# CONTRIBUTION OF EXCHANGE POLARIZATION OF CORE ELECTRONS TO THE MAGNETIC FIELD AT THE NUCLEUS OF Fe

D. A. Goodings and V. Heine
Royal Society Mond Laboratory, Cambridge, England

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Recent experiments[1,2] on the hyperfine spectrum of $\text{Fe}^{57}$ showed that the effective magnetic field at the nucleus in ferromagnetic iron is directed oppositely to the magnetization with a value of -333 kgauss. Because of the negative sign it was recognized[2] that the dominant contribution to $H_{\text{eff}}$ must arise from the contact interaction of *s* electrons in the iron core. Results of calculations are reported here which confirm this view and give greater insight into the effect.

Following Marshall,[3] the $3d+4s$ "conduction" electrons give a positive contribution to $H_{\text{eff}}$. About 50 kgauss come from some unquenched orbital motion due to spin-orbit coupling. There is also some exchange polarization of the "4*s* band" and some admixture of 4*s*-like functions into the "3*d* band." Together they are equivalent to having about 0.04 to 0.15 unpaired 4*s* electrons per atom, giving an $H_{\text{eff}}$ of 70 to 250 kgauss. Thus the core electrons must contribute an $H_{\text{eff}}$ of at least -450 kgauss to account for the experimental result.

Let the majority of 3*d* electrons have spin ↑. Then since exchange acts only between electrons of parallel spin, a core electron with spin ↑ experiences a stronger exchange force than the corresponding core electron with spin ↓. If the Hartree-Fock formalism is modified to allow such pairs of electrons to have different radial functions,[4] one can calculate $\psi_{nl\uparrow}(\vec{r})$ and $\psi_{nl\downarrow}(\vec{r})$ for each *nl* pair in a self-consistent manner. This is known as the unrestricted Hartree-Fock (UHF) method. In particular one obtains nonzero values for the quantities

$$\rho_{ns} = |\psi_{ns\uparrow}(0)|^2 - |\psi_{ns\downarrow}(0)|^2,$$

giving a contribution to $H_{\text{eff}}$ from the contact interaction

$$H_{\text{core}} = (8\pi/3)\mu_B(\bar{S}/S)\sum\nolimits_{\text{core}}\rho_{ns}.$$

Here $\bar{S}$ is the effective spin from the measured net magnetic moment per atom, and $S$ is the spin of the configuration for which the $\rho_{ns}$ are calculated.

A UHF calculation was carried out by numerical methods[5] for the $(3d)^6(4s)^2\ {}^5D_4$ ground term of the free iron atom. The results, given in the first line of Table I, exemplify features found generally in exchange polarization of core electrons.[4,6] The additional exchange force from one or more unpaired *p* or *d* electrons tends to pull out $\psi_{ns\uparrow}(\vec{r})$ relative to $\psi_{ns\downarrow}(\vec{r})$ for inner *ns* levels, giving a large negative contribution to $H_{\text{core}}$. The opposite is true for outer levels. For example, in the free iron atom, the calculated value of $\rho_{4s}$ was +1.02 which almost completely cancels the negative core contribution. In the metal, however, the contribution of the 4*s* electrons is expected to be much smaller in accordance with the estimates already given above. We note that the value $H_{\text{core}} = -355$ kgauss is not quite enough to explain the experimental result.

Another factor must be considered, namely that the 3*d* electrons may be more spread out in the metal than in the free atom.[7,8] The calculation was therefore repeated with 3*d* functions artificially expanded by about 5% at the maxima and 10% over the tail regions, and the results are shown in the lower line of Table I. The expanded 3*d* functions make the 3*s* electrons behave more like an "inner" shell, with the net result that $H_{\text{core}}$ has a larger negative value. We conclude that it seems difficult to explain the large negative $H_{\text{eff}}$ in the metal without assuming that the

Table I. Results of the UHF calculations. The $\rho$'s are given in units of (Bohr radius)$^{-3}$.

| | $\rho_{1s}$ | $\rho_{2s}$ | $\rho_{3s}$ | $\sum_{\text{core}}\rho_{ns}$ | $H_{\text{core}}$(kgauss) |
|---|---|---|---|---|---|
| Free atom | -0.03 | -2.41 | 1.22 | -1.22 | -355 |
| Expanded 3*d* functions | 0.00 | -2.10 | 0.67 | -1.44 | -420 |

3*d* electrons are 5 to 10% more spread out than in the free ion and that the amount of 4*s* admixed into the 3*d* band is rather small, unless there is some new additional effect such as a negative polarization of the conduction band.[7]

Incidentally the calculations show that if iron were a paramagnetic metal it would have a negative Knight shift.[9] Thus there is no difficulty in principle of understanding the occurrence of negative Knight shifts in platinum[10] and manganese.[11]

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# TOROIDAL ENERGY SURFACES IN CRYSTALS WITH WURTZITE SYMMETRY

R. C. Casella
International Business Machines Research Laboratory, Poughkeepsie, New York

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This note describes the results of an investigation which demonstrates the possibility of toroidal energy surfaces in wurtzite-type solids. The model leads to an anisotropy in the Hall effect, which, in principle, can be made as large as one pleases by lowering the sample temperature.

Based on an earlier symmetry analysis,[1] the shapes of the constant-energy surfaces in the vicinity of the conduction and valence band extrema have been obtained for several crystals having the wurtzite symmetry. Analyses[1-6] of data on the optical absorption in hexagonal CdS, ZnS, ZnO, and CdSe indicate that for these materials the extrema lie at (or very close to) $\vec{k}=0$, where $\vec{k}$ is the electron wave vector. Therefore, the dispersion of the single-particle energy $E(\vec{k})$ has been investigated only in the neighborhood of the origin of the Brillouin zone. Study of the optical data also indicates that the conduction band wave functions at $\vec{k}=0$ transform according to the representation $\Gamma_7$ of the point group $C_{6v}$ (including the effects of spin-orbit interaction), and that the corresponding wave functions associated with the upper and lower "split-off" valence bands belong to the representations $\Gamma_9$ and $\Gamma_7$, respectively. Expanding $E(\vec{k})$ about its value at $\vec{k}=0$ to second order in the wave vector components by means of the well-known $\vec{k}\cdot\vec{p}$ perturbation technique, where $\vec{p}$ is the electron momentum, the following results were obtained: (1) The constant-energy surfaces for the upper ($\Gamma_9$) valence band are doubly degenerate ellipsoids of revolution about the $k_z$ axis ($z \parallel c$). (2) For the $\Gamma_7$ conduction and valence bands, the possibility of finite slopes[7] in $E(\vec{k})$ at $\vec{k}=0$ together with the existence of a single rotational axis in wurtzite-type materials (the *c* axis) allows the possibility of toroidal energy surfaces. Henceforth, we shall confine our attention to the toroidal surfaces and the physical properties of wurtzite-type crystals which one might expect to result therefrom.

For the $\Gamma_7$ bands $E(\vec{k})$ has two roots ($\mp$) of the form

$$E_{\mp}(\vec{k}) = E_0(0) \mp Lk_\perp + Ak_\perp{}^2 + Ck_z{}^2, \tag{1}$$

where

$$k_\perp = (k_x{}^2 + k_y{}^2)^{1/2}, \quad L = m^{-1} |(1|\pi_y|2)|,$$

$$A = (2m)^{-1} + \textstyle\sum_i (m^2\omega_{0i})^{-1} |(1|\pi_x|i)|^2, \tag{2}$$

and *C* is given by the right side of Eq. (2) with $\pi_z$ substituted for $\pi_x$. In the above expressions, *m* is the free-electron mass, $\vec{\pi}$ is the generalized