

Calculated hyperfine fields and their pressure derivatives in Fe, Co, and Ni

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The hyperfine field and its pressure derivative have been calculated for the metallic ferromagnets Fe, Co, and Ni using a local approximation for exchange and correlation. Good agreement with experiment is obtained. A short discussion is given of the behavior under pressure of the core and valence contributions to the hyperfine field in these materials.

In the previous paper,¹ Riedi has reported measurements of the pressure dependence of the hyperfine field of ferromagnetic nickel. The hyperfine field in this material increases under pressure, as it does in fcc² and hcp³ cobalt, while it decreases under pressure in bcc iron.⁴

The purpose of this paper is to point out that self-consistent, spin-polarized energy-band calculations for iron, cobalt, and nickel using the local-spin-density (LSD) approximation for exchange and correlation⁵ give results for the hyperfine field and its pressure dependence which are in good agreement with experiment. This is of interest because the LSD approximation assumes that the exchange and correlation forces on an electron at a given point depend only on the electronic charge density and magnetization at the same point, whereas the exchange polarization⁶ of the core electrons by the valence $3d$ electrons (the source of most of the hyperfine field) is a highly nonlocal effect in the Hartree-Fock approximation. It is surprising that the LSD approximation, which can produce exchange polarization effects only through the direct spatial overlap of the core and valence charge densities, works as well as it does for the hyperfine field.

In this Comment, the results of the calculations will first be described and compared to experiment, and a discussion of the meaning of these results will then be given.

In order to calculate the pressure dependence of a quantity in energy-band theory, self-consistent calculations are performed at two or more lattice constants, and a numerical derivative is taken (conversion to a pressure derivative is accomplished using the calculated value of the bulk modulus). The mechanics and details of the energy-band calculations required at each lattice constant have been described elsewhere,⁷ and will not be discussed here. The only features of the calculations that are relevant here are (i) they were performed using the same treatment of exchange and correlation which was earlier found^{8,9} to give good results for the magnetic moment, bulk modulus, lattice constant, etc., of spin-polarized ma-

terials (this treatment is based on the exchange-correlation functional proposed by von Barth and Hedin¹⁰); (ii) their only input parameters are the atomic number and lattice structure (the lattice constant is determined by minimization of the total energy); and (iii) they were performed nonrelativistically in the "muffin-tin" approximation.

The calculated values of the hyperfine field, its pressure derivative, and the pressure derivative of the magnetic moment per atom for bcc Fe, fcc Co, and fcc Ni are compared to experiment in Tables I-III. The decomposition of the pressure derivative of the hyperfine field into core and valence¹⁶ contributions is also given in these tables. The hyperfine field is proportional to the electronic spin density at the nucleus¹⁷ (the field in kG is 524 times the spin density in electrons/Bohr³), and the logarithmic derivatives of the hyperfine field and the experimentally measured hyperfine frequency should be equal, since the nuclear magneton and g factor are not expected to change with pressure.

The calculated values of the hyperfine field at equilibrium are in good agreement with those obtained by Callaway and Wang (who used a similar form for the exchange-correlation potential) for iron¹⁸ and nickel¹⁹; agreement with experiment is satisfactory in cobalt and nickel, but less satisfactory in iron. Although the reason for this is not known, it may be relevant that, of the three, only iron has a partially filled majority-spin d band.

The theoretical values of the pressure derivative of the hyperfine field represent second differences of small quantities (the change with lattice constant or pressure of the spin polarization at the nucleus, which is itself a very small fraction of the total charge density there), and are therefore given to only one significant figure. While the agreement between theoretical and experimental values of the pressure derivative of the hyperfine field is less than perfect, the theory correctly gives the trend in this quantity with atomic number, and it is especially noteworthy that the theory reproduces the change in sign between iron and cobalt.

TABLE I. Hyperfine field H in kG, pressure derivatives of the core and valence contributions to the hyperfine field (kG/Mbar), and logarithmic derivatives of the hyperfine field and magnetic moment per atom (Mbar⁻¹) for bcc iron (calculations performed for a lattice constant of 5.27 a.u.).

	H	$\partial H_c/\partial P$	$\partial H_v/\partial P$	$\partial \ln H/\partial P$	$\partial \ln M/\partial P$
Theory	-260	+1050	-980	-0.3	-0.49
Expt.	-339 ^a	-0.17 ^b	-0.32 ^c

^aReference 11. ^bReference 4. ^cReference 12.

We now turn to a discussion of these results. As is well known, the total electron spin density or microscopic magnetization (whose integral over the unit cell is the magnetic moment per atom) is positive (parallel to the net magnetic moment) in the regions where the $3d$ electronic wave functions have their maximum, but becomes negative both near the nucleus (the hyperfine field is opposite to the magnetic moment¹⁷), and in the interstitial region of the unit cell (in that part of the unit cell outside the $3d$ wave functions), as has been observed by neutron diffraction.²⁰ This is due⁶ to exchange polarization: the exchange interaction is attractive, but operates only on electrons of like spin. Thus the majority-spin d electrons tend to pull majority-spin electrons (mainly the $2s$ electrons) out of the core region,²¹ and also pull valence electrons (mainly the $4s$ electrons) out of the interstitial region, leading to a deficit of majority-spin electrons in both the core and the interstitial regions.

The hyperfine field found in these calculations is negative, in agreement with experiment, because both the core and valence spin densities prove to be negative at the nucleus.²² Its pressure dependence will be a complicated balance of the pressure dependences of the core and valence spin densities at the nucleus. The net magnetic moment per atom de-

TABLE II. Hyperfine field H in kG, pressure derivatives of the core and valence contributions to the hyperfine field (kG/Mbar), and logarithmic derivatives of the hyperfine field and magnetic moment per atom (Mbar⁻¹) for fcc cobalt (calculations performed for a lattice constant of 6.54 a.u.).

	H	$\partial H_c/\partial P$	$\partial H_v/\partial P$	$\partial \ln H/\partial P$	$\partial \ln M/\partial P$
Theory	-220	+210	-280	+0.3	-0.17
Expt.	-217 ^a	+0.60 ^b	-0.22 ^c

^aReference 13. ^bReference 2. ^cReference 14.

TABLE III. Hyperfine field H in kG, pressure derivatives of the core and valence contributions to the hyperfine field (kG/Mbar), and logarithmic derivatives of the hyperfine field and magnetic moment per atom (Mbar⁻¹) for fcc nickel (calculations performed for a lattice constant of 6.55 a.u.).

	H	$\partial H_c/\partial P$	$\partial H_v/\partial P$	$\partial \ln H/\partial P$	$\partial \ln M/\partial P$
Theory	-80	+10	-65	+0.7	-0.21
Expt.	-75 ^a	+0.81 ^b	-0.30 ^c

^aReference 15. ^bReference 1. ^cReference 12.

creases with pressure in all three materials, because the spin density associated with the $3d$ electrons decreases under pressure; this implies a decrease in the exchange polarization forces. Thus the core spin density at the nucleus decreases in magnitude (becomes less negative) under pressure, an effect which is apparent in Tables I–III.

However, the valence spin density at the nucleus *increases* in magnitude (becomes more negative) under pressure in all three materials, as is noted in Tables I–III; this is opposite to what might be expected from the decrease in the exchange polarization forces.²³ One explanation is that the $4s$ orbitals are slightly squeezed by a lattice compression, so that the valence charge density at the nucleus increases under pressure.²⁴ This additional valence charge can become negatively polarized through the exchange interaction with the (already polarized) core orbitals near the nucleus. The net change in the hyperfine field is the result of the competition between these opposing changes in the core and valence spin densities: in Fe, the change in core density outweighs the change in valence spin density, so that the hyperfine field decreases in magnitude under pressure, while in Co and Ni, the valence contribution outweighs the core contribution, so that the hyperfine field increases in magnitude.

An explanation for this difference follows from the fact that, according to the calculations, iron is a "weak" ferromagnet (its majority-spin d band is not filled) while fcc cobalt and nickel are "strong" ferromagnets (their majority-spin d bands are filled). In a ferromagnet, the net magnetic moment per atom decreases with pressure because of conversion of majority-spin d electrons into minority-spin electrons of both s - p and d character (a similar conversion of majority-spin s - p electrons occurs, but is a smaller effect). When the majority-spin d band is filled, as in a strong ferromagnet, its occupancy does not change with pressure (the decrease of the net moment under pressure in this case is caused by increased occupation of the minority-spin d band, because of s - d

conversion). Thus the pressure derivative of the magnetic moment should be larger in weak than in strong ferromagnets, as is observed for the 3d transition metals. The core contribution to the pressure derivative of the hyperfine field should also be larger in weak than in strong ferromagnets, because of the larger pressure dependence of the exchange polarization (both these effects can be seen in Tables I–III), and it may be that the core contribution to the pres-

sure derivative of the hyperfine field outweighs the valence contribution in iron, because of its partially filled majority-spin *d* band.

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¹P. C. Riedi, Phys. Rev. B **20**, 2203 (1979) (preceding paper).

²R. V. Jones and I. P. Kaminow, Bull. Am. Phys. Soc. **5**, 175 (1960).

³D. H. Anderson and G. A. Samara, Bull. Am. Phys. Soc. **2**, 24 (1964).

⁴J. D. Litster and G. B. Benedek, J. Appl. Phys. **34**, 688 (1963).

⁵L. Hedin and B. I. Lundqvist, J. Phys. C **4**, 2064 (1971).

⁶R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 2027 (1961).

⁷V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

⁸J. F. Janak and A. R. Williams, Phys. Rev. B **24**, 4199 (1976).

⁹J. F. Janak, Solid State Commun. **25**, 53 (1978).

¹⁰U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972); see also A. K. Rajagopal and J. Callaway, Phys. Rev. B **7**, 1912 (1973); and O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

¹¹J. I. Budnick, L. J. Bruner, R. J. Blume, and E. L. Boyd, J. Appl. Phys. **32**, 120S (1961).

¹²E. I. Kondorskii and V. L. Sedov, Sov. Phys. JETP **11**, 561 (1960).

¹³A. M. Portis and A. C. Gossard, J. Appl. Phys. **31**, 205S (1960).

¹⁴J. S. Kouvel and C. C. Hartelius, J. Appl. Phys. **35**, 940 (1964).

¹⁵P. C. Riedi, Phys. Rev. B **15**, 5197 (1977).

¹⁶The core electrons are those in the filled argon shell, and the valence electrons include both the 3*d*- and 4*s*-electrons.

¹⁷See, e.g., A. M. Portis and R. H. Lindqvist, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1965), Vol. IIA, p. 357.

¹⁸J. Callaway and C. S. Wang, Phys. Rev. B **16**, 2095 (1977).

¹⁹C. S. Wang and J. Callaway, Phys. Rev. B **15**, 298 (1977).

²⁰See, e.g., G. E. Bacon, *Neutron Diffraction* (Oxford University, New York, 1975), p. 226.

²¹There is also a positive contribution from the 3*s* core electrons, but this is outweighed by the negative contribution from the 2*s* orbitals.

²²In these calculations, it would have been difficult to divide the valence (3*d* + 4*s*-4*p*) contribution to the hyperfine field into component parts, as was done, e.g., in Ref. 6. The calculated valence contribution from all sources is 25–30% of the total hyperfine field in all three metals.

²³This is not necessarily due to an increase in magnitude of the 4*s* spin density everywhere; for example, the calculated interstitial magnetic moment increases (becomes less negative) under pressure in Co and Ni, while it decreases (becomes more negative) in Fe.

²⁴Values of the logarithmic derivative of the valence charge density with respect to pressure are 0.405, 0.351, and 0.756 Mbar⁻¹ for Fe, Co, and Ni, respectively.