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Theoretical paramagnetic form factors for hcp transition metals

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The paramagnetic form factor of a metal gives detailed information about the response of the metal to an external static magnetic field. Measurements of this quantity by elastic neutron scattering have been carried out for many paramagnetic transition metals in the past decades. Theoretical understanding of these results has been slow to develop because the orbital contribution of the band electrons to the magnetic moment is difficult to calculate. Recently, we have performed a series of rather accurate form-factor calculations for cubic transition metals and in this paper the same considerations are extended to hexagonal-closed-packed systems. Results based on local-density bands have been obtained for Sc, Lu, Zr, and Y, and there is reasonable overall agreement between theory and experiments.

I. INTRODUCTION

When a uniform static magnetic field is applied to a paramagnetic metal, it responds by forming a spatial-dependent-induced magnetic moment whose Fourier transform, the form factor, can be measured by elastic neutron scattering. The moment distribution, which consists of an orbital and a spin part, is determined by the energy levels and wave functions of the electrons in the metal, mostly the itinerant electrons. The spin contribution of the band electrons is determined by the charge density of the electrons at the Fermi level, and has been calculated for most transition metals. The orbital contribution proves to be difficult to calculate, and for many years it was approximated by using the atomic model. Recently we have developed a quite accurate method to calculate the orbital form factor of cubic transition metals starting from *ab initio* energy bands and wave functions.[1] We have found that, aside from Cr, the orbital form factor of the metal differs significantly from that of the atom, and the calculated form factors are in reasonable agreement with experimental data for many metals. In this paper we report the extension of this work to hexagonal-closed-packed systems.

As in the cubic case we calculate the form factor by relating it to the wave-vector-dependent susceptibility function of the band electrons. The hcp structure has two atoms in a unit cell, and this introduces complications both in the relation between the form factor and the susceptibility function and in the calculation of the matrix elements in the susceptibility expression. We will concentrate on these new features in this paper and refer to our earlier paper[1] for that part of the formulation which is common to both cubic and hcp systems.

II. THEORY

The general expression for the wave-vector-dependent susceptibility for hexagonal systems is, of course, the same as for cubic systems. The expression for the susceptibility for itinerant electron systems was derived by Oh *et al.*[2] The derivation was based on linear-response theory.[3] For a paramagnet in a uniform static magnetic field **B**, the itinerant electron contribution to the total susceptibility is composed of spin, χ_s, and orbital, χ_0, terms:

$$\chi(\mathbf{G})=\mu_B^2 N_0 \mathrm{Re}[\alpha_s\chi_s(\mathbf{G})+\chi_0(\mathbf{G})] \tag{1}$$

$$=2.377\times 10^{-6}[\alpha_s\chi_s(\mathbf{G})+\chi_0(\mathbf{G})]\ \text{emu/mol}\ , \tag{2}$$

$$\chi_s(\mathbf{G})=2\sum_{n,\mathbf{k}}\langle n\mathbf{k}\,|\,e^{-i\mathbf{G}\cdot\mathbf{r}}\,|\,n\mathbf{k}\rangle\delta(E(n\mathbf{k})-E_f)\ , \tag{3}$$

$$\chi_0(\mathbf{G})=-\frac{8}{G}\lim_{\mathbf{q}\to 0}\hat{\mathbf{G}}\cdot\nabla_{\mathbf{q}}\sum_{\substack{n,n',\\ \mathbf{k}}}\frac{f_{n\mathbf{k}}-f_{n',\mathbf{k}+\mathbf{q}}}{E(n',\mathbf{k}+\mathbf{q})-E(n\mathbf{k})}\langle n\mathbf{k}\,|\,(\hat{\mathbf{G}}\times\hat{\mathbf{B}})\cdot\nabla e^{-i(\mathbf{G}+\mathbf{q})\cdot\mathbf{r}}\,|\,n',\mathbf{k}+\mathbf{q}\rangle\langle n',\mathbf{k}+\mathbf{q}\,|\,(\hat{\mathbf{G}}\times\hat{\mathbf{B}})\cdot\nabla e^{i\mathbf{q}\cdot\mathbf{r}}\,|\,n\mathbf{k}\rangle\ , \tag{4}$$

where **G** is a reciprocal-lattice vector, $V=|\mathbf{V}|$, μ_B is the Bohr magneton, N_0 is Avogadro's number, and α_s is the spin enhancement factor. The wave vector **q** is an infinitesimal vector parallel to **G**. The electronic energy $E(n,\mathbf{k})$ is assumed to be in units of rydbergs, and ^ denotes a unit vector. The matrix elements must be evaluated over the unit cell. As was argued in the case of cubic systems, the expression for the orbital susceptibility can be simplified considerably by neglecting all terms which contain the dipole matrix element $\langle n\mathbf{k}\,|\,\nabla\,|\,n'\mathbf{k}'\rangle$ as a factor. This follows from the same argument used in the cubic case; i.e., most of the contribution to the orbital term comes from states near the Fermi surface, which for transition metals are predominantly d in character, and the dipole matrix element between such states is very small. This approximation has been verified by direct numerical calculation. With this approximation

$$\chi_0(\mathbf{G}) = -\frac{8i}{G}\sum_{\substack{n,n',\\ \mathbf{k}}}\frac{f_{n\mathbf{k}}-f_{n'\mathbf{k}}}{E(n'\mathbf{k})-E(n\mathbf{k})} \times\langle n\mathbf{k}\,|\,(\hat{\mathbf{G}}\times\hat{\mathbf{B}})\cdot\nabla e^{-i\mathbf{G}\cdot\mathbf{r}}\,|\,n'\mathbf{k}\rangle \times\langle n'\mathbf{k}\,|\,(\hat{\mathbf{G}}\times\hat{\mathbf{B}})\cdot\nabla(\hat{\mathbf{G}}\cdot\mathbf{r})\,|\,n\mathbf{k}\rangle \; . \tag{5}$$

The first step in evaluating the susceptibility is to determine the band structure. At this point the procedure begins to deviate from that used in the cubic case. The band structure was generated from a self-consistent nonrelativistic Koringa-Kohn-Rostoker (KKR) method using the muffin-tin approximation. The Kohn-Sham approximation for the exchange-correlation potential was used. The hcp structure has two atoms in a unit cell. We choose the unit cell such that the atoms are situated at the origin and at $\boldsymbol{\delta}=(a/\sqrt{3})\hat{\mathbf{x}}+(c/2)\hat{\mathbf{z}}$, where a and c are relevant lattice parameters. Inside the muffin tin the wave functions are expanded in terms of symmetry orbitals, $\phi_\mu(\mathbf{r},E)$, where E is the state energy and μ is a composite symmetry index for conventional angular momentum indices (l,m).

$$|\,n\mathbf{k}\rangle=\sum_{\mu,j}(i)^{l_\mu}a^j_{n\mu}(\mathbf{k})\phi_\mu(\mathbf{r}-\boldsymbol{\delta}_j,E(n\mathbf{k})) \; , \tag{6}$$

where j is a site index and $\boldsymbol{\delta}_j$ locates the atomic sites in the unit cell (either 0 or $\boldsymbol{\delta}$). The $\{a^j_{n\mu}(\mathbf{k})\}$ are relevant expansion coefficients and are complex. As in the cubic case, the symmetry orbitals are chosen to be products of real spherical harmonics and radial functions.

$$\phi_\mu(\mathbf{r},E)=R_l(r,E)y_\mu(\hat{\mathbf{r}}) \; . \tag{7}$$

A site-diagonal approximation is used to evaluate the matrix elements which appear in the expression for the susceptibility. That is, products of radial functions located on different sites are neglected. This is a good approximation for d-symmetry terms. This approximation is not as good for s- and p-symmetry terms but their contribution is relatively small. The matrix elements can then be written in the form

$$\langle n\mathbf{k}\,|\,\mathcal{O}\,|\,n'\mathbf{k}\rangle=\sum_{\substack{\mu,\nu,\\ j}}\bar{a}^{\,j}_{n\mu}(\mathbf{k})a^j_{n\nu}(\mathbf{k})D_{\mu\nu}(\mathcal{O}) \; , \tag{8}$$

$$D_{\mu\nu}(\mathcal{O})=\int\phi_\mu(\mathbf{r},E(n\mathbf{k}))\mathcal{O}\phi_\nu(\mathbf{r},E(n'\mathbf{k}'))d^3r \; , \tag{9}$$

and $\bar{a}^{\,j}_{n\mu}=(a^j_{n\mu})^*$. Note that $D_{\mu\nu}$ depends on both the state energies as well as on symmetry.

III. COMPUTATIONAL PROCEDURE

The general matrix element given in Eq. (8) is evaluated by using a Wigner-Seitz sphere approximation. That is, the unit cell integrals are replaced by an integration over spheres located at each of the two atomic positions in the cell. The volume of each sphere is chosen to be equal to half the unit cell volume. The wave function between the muffin-tin and Wigner-Seitz sphere radii is obtained by extrapolating the radial function $R_l(r,E)$ in Eq. (7). The contribution from the muffin-tin spheres is exact. The contribution from outside the muffin-tin sphere is approximate but also relatively small. At this point we also drop the energy dependence of the radial functions. The spin susceptibility given in Eq. (3) depends only on the wave functions evaluated at the Fermi energy. Since the predominant contribution to the orbital susceptibility comes from states near the Fermi energy and energy dependence of the radial functions is intrinsically weak, it appears, to a good approximation, that the orbital susceptibility can also be calculated using radial functions evaluated at the Fermi energy. These approximations do not alter significantly the numerical accuracy of the result but they do lead to two important numerical simplifications. First, it is clear from the result in Eq. (8) that all of the band and wave-vector dependence of the matrix elements comes from the expansion coefficients and that the $D_{\mu\nu}$ can be factored out of any Brillouin zone sum. Second, the Wigner-Seitz approximation leads to a representation for $D_{\mu\nu}$ which is straightforward to evaluate.

There are three different integrals which must be determined. Since the wave functions have been expanded in terms of real spherical harmonics, we can use the same expansions derived from the cubic case. For completeness the outline of the derivation is reproduced in the Appendix. The general results are

$$D_{\mu\nu}(r_\alpha\nabla_\beta)=\sum_{\xi=\pm}T^{\alpha\beta}_{\mu\nu}(\xi)B^{\xi}_{\mu\nu} \; , \tag{10}$$

$$D_{\mu\nu}(e^{-i\mathbf{G}\cdot\mathbf{r}}\nabla_\alpha)=\sum_{\substack{L,M\\ \xi=\pm}}K^{LM}_{l_\mu,m_\mu;l_\nu m_\nu}(\xi,\alpha) \times W^{\xi}(l_\mu,l_\nu,L:G)y_{L,M}(\hat{\mathbf{G}}) \; , \tag{11}$$

$$D_{\mu\nu}(e^{-i\mathbf{G}\cdot\mathbf{r}})=4\pi\sum_{L,M}(-1)^{(l_\mu-l_\nu+L)/2} \times A(l_\mu,l_\nu,L:G)y_{L,M}(\hat{\mathbf{G}}) \; , \tag{12}$$

where the various terms are defined in the Appendix.

Let $\{g_s\}$ represent the 24 operations of the hcp space group. These are related to 12 simple rotation-reflection operations $\{\alpha_s\}$ as follows:

$$g_s\mathbf{r}=\alpha_s\mathbf{r}, \quad s=1,\ldots,12 \tag{13}$$

$$g_s\mathbf{r}=\sigma\alpha_s\mathbf{r}+\boldsymbol{\delta}, \quad s=13,\ldots,24 \tag{14}$$

where σ is the inversion operation and $\boldsymbol{\delta}$ locates the atom not at the origin. The computer time and core requirements can be reduced significantly by building in the symmetry where possible. For example, the full Brillouin zone sums can be reduced to irreducible zone sums. In addition, it turns out that dividing the space group operations into the two parts given above leads directly to a result for the form factor which is easier to treat numerically.

Then from Eqs. (8), (12), and (15) and the space group operations given in Eqs. (13) and (14), the spin contribution to the susceptibility becomes

$$\chi_s(\mathbf{G})=\chi_1(\mathbf{G})+\chi_1(-\mathbf{G})e^{-i\mathbf{G}\cdot\boldsymbol{\delta}} , \tag{15}$$

$$\chi_1(\mathbf{G})=\sum_{n,k}{}' P_{n\mathbf{k}}^{(s)}(\mathbf{G})\delta(E(n\mathbf{k})-E_f) , \tag{16}$$

where E is the Fermi energy, $\sum'_{\mathbf{k}}$ denotes a sum only over the irreducible Brillouin zone, and

$$P_{n\mathbf{k}}^{(s)}(\mathbf{G})=\sum_{s=1}^{12}\int \bar{\psi}_{nk}(\mathbf{r})e^{-i\alpha_s^{-1}\mathbf{G}\cdot\mathbf{r}}\psi_{nk}(\mathbf{r})d^3r . \tag{17}$$

Substitution of the result given in Eq. (8) yields

$$\chi_s(\mathbf{G})=\sum_{\mu,\nu}[1+(-1)^{l_\mu+l_\nu}e^{-i\mathbf{G}\cdot\boldsymbol{\delta}}]\rho_{\mu\nu}\sum_{s=1}^{12}D_{\mu\nu}(e^{-i\alpha_s^{-1}\mathbf{G}\cdot\mathbf{r}}) , \tag{18}$$

where

$$\rho_{\mu\nu}=\rho_{\mu\nu}^{(1)}+(-1)^{l_\mu+l_\nu}\rho_{\mu\nu}^{(2)} \tag{19}$$

and

$$\rho_{\mu\nu}^{(j)}=\sum_{n,\mathbf{k}}{}'\bar{a}_{n\mu}^{j}(\mathbf{k})a_{n\nu}^{j}(\mathbf{k})\delta(E(n\mathbf{k})-E_f) . \tag{20}$$

The orbital contribution can be written in a form similar to the spin contribution given in Eq. (15):

$$\chi_o(\mathbf{G})=\chi_2(\mathbf{G})+\chi_2(-\mathbf{G})e^{-i\mathbf{G}\cdot\boldsymbol{\delta}} , \tag{21}$$

where

$$\chi_2(\mathbf{G})=\frac{8}{G}\sum_{n,n',\mathbf{k}}\frac{f_{n\mathbf{k}}-f_{n'\mathbf{k}}}{E(n'\mathbf{k})-E(n\mathbf{k})}P_{nn'\mathbf{k}}^{(o)}(\mathbf{G}) \tag{22}$$

and

$$P_{nn'\mathbf{k}}^{(o)}(\mathbf{G})=\sum_{s=1}^{12}\langle n\mathbf{k}\,|\,e^{-i\alpha_s^{-1}\mathbf{G}\cdot\mathbf{r}}\alpha_s^{-1}\hat{\mathbf{G}}\times\hat{\mathbf{B}}\cdot(-i\nabla)\,|\,n'\mathbf{k}\rangle \times\langle n'\mathbf{k}\,|\,\alpha_s^{-1}\hat{\mathbf{G}}\cdot\mathbf{r}\alpha_s^{-1}\hat{\mathbf{G}}\times\hat{\mathbf{B}}\cdot\nabla\,|\,n\mathbf{k}\rangle . \tag{23}$$

In order to calculate the orbital contribution some further manipulation of the result given in Eq. (5) is required. The first step is to separate the inter- and intraband terms. Equation (5) becomes

$$\chi_o(\mathbf{G})=\chi_{\text{intra}}(\mathbf{G})+\chi_{\text{inter}}(\mathbf{G}) , \tag{24}$$

where

$$\chi_{\text{intra}}(\mathbf{G})=\frac{8}{G}\sum_{n,\mathbf{k}}{}'\delta(E(n\mathbf{k})-E_f)P_{nn\mathbf{k}}^{(o)}(G) , \tag{25}$$

$$\chi_{\text{inter}}(\mathbf{G})=\frac{8}{G}\sum_{\substack{n,n',\mathbf{k}\\(n\neq n')}}{}'\frac{f_{n\mathbf{k}}-f_{n'\mathbf{k}}}{E(n'\mathbf{k})-E(n\mathbf{k})}P_{nn'\mathbf{k}}^{(o)}(\mathbf{G}) \tag{26}$$

$$=\frac{8}{G}\sum_{\substack{n,n',\mathbf{k}\\(n\neq n')}}{}'\frac{f_{n\mathbf{k}}(1-f_{n'\mathbf{k}})}{E(n'\mathbf{k})-E(n\mathbf{k})} \times[P_{nn'\mathbf{k}}^{(o)}(\mathbf{G})+P_{n'n\mathbf{k}}^{(o)}(\mathbf{G})] . \tag{27}$$

Substitution of results given in Eqs. (A8), (A12), and (A21) yields

$$P_{nn'\mathbf{k}}^{(o)}(\mathbf{G})=\sum_{\beta,\beta'}H_{nn'}^{\beta\beta'}(\mathbf{k},\mathbf{G})Q_{n'n}^{\beta\beta'}(\mathbf{k}) , \tag{28}$$

$$\begin{aligned}H_{nn'}^{\beta\beta'}(\mathbf{k},\mathbf{G})=\sum_{\mu,\nu}{}'(&[\bar{a}_{n\mu}^{1}(\mathbf{k})a_{n'\nu}^{1}(\mathbf{k})e^{-i\mathbf{G}\cdot\boldsymbol{\delta}}\\&+\bar{a}_{n\mu}^{2}(\mathbf{k})a_{n'\nu}^{2}(\mathbf{k})]A_{\mu\nu}^{\beta\beta'}(\mathbf{G})\\&+[\bar{a}_{n\mu}^{1}(\mathbf{k})a_{n'\nu}^{1}(\mathbf{k})-\bar{a}_{n\mu}^{2}(\mathbf{k})a_{n'\nu}^{2}(\mathbf{k})]\\&\times(1-e^{-i\mathbf{G}\cdot\boldsymbol{\delta}})B_{\mu\nu}^{\beta\beta'}(\mathbf{G})) ,\end{aligned} \tag{29}$$

$$A_{\mu\nu}^{\beta\beta'}(\mathbf{G})=\sum_{\substack{\eta,\alpha''\\\xi=\pm}}[1-(-1)^{L\eta}]K_{\mu\nu}^{\eta}(\xi,\alpha'') \times W^{\xi}(l_\mu,l_\nu,L_\eta:G)S_\eta^{\beta\beta'\alpha''}(\hat{\mathbf{G}}) , \tag{30}$$

$$B_{\mu\nu}^{\beta\beta'}(\mathbf{G})=\sum_{\substack{\eta,\alpha''\\\xi=\pm}}K_{\mu\nu}^{\eta}W^{\xi}(l_\mu,l_\nu,L_\eta;G)S_\eta^{\beta\beta'\alpha''}(\hat{\mathbf{G}}) , \tag{31}$$

$$Q_{n'n}^{\beta\beta'}(\mathbf{k})=\sum_{\substack{\mu,\nu,\\j}}\bar{a}_{n'\mu}^{j}(\mathbf{k})a_{n\nu}^{j}(\mathbf{k})\sum_{\xi=\pm}B_{\mu\nu}^{\xi}T_{\mu\nu}^{\beta\beta'}(\xi) , \tag{32}$$

and

$$S_\eta^{\beta\beta'\alpha''}(\hat{\mathbf{G}}) =\sum_{s=1}^{12}(\alpha_s^{-1}\hat{\mathbf{G}})_\beta(\alpha_s^{-1}\hat{\mathbf{G}}\times\hat{\mathbf{B}})_{\beta'}(\alpha_s^{-1}\hat{\mathbf{G}}\times\hat{\mathbf{B}})_{\alpha''}y_\eta(\alpha_s^{-1}\hat{\mathbf{G}}) . \tag{33}$$

Notice that since $A_{\mu\nu}^{\beta\beta'}(\mathbf{G})$ does not contain terms for L_η even, and in particular for $L_\eta=0$, the orbital contribution, which has $1/G$ as a factor [see Eq. (5)], remains finite as $G\rightarrow 0$.

IV. NUMERICAL RESULTS

The results given in Eqs. (18), (25), and (26) for the spin and orbital susceptibility are straightforward to evaluate. Computer programs have been developed to evaluate accurately the band structure, Wigner-Seitz sphere integrals, and spherical harmonic integrals. The tetrahedron method was used to evaluate the irreducible zone sums. We have included terms of s, p, and d symmetry (nine terms altogether), and the six lowest energy bands.

The itinerant electron contribution to the susceptibility was calculated for Sc, Lu, Zr, and Y. These are all of the hcp paramagnets for which experimental form factor

TABLE I. Calculated values of the spin (α_s,χ_s), orbit (χ_o), and total $(\chi=\alpha_s\chi_s+\chi_o)$ susceptibility. All values are in 10^{-6} emu/mol.

		Sc			Lu	
		$\alpha_s=2.2$			$\alpha_s=1.0$	
G	$\alpha_s\chi_s$	χ_o	χ	$\alpha_s\chi_s$	χ_o	χ
000	301.048	13.661	314.709	105.790	9.640	115.430
100	86.700	11.893	98.593	23.689	3.579	27.268
002	61.565	12.025	73.590	13.426	3.034	16.460
101	19.516	12.051	31.567	−2.307	3.040	0.733
102	19.452	10.297	29.749	−1.500	1.680	0.180
110	15.545	8.781	24.326	−0.555	1.158	0.603
202	27.185	5.088	32.273	6.959	0.164	7.123
103	18.330	8.299	26.629	1.299	1.436	2.735
200	17.664	6.685	24.349	2.543	0.245	2.788
201	28.092	6.290	34.382	5.523	0.436	5.959
300	−0.821	1.449	0.628	−2.253	−0.807	−3.060
004	31.436	4.844	36.280	8.010	−0.506	7.504
400	−8.151	0.157	−7.994	−0.838	−0.256	−1.094
203	8.309	3.317	11.626	0.403	−0.331	0.072

data exist. The total susceptibility, $\chi_T(\mathbf{G})$, determined experimentally is a combination of the itinerant electron contribution discussed above and the diamagnetic contribution from the core electrons, $\chi_{\rm dia}^{\rm core}(\mathbf{G})$,

$$\chi_T(\mathbf{G})=\chi(\mathbf{G})+\chi_{\rm dia}^{\rm core}(\mathbf{G}) , \tag{34}$$

where

$$\chi_{\rm dia}^{\rm core}(\mathbf{G})=-0.7923\times10^{-6}\langle r^2\rangle f_{\rm dia}(\mathbf{G})\ \text{emu/mol} , \tag{35}$$

and r is in units of the Bohr radius. The diamagnetic form factor $f_{\rm dia}$ is given by Stassis.[4] In many cases, experimentalists give $\chi_T(\mathbf{G})$ directly by subtracting out the core diamagnetism from their data.

Numerical results for the wave-vector-dependent susceptibility in units of emu/mol are given in Table I for Sc and Lu and in Table II for Zr and Y. Since the spin enhancement factor α_s has not been calculated for these materials, values were estimated by requiring that the calculated bulk susceptibility $\chi_T(0)$ fall within the range of experimental data. No attempt was made to determine a best fit to the form factor data. As can be seen from Tables I and II, the spin term dominates in all cases except Zr. As was found for the cubic case, the orbital term falls off more slowly and, in general, exhibits less anisotropy than the spin term. This appears to be a universal feature of both cubic and hcp paramagnets. The Wigner-Seitz sphere approximation may smooth out inherent anisotropy but there is no reason to believe that it would affect one term more than the other.

The induced magnetic form factor is more complicated for hcp than for cubic systems. The form factor is defined in terms of the neutron spin-flip ratio $R(\mathbf{G})$,

$$R(\mathbf{G})\sim\frac{4\,\mathrm{Re}\{F_N(\mathbf{G})\chi_T(\mathbf{G})\}}{|F_N(\mathbf{G})|^2} , \tag{36}$$

where $F_N(\mathbf{G})$ is the nuclear structure factor

$$F_N(\mathbf{G})=b(1+e^{i\mathbf{G}\cdot\boldsymbol{\delta}}) , \tag{37}$$

TABLE II. Calculated values of the spin $(\alpha_s\chi_s)$, orbit (χ_o), and total $(\chi=\alpha_s\chi_s+\chi_o)$ susceptibility. All values are in 10^{-6} emu/mol.

		Zr			Y	
		$\alpha_s=1.14$			$\alpha_s=1.52$	
G	$\alpha_s\chi_s$	χ_o	χ	$\alpha_s\chi_s$	χ_o	χ
000	54.133	65.810	119.943	184.969	5.517	190.486
100	11.243	33.051	44.294	41.709	3.892	45.601
002	6.873	23.904	30.777	23.926	4.172	28.098
101	3.853	22.444	26.297	−3.987	3.572	−0.415
102	−0.246	11.424	11.178	−2.224	3.053	0.829
110	−0.010	10.178	10.168	1.663	1.940	3.603
202	2.562	2.604	5.166	14.484	0.294	14.778
103	1.411	5.443	6.854	4.302	2.368	6.670
200	1.720	5.555	7.275	8.416	1.072	9.488
201	1.979	4.050	6.029	11.388	0.893	12.281
300	−0.732	0.703	−0.029	−4.127	−0.783	−4.910
004	3.081	3.346	6.427	16.481	0.091	16.572
400	0.442	0.529	0.971	−1.602	−0.322	−1.924
203	0.431	1.289	1.720	1.140	−0.451	0.689

and b is the nuclear scattering amplitude. Then the form factor, normalized to $\chi_T(0)$ at $G=0$, is given by

$$F(\mathbf{G})=\chi_T'(\mathbf{G})+\frac{\sin(\mathbf{G}\cdot\boldsymbol{\delta})}{1+\cos(\mathbf{G}\cdot\boldsymbol{\delta})}\chi_T''(G)\ , \tag{38}$$

where

$$\chi_T(\mathbf{G})=\chi_T'(\mathbf{G})+i\chi_T''(\mathbf{G})\ . \tag{39}$$

The results given in Tables I and II are reproduced in terms of conventional form factor plots (normalized to unity at $G=0$) in Figs. 1–4. Experimental results are given where available.[5-8] The core diamagnetic term has been subtracted from the experimental data so that the comparison in Figs. 1–4 is for the itinerant electron contribution alone. As was found in the cubic case, the overall agreement is reasonable but not spectacular.

Calculations of the spin contribution from band structure have been carried out before. The results given in this paper are the first to include the itinerant electron orbital term for hcp structures. In previous work, the orbital contribution was taken from atomic theory. A comparison of the orbital part of the normalized form factor for Zr calculated from atomic and itinerant models is given in Fig. 5. These results are typical and indicate that the itinerant result falls off somewhat faster than the atomic result and is not smooth, but exhibits anisotropy.

V. DISCUSSION AND CONCLUSION

As in the previous case, comparison between theory and experiments for hcp metals is subject to the same uncertainties, namely, the spin enhancement factor α_s, the considerable scatter of bulk susceptibility data, and the absolute scale of the form factor data. Unlike the cubic systems, there exists no independent estimate of the spin enhancement factor for hcp transition metals. We have determined α_s by requiring that the bulk susceptibility falls within the range of experimental results. Different choices of the enhancement factor would affect both the absolute value and the shape of the form factor. A possible reason for the scatter of the bulk susceptibility data is the amount of magnetic impurities in the samples.

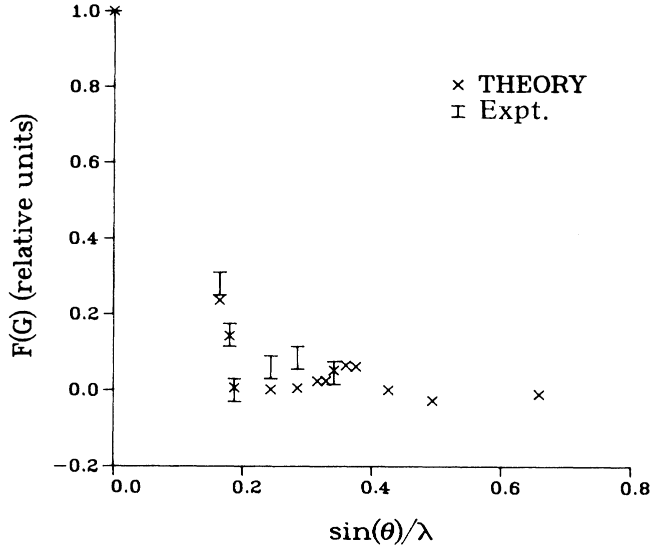

FIG. 2. Form factor for lutetium. Experimental data from Stassis *et al.* (Ref. 6).

While we have tabulated our best estimate of the absolute values of the form factors, we continue to adhere to the convention by comparing theoretical and experimental results in terms of normalized form factors. Experimental data in absolute units are often unavailable.

There is one feature in the Zr data worth mentioning; namely that the bulk susceptibility shows considerable

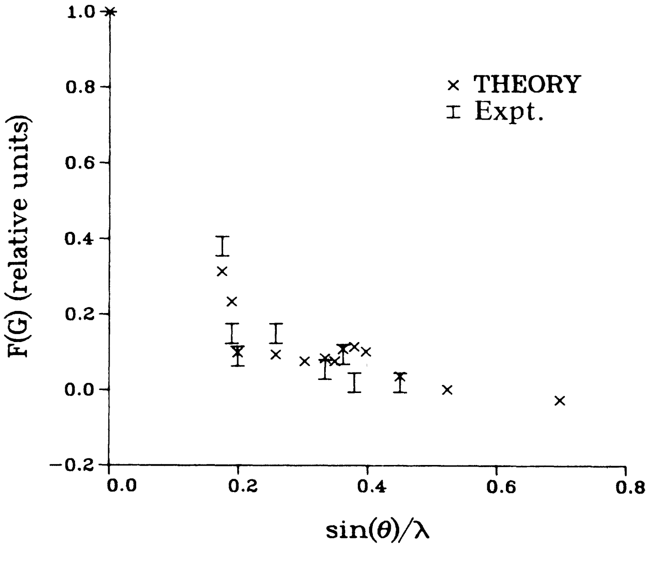

FIG. 1. Form factor for scandium. Experimental data from Koehler *et al.* (Ref. 5).

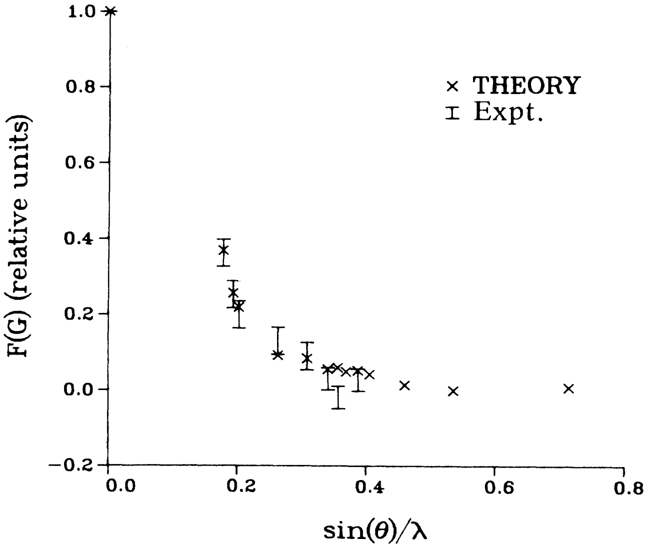

FIG. 3. Form factor for zirconium. Experimental data from Stassis *et al.* (Ref. 7).

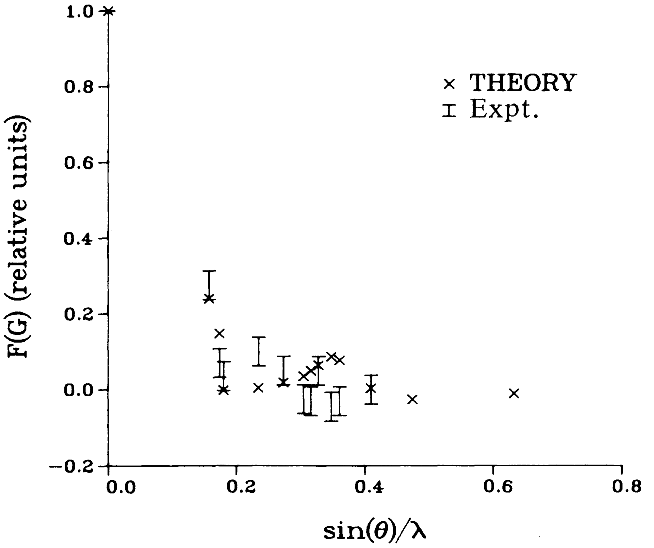

FIG. 4. Form factor for yttrium. Experimental data from Moon *et al.* (Ref. 8).

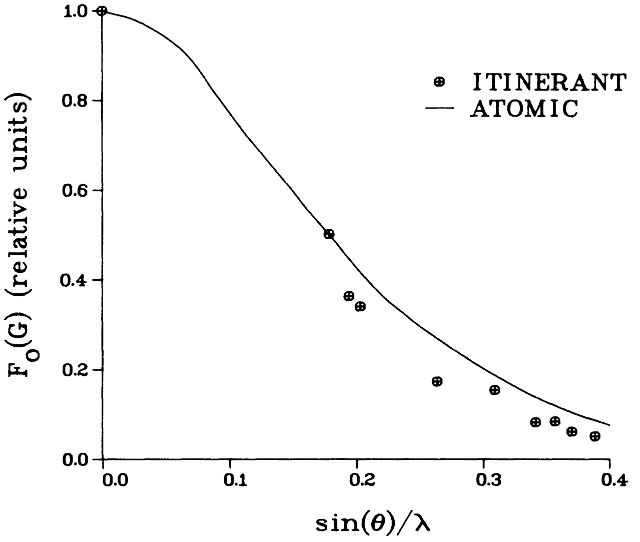

FIG. 5. Comparison of orbital part of the form factor calculated from itinerant and atomic theory for zirconium.

anisotropy depending on whether the field is applied parallel or perpendicular to the c axis of the crystal.[7] On the other hand the form factor data show no such anisotropy. The theoretical results are also insensitive to the field direction. Thus, whatever causes the anisotropy in the bulk susceptibility must be a uniform magnetization. This could be the Landau diamagnetic contribution, but we have no way to confirm this speculation.

ACKNOWLEDGMENT

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APPENDIX

The derivation of expressions for the unit cell integrals necessary for calculating the static susceptibility is outlined in this appendix. There are three integrals which must be evaluated, namely $D(r_\alpha \nabla_\beta)$, $D(e^{-i\mathbf{G}\cdot\mathbf{r}}\nabla_\alpha)$, and $D(e^{-i\mathbf{G}\cdot\mathbf{r}})$ for $\alpha,\beta=x,y,z$. Since the radial functions are to be evaluated at the Fermi energy, we drop the energy variable, i.e., $R_l(r,E_f)\rightarrow R_l(r)$. By convention, composite symmetry indices will be used where possible to represent angular momentum indices, e.g., $\mu=(l_\mu,m_\mu)$. It follows from the properties of spherical harmonics and the identities

$$\nabla_\alpha R_l(r) y_{l,m}(\hat{\mathbf{r}}) = \tfrac{1}{2}\{\nabla^2[r_\alpha R_l(r) y_{l,m}(\hat{\mathbf{r}})] - r_\alpha \nabla^2[R_l(r) y_{l,m}(\hat{\mathbf{r}})]\} , \tag{A1}$$

$$r_\alpha = \left[\frac{4\pi}{3}\right]^{1/2} r y_{l,m_\alpha}(\hat{\mathbf{r}}) , \tag{A2}$$

where $m_\alpha = 1,-1,0$ for $\alpha=x,y,z$, respectively,

$$y_{l,m}(\hat{\mathbf{r}}) y_{l',m'}(\hat{\mathbf{r}}) = \sum_{L,M} C^{L,M}_{l,m;l'm'} y_{L,M}(\hat{\mathbf{r}}) , \tag{A3}$$

$$C^{L,M}_{l,m;l'm'} = \int y_{L,M}(\hat{\mathbf{r}}) y_{l,m}(\hat{\mathbf{r}}) y_{l',m'}(\hat{\mathbf{r}}) d\hat{\mathbf{r}} , \tag{A4}$$

and

$$\nabla_\alpha R_l(r) y_{l,m}(\hat{\mathbf{r}}) = \left[\frac{4\pi}{3}\right]^{1/2} \left[\left[\frac{d}{dr} - \frac{l}{r}\right] R_l(r) \sum_M C^{l+1,M}_{1,m_\alpha;l,m} y_{l+1,M}(\hat{\mathbf{r}}) + \left[\frac{d}{dr} + \frac{l+1}{r}\right] R_l(r) \sum_M C^{l-1,M}_{1,m_\alpha;l,m} y_{l-1,M}(\hat{\mathbf{r}}) \right] , \tag{A5}$$

where $m_\alpha = 1,-1,0$ for $\alpha=x,y,z$, respectively.

Then with

$$e^{-i\mathbf{G}\cdot\mathbf{r}} = 4\pi \sum_{L,M} (i)^{-L} j_l(Gr) y_{L,M}(\hat{\mathbf{G}}) y_{L,M}(\hat{\mathbf{r}}) , \tag{A6}$$

$$P_l(r) = r R_l(r) , \tag{A7}$$

where $j_L(Gr)$ is a spherical Bessel function, it follows that

$$D_{\mu\nu}(r_\alpha \nabla_\beta) = [B^{+}_{\mu\nu} T^{\alpha\beta}_{\mu\nu}(+) + B^{-}_{\mu\nu} T^{\alpha\beta}_{\mu\nu}(-)] , \tag{A8}$$

$$T^{\alpha\beta}_{\mu\nu}(\pm) = \left[\frac{4\pi}{3}\right]^{1/2} (-1)^{(l_\mu - l_\nu)/2} \times \sum_M C^{l_\nu \pm 1,M}_{1,m_\alpha;l_\mu,m_\mu} C^{l_\nu \pm 1,M}_{1,m_\beta;l_\nu,m_\nu} , \tag{A9}$$

$$B^{+}_{\mu\nu}=\int_0^{R_{\rm WS}} rP_{l_\mu}(r)\left[\frac{d}{dr}-\frac{l_\nu+1}{r}\right]P_{l_\nu}(r)dr\ , \tag{A10}$$

$$B^{-}_{\mu\nu}=\int_0^{R_{\rm WS}} rP_{l_\mu}(r)\left[\frac{d}{dr}+\frac{l_\nu}{r}\right]P_{l_\nu}(r)dr\ , \tag{A11}$$

$$\begin{aligned}D_{\mu\nu}(e^{-i\mathbf{G}\cdot\mathbf{r}}\nabla_\alpha)=\sum_{L,M}[&K^{L,M}_{l_\mu,m_\mu;l_\nu,m_\nu}(+,\alpha)W^{+}(l_\mu,l_\nu,L:G)\\&+K^{L,M}_{l_\mu,m_\mu;l_\nu,m_\nu}(-,\alpha)\\&\times W^{-}(l_\mu,l_\nu,L:G)]y_{L,M}(\hat{\mathbf{G}})\ ,\end{aligned} \tag{A12}$$

$$\begin{aligned}K^{\eta}_{\mu,\nu}(\pm,\alpha)=&(-1)^{(l_\mu-l_\nu+l_\eta+1)/2}4\pi\left[\frac{4\pi}{3}\right]^{1/2}\\&\times\sum_{M}C^{l_\nu\pm1,M}_{l_\eta,m_\eta;l_\mu,m_\mu}C^{l_\nu\pm1,M}_{1,m_\alpha;l_\nu,m_\nu}\ ,\end{aligned} \tag{A13}$$

$$\begin{aligned}W^{+}(l_\mu,l_\nu,L:G)=&\int_0^{R_{\rm WS}}P_{l_\mu}(r)j_L(Gr)\\&\times\left[\frac{d}{dr}-\frac{l_\nu+1}{r}\right]P_{l_\nu}(r)dr\ ,\end{aligned} \tag{A14}$$

$$\begin{aligned}W^{-}(l_\mu,l_\nu,L:G)=&\int_0^{R_{\rm WS}}P_{l_\mu}(r)j_L(Gr)\\&\times\left[\frac{d}{dr}+\frac{l_\nu}{r}\right]P_{l_\nu}(r)dr\ ,\end{aligned} \tag{A15}$$

$$\begin{aligned}D_{\mu\nu}(e^{-iG\cdot r})=&4\pi\sum_{L,M}(-1)^{(l_\mu-l_\nu+L)/2}A(l_\mu,l_\nu,L:G)\\&\times C^{L,M}_{l_\mu,m_\mu;l_\nu,m_\nu}y_{LM}(\hat{\mathbf{G}})\ ,\end{aligned} \tag{A16}$$

$$A(l,l',L:G)=\int_0^{R_{\rm WS}}P_l(r)j_L(Gr)P_{l'}(r)dr\ . \tag{A17}$$

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[1] J. F. Cooke, S. H. Liu, and A. J. Liu, Phys. Rev. B (to be published).

[2] K. H. Oh, B. N. Harmon, S. H. Liu, and S. K. Sinha, Phys. Rev. B **14**, 1283 (1976).

[3] J. E. Hebborn and N. H. March, Adv. Phys. **19**, 175 (1970).

[4] C. Stassis, Phys. Rev. Lett. **24**, 1415 (1970).

[5] W. C. Koehler and R. M. Moon, Phys. Rev. Lett. **36**, 616 (1976).

[6] C. Stassis, G. R. Kline, and C.-K. Loong, Solid State Commun. **23**, 159 (1977).

[7] C. Stassis, G. Kline, B. N. Harmon, R. M. Moon, and W. C. Koehler, J. Magn. Magn. Mater. **14**, 303 (1976).

[8] R. M. Moon, W. C. Koehler, and J. W. Cable, in Proceedings of the Conference on Neutron Scattering, Gatlinburg, Tennessee [U.S. Energy Research and Development Administration, Oak Ridge National Laboratory, Oak Ridge, Tennessee, Report No. CONF-7670601-P2, 1976 (unpublished)].