. The *individual* $4s$-electron contributions increase with increasing Z. This is, of course, not due to the exchange interaction with the $3d$ shells but is due to the variation in nuclear charge.

We have seen that χ_3 (and for that matter χ_4) becomes increasingly negative with increasing Z. A similar trend has been observed[44] in experimental Knight shift data in which there is a tendency towards positive Knight

TABLE VII. Excited configurations of the same symmetry and differing by two one-electron orbitals from the ground configuration as listed in Moore's tables[a] of atomic spectra for divalent and neutral iron series ions.

Divalent ion		V^{++}(^4F)	Mn^{++}(^6S)	Co^{++}(^4F)	Cu^{++}(^2D)
Ground configuration		$3d^3$	$3d^5$	$3d^7$	$3d^9$
Excited configurations		None	None	None	None
Neutral atom	Sc(^2D)	V(^4F)	Mn(^6S)	Co(^4F)	Cu(^2D)[b]
Ground configuration	$3d^14s^2$	$3d^34s^2$	$3d^54s^2$	$3d^74s^2$	$3d^94s^2$
Excited configurations	None	$3d^5$	None	$3d^85s$ $3d^84d$	$3d^{10}4d$ $3d^{10}5d$ $3d^{10}6d$ $3d^{10}7d$ $3d^{10}8d$ $3d^{10}9d$ $3d^{10}10d$ $3d^{10}11d$

[a] See reference 39.
[b] Note that this is not the ground state of this atom.

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[42] See E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1953), Chap. VI.

[43] W. Marshall, Proceedings of the Mössbauer Effect Conference, University of Illinois, 1960, edited by H. Frauenfelder and H. Lustig [University of Illinois Report AFOSR TN 60-698 (unpublished), p. 44].

[44] A. M. Clogston (private communication) has informed us that workers at the Bell Telephone Laboratories have observed this trend. Some of the data on which this observation rests have appeared in: W. E. Blumberg, J. Eisinger, V. Jaccarino, and B. T. Matthias, Phys. Rev. Letters **5**, 52 (1960); V. Jaccarino, M. Peter, and J. H. Wernick, *ibid.* **5**, 53 (1960); and W. E. Blumberg, J. Eisinger, V. Jaccarino, and B. T. Matthias, *ibid.* **5**, 149 (1960). We are indebted to Dr. Clogston for pointing this out and for helpful discussions.

TABLE VIII. H_3 and the individuals $4s$ contributions to H_4 for the neutral iron series atoms (in kgauss).

Atom	Sc($3d^14s^2$)	V($3d^34s^2$)	Mn($3d^54s^2$)	Fe($3d^64s^2$)	Co($3d^74s^2$)	Cu($3d^94s^2$)
$4s\uparrow$ (i.e., parallel to the $3d$-shell spin)	+937	+1328	+1750	+1850	+1951	+2155
$4s\downarrow$ antiparallel	−825	−985	−1149	−1361	−1574	−2027
H_3	−120	−400	−715	−585	−453	−158

shifts for the elements of lower Z with an increasing tendency toward negative Knight shifts for higher Z. The parallel is not exact since Knight shift measurements are made in nonzero magnetic fields and the magnetic field contributes a polarization term missing from our discussions. Investigations concerning the Knight shifts in transition metals have been carried out and these will be reported on in a forthcoming publication.[45]

Before leaving this section we wish to indicate what we think may be the two most important features of the results reported here. First, we have seen a trend to more negative χ_3's with increasing Z, a trend which parallels experimental observations. Secondly, we have seen the spin-polarized Hartree-Fock formalism fail in its predictions of χ for three of the neutral atoms. We believe that substantial improvements can be made by using limited configuration interaction *providing* that the ground-configuration orbitals "see" the excited configurations.

V. EFFECTIVE MAGNETIC FIELD IN FERROMAGNETS

In the previous sections we have observed the role of the core polarization on the hyperfine fields in divalent ions and atoms. Let us now examine the situation in the more involved case of effective fields in magnetic solids. In Table IX we summarize some of the data currently available for a number of these materials. The striking features of this table are (1) the internal fields are large (300 to 750 kgauss) and (2) for the ferromagnets (and antiferromagnets) some of these fields are negative (i.e., antiparallel to the direction of magnetization). We shall discuss the origin of these fields in ferromagnets in this section with particular regard to metallic iron and the remaining cases in the one that follows.

In the case of the iron series ferromagnetic metals the core polarization is only one of a number of contributions to the effective field (H_e) which interacts with the nuclear-spin magnetic moment. Marshall[9] first discussed these terms in an investigation of the problem of nuclear alignment. Aside from the core polarization contribution to the effective field and the local magnetic field (which is composed of the external plus demagnetizing fields and the Lorentz field) these terms included the contribution from the outer electrons as follows:

(1) the field from the contact interaction with the $4s$ electrons, polarized by the $3d$'s,

(2) the field from the contact interaction with the $4s$ electrons partly admixed into the $3d$ band,

(3) a contribution from the dipolar field of the $3d$ electrons (zero for cubic symmetry),

(4) an orbital contribution from any unquenched angular momentum of the $3d$ electrons.

(As we shall see there may be other contributions and these are discussed later in this section.) In his pioneering paper Marshall made the following estimates for the various contributions to H_e in Co: +40 kgauss for term (1), +81 kgauss for term (3) (for hexagonal Co), and +83 kgauss for term (4). Then assuming a core polarization contribution of −128 kgauss[46] and the measured H_e from specific heat data to be +219 kgauss he determined (2) to be +137 kgauss.

A. Effective Field at a Nucleus in Iron

Recent Mössbauer experiments by Hanna *et al.*,[47] showed however that the effective field at the nucleus in Fe^{57} was in fact negative, i.e., directed opposite to the direction of magnetization. These workers[47] concluded that the dominant contribution to H_e must come from the core contribution since the other sources are (or are generally presumed to be) positive. We now wish to see whether a computed core polarization will, in competition with the other terms, yield an H_e which is in agreement with experiment.

In an effort to estimate some of these positive terms, let us see what we can glean from Wood's augmented plane wave[48] and Stern's modified tight binding[49] calculations for metallic iron. Wood[48] has recently obtained a density of states curve which shows 0.4 electron in the

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[45] R. E. Watson and A. J. Freeman, Bull. Am. Phys. Soc. **6**, 166 (1961); A. J. Freeman and R. E. Watson (to be published).

[46] Since Marshall used the χ appropriate to neutral Co he was in part counting the $4s$ polarization twice. Actually the χ for Co^{++} is the correct value to use.

[47] S. S. Hanna, J. Heberle, C. Littlejohn, G. J. Perlow, R. S. Preston and D. H. Vincent, Phys. Rev. Letters **4**, 177 (1960) and S. S. Hanna, J. Heberle, G. J. Perlow, R. S. Preston, and D. H. Vincent, *ibid.* **4**, 513 (1960) first measured the effective field and its sign in Fe. See also D. E. Nagle, H. Frauenfelder, R. D. Taylor, D. R. F. Cochran and B. T. Matthias, Phys. Rev. Letters **5**, 364 (1960) for the temperature dependence of the internal field as determined by Mössbauer measurements.

[48] J. H. Wood, Phys. Rev. **117**, 714 (1960) and Quarterly Progress Report, Solid State and Molecular Theory Group, Massachusetts Institute of Technology, January 15, 1961 (unpublished), p. 79; and private communications for which we are grateful.

[49] F. Stern, Phys. Rev. **116**, 1399 (1959).

TABLE IX. Effective fields, H_e, in units of 10^5 gauss at nuclei in various hosts. T (°K) is the temperature (in degrees Kelvin) at which the measurements were made, and symbolically, M = Mössbauer, NMR = nuclear magnetic resonance, EPR = electron paramagnetic resonance, C_v = specific heat, and NP = nuclear polarization. Where the symmetry of the ion site has been given by the author this information has been included (e.g., tet = tetrahedral, oct = octahedral). Where a sign has been given for H_e it is the one which has been determined; no sign (+ or −) means no such determination has been made.

Nucleus	Host	H_e (in 10^5 gauss)	Method	T (°K)	Reference
^{57}Fe	Fe	−3.42	M	0	47
		3.30	NMR	295	a
	Co	3.12 ± 0.05	M	0	75
	Ni	2.80 ± 0.05	M	0	75
	CoPd	3.3	M	88	b
^{57}Fe^{3+} (tet)	YIG	3.92 ± 0.05	M	room	c
		3.90	M	room	65
		3.9	NMR	room	d
		3.90 ± 0.07	M	room	76
		4.6	M	liquid air	65
^{57}Fe^{3+} (oct)	YIG	4.74 ± 0.06	M	room	c
		4.85	M	room	65
		4.7	NMR	room	d
		4.90 ± 0.07	M	room	76
		5.4	M	liquid air	65
^{57}Fe^{3+} (tet)	DyIG	3.90	M	room	65
		4.6	M	liquid air	65
^{57}Fe^{3+} (oct)	DyIG	4.85	M	room	65
		5.4	M	liquid air	65
^{57}Fe^{3+}	GdIG	4.0 and 4.9	NMR	room	d
^{57}Fe	Fe_3O_4	5	M	room	75
		4.70 ± 0.20 4.50 ± 0.20	M	room	76
		5.0 ± 0.20 4.5 ± 0.20	M	room	77
		5.1 ± 0.20 (tet) 4.5 ± 0.20 (oct)	M	85	77
^{57}Fe^{3+}	NiO·Fe_2O_3	5.1	M	room	75
		5.1 ± 0.20	M	room	77
^{57}Fe^{3+}	αFe_2O_3	5.15	M	room	e
	γFe_2O_3	5.0 ± 0.1	M	room	f
		5.05 ± 0.20	M	300	77
		5.15 ± 0.20	M	85	77
^{57}Fe^{3+}	MgO	5.50	EPR	1.3	g
^{57}Fe^{3+}	FeF_2	3.40	M	0	h
^{59}Co	Co (fcc)	2.134	NMR	room	6
	Co (hex)	2.28	NMR	0	7
	Co	2.20	C_v	0	i
	Fe	3.20	C_v	0	i
	Ni	0.80	C_v	0	i
	Fe	3.0 ± 0.2	M	4.5	j
	$Co_{0.83}Fe_{2.17}O_4$	4.10 ± 10	C_v	0	87
^{61}Ni	Ni	1.70	NMR	room	k
		−1.70	M	room	l
^{119}Sn	Fe	−0.81 ± 0.04	M	100	m
	Co	−0.205 ± 0.015	M	100	m
	Ni	+0.185 ± 0.01	M	100	m
	Mn_2Sn	−0.45	M	0	n
	Mn_4Sn	+2.00	M	0	n
^{198}Au	Fe	7.5	NP	0.015	o
^{114}In	Fe	1.8	NP	0.015	o
^{122}Sb	Fe	2.0	NP	0.015	o

[a] A. C. Gossard, A. M. Portis, and J. W. Sandle[7]; C. Robert and J.-M. Winter[7] and J. I. Budnick, L. J. Brunner, R. J. Blume, and E. L. Boyd, J. Appl. Phys. **32**, 120S (1961). See the last named authors for the temperature dependence of the NMR frequency, and G. B. Benedek and J. Armstrong [J. Appl. Phys. **32**, 106S (1961)] for the pressure and temperature dependence of the resonance frequency.

[b] D. E. Nagle *et al.*[47] and R. D. Taylor, D. E. Nagle, H. Frauenfelder, and D. R. F. Cochran (to be published).

[c] C. Alf and G. K. Wertheim, Bull. Am. Phys. Soc. **5**, 428 (1960) and reference 75.

[d] E. L. Boyd, L. J. Brunner, J. I. Budnick, and R. J. Blume, Bull. Am. Phys. Soc. **6**, 159 (1961).

[e] O. C. Kistner and A. W. Sunyar, Phys. Rev. Letters **4**, 412 (1960).

[f] W. H. Kelly, M. Hass, W. N. Schreiner, and G. B. Beard, Bull. Am. Phys. Soc. **6**, 135 (1961), and to be published.

[g] E. S. Rosenvasser and G. Feher, Bull. Am. Phys. Soc. **6**, 117 (1960).

[h] G. K. Wertheim, Phys. Rev. **121**, 63 (1961).

[i] See V. Arp, D. Edmonds, and R. Petersen (reference 2) for these data and effective field data for Co in CoNi and CoFe alloys and G. K. Wertheim (reference 75, J. Appl. Phys.) for a discussion.

[j] J. G. Dash, R. D. Taylor, D. E. Nagle, P. P. Craig, and W. M. Visscher, Bull. Am. Phys. Soc. **6**, 136 (1961), and to be published.

[k] L. J. Brunner, J. I. Budnick, and R. J. Blume, Phys. Rev. **121**, 83 (1961).

[l] H. F. Wegener and F. E. Obenshain, Phys. Rev. (to be published).

[m] A. J. F. Boyle, D. St. P. Bunbury, and C. Edwards, Phys. Rev. Letters **5**, 553 (1960) and Boyle *et al.* and H. E. Hall, Proc. Phys. Soc. **77**, 129 (1961).

[n] L. Meyer-Schützmeister, R. S. Preston, and S. S. Hanna, Phys. Rev. (to be published).

[o] B. N. Samoĭlov, V. V. Sklyarevskiĭ, and E. P. Stepanov, J. Exptl. Theoret. Phys. (U.S.S.R.) **36**, 644 (1959); **36**, 1944 (1959); **38**, 359 (1960). The values quoted in Table IX are those obtained by applying the correction suggested by these authors as a Note Added in Proof.

$4s$ band for energies lying beneath the onset of the $3d$ bands. If one considers the nonmagnetic state and fills the energy levels until there are eight electrons per atom in them, one has put approximately one electron in the $4s$ band (i.e., 0.6 electron in the region overlapping the partially filled $3d$ bands). This estimate is of necessity crude. Stern also predicted approximately one electron in the $4s$ band, as did Walker *et al.*,[50] from an interpretation of the Fe^{57} isomer shift.[51] Let us now go to the magnetic state by depopulating states of one spin (and filling the other) until there are 2.2 unpaired electrons per atom. Let us assume that the exchange interactions causing the creation of the net spin are of the same sign and magnitude for both the $4s$ and $3d$ shells (naive arguments based on the overlap of wave functions would suggest that the $4s$ exchange parameter is smaller). Then there would be roughly 0.05 to 0.1 unpaired electrons in the $4s$ band. In order to use these observations in an estimate of contributions to the effective field one must remember that while the bottom of the $4s$ band may be of almost pure $4s$ character, it is dangerous to assume that this is the case for states halfway up in the band. Thus, 0.05 to 0.1 unpaired $4s$-band electrons does not necessarily imply this much unpaired $4s$ character. Bearing this (and the possibilities of overestimating the $4s$-band exchange parameter) in mind let us assume that there are 0.8 paired and 0.05 unpaired (with spin parallel with the $3d$) $4s$ electrons in the "$4s$ band." Using the data of Table VIII these yield contributions to H_e of +105 and +90 kgauss respectively. These are, we believe, overestimates of the effects but they provide us with a framework for our discussions. If we estimate the contribution of the core electrons by using the "observed" divalent ion χ of about −3 a.u., then the effective field for the metal (with 2.2 unpaired $3d$ spins, i.e.,

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[50] L. R. Walker, G. K. Wertheim, and V. Jaccarino, Phys. Rev. Letters **6**, 98 (1961).

[51] We shall have only a brief opportunity to refer to the important data obtained from the isomer shift (see reference e in Table IX). This gives a measure of the total *charge* density at the nucleus whereas the contact part of the hyperfine field measures the total *spin* density at the nucleus.

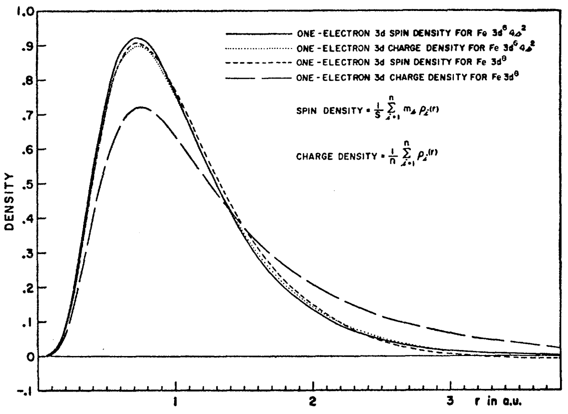

FIG. 1. One-electron $3d$ spin and charge densities for Fe $3d^64s^2$ and Fe $3d^8$.

we assume[52] that the spin moment in the metal is entirely due to the $3d$ band) from the core contact interactions, H_c, is -275 kgauss. This by itself is not as large as the measured field of -333 kgauss. Using the computed neutral Fe atom χ_3 (which we believe is overestimated by ~ -30 kgauss) H_c becomes -320 kgauss, still too small to overcome the positive contributions. Assuming that the estimates of the positive terms are at least reasonable, either the neutral atom (and divalent ion) χ_3 is inappropriate for the metal or there are other negative terms. We will concentrate on the former possibility in this section but will discuss the latter briefly.

In investigating possible sources of a large difference between core polarizations in metals and ions, several factors have been considered. It is generally assumed that in metallic iron there are between 7 and 8 electrons in the $3d$ band (as against 6 for the neutral atom or divalent ion). Furthermore, energy band calculations by Wood[48] and Stern[49] indicate that the $3d$ electrons in the metal are more expanded than in the free ($3d^64s^2$) atom. We have therefore done full spin-polarized Hartree-Fock calculations for Fe in both the $3d^64s^2$ and the $3d^8$ configurations. As shown in Fig. 1, even though the $3d^8$ one-electron $3d$-*charge* density is expanded relative to the $3d^64s^2$, the resultant one-electron $3d$-*spin* density (which to the first approximation is the relevant factor determining H_c) is not significantly changed. This spin density which is actually slightly contracted relative to the free $3d^64s^2$ atom agrees well with neutron measurements[53] and observations from energy band calculations.[48,49] For[17] Ni^{++} in a cubic crystalline field, such a contraction in spin density was shown to reduce H_c.

A calculated H_c of -350 kgauss was obtained for the $3d^8$ state. This is 30 kgauss lower than the $3d^64s^2$ value (and is also overestimated by about 30 kgauss). This improvement is however too small to overcome the positive contribution and so cannot account for the experimental result.

Goodings and Heine[54] did a $3d^64s^2$ free atom spin polarized calculation for Fe and obtained a χ of -3.8 a.u. (-355 kgauss) from the core. The difference between this value and our own arises from the computational sensitivity of the calculations (thus the best one can hope to do is to provide a consistent set of computations). Their χ (and ours) shows the overestimation discussed above. To estimate the effect in a metal, they repeated the calculation with *fixed* "$3d$ functions artificially expanded by about 5% at the maxima and 10% over the tail regions." This lowered H_c (by 65 kgauss) to -420 kgauss. This, they felt, sufficiently balanced the positive contribution at their lower limit (taken to be $+120$ kgauss) to make the calculated H_c explain the experimental H_e.

We do not agree. If their free atom overestimate of H_c is corrected (from -355 to ~ -300 kgauss), then their expanded $3d$ value of H_c would be changed from -420 kgauss approximately back to their quoted free atom value. Furthermore, their "artificial $3d$ expansion" gives a *spin density* in direct disagreement with the neutron diffraction and energy band results cited above.

An investigation of H_c as a function of the position of $3d$ density in the atom helps to clarify the theoretical picture. For a series of fixed $3d$ functions (which for computational simplicity we took as a single Slater atomic orbital), we determined H_c via spin-polarized H-F calculations. The results are shown in Fig. 2 as a function of the maxima of the $3d$ orbitals. We see that a large, *but unrealistic*, expansion *or* contraction of the

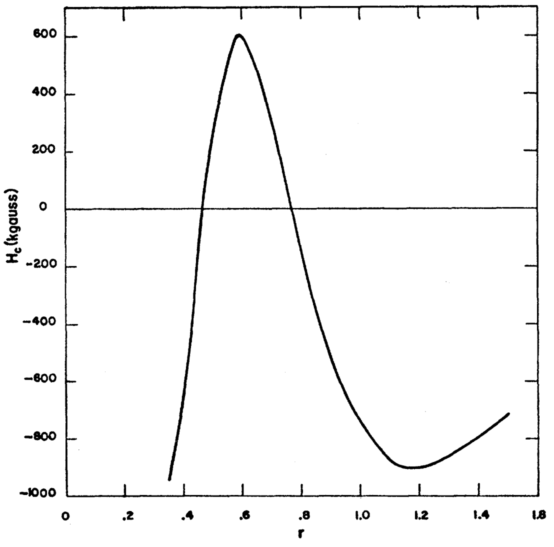

FIG. 2. Core effective field, H_c, as a function of the maximum of the $3d$ orbital for Fe $3d^8$.

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[52] We neglect here the 0.05 unpaired $4s$ electron in the $4s$ band.

[53] R. J. Weiss and A. J. Freeman, J. Phys. Chem. Solids **10**, 147 (1959) and R. Nathans, C. G. Shull, A. Andreson, and G. Shirane, *ibid.* **10**, 138 (1959).

[54] D. A. Goodings and V. Heine, Phys. Rev. Letters **5**, 370 (1960).

3*d*-shell spin density will yield an H_c which is more than sufficient to "explain" the *metal* results. Simple scaling does not appear to be the answer to the problem.[55] On the other hand, Fig. 2 suggests that any (other) *ad hoc* small change of shape in the 3*d* functions which removes spin density from the region roughly between 0.5 and 0.75 a.u. will yield a substantial lowering of H_c. This can be devised while maintaining reasonable compatibility with the neutron measurements. Unfortunately the ability to devise one or a number of "reasonably compatible" 3*d*-electron distributions which yield H_c's of -500 kgauss or better does not constitute proof that the core electron polarization in the metal takes on such a value. What is needed is a theoretical treatment which gives a more realistic, hence more difficult to handle, description of the atom's environment.

The individual 2*s*- and 3*s*-shell contributions to the H_c of Fig. 2 appear in Fig. 3. We believe they supply some insight into the spin-polarization mechanism. In viewing Fig. 3 note that the bulk of the 2*s*-charge density lies between 0.1 and 0.4 a.u. and that the 3*s* is concentrated between 0.5 and 1.0 a.u. The behavior of the curves can be understood in the crude terms used earlier, namely, that when the 3*d* shell lies "outside" a given *s* shell the shell's contribution to H_c is negative (since that *s* electron of majority spin has been "attracted" outwards) and when the 3*d* shell lies "inside" the reverse occurs. One would expect that further computations for more contracted 3*d* shells would show the H_c of Fig. 2 turning positive due to the 2*s*-shell contribution turning positive and then turning negative again as the 1*s* shell becomes most important. Since such contracted *d* shells are well outside of reason such computations have not been done.

We have seen that there is some uncertainty as to whether the core contact term alone can overcome the positive contributions to H_e in order to yield the experimentally observed effective field of -333 kgauss in Fe. In fact there is some doubt as to whether the 4*s* "conduction" electron contributions are always positive. Carr[56] and Anderson and Clogston[57] have suggested that aside from the positive contribution from the *s*-*d* admixture there is a negative contribution (antiferromagnetic polarization) which also comes from the covalent mixing of the *s* and *d* functions. They suggested, on the basis of perturbation theory, that these contributions would cancel. We will mention four ways in which this will affect H_e. All of these tend to bring the computed H_e into better agreement with experiment. First and most obviously if the positive (estimated earlier to be +0.05-electron spin) and negative tendencies approximately cancelled each other, the computed H_e would be modified by -90 kgauss. Secondly, in order to preserve the given net spin per atom there will have to be a small increase in the number of unpaired 3*d* orbitals and this will increase the polarization of both core and paired 4*s* electrons. Thirdly, the unpaired 4*s* electrons will also contribute to the polarization of the core electrons (an affect hitherto neglected). Investigations[45] show that a χ of approximately +4 a.u. can be associated with the core polarization due to a single unpaired 4*s* electron. A 4*s*-net spin which is antiparallel to the 3*d* will thus contribute a core polarization of the same sign as the 3*d*'s. The combined effect of a change in net 3*d* and 4*s* spin will yield a change in H_c which is of the same sign and approximately fifteen percent of the size of the first effect. Finally, the 4*s*-band wave functions are expanded (radially) relative to the unpaired 3*d* functions. If there is an antiparallel 4*s* net spin, the combined spin density will appear *contracted* relative to the actual 3*d*-spin density. Now the experimental neutron form factor is based on the combined spin density and we have relied on this for evidence of 3*d*-spin density behavior. This may mean that the "true" 3*d*-spin density is more expanded than we have presumed and this would very likely increase (make more negative) any estimate of H_e and thus bring about better agreement with experiment. One should note that the counterparts of the last three effects were not considered in any of our earlier discussions; they should be included in any detailed treatment of this problem.

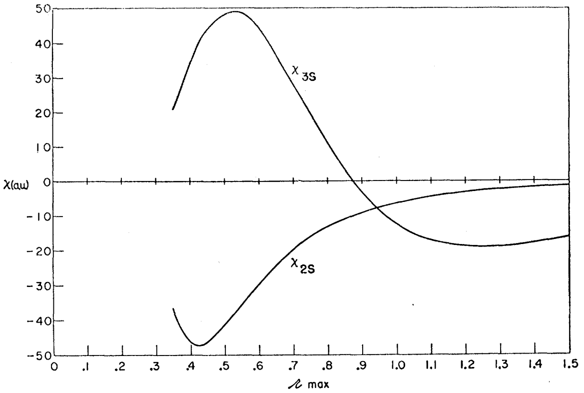

FIG. 3. Individual 2*s* and 3*s* contributions to H_c as a function of the position of the 3*d* maximum for Fe 3d^8.

B. Effective Field at Other Ferromagnetic Metals

Let us now turn to some of the remaining data in Table IX for H_e in ferromagnetic metals. The Mössbauer data for Fe^{57} as an impurity in CoPd gave an H_e of $|330|$ kgauss in precise agreement with the Fe^{57} in Fe value, as we assume the sign to be negative. This plus the data for Fe^{57} in Co and Ni (which show a small decrease in H_e), and Fe^{57} as impurity in the Cu–Ni alloy system indicate that the field at the iron nucleus is

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[55] It is apparently always the case that shape and not scaling is the important feature.[15,17]

[56] W. J. Carr, Jr., Winter Institute in Quantum Chemistry and Solid State Physics, Sanibel Island, Florida, January 1–13, 1961 (unpublished).

[57] P. W. Anderson and A. M. Clogston, Bull. Am. Phys. Soc. **6**, 124 (1961).

predominantly due to its own electrons and depends only to a small degree on the magnetization of the host. Indeed one is tempted to make much of the observation (by way of a semiempirical rule of thumb) that if one wants an estimate of H_e he should calculate H_c and neglect all the remaining terms. We have seen that this "works" for metallic Fe; for metallic cobalt using a χ of -3.0 and 1.7 unpaired spins one obtains an H_c of -215 kgauss in remarkable agreement with experiment (see Table IX). For ferromagnetic Ni with 0.6 unpaired spins and a χ of -3.0 this simple procedure fails completely in that it predicts an H_c of -75 kgauss whereas the measured value is -170 kgauss. (The calculated χ, -3.94, listed in Table II, gives a larger field and hence better agreement, but this value is surely overestimated.) This can be taken to mean that it is not enough to merely take the conduction electron contributions as cancelling each other—the need for an additional negative contribution to H_e in Ni is indicated. The observed H_e must of course come about as a result of the detailed balancing of the various conduction electron contributions with the core polarization terms but it is not currently possible to give anything more than a qualitative estimate of these effects. The accumulation of data (which is now well under way) on H_e, as well as measurements of the isomer shift,[58] for a wide class of materials offers the best hope for providing a detailed understanding of the various contributions.

We have seen that the assumption that χ is linear in the number of unpaired $3d$ electrons gave reasonable results. In this way measurements of H_e at nuclei in various environments would give information about the local moment at these sites. Such measurements have been made (cf. Co in Fe; Fe in Co and Ni; Fe in Cu—Ni alloys; etc.) and detailed correlation with the local moment per impurity atom can be attempted. A discussion of this data is well beyond the scope (and purpose) of this paper. We shall only comment that in these materials the dominant contribution also comes from the polarization of the core electrons; e.g., the increase in H_e for Co in going from the pure metal to an impurity in Fe can best be explained as due to an increase in the local moment of a Co atom which increases (the magnitude of) H_e.

C. Effective Field at the Nuclei of Nonmagnetic Atoms in Ferromagnets

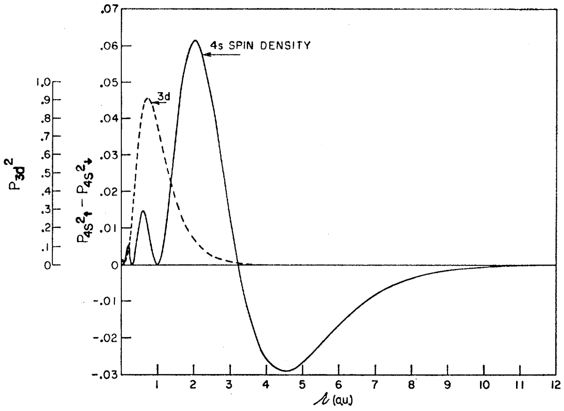

FIG. 4. The $3d$ and $4s$ one-electron spin densities for exchange-polarized neutral Fe $3d^6 4s^2$.

H_e has now also been observed at the nuclei of nonmagnetic atoms when these are impurities in, or alloyed with, ferromagnets (e.g., Sn as impurities in Fe, Co, and Ni; Au, Sb, and In as impurities in Fe; and Sn alloyed with Mn in Mn_2Sn and Mn_4Sn). Several mechanisms suggest themselves as explaining the observed fields: (1) The admixture of the $3d$-spin density from the ferromagnetic atom into the "paired" closed shells of the nonmagnetic atom produces an unpairing of the latter's wave functions. This results in an H_e in the same way as is observed for the effective field at the nuclei of normally diamagnetic atoms (like F^-) in transition metal salts.[59] (2) The nonmagnetic atom is polarized by the exchange field of the magnetic electrons on the ferromagnetic atoms and this produces an unpairing of the s electrons which then contribute a field at the nucleus via the Fermi contact term. This mechanism has been shown[60] to produce large effects on neighboring atoms and, as we have seen, produces the large negative fields in the ferromagnets via the core electrons. (3) The conduction electrons are polarized and this polarization produces an H_e at the nucleus via the Fermi contact term. The polarization can be via the Ruderman-Kittel-Yosida-Kasuya[61] exchange interaction and/or via the ordinary exchange polarization which we[19] have shown to be important for the rare earth elements; the former would produce a positive H_e whereas the latter would produce a negative field at the nucleus of the nonmagnetic atom. As a crude indication of the exchange polarization of "conduction" electrons, we show in Fig. 4 the spin density of the paired $4s$ electrons in Fe as calculated from the exchange-polarized H-F calculation for Fe ($3d^6 4s^2$) which was discussed earlier (cf. Secs. IV and V). The outer region of the atom has a negative spin density which by admixture into the (say) Sn wave functions would produce a negative field at the

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[58] See reference e in Table IX and reference 50, and S. DeBenedetti, G. Lang, and R. Ingalls, Phys. Rev. Letters **6**, 60 (1961).

[59] M. Tinkham, Proc. Roy. Soc. (London) **A236**, 535 and 549 (1956). R. G. Shulman and V. Jaccarino, Phys. Rev. **103**, 1126 (1956) and **108**, 1219 (1957). F. Keffer, T. Oguchi, W. O'Sullivan, and J. Yamashita, *ibid.* **115**, 1553 (1959). A. Mukherji and T. P. Das, *ibid.* **111**, 1479 (1958); W. Marshall (unpublished); and G. Benedek and T. Kushida, *ibid.* **118**, 46 (1960). See also A. J. Freeman and R. E. Watson, Phys. Rev. Letters **6**, 343 (1961) for a recent discussion of this problem.

[60] A. J. Freeman and R. E. Watson, Bull. Am. Phys. Soc. **6**, 234 (1961), and R. E. Watson and A. J. Freeman (to be published).

[61] M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954); T. Kasuya, Progr. Theoret. Phys. (Kyoto) **16**, 45 (1956); K. Yosida, Phys. Rev. **106**, 893 (1957).

Sn nucleus. This effect is, however, of less importance for transition metal alloys and intermetallic compounds than it is for the rare earths (in which the $4f$ electrons are well inside the atom) since the $3d$ overlap is considerable, but for these atoms as impurities the long-range polarization of the conduction electrons may be important.

The limited data available to date (cf. Table IX) indicate that most probably the observed fields are due to a competition between the core and conduction electron contributions, but it is too early to make any quantitative estimates of the magnitude of these effects. (We are in the process of carrying out some calculations for Sn which we hope will shed some light on these matters). Our own experience[60] shows that exchange polarization can produce large fields at neighboring nuclei via polarization of their closed s shells and this leads us to favor this mechanism. Clearly more data, particularly determinations of the sign of H_e, are needed to resolve the issue.

VI. EFFECTIVE FIELD AT NUCLEI IN SALTS

Effective fields at the nuclei of a number of magnetic materials other than the common ferromagnets have now been observed. Mössbauer and NMR techniques represent a rapidly expanding field with new data being determined at a rapid pace. Some of the data currently available was given previously in Table IX. In this section we shall discuss some aspects of this information for salts in the light of the theoretical results reported in earlier sections. The theoretical situation for ions in salts is much simpler than that for metals since the most troublesome terms, which come from the conduction electrons, are absent. This leaves just three terms which must be considered (cf. Sec. V); these are the contribution of the polarized core s electrons, a contribution from any unquenched orbital angular momentum and a dipolar contribution from the $3d$ electrons at other sites (which is zero when the ion is in a spherical or cubic environment). We shall see that the dominant contribution from the polarization of the core s electrons can be taken to be the value calculated for the free ion and that environmental factors can be considered as a correction to the free ion result.

There is a considerable body of data available, particularly from paramagnetic resonance measurements, concerning the $3d$-transition metal ions in salts. In Sec. III we considered the Abragam, Horowitz, and Pryce data which showed that χ was roughly constant (~ -3 a.u.) for the divalent ions. As observed by Low,[4] Van Wierengen,[5] and others, this is true only in first approximation and covalent bonding effects bring about certain essential differences in the observed hyperfine fields. The measurements show that the hyperfine field depends on the compound in which the ion is dissolved; for the groups of fluorides, oxides, and sulfides the hfs is roughly the same and is determined by the negative-ion neighbors.[5] The lattice parameter is apparently of little importance in these compounds but covalent bonding plays an important role. We shall see that the Mössbauer, NMR, and specific-heat data complement the observations made by EPR.

TABLE X. Hyperfine fields, H_e (in kgauss), for Mn^{++}, for various ligand neighbors (after Van Wierengen[5]).

Ligand neighbor	H_2O	F^-	CO_3^{--}	O^{--}	S^{--}	Se^{--}	Te^{--}
H_e	695	695	665	570–640	490	460	420

A. Field at the Nucleus of Mn^{++} Ions

The simplest case to discuss is Mn^{++} in the $3d^5$, ^6S state since the only contribution to H_e is H_c, the core polarization term. Fe^{3+}, the ion isoelectronic with Mn^{++}, has no common isotope with a nuclear moment and so H_e has not been observed by EPR methods. This makes the Mössbauer data for Fe^{3+} listed in Table IX all the more valuable and interesting. We shall first indicate some of the EPR results for Mn^{++} before discussing the NMR and Mössbauer data for Fe^{3+} and our own calculations for these ions.

Van Wierengen[5] lists H_e for Mn^{++} in a variety of hosts which we reproduce in Table X below with H_e in kgauss. The interpretation is clear that H_e depends on covalent bonding; the more covalent the bonding the smaller the observed H_e. These values are to be compared with the AHP value (cf. Table I) of -650 kgauss and our calculated value (cf. Table II) of -700 kgauss. If one compares Van Wierengen's data with the detailed measurements of Ogawa,[62] the H_e listed in Table X are apparently a bit too large in magnitude for H_2O and F^- as neighbors. Ogawa[62] finds that Mn^{++} in such compounds as $KMgF_3$, $KCdF_3$, $KCaF_3$, K_2MgF_4, and $NaMgF_3$ gives an H_e lying between -640 and -670 kgauss. Low's[4] value for Mn^{++} in CaF_2 (about 675 kgauss) is closer to the Ogawa data than Van Wierengen's, whereas Tinkham's[59] value of -680 ± 20 kgauss for Mn^{++} in ZnF_2 is too uncertain to cast any light on the question. Our calculated value (cf. Table II) of -700 kgauss is in surprisingly good agreement with these data (due probably to a cancellation of errors) considering the approximations and inaccuracies discussed earlier for these free-atom calculations (see also Appendix II). What we must emphasize is the qualitative rather than the quantitative agreement that is possible with the current state of exchange-polarized calculations. Low[4] lists some other data for Mn^{++} which is of interest and relevant to what follows below. For Mn^{++} in NaCl, $BaTiO_3$, and MgO, H_e is -575 kgauss but in ZnS it is -445 kgauss and in Ge it is -318 kgauss, showing a large departure from the ionic value.

In some of these hosts Mn^{++} is obviously not in a pure ^6S state and so there is some orbital contribution to the

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[62] S. Ogawa, J. Phys. Soc. (Japan) **15**, 1475 (1960).

field as well. As Van Wierengen has shown, the exchange interactions between Mn^{++} ions would also reduce H_e. These factors plus the strong effect of covalent bonding indicate the complexity of the physical situation in all but the case in which the purely ionic approximation is valid—the case where an application of our free ion results may be best applied. Such effects as the expansion of the $3d$ density[63] and crystalline environments[17,63] have not been included in our calculations (except for Ni^{++}) although the discussion of Sec. V showed that H_e was sensitive to the position of the $3d$ density.

B. The Field at the Nucleus of Fe^{3+} Ions

Exchange Polarized H-F Calculation for Fe^{3+}

We have calculated H_c for Fe^{3+} in its $3d^5$, ^6S state via a full exchange-polarized H-F calculation. This gave a χ of -3.00 a.u. or an H_c of -630 kgauss; the individual contributions from the $1s$, $2s$, and $3s$ shells being -0.25, -8.51, and $+5.77$ a.u. respectively. This is to be compared with the Mn^{++} ion to which it is isoelectronic. From Table II we see that while the individual s shell contributions are greater for Fe^{3+} than for Mn^{++} the calculated χ (-3.34 a.u.) for Mn^{++} is larger (in magnitude) than the χ for Fe^{3+}. In part this is to be expected from our earlier discussion of the dependence of χ on the position of the $3d$-spin density since the $3d$ functions in Fe^{3+} are in the field of a higher Z (the atomic number) and so are more tightly bound than are the $3d$ functions in Mn^{++}. This shift must of course be relative to that of the core s electrons and observations of calculated wave functions[21] show that this is so. Both values of χ undoubtedly show the overestimation noted earlier for the results of such calculations.

Field for Fe^{3+} in Ferrites

Some recent observations of H_e and Fe^{3+} were listed in Table IX. While the sign has not been determined for any of these cases it is almost certainly negative and we shall make this assumption. In αFe_2O_3 (hexagonal), γFe_2O_3 (cubic), and $NiO\cdot Fe_2O_3$ the measured H_e at an Fe^{3+} site is the same, indicating that for the ferrites H_e is independent of the structure and the same for the ions on both the tetrahedral and octahedral sites in keeping with the above discussion. (The field at a tetrahedral site in Fe_3O_4 is also about the same; this case will be discussed in greater detail later on.) This is not too surprising since experimental indications are that Fe^{3+} is in a $3d^5$, ^6S state. The room temperature value ($\sim$510 kgauss), when reduced to 0°K, increases H_e by approximately 10%[64] giving a field of 550 kgauss which also is the value observed (see Table IX, reference 9) by EPR measurements for Fe^{3+} in MgO.

Our calculated value for Fe^{3+} (-630 kgauss) is in good agreement with this measured value. It shows in part the overestimation discussed earlier. We do not expect the Fe^{3+} field to agree with the Mn^{++} value for the reason given earlier and indeed the field[4] for Mn^{++} in MgO (-575) does show this difference. This is encouraging for it means that even though the exchange-polarized H-F calculations give fields which are sensitive to various factors they can reproduce essential physical differences.

Field for Fe^{3+} in Some Rare-Earth Garnets

Mössbauer and NMR measurements have revealed the field at the Fe^{3+} sites in some magnetic rare earth–iron garnets. For YIG and DyIG the fields at the tetrahedral and octahedral sites are 3.9×10^5 and 4.8×10^5 gauss, respectively, at room temperature and 4.6×10^5 and 5.4×10^5 gauss at liquid air temperature. For GdIG, NMR results show two resonances at room temperature corresponding to H_e's of 4.0×10^5 and 4.9×10^5 gauss, in very close agreement with the other garnet data. Clearly H_e at the octahedral site corresponds to the Fe^{3+} value found in the ferrites and is close to the free ion value we have calculated whereas the tetrahedral site ions have fields which are diminished by about 100 kgauss. The reason for this is not known but we can suggest several ways this difference comes about. Two mechanisms stand out—covalent bonding and distortions from cubic symmetry (which produce dipolar fields arising from a lowering of the crystal symmetry at the tetrahedral site) which we feel are supported by experimental data. Mössbauer isomer shift data[51] for YIG shows a shift of 0.026±0.005 cm/sec at a tetrahedral site and 0.057±0.005 cm/sec for a tetrahedral site ion (Bauminger *et al.*[65] find shifts of 0.04±0.005 cm/sec and 0.06±0.005 cm/sec for these sites in both YIG and DyIG). Walker *et al.*[50] plotted isomer shift data for Fe^{++} and Fe^{3+} ions as $3d^64s^x$ and $3d^54s^x$ curves, respectively, thus relating covalency with the idea that the $4s$-atomic orbitals are partially occupied by electrons from the ligand ions. The octahedral shift is consistent with $x=0$ whereas the tetrahedral shift requires $x=0.1$. Consistent with this are the observations of Geller and Gilleo[66] who found that the tetrahedral-oxygen distance in YIG is 1.88 A, whereas the octahedral-oxygen distance is 2.00 A; on the simple picture of the relation of covalent bonding to degree of overlap this difference indicates that the covalent bonding for the tetrahedral ions is greater than that for the octahedral ions. As we have seen earlier in our discussion of Mn^{++}, the greater the degree of covalency the lower the observed H_e. The

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[63] A. J. Freeman and R. E. Watson, Phys. Rev. **118**, 1168 (1960); J. Appl. Phys. **31**, 374S (1960).

[64] M. Hass (private communication). *Note added in proof.* Dr. Hass has kindly informed us that the field at 0°K should be larger by about 4% (rather than his original estimate of 10%) since it is the sublattice magnetization, rather than the saturation magnetization, which is the relevant quantity.

[65] R. Bauminger, S. G. Cohen, A. Marinov, and S. Ofer, Phys. Rev. (to be published).

[66] S. Geller and M. A. Gilleo, Acta Cryst. **10**, 239 and 787 (1959).

$3d^5 4s^x$ picture of Walker *et al.*[50] should really be taken to express the configuration mixing of higher states (containing *s* electrons) into the ground state $3d^5$ configuration since there is experimental evidence from paramagnetic resonance for this for Mn^{++} ($3d^5$, ^6S state). The contribution to H_e via the contact term of these excited *s* states is positive, thus decreasing the negative core polarization value in keeping with the observed results.

Rodrique *et al.*[67] have used Pauthenet's[68] magnetization data for YIG to determine from the observed anisotropy[69] an anisotropy per unit cell for the tetrahedral and octahedral sublattices. They find the anisotropy coefficients to be -6.4×10^{-3} cm^{-1} for the octahedral cell but 101×10^{-3} cm^{-1} for the tetrahedral cell. While the distortions in the lattice due to magnetostriction are very small, the point of this discussion is to show that differences in distortions away from cubic symmetry are expected for the tetrahedral and octahedral sites. Crystal field effects are, however, expected to be more important for producing these distortions. There are several ways this can come about. The oxygen positions are sensitive to the magnetic ions which occupy the tetrahedral and octahedral sites, with the crystal fields of some of these ions tending to distort the structures to lower symmetry.[70] Further, differences in distortions at tetrahedral and octahedral sites may be understood in terms of a dynamical Jahn-Teller effect since the first excited state for a d^5 ion in a tetrahedral field will distort more than in an octahedral environment.[71] The lowering of the crystal field symmetry at the tetrahedral site (and to a lesser degree at the octahedral site as well) would introduce dipolar fields from the neighboring magnetic ions. (These dipolar fields are of course smaller than the reduction due to covalency for this case but may be more important for other cases.) Since this is usually a positive contribution it will partially cancel the negative core polarization term and so contribute to the observed difference in internal fields at the two sites in the garnets.

Field for Fe^{3+} in Fe_3O_4

Magnetite, Fe_3O_4, is a much more complicated system to understand. It is an inverse spinel with trivalent iron on tetrahedral and octahedral sites and divalent iron only on octahedral sites. There is a transition at about 120°K which brings on a remarkable change in its physical properties. Verwey and de Boer[72] postulated that the high conductivity of magnetite above the transition temperature is due to rapid electron transfer between Fe^{++} and Fe^{3+} ions in the octahedral site. This dynamic disarrangement between the ferric and ferrous ions is halted below the transition temperature with an ordering of the ions. The ordering scheme proposed by Verwey has orthorhombic symmetry—a scheme that has been shown to be correct.[73] On the basis of this exchange picture (electron transfer), Anderson[74] suggested that Mössbauer measurements be carried out to observe this transition. At room temperature one would expect no observable difference between sites since the rapid exchange of electrons between the ferrous and ferric ions would wash out any difference between the two types of ions.

The first Mössbauer observations on Fe_3O_4 by Wertheim[75] at room temperature found only a single field (5.1×10^5 gauss). Later Solomon[76] found two fields [$(4.7\pm0.2)\times10^5$ and $(4.5\pm0.2)\times10^5$ gauss], while recent measurements by Bauminger *et al.*[77] at room temperature found two hyperfine fields, 5.0×10^5 gauss and 4.5×10^5 gauss, which, on the basis of intensity arguments, were assigned to the tetrahedral Fe^{3+} ions and the octahedral ions (Fe^{3+} and Fe^{++}), respectively. At 85°K two fields, 5.1×10^5 gauss and 4.5×10^5 gauss, were observed and these were assigned to the Fe^{3+} and the Fe^{++} ions, respectively. These authors interpreted their observations as confirming Verwey's hypothesis.

Some very recent measurements by Boyd[78] have revealed a different picture for magnetite. Three separate resonances were found at 300°, 273°, and 200°K which were tentatively assigned to the two trivalent ions and the divalent ion as one might expect from the static model of Fe_3O_4. The reason for the difference between the NMR and the Mössbauer room temperature results is not known but may lie in the difficulty of resolving the hyperfine patterns obtained in the latter method. Since further studies are under way to resolve these differences we shall await further developments in this field. We shall only look at the low-temperature data in the light of our theoretical calculations.

We have discussed the Fe^{3+} ion earlier and have seen several ways in which H_c for an ion in a ^6S ground state is reduced from its calculated free ion value. The effective field, 5.1×10^5 gauss, agrees with the measurements

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[67] G. P. Rodrique, H. Meyer, and R. V. Jones, J. Appl. Phys. **31**, 376S (1960).

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[69] See the magnetostriction studies of, e.g., K. P. Belov and A. V. Pedko, J. Appl. Phys. **31**, 55S (1960) and the review article by J. C. Slonczewski, *ibid.* **32**, 253S (1961).

[70] S. Geller, J. Appl. Phys. **31**, 30S (1960); D. S. McClure, J. Phys. Chem. Solids **3**, 311 (1957), and references therein.

[71] M. H. L. Pryce, U. Opik, H. C. Lonquet-Higgins, and R. A. Sack, Proc. Roy. Soc. (London) **A244**, 1 (1958) and C. S. Naiman (private communication).

[72] E. J. W. Verwey, Nature **144**, 327 (1939); E. J. Verwey and J. H. de Boer, Rec. trav. chim. **55**, 531 (1936); E. J. Verwey and P. W. Haayman, Physica **8**, 979 (1941).

[73] See W. C. Hamilton, Phys. Rev. **110**, 1050 (1958), and references therein.

[74] P. W. Anderson, Proceedings of the Mössbauer Effect Conference, University of Illinois, 1960, edited by H. Frauenfelder and H. Lustig [University of Illinois Report AFOSR TN 60-698 (unpublished), p. 39].

[75] G. K. Wertheim, Phys. Rev. Letters **4**, 403 (1960) and J. Appl. Phys. **32**, 110S (1960).

[76] I. Solomon, Compt. rend. **251**, 2675 (1960).

[77] R. Bauminger, S. G. Cohen, A. Marinov, S. Ofer, and E. Segal, Phys. Rev. (to be published).

[78] E. L. Boyd (private communication; and to be published).

discussed above for Fe^{3+} in the ferrites and in the octahedral sites in the garnets—a not too surprising result in view of the data in Table X above. Small differences between the Fe^{3+} ions on the tetrahedral and octahedral sites would arise from differences in covalent bonding effects (due mainly to different internuclear distances from the O^{--} ions). The main result to be discussed is the difference between the observed trivalent and divalent ion fields. This will be done in the next subsection where the effective field for Fe^{++} ions is discussed.

C. Field at the Nucleus of Fe^{++} Ions

With no common isotope having a nuclear moment, effective fields at iron nuclei were not determined until recently when Mössbauer work with Fe^{57} revealed the effective field for some materials (cf. Table IX). This means that Mössbauer and NMR measurements go beyond simply augmenting the techniques previously used for measuring hyperfine interactions; rather, they provide us with new information about H_e in a variety of materials. Even now very little information is available for the effective field at the nucleus of an Fe^{++} ion —only Fe_3O_4 and FeF_2 have been studied to date—but this situation will no doubt be changed rather quickly.

Since it is easier to understand the measured field in FeF_2 than in Fe_3O_4 (which was discussed in part earlier) we shall discuss the former first and then use this discussion to try to understand the results in the latter.

Field for Fe^{++} in FeF_2

The effective field in FeF_2 at 0°K is observed to be $|340|$ kgauss (and as with the other data is undoubtedly negative) whereas our calculated value for Fe^{++} is -550 kgauss (see Table II). Even if one allows for a small overestimate in our calculated value of χ, the observed field is considerably less than this calculated value. Actually one cannot compare theory with experiment until one includes several other contributions to H_e aside from the core polarization term. Since Fe^{++} as a free ion is in a $3d^6$, ^5D state we expect that orbital contributions to the field [see Eq. (1)] will be important. Indeed it is known[79] that for Fe^{++} in salts the free ion orbital angular momentum is not completely quenched and so we must expect a (positive) contribution to H_e from this source.[80] In addition FeF_2 has a rutile-type structure[81] with the Fe^{++} ions forming a body-centered tetragonal structure. The environment of an Fe^{++} is therefore not cubic and so the dipolar contributions to the field from the surrounding magnetic ions is nonzero. These two *positive* contributions will therefore tend to reduce the negative field due to exchange polarization of the core s electrons, in agreement with experiment. Detailed quantitative estimates of these effects are difficult to make. If one uses the g value determined[82] for FeF_2 ($g=2.24\pm0.05$) and estimates an unquenched orbital contribution (as indicated by Abragam *et al.*[3] and by Marshall) from our calculated $\langle r^{-3}\rangle$ value of 5.1 (gotten by averaging the ↑ and ↓ values), we find a dipolar contribution to the field of about 200 kgauss. This is rather a large field and surely overestimated, but nonetheless it gives the expected order of magnitude for this contribution. (As Abragam *et al.*[3] also pointed out, not much reliance can be placed on such crude calculations because of uncertainties introduced by a number of factors which have been omitted.) Its chief value is that it indicates, however, that the effective field for Fe^{++} in FeF_2 can be qualitatively understood with the simple theory already propounded.

Field for Fe^{++} in Fe_3O_4

The effective field at the Fe^{++} nucleus in Fe_3O_4, 4.5×10^5 gauss at 85°K, is some 100 kgauss smaller than the value calculated from the exchange polarization of the core. This is not surprising since, as we have seen, orbital contributions and covalent bonding will affect the observed fields. What needs to be understood is (a) the rather small difference between the Fe^{++} and Fe^{3+} effective fields (only about 60 kgauss at 85°K) and (b) the difference in fields for Fe^{++} in FeF_2 and Fe_3O_4.

Our calculations for H_c gave core polarization differences of about 75 kgauss between trivalent and divalent irons, and this alone can apparently account for the difference in observed fields. Measured[83] g values for Fe^{++} in Fe_3O_4 show but a very small difference (0.06) from 2.00 at low temperatures indicating that unquenched orbital angular momentum effects are small. Differences in fields due to covalent bonding effects are also expected. Both theoretical free atom calculations[21] and neutron magnetic form factor measurements[84] indicate that the $3d$ charge density is more expanded for Fe^{++} than for Fe^{3+} which means a greater degree of covalent bonding (hence a smaller H_c) for the former. The different bonding distances to the O^{--} ions (some 15% smaller for the tetrahedral sites) however tend to decrease these differences in covalency effects.

D. Effective Field at the Nucleus of Co^{++} Ions

Very few data are presently available for the hyperfine fields of Co^{++} ions in salts. The free-ion ground

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[79] See, e.g., Low[4]; T. Moriya, K. Motizuki, J. Kanamori, and T. Nagamiya, J. Phys. Soc. Japan **11**, 211 (1956); A. L. Loeb and J. B. Goodenough, *Proceedings of the Conference on Magnetism and Magnetic Materials, Boston, 1956* (American Institute of Electrical Engineers, New York, 1957), AIEE Spec. Publ. T-91.

[80] These fields can be very large as is discussed later on. For a single unpaired $3d$ electron a typical value for the dipolar field is on the order of 500 kgauss.

[81] J. W. Stout and S. A. Reed, J. Am. Chem. Soc. **76**, 5279 (1954).

[82] R. C. Ohlmann and M. Tinkham, Bull. Am. Phys. Soc. **3**, 416 (1958), and to be published.

[83] J. Smit and H. P. J. Wijn, *Ferrites* (John Wiley & Sons, Inc., New York, 1959).

[84] R. Nathans, S. Pickart and H. Alperin, Bull. Am. Phys. Soc. **5**, 455 (1960).

state $3d^7$, ^4F is orbitally degenerate and, as with Fe^{++}, it is found that the orbital angular momentum is not completely quenched in a crystalline field. The value of χ quoted in Table I was obtained by Abragam *et al.*[3] using a complicated theoretical procedure[3,85] to separate out the orbital contributions, due to the $3d$ electrons, from the contact term. In view of the various approximations and uncertainties involved in such a procedure, particularly the neglect of charge transfer and covalent bonding effects (which we have seen can be very important), much more theoretical and experimental work is needed in order to obtain an accurate separation of the orbital from the s electron part of the hyperfine field.

As an indication of the complexity of some of the experimental data,[86] the fluosilicate and the ammonium and potassium Tutton salts which AHP analyzed had (nearly) tetragonal or trigonal symmetry (or lower). In $3\ Co(NO_3)_2 \cdot 2\ Bi(NO_3)_2 \cdot 24\ H_2O$ there are two types of Co^{++} ions in each unit cell having very different hyperfine fields. The measured g values are greatly anisotropic, vary over a wide range and show large deviations from the spin-only value ($g_{\parallel}=6$ and $g_{\perp}=3$ are typical values). Hence one suspects, and indeed observes, that orbital angular momentum contributions will be large. (By contrast, Mn^{++} behaves normally in these compounds.) The hf splittings are not constant but involve effective fields of about 10^6 gauss. The contact part of this field was estimated by AHP (see Table I) to be -315 kgauss whereas we would estimate (on the basis of the results reported in Tables II and V) that the computed value for χ would be between -3.4 and -3.6 a.u. or a field of -425 to -450 kgauss. From this we see that the orbital contributions are large and since they can be greater than the purely contact part the observed fields need not be negative. (For the cases discussed earlier, like FeF_2, the g values indicated small deviations from the spin only value and so we were justified in assuming the measured field to be negative.)

Let us now examine some recent experimental determinations of H_e for Co^{++} ions. Pollack[87] has measured the specific heat of $Co_{0.83}Fe_{2.17}O_4$ from which the nuclear contribution (due only to the Co^{++} nuclei) was extracted. This gave a field of $|410|\pm10$ kgauss, in remarkable agreement with our estimated value. The g value[83] for Fe^{++} in Fe_3O_4 is only slightly larger than 2 so that, if one assumes a similar value for Co^{++} in this Co ferrite, the unquenched orbital angular momentum should make only a small contribution. As in the case of Fe_3O_4 ,distortions from cubic symmetry are small and so the dipolar contribution from neighbors can be neglected. The observed effective field should then be mainly due to the polarization of the core electrons, and indeed the agreement between our estimated value and experiment can be understood on this basis.

Low[4] found that the internal field for Co^{++} in MgO was about 435 kgauss, which at first sight one might imagine to arise solely from the polarization of the core electrons. This cannot be the case here since the observed g value (4.278) indicates a large contribution from orbital angular momentum. The observed field is then best understood as being positive with the orbital contribution amounting to twice the negative of the core polarization term. Clearly, more data are needed for a better detailed understanding of this ion in salts.

E. Effective Field at the Nucleus of Rare-Earth Ions

We have confined our attention in this paper to effective fields for the $3d$ transition elements. Mössbauer and NMR measurements of H_e in some rare earth metals and salts[88] have recently been reported and active work on other systems is well under way. Our own investigations[89] of some rare-earth ions, which we shall mention only briefly here, indicate that for ions with a half-closed shell (like Gd^{3+} and Eu^{++}) the dominant contribution arises from the exchange polarization of the core electrons by the unfilled $4f$-shell electrons, whereas for the other unfilled $4f$-shell elements the dominant contribution comes from the orbital angular momentum of the $4f$ electrons which, unlike the case for $3d$ elements, is almost completely unquenched. These orbital contributions are large (approximately 10^6 gauss) and can easily account for the observations. This work will be fully discussed in a future publication.

VII. SUMMARY AND CONCLUSION

We have been studying the origin of the effective fields observed at the nuclei of a variety of magnetic materials. Our investigations were based on (a) accurate exchange- (or spin-) polarized Hartree-Fock calculations for free transition-metal ions and neutral atoms (b) on calculations for ions in a (crude) crystalline field (as in a salt) and (c) on calculations in which modifications of the wave functions (and spin density) were made in order to conform with energy band and neutron magnetic scattering observations for the ferromagnetic metals. It was shown that for the metals and for most transition-element ions in salts the dominant contribution to the effective field acting on the nucleus was the field arising from the exchange polarization of the core electrons by the spin density of the unpaired $3d$ electrons. Further, the exchange polarization method and

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[85] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. **A205**, 135 (1951); **A206**, 164 and 173 (1951).

[86] B. Bleaney and D. J. E. Ingram, Proc. Roy. Soc. (London) **A208**, 143 (1951); R. S. Trenam, Proc. Phys. Soc. (London) **66**, 118 (1953).

[87] S. R. Pollack, Bull. Am. Phys. Soc. **6**, 169 (1961).

[88] J. Hervé and P. Viellet, Compt. rend **252**, 99 (1961) found a field of $(4.0\pm0.1)\times10^6$ gauss at 0°K for Tb^{109}; S. Ofer, P. Avivi, R. Bauminger, A. Marinov, and S. G. Cohen [Phys. Rev. **120**, 406 (1960)] measured a field of $\sim2\times10^6$ gauss for Dy^{161} in DyIG; N. Kurti and R. S. Safrata, Phil. Mag. **3**, 780 (1958), did the original nuclear specific heat measurements on Tb.

[89] Reference 19 and A. J. Freeman and R. E. Watson (to be published).

the accuracy of the spin-polarized H-F solutions were discussed with regard to various factors, i.e., sensitivity of H_e to orbital descriptions (both for s electrons in the region near the nucleus and to greater variational freedom for the other electrons), the effect of crystal environments, and to expansion or contraction of the $3d$-spin density; the effect of each of these factors was illustrated by accurate detailed calculations. While it was found that H_e was strongly dependent on all these factors, which made for a certain ambiguity in the exact value of the field, a consistent set of calculations was reported which was able to reproduce essential differences between various ions and to agree quite well with some of the experimental data.

We have seen that the negative fields found for the ferromagnetic metals was predominantly due to the core polarization term. The other terms arising from the conduction electrons, initially discussed by Marshall, were analyzed and it was shown that another negative field (introduced by Anderson and Clogston, and by Carr) arising from covalent bonding of the conduction electrons with the unfilled $3d$ electrons gave rise to several other (smaller) negative terms which together could explain the magnitude and sign of H_e in the metals. These extra terms are particularly needed in the case of nickel.

For H_e at the nucleus of ions like Fe^{3+} in some rare-earth garnets, ferrites, and salts, the dominant contribution is again that due to core polarization. Such factors as charge transfer, covalent bonding, and crystal field effects, e.g., distortions from cubic symmetry, were shown to reduce the free-ion value of H_e and needed in order to understand the data. Differences between ions in the same environment (like Mn^{++} and Fe^{3+}) were found to be reflected in the H-F calculations. For ions like Fe^{++} and Co^{++} (particularly the latter), large positive contributions from unquenched orbital angular momentum were found to compete with the core polarization term and were needed to interpret the Mössbauer, NMR, and paramagnetic resonance results. (For the rare earth ions, these orbital contributions will dominate over the core polarization contact term, except for half-closed shell ions like Eu^{++} and Gd^{3+}.)

While the main features of the experimental data may be understood (and reproduced) in terms of our calculations, more realistic calculations for these ions, i.e., ones which take the environment into account, are needed in order to obtain detailed quantitative agreement with experiment.

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APPENDIX I. THE EXPECTATION VALUE OF S^2 FOR SPIN-POLARIZED Mn^{++}, Ni^{++}, AND Fe

As noted in Sec. II, the spin-polarized single-determinant Hartree-Fock functions are not exact spin eigenfunctions. This is due to the unpairing of the "paired" electrons. Spin-polarized Hartree-Fock radial functions for orbitals of common l and m_l but differing m_s have overlap integrals which are, in general, neither zero nor one as would be the case for conventional Hartree-Fock orbitals. This lack of orthonormality produces nonzero contributions to the total spin expectation value, $\langle S^2\rangle$, of the ion. This causes a deviation in the value of $\langle S^2\rangle$ from $S(S+1)$, i.e., what it would be for an exact spin eigenfunction. As examples of this, let us consider the expectation values of S^2 for our Mn^{++} $3d^5$, Ni^{++} $3d^8$, and Fe $3d^6 4s^2$ exchange-polarized functions. These are obtained by applying the operator

$$S^2 = S_z^2 + S_z + S_- S_+ \tag{8}$$

to the single-determinant Φ_0 in question and integrating over space and spin. The S_z terms can be evaluated by inspection, whereas the $S_- S_+$ term involves more work. $S_- S_+$ projects from Φ_0 a linear combination of determinants which are either identical with the original determinant, or differ from it by flipping a pair of orbital spins. One obtains the contribution to $\langle S^2\rangle$ by multiplying this linear combination by the original determinant and integrating. The problem thus involves evaluating a series of overlap determinants involving nonorthogonal one-electron wave functions.[90] Due to orthogonality, only those determinants obtained by flipping orbitals of common l and m_l values make nonzero contributions and $\langle S^2\rangle$ becomes

$$\langle S^2\rangle = \langle S_z^2\rangle + \langle S_z\rangle + \sum_l \sum_m \sum_\beta \left(1 - \sum_\alpha d_{\alpha\beta}^2\right), \tag{9}$$

where $\sum_\alpha$ and $\sum_\beta$ are sums over the spin ↑ and ↓ orbitals, respectively, of the original determinant and the $d_{\alpha\beta}$'s are radial overlap integrals, i.e.,

$$d_{\alpha\beta} = \int_0^\infty \phi_\alpha^*(r)\phi_\beta(r)dr. \tag{10}$$

In obtaining Eq. (9) use was made of the fact that orbitals of common l, m_l, and m_s values are orthogonal.

Since our determinants are approximate spin eigenfunctions for the case $M_s = S$, the S_z terms yield what $\langle S^2\rangle$ would be if we had exact eigenfunctions and the $S_- S_+$ term measures the deviation from that value. The

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[90] For this the methods of Löwdin [P. O. Löwdin, Phys. Rev. **97**, 1474 (1955)] are valuable.

TABLE XI. The calculated $\langle S^2\rangle$ for the single-determinant spin-polarized functions, the exact eigenfunction value of $\langle S^2\rangle$, and individual shell contributions (Δ_l) to the deviation for spin-polarized Mn^{++}, Fe, and Ni^{++}.

	Mn$^{++}(3d^5,{}^6S)$	Fe$(3d^64s^2,{}^5D)$	Ni$^{++}(3d^8,{}^3F)$
$\langle S^2\rangle_{\text{single determinant}}$	8.75043	6.01362	2.00085
$S(S+1)$	8.75	6.0	2.0
Δ_s	0.00001	0.01107	0.000002
Δ_p	0.00042	0.00027	0.00006
Δ_d	0.00000	0.00228	0.00079

form of Eq. (9) lets us catalog the contribution (Δ_l) associated with orbitals of a specific l value. $\langle S\rangle$'s, Δ_l's and the exact eigenfunction values of $\langle S^2\rangle$, i.e., $S(S+1)$, appear in Table XI. The deviations are not large. They are larger than the deviation of 0.000016 obtained by Sachs[13] for Li and except for Fe are smaller than the deviation of 0.0079 obtained by the writers[91] for spin-polarized N. The larger deviation in Fe is due to the Δ_s which in turn is largely due to the 4s shell. The contribution from the 1s, 2s, and 3s shells is of the same order of magnitude as the Mn^{++} and Ni^{++} Δ_s's. The small size of the deviations indicates that there has been but a small admixture of states of higher multiplicity into our single determinants. Despite the smallness of the admixture, the H_c's obtained for[13] Li and[91] N are appreciably perturbed on projecting the properly symmetrized functions.

It should be noted that similar deviations do *not* occur for expectation values of the angular momentum operator L^2. This would not be the case if the restriction of having common radial functions for orbitals differing only in m_l value was relaxed. Relaxation of this constraint would complicate an already complicated situation.

In the text it is noted that applying the variational principle to the properly symmetrized many-determinant function or obtaining the properly symmetrized function after the SCF solution are both beyond the scope of present computational facilities for many-electron systems of the size of the iron series ions. The complications are associated with the number of determinants necessary for a properly symmetrized spin polarized function. There are 3 determinants for Li ($1s^22s,{}^2S$), 21 for N ($2p^3,{}^4S$), 5005 for P ($3p^3,{}^4S$) and 817 190 for Mn^{++} ($3d^5,{}^6S$). It is therefore apparent that such computations become quite out of hand for systems of the size of the iron series atoms.

APPENDIX II. SENSITIVITY OF χ TO ORBITAL ACCURACY

The sensitivity of χ to the accuracy of the Hartree-Fock solutions was investigated by means of several spin-polarized calculations in which the basis set (the R_j's) was augmented in two ways. If we call the basis set referred to in the text as set I then the new set, set II, contains one more basis function than set I and this function has an A_j [see Eq. (6)] equal to zero (i.e., is "1s-like") and a Z_j chosen so that it contributes to the construction of s orbitals in the region inside the 1s maximum. Set III contains four more basis functions than set II and these give greater freedom to the solution for the 2p, 3p, 3d, and the (outer part of the) 3s orbitals. A calculation with set II yields solutions in which we have improved the description of s electron behavior at and near the nucleus but otherwise gives Hartree-Fock orbitals which are the same as set I results. Set III, in turn, yields no further freedom for s orbital construction in this region while otherwise allowing for more accurate Hartree-Fock solutions. Calculations utilizing these basis sets allow us to test (1) the sensitivity of a computed χ to the choice and number of basis orbitals contributing to H_c (s orbitals with $A_j=0$) and (2) the sensitivity of χ to details in the descriptions of all the orbitals. Set III has been used in spin polarized *and* restricted Hartree-Fock calculations. The resulting Hartree-Fock orbitals are given in Appendix III along with a discussion comparing restricted Hartree-Fock results for sets I[21] and III. Before discussing the results of using the various sets we wish to stress that the accuracy of the set I restricted Hartree-Fock solution appears to be that of existing numerical solutions.[36] The total energies, χ's, and individual shell contributions to χ for the various calculations appear in Table XII. One sees that only a small (~0.0001%) energy improvement is associated with going from the restricted to the spin-polarized formalism. *This is important* for if it were otherwise we would not be justified in relying on the restricted Hartree-Fock formalism as we usually do, both in computation and in the parametrization of experimental results. Also one would expect that effects associated with such a small energy change will be sensitive to computational details. Inspection of the χ's of Table XII shows that this is so. We see that for Mn^{++} the total χ and its individual shell contributions are sensitive both to improvements in s orbital descriptions

TABLE XII. Mn^{++} total energies, contact term χ's, and individual s-shell contributions to χ as obtained in restricted and spin-polarized Hartree-Fock calculations of varying accuracy. See the text for a description of the sets.

Calculation	Total ion energy (ry)	χ (a.u.)	Individual shell contributions to χ (a.u.) 1s	2s	3s
restricted H-F set I	−2298.210	⋯	⋯	⋯	⋯
spin-polarized H-F set I	−2298.212	−3.34	−0.16	−6.73	+3.55
spin-polarized H-F set II	−2298.213	−4.45	−0.19	−7.22	+2.96
restricted H-F set III	−2298.216	⋯	⋯	⋯	⋯
spin-polarized H-F set III	−2298.219	−4.13	−0.19	−7.15	+3.22

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[91] A. J. Freeman and R. E. Watson (to be published).

near the nucleus (sets I and II) and to small improvements elsewhere in the orbitals (sets II and III). We see that sets II and III yield χ's which are larger in magnitude and more negative, thus further away from the experimental value of Table I. We have done calculations equivalent to sets II or III for several other ions and comparison with set I results shows differences similar to those seen in Table XII. From this, one sees that it is therefore highly desirable to use a set of calculations of consistent accuracy so that comparisons between calculations are meaningful. We have used and in the text report results of calculations using basis sets which are equivalent to set I. Considerations of computer time and capacity[92] have required this since calculations for the neutral $3d^n4s^2$ atoms, using sets equivalent to set III, are beyond the capacity of the programs and available machine size. In viewing set I results, it should now be remembered that these, if anything, underestimate the 1*s*, 2*s*, and 3*s* contact term predictions of the spin-polarized Hartree-Fock formalism but overestimate H_c as compared with experiment. (As discussed in the text, it is expected that a proper treatment, i.e., one in which the total wave function is an eigenfunction of S^2, would produce greater agreement with experiment.)

TABLE XIII. Parameters defining the radial basis orbitals (R_j's) used in the set III calculations for Mn^{++}. See Eq. (6) for a definition of the parameters.

Orbitals used in the construction of	j	N_j	A_j	Z_j
s functions	1	1224.7989	0	72.1146
	2	261.85019	0	25.7839
	3	2780.1222	1	22.5236
	4	506.67737	1	11.4000
	5	1688.7636	2	10.6985
	6	262.22168	2	6.2836
	7	60.833973	2	4.1392
	8	9.6184780	2	2.4437
p functions	9	5232.9774	0	29.0076
	10	1173.4732	0	15.9515
	11	318.20140	0	9.4644
	12	868.61621	1	8.8476
	13	130.31498	1	5.1457
	14	27.470219	1	3.2981
	15	4.9052944	2	2.3130
d functions	16	3.0714190	0	1.7636
	17	11.877153	0	2.5955
	18	78.366500	0	4.4498
	19	554.11740	0	7.7812
	20	3774.5698	0	13.4624

APPENDIX III. RESULTS FOR Mn^{++}

Results for spin-polarized and restricted Hartree-Fock calculations for Mn^{++} appear in this Appendix. These are "set III" (see Appendix II) results. The restricted Hartree-Fock results are superior to (and will be compared with) the previously available analytic

TABLE XIV. Eigenvectors (C_{ij}'s) defining the Mn^{++} restricted and spin-polarized Hartree-Fock radial functions in terms of the basis orbitals. [See Eq. (4).]

$i \diagdown j$	1	2	3	4	5	6	7	8
1*s* restricted	0.00095262	0.93219341	0.08256074	−0.00102360	0.00119986	−0.00040714	0.00012154	−0.00002815
1*s* ↑ spin pol.	0.00095231	0.93219166	0.08255771	−0.00101831	0.00121136	−0.00040865	0.00012332	−0.00002842
1*s* ↓ spin pol.	0.00095298	0.93219597	0.08256481	−0.00103419	0.00119281	−0.00040765	0.00012115	−0.00002835
2*s* restricted	−0.00022792	−0.28140575	−0.16281069	0.76530851	0.37083125	0.04069852	−0.00804737	0.00185071
2*s* ↑ spin pol.	−0.00021542	−0.28100120	−0.16227204	0.76321451	0.37014813	0.04416826	−0.00829855	0.00202661
2*s* ↓ spin pol.	−0.00024049	−0.28180739	−0.16335366	0.76742189	0.37146610	0.03726043	−0.00778938	0.00167815
3*s* restricted	0.00021295	−0.10440284	−0.05594452	0.27669587	0.31041248	−0.26001952	−0.86604390	−0.05498650
3*s* ↑ spin pol.	0.00023911	−0.10508183	−0.05572422	0.27665827	0.31289328	−0.25772116	−0.87244376	−0.04968453
3*s* ↓ spin pol.	0.00018706	−0.10370366	−0.05614773	0.27666369	0.30787470	−0.26236141	−0.85894319	−0.06105758

$j=$	9	10	11	12	13	14	15
2*p* restricted	0.00143951	0.15759096	0.86258283	−0.01397536	0.02904026	−0.01011309	0.00241103
2*p* ↑ spin pol.	0.00136924	0.15811721	0.85820607	−0.01089018	0.03171642	−0.01004644	0.00253086
2*p* ↓ spin pol.	0.00150845	0.15706754	0.86693095	−0.01708712	0.02643833	−0.01017499	0.00229375
3*p* restricted	−0.00105760	−0.04420328	−0.34753116	−0.00671697	0.53148740	0.57696816	0.02049388
3*p* ↑ spin pol.	−0.00082579	−0.04739754	−0.34456941	−0.01617902	0.54332079	0.57271426	0.01481919
3*p* ↓ spin pol.	−0.00128849	−0.04098625	−0.35025844	0.00275979	0.51914348	0.58057789	0.02782140

$j=$	16	17	18	19	20
3*d* restricted	0.19363690	0.41062251	0.42609849	0.10403286	0.00663517
3*d* ↑ spin pol.	0.19267643	0.41028202	0.42731074	0.10394168	0.00667143

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[92] These calculations were done on a 32 000 word core IBM 704.

functions and we believe[93] them to be superior to existing[36,94] numerical solutions. The parameters defining the basis functions [see Eq. (6)] appear in Table XIII and the eigenvectors, i.e., the C_{ij}'s [see Eq. (4)], appear in Table XIV. The total energies, the one-electron energies (ϵ_i), and the one-electron kinetic + nuclear potential energies (K_i) appear in Table XV along with the values obtained for the earlier restricted solution (set I). The difference in total energy between the set I and III restricted Hartree-Fock results is 0.003 a.u. or less than one thousandth of a percent, whereas the variation in several of the K_i's and ϵ_i's is greater than this. The largest changes in one-electron orbitals (as evidenced by K_i variations) are a small contraction of the $3d$ and a smaller expansion of the $3s$. One might note that while the largest K_i variation is associated with the $3d$ orbital, ϵ_{3d} and ϵ_{1s} share in showing the smallest change between calculations. We believe that the changes in total energies, one-electron energies, ϵ_i's, and K_i's can serve as an estimate of the maximum change which would come with further wave function improvement. Now the change we have seen in the total energy is less than one percent of the correlation energy[95] (i.e., the difference between the exact eigenvalue of our many-electron Hamiltonian and the Hartree-Fock total energy). Therefore one should perhaps be more preoccupied with wave-function improvements that go beyond the Hartree-Fock formalism than with worrying about increased numerical accuracy in the Hartree-Fock solutions themselves.

TABLE XV. Total energies, one-electron energies (ϵ_i's), and one-electron kinetic + nuclear potential energies (K_i's) as obtained for $Mn^{++}(^6S)$ in sets I[a] and III restricted Hartree-Fock calculations and in a set III spin-polarized Hartree-Fock calculation. All energies are in atomic units (1 a.u. = 2 ry).

	Set I[a] restricted H-F	Set III restricted H-F	Set III spin-polarized H-F	
			spin ↑	spin ↓
ϵ_{1s}	−241.192	−241.188	−241.185	−241.187
ϵ_{2s}	−29.757	−29.751	−29.817	−29.682
ϵ_{3s}	−4.461	−4.456	−4.661	−4.247
ϵ_{2p}	−25.464	−25.458	−25.522	−25.390
ϵ_{3p}	−3.131	−3.126	−3.376	−2.873
ϵ_{3d}	−1.292	−1.288	−1.288	···
K_{1s}	−312.357	−312.356	−312.356	−312.356
K_{2s}	−76.342	−76.344	−76.309	−76.377
K_{3s}	−29.243	−29.237	−29.272	−29.199
K_{2p}	−75.670	−75.670	−75.618	−75.720
K_{3p}	−27.448	−27.449	−27.546	−27.339
K_{3d}	−22.955	−22.980	−22.996	···
Total energy	−1149.105	−1149.108	−1149.110	

[a] See reference 21.

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[93] In general comparisons with numerical H-F calculations have been difficult to make because total energies are generally not listed for these. See reference 92.

[94] D. F. Mayers has just informed us that he has recently obtained a highly accurate numerical solution for Mn^{++} as part of his program to produce numerical Hartree-Fock solutions with an accuracy superior to those in the literature. His ion total energy is −1149.11 a.u. (cf. Table XV) and his one-electron energies generally agree with our set III values to 0.001 a.u., the last digit reported by him. The agreement of the analytic and numerical results is striking, and bears out the belief that the analytic functions represent good Hartree-Fock solutions.

[95] See the discussion in reference 32 and the estimates of the correlation effects in reference 21.