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# Exchange Polarization and the Magnetic Behavior of Transition Metal and Rare Earth Ions

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Investigations have been carried out for the contribution of "paired" electrons to the magnetic properties of solids utilizing the spin or exchange polarization mechanism in the Hartree-Fock formalism.

Three different physical properties have been studied, each distinguished by the particular region in which the spin density predominates:

(1) The magnetic interaction of a rare earth ion with its neighbors and with its own conduction electrons (which may explain some negative Knight shift measurements by Jaccarino et al.).

(2) The contribution of the core polarization (via the Fermi contact term) to (a) the effective magnetic fields observed by Mössbauer, NMR, EPR and specific heat measurements, (b) to the observed Knight shifts (positive and negative) for systems with unpaired s and d (or f) electrons.

(3) The contribution of the "paired" electrons to the magnetic scattering of neutrons by transition metal and rare earth ions.

## Introduction

The Hartree-Fock method, as conventionally applied to multielectron systems, has a number of restrictions associated with it which limit its applications to physical problems<sup>1)</sup>. One of these restrictions is the requirement that orbitals in the same shell but differing in spin have common radial Relaxation of this constraint, functions. known as spin or exchange polarization, leads to solutions which, as we have found, profoundly affect the interpretation of the magnetic behavior of solids. Since the discussion naturally divides itself into three parts, each distinguished by the particular physical region in space in which the spin density predominates, we shall briefly indicate in the space available to us some of the qualitative results of these investigations.

## 1. Magnetic Interactions of Rare Earths

The contribution of spin or exchange polarization to the magnetic interaction of a rare earth ion with its neighbors and with its own conduction electrons was studied by means of conventional analytic Hartree-Fock calculations for the trivalent rare earth ions and a

spin polarized H-F calculation for the Gd<sup>3+</sup> ion<sup>2)</sup>.

Since the conventional H-F results are of interest in themselves, as they represent the first time that such information has been available, we show in Fig. 1 the one-electron radial charge densities,  $P^2(r)$ , for the outer electrons in Gd<sup>+</sup>. For the metal the 6s electrons would become part of the conduction band but it is not expected that the "core"

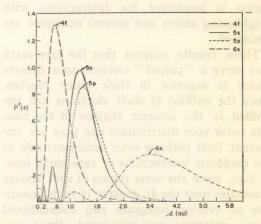


Fig. 1. The one-electron radial charge densities,  $P^{2}(r)$ , for the outer electrons in Gd<sup>+</sup>.

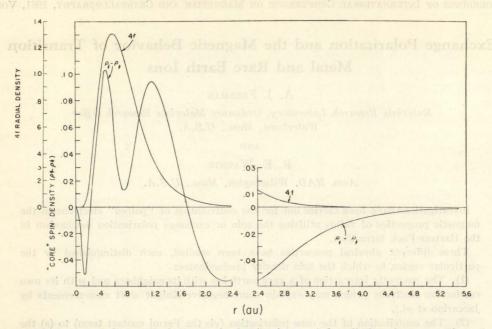


Fig. 2. The computed "core" electron spin density  $(\rho_1 - \rho_1)$  for all the electrons other than the 4f shell and, for comparison, the 4f density as well. Note the change at r=2.4 a.u. to a common scale for both curves.

electrons, i.e., the 4f, 5s, and 5p would be greatly affected from their free ion value.

Fig. 2 shows the computed "core" (i.e., no 6s) electron spin density  $(\rho_{\uparrow} - \rho_{\downarrow})$  for all the electrons other than the 4f shell and, for comparison, the 4f density as well. (Note the change of scales at r=2.4 au to a common scale for both  $\rho_{\uparrow} - \rho_{\downarrow}$  and the 4f density.) The two negative regions indicate densities associated with a spin antiparallel to the net spin of the ion. The region near the nucleus produces the negative effective fields of the type to be discussed below in 2. The outer region is important for interactions with neighboring atoms and several examples are discussed.

These results suggest that the rare earth ions carry a "paired" electron spin density which is negative in their outer reaches. Since the unfilled 4f shell electrons are imbedded in the interior regions of the ions, this outer spin distribution can play an important (and perhaps even dominant) role in the magnetic interactions of rare earth ions. In fact, since the outer region of spin density dominates over the 4f density if such quantities as overlap integrals and conventional  $\langle 1/r_{12} \rangle$  integrals are calculated, these ions may even appear to their neighbors as hav-

ing negative spins (i.e., antiparallel to the 4f spin direction) and some experimental results can perhaps be understood on this basis. In this way, the negative Knight shifts recently observed for GdAl<sub>2</sub> by Jaccarino et al.3) may possibly be qualitatively understood without invoking a negative exchange interaction between the 4f and the conduction electrons.

## 2. Hyperfine Fields and Knight Shifts

The origin of the effective fields, He, observed at the nuclei of a variety of magnetic materials by Mössbauer, NMR, EPR, specific heat and nuclear polarization methods, was investigated by means of (a) accurate exchange (or spin) polarized Hartree-Fock calculations for free transition metal ions and neutral atoms (b) calculations for ions in a (crude) crystalline field (as in a salt) and (c) 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<sup>4)</sup>. It was found 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. While it was found that  $H_e$  was strongly dependent on such factors as the sensitivity of the core polarization 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, which made for a certain ambiguity in the exact value of the field, a consistent set of calculations was carried out which was able to reproduce essential qualitative differences between various ions and to agree quite well with some of the experimental data.

The negative fields found for the ferromagnetic transition metals is 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 mixing of the conduction electrons with the unfilled 3d electrons, gave rise to several other (smaller) negative terms which together can perhaps explain the magnitude and sign of  $H_e$ in the metals. These extra terms are particularly needed in the case of nickel, because the situation here is less understood.

For  $H_e$  [at the nucleus of ions like Fe<sup>+++</sup> 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 found to reduce the free ion value of  $H_e$  and are necessary in order to understand the data. Differences between ions in the same environment (like Mn<sup>++</sup> and Fe<sup>+++</sup>) were found to be reflected in the H-F calculations. For ions like Fe<sup>++</sup> and Co<sup>++</sup> (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 dominate over the core polarization contact term, except for half-closed shell ions like Eu++ and Gd<sup>+++</sup> (for which the orbital contribution

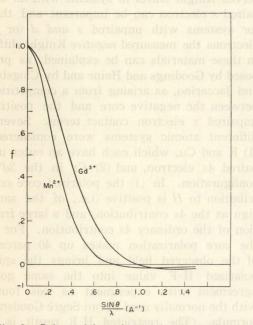
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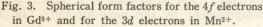
While certain features of the experimental data may be understood (and qualitatively reproduced) in terms of our calculations, more realistic calculations for these ions (e.g., ones which take correlation, relativistic effects and the environment into account) are needed in order to obtain detailed quantitative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

In a parallel study we have also found that the core polarization contributions to the observed Knight shifts in systems with an unpaired s electron can be important and that for systems with unpaired s and d (or f) electrons the measured negative Knight shifts in these materials can be explained, as proposed by Goodings and Heine and by Clogston and Jaccarino, as arising from a competition between the negative core and the positive unpaired s electron contact terms. Several different atomic systems were considered: (1) K and Cu, which each have an outer unpaired 4s electron, and (2) Cr in the  $3d^{5}4s$ configuration. In (1) the polarized core contribution to H is positive (i.e., of the same sign as the 4s contribution) and a large fraction of the ordinary 4s contribution. For K the core polarization makes up 40 percent of the observed field and brings the spinpolarized H-F value into the same good agreement with experiment as was found with the normally used Fermi-Segrè-Goudsmit formula. (The restricted H-F result is in disagreement by the same amount.) In (2) the core polarization contribution is due to a competition between the unpaired 3d (which tend to produce a negative core contribution) and 4s electrons with the net hyperfine field being negative, if the magnetic susceptibility of the 3d electrons is roughly two times that of the "4s" conduction electrons.

# 3. Neutron Magnetic Scattering

The contribution of the "paired" electron spin density to the magnetic scattering of neutrons was investigated using the results for the transition metal and rare earth ions discussed above. Previously reported calculations by ourselves<sup>5</sup> suggested that this contribution was observable, a suggestion which has apparently been borne out in part for<sup>6</sup> NiO. It should be noted that the scattering due to unquenched angular momentum<sup>7</sup> affects the measured form factor in a similar way and that estimates of the two effects together are too small to yield agreement with experiment. Magnetic form factors were determined for the 4*f* electrons including the spin density from the core electrons; the latter is found to increase the 4*f* form factor at low  $\sin \theta/\lambda$  but to decrease it at high  $\sin \theta/\lambda$ . Comparisons are made between our theoretical qualitative predictions and previous theoretical estimates and experimental





values for the 4f electrons in the rare earths and the 3d electrons of the transition elements. The relative closeness of the 4felectron density to the nucleus is shown in Fig. 3 which shows the spherical form factors for the 4f electrons in  $Gd^{3+}$  and the 3d electrons in  $Mn^{2+}$  (its corresponding half-closed shell element). Calculations have been made for the orbital contribution to the magnetic scattering from the 4f electrons; unlike the case for the transition metals this contribution is considerable, since the orbital angular momentum is almost completely unquenched.

#### References

- See R. E. Watson and A. J. Freeman: Phys. Rev. **120** (1960) 1125; for a recent discussion of the Hartree-Fock formalism, with and without restrictions.
- 2 A preliminary report was given earlier (R. E. Watson and A. J. Freeman: Phys. Rev. Letters 6 (1961) 277). A. J. Freeman and R. E. Watson: Phys. Rev. to be published for a more complete discussion.
- 3 V. Jaccarino, B. J. Matthias, M. Peter, H. Suhl and J. H. Wernick: Phys. Rev. Letters 5 (1960) 251.
- 4 See A. J. Freeman and R. E. Watson: Phys. Rev. Letters 5 (1960) 498. R. E. Watson and A. J. Freeman: Phys. Rev. 123 (1961) 2027.
- 5 A. J. Freeman and R. E. Watson: J.A.P. 31 (1960) 374S; Phys. Rev. 118 (1960) 1168.
- 6 H. Alperin: Phys. Rev. Letters **6** (1961) 55; and see the corresponding article in these proceedings.
- 7 M. Blume: Phys. Rev. **124** (1961) 96; see also the paper by W. Marshall in these proceedings.

# DISCUSSION

**R.** NATHANS: I would like to take issue with your statement that the situation with respect to the hyperfine fields in the iron metals is "well in hand". At Brookhaven Mössbauer measurements on Fe<sub>2</sub>Zr and Fe<sub>2</sub>Ti, two iron alloys where the iron magnetic moments are significantly reduced from that in pure iron, have shown that the hyperfine field depends only on the net magnetic moment over a wide range of values. These results are consistent with those of the Harwell group. From your calculations you suggest that the contact term contribution to the hyperfine field is exceedingly sensitive to the detailed shape of the 3d spin density. You also note that the orbital contribution to the total magnetic moment will affect the hyperfine field rather drastically.

Now, from the band calculations on iron metal which shows a strong dependence of the radial extension of the electrons on their relative position in the band, we would expect that the unpaired electron distribution on the iron atoms in alloys with intrinsic moments far different from  $2.2 \mu_B$ , to be quite different from that of pure iron. Further in view of differences in the iron atom environments—the alloys studied at Brookhaven possess a Laves phase structure—we may expect a variation from material to material in the orbital contribution. In spite of all these changes which are now being checked with polarized neutrons, the field at the iron nucleus seems to depend only on the net magnetic moment. The theoretical aspects of this problem do not appear to be entirely exhausted.

W. MARSHALL: The viewpoints of Freeman and Nathans are not really contradictory. Nathans is correct in drawing attention to the deficiencies in our understanding of these matters, but Freeman is probably correct to maintain that our progress is so rapid that we may consider the problem to be well in hand.

V. JACCARINO: It appears doubtful that the exchange polarization mechanism is responsible for the negative spin density observed at the Al sites in  $GdAl_2$ , for example. The reasons for this are as follows:

1. NMR studies of F in  $GdF_3$  and ESR studies of Gd in  $CaF_2$  offer no evidence of a net spin density, of either sign, at the F site.

2. The NMR experiments on LaAl<sub>2</sub> containing 0.1% Gd indicate that a rare-earth conduction electron interaction exists, the magnitude of which is equal to that which is deduced from the Knight shift in the magnetically dense  $GdAl_2$ . Only an interaction that decreased as slowly as  $1/r^3$  at large distance could account for the dilute NMR experiments which is certainly not the case for the exchange polarization mechanism.

A. J. FREEMAN: You are quite correct in pointing out that our qualitative free ion results cannot explain the NMR experiments on LaAl<sub>2</sub> containing Gd. Clearly a proper conduction electron treatment is needed here.

The  $Gd^{3+}$  experiment however involves no conduction electrons and so is a separate case. The reason why no super h.f.s. has been observed in the examples you cited is not clear; a small effect has been observed for  $F^{19}$  in the case of Gd in solution.

to examine this point further; evaluat-