

CONTRIBUTION OF THE FERMI CONTACT TERM TO THE MAGNETIC FIELD
AT THE NUCLEUS IN FERROMAGNETS*

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Recent Mössbauer measurements¹ have revealed a large but unexpectedly² negative (-333 kgauss) effective magnetic field, H_e , at the Fe⁵⁷ nucleus in ferromagnetic iron. These results led to the recognition¹ that the dominant source of H_e must come from the polarization of the core s electrons which then contribute a field, H_C , through the Fermi contact interaction. We are here reporting results for a set of calculations³ for H_C which are based on a model consistent with neutron diffraction⁴ and energy band results.⁵ These results are compared with those just reported by Goodings and Heine⁶ for a less realistic model. Both calculations are shown to be deficient in that the experimental value of H_e is not realized, and hence that the dominance of the core contribution has not been proven. Some striking results are also reported for an investigation of H_C as a function of the position of the $3d$ density in the atom. These results help to clarify the theoretical picture and should lead to a proper theoretical treatment of the problem.

Our investigations are based on "spin (exchange) polarized" Hartree-Fock³ calculations, i.e., calculations in which electrons in the same shell, but differing in spin direction (m_s) are allowed different radial distributions. Physically, this difference arises, in atoms having a net spin, from the different exchange interactions experienced by electrons of majority (say up, \uparrow) and minority (\downarrow) spins. The resultant difference in radial distributions leads to a difference in density for s electrons at the nucleus, $|\psi_{\uparrow}(0)|^2 - |\psi_{\downarrow}(0)|^2$, which contributes to H_e through the Fermi contact interaction. A convenient measure of this interaction is given by

$$\chi = (4\pi/S) \sum_{\text{shells}} \{ |\psi_{\uparrow}(0)|^2 - |\psi_{\downarrow}(0)|^2 \},$$

where S designates the number of unpaired electrons. For divalent transition element ions, experimental values of χ are known⁷ to be roughly

constant (~ -3 atomic units) and this has led to the general assumption of spin polarization effects linear in total spin.

We have calculated χ for the free ions Mn⁺², Fe⁺², and Ni⁺²; the resulting χ 's are -3.34, -3.29, and -3.94 a.u., respectively. We also obtained a χ of -3.27 a.u. for Ni⁺² in a crude (i.e., point charge) crystalline field. The variation in χ for the Ni⁺² calculations is due to its extreme sensitivity to the behavior of the $3d$ spin distribution. The calculated χ 's are consistently more negative than experimental values and this overestimation appears to be a general result of such calculations.⁸

Marshall's² estimates for the outer electrons in metallic Co gave a contribution to the magnetic field of about +260 kgauss. Such estimates are necessarily crude, but probably 200 kgauss for these terms in Fe is reasonable. (Goodings and Heine estimated this to be between +120 and +300 kgauss.) To give a net H_e of -333 kgauss in Fe⁵⁷, the actual H_C must be ~ -530 kgauss (or there must be another, as yet uninvestigated negative contribution). If we estimate by assuming, as for the divalent ions, that χ is about -3 a.u., then H_C for the metal core (with 2.2 unpaired spins) is only -280 kgauss and this is clearly not enough.

To account for this large difference between core polarizations in metals and ions, several factors were 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, theoretical evidence⁵ indicates that the $3d$ electrons in the metal are more expanded than in the free ($3d^6 4s^2$) atom. We have therefore done a full Hartree-Fock spin (exchange) polarized calculation for Fe in both $3d^6 4s^2$ and $3d^8$ configurations. As shown in Fig. 1, even though the $3d^8$ one-electron $3d$ charge density is expanded relative to the $3d^6 4s^2$, the resultant one-electron $3d$ spin density (the relevant factor determining H_C)³ is not significantly changed. This spin density agrees with

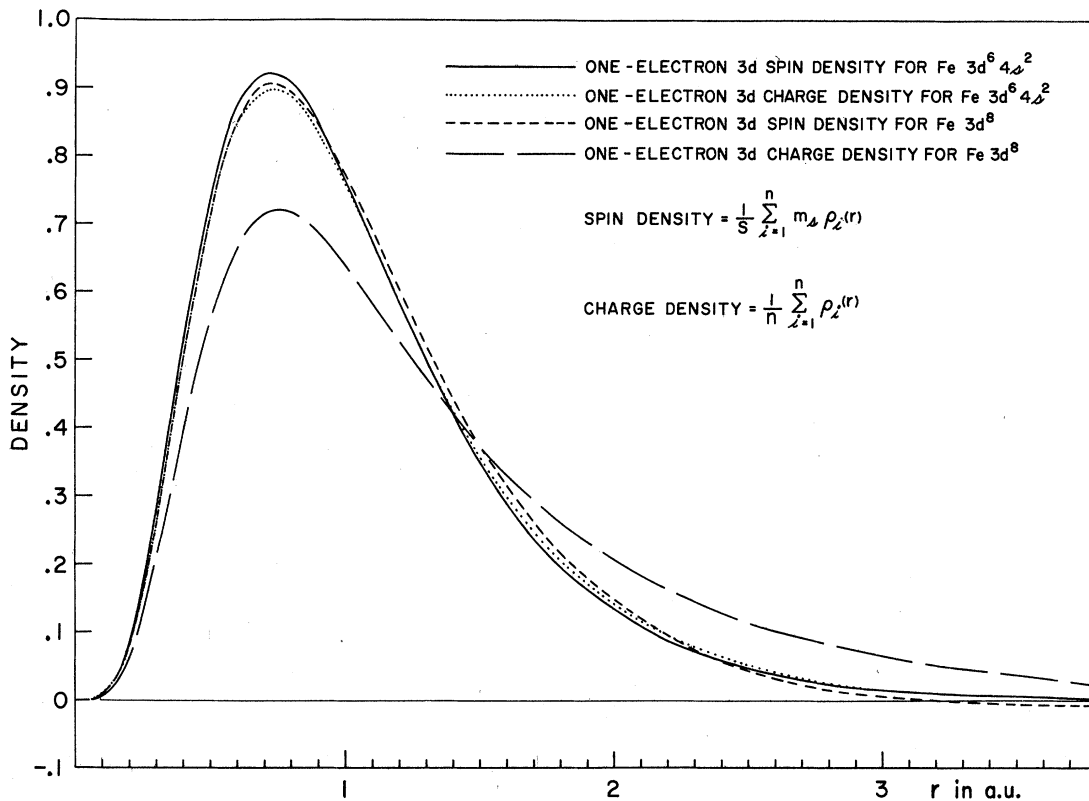


FIG. 1. One-electron $3d$ spin and charge densities for $Fe 3d^6 4s^2$ and $3d^8$.

neutron measurements⁴ and energy band calculations⁵ which give a spin density which is actually slightly contracted relative to the free $3d^6 4s^2$ atom. For Ni^{+2} , such a contraction in spin density was shown to reduce H_C .³

For the $3d^8$ state, the calculated H_C (-350 kgauss) is 30 kgauss lower than the $3d^6 4s^2$ value (both are overestimated by about 40 kgauss). This improvement is too small to overcome the positive contributions and so cannot account for the experimental result.

Goodings and Heine⁶ did a $3d^6 4s^2$ 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 (+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 ~-280 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 the $3d$ 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 Hartree-Fock 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 $3d$ 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.⁹ On the other hand, Fig. 2 suggests that any (other) ad hoc small change of shape in the $3d$ functions

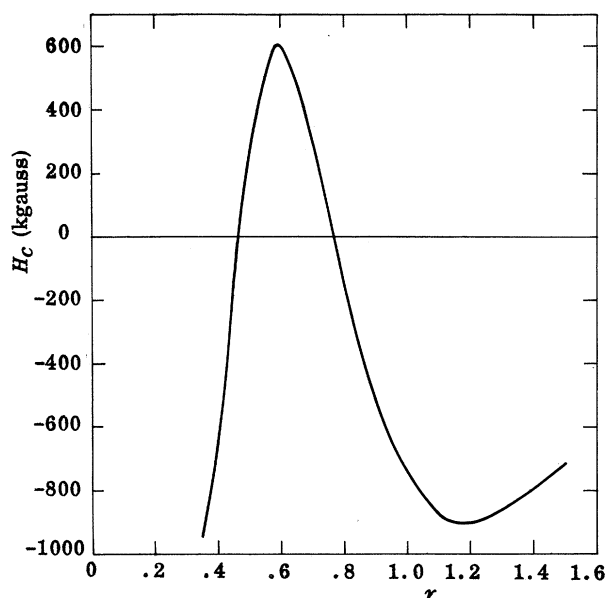


FIG. 2. Core effective field, H_C , as a function of the maximum of the $3d$ orbital for $Fe\ 3d^8$.

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.

What is needed is a theoretical treatment which gives a more realistic description of the atom's

environment, the importance of which is indicated by the experimental results¹⁰ for Fe^{57} in Fe, Co, and Ni.

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⁸This is in large part due to lack of symmetrization, i. e., the total wave function is not, but should be, an eigenfunction of S^2 .

⁹It is apparently always the case that shape and not scaling is the important feature.³

¹⁰See a recent review by G. K. Wertheim, Suppl. J. Appl. Phys. (to be published).

OPTICAL ACTIVITY IN TELLURIUM

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The crystal structure¹ of the elemental semiconductor, tellurium, has a symmetry which places it in an enantiomorphous class. Since this kind of symmetry constitutes only a necessary condition for the existence of optical activity, this effect was examined in single crystals and tellurium was found to have a large rotatory power. Thus, this is the first of the space-group-dependent properties to be measured in this semiconductor.

Both left- and right-handed single crystals were grown by the Czochralski method² which correspond to the space groups D_3^6 and D_3^4 , respectively.

Such crystals are levo- and dextrorotatory. At the initial stages of this work, all of our crystals were found to be dextrorotatory. This, of course, was to be expected since all of our crystals were "descended" from the same parent seed of a few years ago. The levorotatory crystals were grown from seeds which were randomly grown as needles in a hydrogen atmosphere. We would reasonably expect that such needles would have equal likelihood of being left- or right-handed. Quite fortuitously, a levorotatory crystal was grown on the second attempt.

The samples were cut into thicknesses varying