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PARAMAGNETIC FORM FACTORS FROM ITINERANT ELECTRON THEORY

J. F. Cooke, S. H. Liu, and A. J. Liu
Solid State Division, Oak Ridge National Laboratory*
Oak Ridge, TN 37831

ABSTRACT

Elastic neutron scattering experiments performed over the past two decades have provided accurate information about the magnetic form factors of paramagnetic transition metals. These measurements have traditionally been analyzed in terms of an atomic-like theory. There are, however, some cases where this procedure does not work, and there remains the overall conceptual problem of using an atomistic theory for systems where the unpaired-spin electrons are itinerant. We have recently developed computer codes for efficiently evaluating the induced magnetic form factors of fcc and bcc itinerant electron paramagnets. Results for the orbital and spin contributions have been obtained for Cr, Nb, V, Mo, Pd, and Rh based on local density bands. By using calculated spin enhancement parameters, we find reasonable agreement between theory and neutron form factor data. In addition, these zero parameter calculations yield predictions for the bulk susceptibility on an absolute scale which are in reasonable agreement with experiment in all treated cases except palladium.

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A uniform magnetic field induces in a nonmagnetic metal a magnetization density which has the periodicity of the lattice. The bulk susceptibility is proportional to the average of the moment density, and the magnetic form factor as measured by the polarized neutron scattering technique gives the Fourier transform of the moment distribution. In the past two decades the induced moment form factor has been measured for a large number of transition metals, and these data provide detailed information on the response of the metals to an external magnetic field. In principle one should be able to relate the moment distribution to the energy levels and wave functions of the metallic electrons. In practice, however, the orbital part of the magnetic response of the itinerant electrons presents a major obstacle. The difficulty is well-known. In short, the magnetic field $\vec{B}$ enters the Hamiltonian of the electron system via the vector potential $\vec{A} = \frac{1}{2}\vec{B} \times \vec{r}$, where $\vec{r}$ is the spatial coordinate. In an infinite crystal the vector potential diverges so that a perturbative treatment of the field effect fails. An exact treatment is possible only in the free electron limit, which is not applicable to transition metals.

Oh et al.[1] circumvented the divergence problem and derived an exact expression for the generalized susceptibility $F_0(\vec{G})$, which is proportional to the orbital contribution of the magnetic form factor:[1]

$$F_0(\vec{G}) = \frac{8N\mu_B^2}{G} \lim_{q\to 0} \sum_{nn'} \sum_{\vec{k}} \frac{f_{n\vec{k}} - f_{n',\vec{k}+\vec{q}}}{E_{n',\vec{k}+\vec{q}} - E_{n\vec{k}}}$$

$$\times \langle n\vec{k}|i\hat{G}\times\hat{B}\cdot\nabla e^{-i(\vec{G}+\vec{q})\cdot\vec{r}}|n',\vec{k}-\vec{g}\rangle\langle n',\vec{k}+\vec{q}|-i\hat{G}\times\hat{B}\cdot\nabla e^{i\vec{q}\cdot\vec{r}}|n\vec{k}\rangle \ . \qquad (1)$$

In the above expression $\vec{G}$ is a reciprocal lattice vector perpendicular to $\vec{B}$, $G = |\vec{G}|$, $\vec{q} \parallel \vec{G}$, μ_B is the Bohr magneton, N is the number of unit cells in the sample, $E_{n\vec{k}}$ is the energy of the state $|n\vec{k}>$ in the band n and wavevector $\vec{k}$, and $f_{n\vec{k}}$ is the states occupation number. The matrix elements are evaluated in the unit cell. It remains difficult to evaluate this expression, but Oh et al.[1] suggested an approximation scheme and applied it to Cr. Their scheme involved the neglect of certain surface integrals over the unit cell boundary, and they argued that it was justifiable for Cr but not for other transition metals.

An alternative to this approach is to formulate the magnetic response problem in real space, as was done by Benkowitsch and Winter.[2] The orbital part of the bulk susceptibility of Al, V, Nb, and Mo has been calculated by these authors, but no form factor calculation was attempted. In close analogy with Ref. 1, the authors of Ref. 2 also separated the total susceptibility into Van Vleck, Landau and diamagnetic contributions. It was shown in Ref. 1 that such a procedure inevitably generates a number of unit cell surface integrals which are small for Cr and Mo but not small for V and Nb. It appears that these surface integrals were ignored in the algebraic manipulations in Ref. 2. Consequently the expression for χ_L in Ref. 2 is incomplete, and this is the reason for their unphysical result of large "paramagnetic" Landau susceptibility in V and Nb.

We present in this paper a different method to evaluate approximately the expression in Eq. (1). The method is based on two observations: (1) that the largest contribution to the sum comes from states near the Fermi level, and in transition metals these are largely d states; and

(2) that the dipole matrix elements $\langle n\vec{k}|-i\nabla|n'\vec{k}\rangle$ between states in the d bands are very small. Consequently, in carrying out the differentiation with respect to q, we may neglect all terms which contain the dipole matrix element as a factor. The result has a simple form:

$$F_0(G) = \frac{8N\mu_B^2}{G} \sum_{nn'} \sum_{\vec{k}} \frac{f_{n\vec{k}}-f_{n'\vec{k}}}{E_{n'\vec{k}}-E_{n\vec{k}}}$$

$$\times \langle n\vec{k}|i\hat{G}\times\hat{B}\cdot\nabla e^{-\vec{G}\cdot\vec{r}}|n'\vec{k}\rangle\langle n'\vec{k}|(\hat{G}\times\hat{B}\cdot\nabla)(\hat{G}\cdot\vec{r})|n\vec{k}\rangle \ . \qquad (2)$$

Unlike the method in Ref. 1, we do not need to evaluate any surface integrals on the unit cell boundary. As a result, the new scheme is applicable to all transition metals. Neither method is applicable to simple metals, however, because they both neglect the Landau diamagnetism. The evaluation of the expression for the orbital susceptibility given in Eq. (2), remains nontrivial. Because of limited space we will only outline the numerical procedure. Given the crystal potential, the electronic band structure and wave functions are generated from a KKR formalism. Inside the muffin-tin sphere the wave functions can be expanded in terms of symmetry orbitals, $\phi_\mu(\vec{r})$, where μ is the symmetry index:

$$|n\vec{k}\rangle = \sum_\mu a_{n\mu}(\vec{k})\phi_\mu(\vec{r}) \ . \qquad (3)$$

The $\{a_{n\mu}(\vec{k})\}$ are the relevant expansion coefficients. The matrix element of an arbitrary operator O can then be written in the general form

$$\langle n\vec{k}|\mathcal{O}|n'\vec{k}\rangle = \sum_{\mu\nu} a^*_{n\mu}(\vec{k})a_{n'\nu}(\vec{k})D_{\mu\nu}(\mathcal{O}) \ , \qquad (4)$$

$$D_{\mu\nu}(\mathcal{O}) = \int \phi^*_\mu(\vec{r})\mathcal{O}\phi_\nu(\vec{r})d^3r \ . \qquad (5)$$

A Wigner-Seitz (WS) approximation is used to evaluate the $D_{\mu\nu}$. That is, the unit cell is approximated by a sphere and the wave function in Eq. (3) is extrapolated to the WS sphere radius. Then, by using standard numerical techniques, the $D_{\mu\nu}$ integrals can be written in terms of products of Clebsch-Gordon matrices, spherical harmonics, and appropriate radial integrals. In this way, the matrix elements in Eq. (2) can be evaluated for a given band structure. Once the matrix elements are known, the Brillouin zone sums can be obtained using well established analytic integration techniques.

We have used the approach outlined above to calculate the total magnetic form factor

$$F(\vec{G}) = \alpha_s F_s(\vec{G}) + F_0(\vec{G}) + F_c(\vec{G}) \ , \qquad (6)$$

based on local density theory. $F_s(\vec{G})$ is the unenhanced spin susceptibility[1], α_s is the corresponding spin enhancement factor, and F_c is the diamagnetic susceptibility for the core electrons (i.e., electrons not included in the calculation of F_0). All of the quantitites in Eq. (6) are completely determined from the band structure, i.e., there are no adjustable parameters. To date, numerical results for Nb, Mo, Cr, V, Pd, and Rh have been obtained on an absolute scale using potentials and spin enhancement factors determined by Moruzzi, Janak, and Williams.[3] A comparison of our results for Cr and Nb with experiment are shown in Figs. 1 and 2, respectively. These represent the best and worst cases found so far. The results for Cr are in excellent agreement with those of Oh et al.[1] This provides an important crosscheck on our calculations.

The results for Cr are dominated by the orbital contribution and are obviously in excellent agreement with experiment. Niobium is a case where the spin and orbital contributions are comparable at $\vec{G} = 0$. However, the orbital term dominates for $\vec{G} \neq 0$ because of the rapid decrease of the spin term with increasing $|\vec{G}|$. The poor agreement with experiment indicates a problem with the wave functions generated by the local density approximation. A word of caution about comparisons of the type given in Figs. 1 and 2. Experimental form factor results are usually given on a relative scale with F(0)=1. Since F(0) cannot be determined from neutron measurements some sort of extrapolated value must be used to normalize the data. It would be preferable for form factor data to be given on an absolute basis (disregarding F(0)) since this would allow a more detailed test of theoretical predictions.

Calculated results for the bulk susceptibility, F(0), are given in Table 1. Our results for Nb and V are quite different from those of Benkowitsch and Winter[2] while results for Mo are in close agreement. In all cases the difference is almost exactly equal to their value for χ_L. This reinforces our point of view that their final expression for χ_L is incorrect. (We expect χ_L to be quite small and negative.) The reason the Mo results agree is because, unlike Nb and V, the Mo wave functions are approximately zero at the Wigner-Seitz sphere radius and the neglected surface integrals are likewise small. Unfortunately, there is not space here to give a detailed comparison with experiment. Experimental data for the bulk susceptibility for most paramagnetic materials ranges over a wide range of values. Within these limits, it appears that, except for Pd our results are reasonable.

In summary, our first principle calculations appear to be in reasonable agreement with experimental results. There are, however, certain discrepancies which appear to be outside combined numerical and experimental uncertainties. In order to help clarify the current situation it is important that we have more accurate form factor data (in absolute not relative units) as well as reliable bulk susceptibility data on a wide range of pure materials at low temperatures.

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[*] Operated by Martin Marietta Energy Systems, Inc. under contract DE-AC05-84OR21400 with the U. S. Department of Energy.

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Table 1

Calculated values of the spin ($\alpha_s F_s$), orbit (F_o), and core (F_c) contributions to the bulk susceptibility (χ).
All values are in 10^{-6} emu/mole.

	$\alpha_s F_s$	F_o	F_c	χ
Cr	30	138	-7	161
V	126	113	-8	231
Nb	82	94	-14	162
Mo	25	98	-13	110
Pd	352	28	-10	370
Rh	82	51	-10	123

FIGURE CAPTIONS

Fig. 1. Form factor for chromium. Experimental data from Stassis et al.[4]

Fig. 2. Form factor for niobium. Experimental data from Moon et al.[5]

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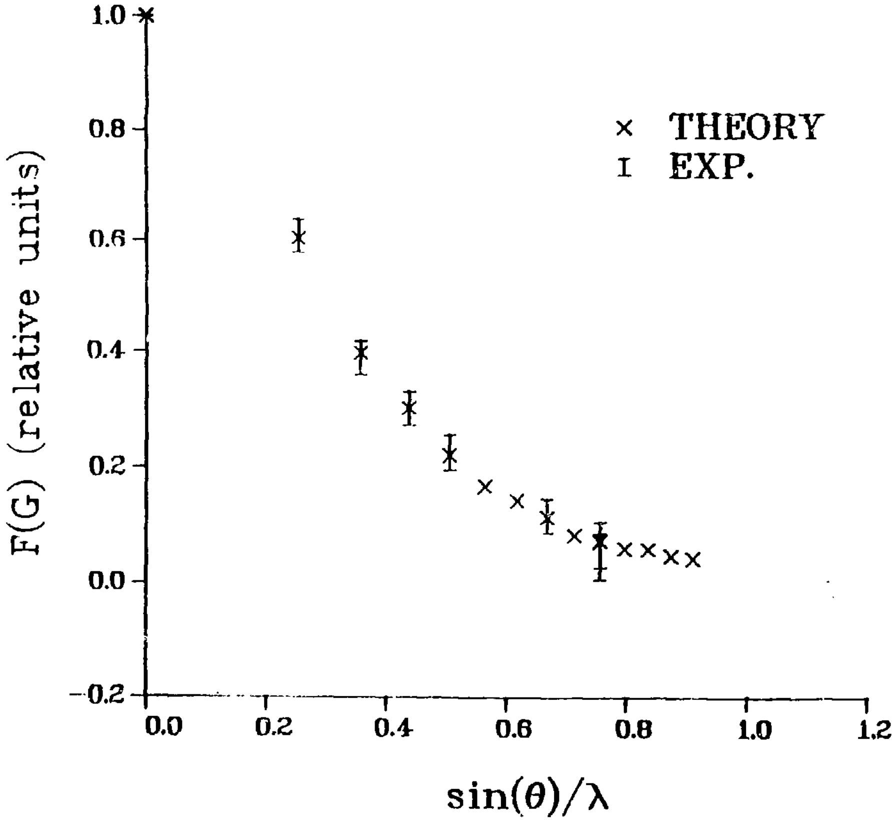

Fig. 1

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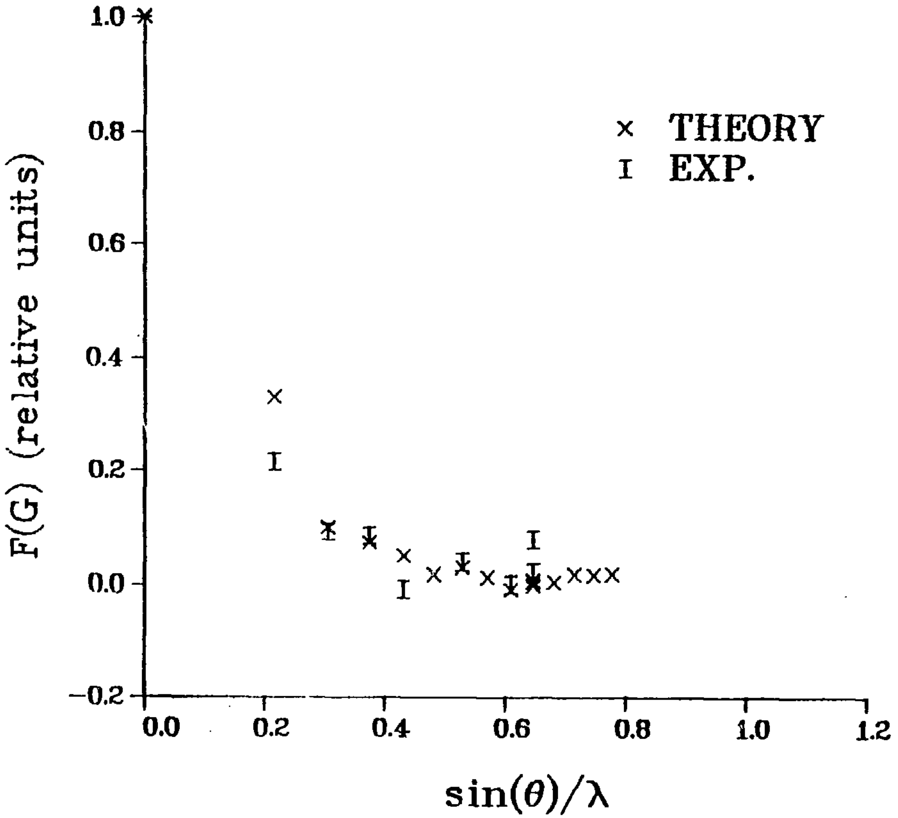

Fig. 2