Polarized-neutron study of the coherent paramagnetic scattering amplitude of metallic erbium*

C. Stassis and G. R. Kline
Ames Laboratory–ERDA and Department of Physics, Iowa State University, Ames, Iowa 50011

A. J. Freeman
Physics Department, Northwestern University, Evanston, Illinois 60201

J. P. Desclaux
Institute Laue-Langevin, Grenoble, France

(Received 3 November 1975)

Polarized-neutron techniques have been used to measure the coherent paramagnetic scattering amplitude of high-purity single crystals of metallic erbium at 300 K. The angular dependence of the coherent-scattering amplitude has been determined with the external magnetic field ($H = 22$ kOe) applied parallel as well as perpendicular to the c axis of the crystal. It has been found that the angular dependence of the scattering amplitude for $\vec{H} \parallel \vec{c}$ as well as $\vec{H} \perp \vec{c}$ is in good agreement, except at small scattering angles, with the $4f$-electron magnetic form factor calculated using relativistic Dirac-Fock wave functions. At small scattering angles the experimental points were found to be systematically higher than the theoretical curves obtained by least-square fitting of the calculated $4f$-electron form factor to the large-angle experimental points. This small-angle contribution, attributed to the polarization of the conduction bands of erbium, has an unusual angular dependence; it is different from either a $5d$ or $6s$ atomic form factor and exhibits a non-negative oscillatory character.

I. INTRODUCTION

Although the electronic band structure and related properties of rare-earth metals appear to be well understood, direct information about the nature of their wave functions has been difficult to obtain. Neutron magnetic scattering experiments allow the possibility of obtaining, through Fourier inversion of the measured magnetic form factor, detailed information about the spatial distribution of the magnetization density. The precision determination of the magnetic form factor of Gd metal by Moon, Kohler, Cable, and Child[1] serves to illustrate both the promise and complexities of the method.

In analyzing their results, Moon *et al.*[1] separated from the measured magnetic form factor a contribution representing the localized $4f$ electrons and obtained a form factor which is presumably characteristic of the polarized conduction electrons. The $4f$ density was found to be spherically symmetric with a radial dependence significantly *expanded* relative to the Freeman-Watson[2] nonrelativistic Hartree-Fock (HF) wave functions for the free trivalent ion. The conduction-electron density was found to be long range and oscillatory, i.e., quite different from that expected for the atomic $5d$ and $6s$ orbitals.

Freeman and Desclaux,[3] using relativistic Dirac-Fock (DF) solutions for the Gd^{3+} ion, obtained a $4f$ electron form factor in excellent agreement with the localized form factor found by Moon *et al.*[1] The expansion of the observed $4f$ radial density relative to the HF results was found to be an indirect relativistic effect, the relativistic contraction of the core electrons which results in a more effective screening of the nuclear charge. The magnetic form factor of Tb^{3+}, obtained by polarized-neturon measurements[4] on a truly ionic material, $Tb(OH)_3$ (in which the magnetization arises only from the unpaired $4f$ electrons), was also found to be in excellent agreement with the calculated DF form factor. The theoretical situation for the conduction-electron contribution to the form factor is less clear. An extensive spin-polarized augmented-plane-wave (APW) study of the band structure, conduction-electron polarization, spin densities, and neutron magnetic scattering in ferromagnetic Gd was performed by Harmon and Freeman.[5] The calculated conduction-electron spin density was found to be in only qualitative agreement with the experimental observations[1] because of lack of agreement at the first of several inner reflections from which the spin density is derived. Harmon and Freeman[5] discussed other possible contributions to the magnetization density and concluded that a nonspherical contribution, possibly arising from the $4f$ shell, was needed to explain the discrepancy.

In this paper, we report results of a detailed experimental and theoretical study of the coherent paramagnetic scattering of neutrons in erbium, a heavy-rare-earth metal whose open $4f$ shell, unlike that of Gd, possesses an orbital magnetic moment giving rise to a relatively large magnetic anisotropy. At room temperature erbium is paramagnetic and the $4f$ shell in the metal is in the $^4I_{15/2}$ state. The $4f$ shell possesses both spin and

orbital magnetic moments and the relatively large magnetic anisotropy can be easily observed in a neutron-diffraction experiment. In the present experiment we have chosen to study the spatial distribution of the field-induced magnetization in paramagnetic erbium by measuring the angular distribution of the coherent paramagnetic scattering amplitude. The polarized-neutron technique has been used to perform the measurements, since this method gives highly precise results when the coherent paramagnetic scattering amplitude is small in comparison with the coherent nuclear scattering amplitude, a condition fulfilled in the present experiment. For the same reason the depolarization of the incident beam by the sample is small and its effect on the measurements can be easily assessed. The measurements have been performed using high-purity single crystals, whose properties have been extensively studied by both magnetization measurements[6] and neutron diffraction techniques[7] at the Ames Laboratory.

We find that the localized part of the form factor agrees well with that determined for the Er^{3+} ion from relativistic DF calculations. The difference between the measured form factor and the DF values, at small scattering angles, is different from that expected for $5d$ and $6s$ atomic orbitals and exhibits a non-negative oscillatory character. This oscillatory contribution may be understood as arising from the polarization of the conduction electrons.

II. THEORY

A. Coherent paramagnetic scattering amplitude for Er^{3+}

The quantity measured by the polarized-neutron technique is the *coherent* paramagnetic scattering amplitude $p(\theta)$. Following Moon *et al.*[1] we assume that $p(\theta)$ consists of a localized part $p_l(\theta)$ due to the field-induced $4f$ magnetization and the contribution $p_c(\theta)$ of the conduction-electron polarization,

$$p(\theta)=p_l(\theta)+p_c(\theta)\,. \tag{1}$$

The conduction electrons are polarized by their exchange coupling to the localized ionic moments as well as by the external magnetic field. As a result of the itinerant character of the $5d$- and $6s$-like electrons in the metal their contribution to the coherent scattering amplitude can be of significance only at small scattering angles. No detailed band-theoretical calculation of the conduction-electron contribution is presently available for paramagnetic erbium. The $4f$-electron contribution $p_l(\theta)$ to the coherent paramagnetic scattering amplitude, on the other hand, can be easily calculated if one assumes that the $4f$ electrons in the metal behave like those of the free tripositive ion.

We assume that in the absence of the external magnetic field the tripositive ion is in a single Russel-Saunders state $|\alpha JM\rangle$, where $\alpha=\gamma SL$. When a magnetic field H is externally applied, this state is split into $2J+1$ levels whose probability of occupation is proportional to $e^{\beta M}$, where $\beta=g\mu_B H/kT$ and g is the Landé splitting factor of the ion. If one denotes by $p_{\alpha JM}(\theta)$ the neutron magnetic scattering amplitude by the ion in the $|\alpha JM\rangle$ state, then the coherent scattering amplitude in the presence of the magnetic field is

$$p_l(\theta)=\langle p_{\alpha JM}(\theta)\rangle=\sum_M\left[e^{\beta M}\left(\sum_M e^{\beta M}\right)^{-1}p_{\alpha JM}(\theta)\right]. \tag{2}$$

The magnetic scattering amplitude $p_{\alpha JM}(\theta)$ can be expressed in terms of odd magnetic moments of the ion, whose order of multipolarity is less than or equal to $2l+1$, where l is the orbital quantum number of the open ionic shell. However, this expression for the coherent scattering amplitude can be considerably simplified if the measurements are performed at high temperatures ($\beta\ll 1$), a condition fulfilled in the present experiment. In this case $e^{\beta M}\simeq 1+\beta M$ and only the magnetic dipole term contributes to the coherent scattering amplitude. Thus the coherent paramagnetic scattering amplitude can be written as

$$p_l(\theta)=(0.484)\chi_{\mathrm{mol}}(T)Hf_m(\theta)\times 10^{-16}\,\mathrm{cm}, \tag{3}$$

where H is the magnetic field in G, $\chi_{\mathrm{mol}}(T)$ is the molar susceptibility, and $f_m(\theta)$, the magnetic form factor, is given by[8]

$$f_m(\theta)=\langle j_0(\theta)\rangle+\left[\frac{J(J+1)+L(L+1)-S(S+1)}{3J(J+1)+S(S+1)-L(L+1)}+\frac{2[J(J+1)(2J+1)]^{1/2}}{3J(J+1)+S(S+1)-L(L+1)}\left(\frac{3l(l+1)(2l+1)}{(2l-1)(2l+3)}\right)^{1/2}\times\begin{Bmatrix}S&S&1\\L&L&2\\J&J&1\end{Bmatrix}(\alpha\|W^{(1,2)}\|\alpha)\right]\langle j_2(\theta)\rangle\,, \tag{4}$$

where $W^{(1,2)}$ is a Racah unit double tensor and $\langle j_0(\theta)\rangle$ and $\langle j_2(\theta)\rangle$ are the zero- and second-order Bessel transforms, respectively, of the electronic radial density. In the case of Er^{3+} ($l=3$, $L=6$,

$S=\frac{3}{2}$, and $J=\frac{15}{2}$) the 9-j symbol is $-\frac{1}{100}\sqrt{\frac{187}{273}}$; from the tables[9] of the reduced matrix elements of the Racah tensors $(\alpha \| W^{(1,2)} \| \alpha)=\frac{5}{3}\sqrt{\frac{13}{11}}$. Substituting these values into Eq. (4) gives

$$f_m(\theta)=\langle j_0(\theta)\rangle+\tfrac{88}{135}\langle j_2(\theta)\rangle . \tag{5}$$

The theoretical problem thus becomes one of obtaining realistic values of the $\langle j_i\rangle$ radial integrals.

B. Dirac-Fock calculations for Er^{3+}

In the absence of accurate solid-state calculations, we assume the validity of a highly localized description of the 4f electrons and approximate the $\langle j_i\rangle$ integrals with those obtained from the "best" free-ion solutions. Using our experience with Gd^{3+} and Tb^{3+}, we have obtained highly accurate solutions of the DF equations for Er^{3+} in its ground-state $^4I_{15/2}$ configuration.

The Dirac-Fock approach, as the relativistic counterpart of the HF scheme, has been discussed in detail elsewhere.[10] Solution of the DF equations yields relativistic one-electron wave functions which are conveniently expressed in four-component spinor form, each with a large and small radial function $P(r)$ and $Q(r)$. However, since the Dirac Hamiltonian explicitly includes the spin-orbit interaction, the one-electron orbitals are no longer simultaneous eigenfunctions of the orbital ($\vec{l}$) and spin ($\vec{s}$) angular momenta, but are only eigenfunctions of the total angular momentum $\vec{j}=\vec{l}+\vec{s}$. Using these one-electron Dirac four-component spinors, the many electron wave function is built up as an antisymmetric product which is an eigenfunction of only the total angular momentum $\vec{J}=\vec{L}+\vec{S}$ of the system. By considering a single configuration in the relativistic case, one is restricted to pure jj coupling. This coupling scheme is not justified for the rare-earth atoms, since the Coulomb interaction is by no means negligible compared to the spin-orbit interaction.

To overcome this difficulty, the most accurate procedure for determining the wave functions would be to consider total wave functions defined in intermediate coupling. While it may be worthwhile to undertake such a calculation to study in detail some particular atomic case, we are dealing here with atoms in a crystal; it would be meaningless to calculate the wave functions for a given term as accurately as we could while ignoring the crystal field.

In the nonrelativistic case, a useful approximation in HF calculations is the concept of the average energy.[11] In this approximation, the wave functions are calculated not for each (L, S) state but for the center of gravity of all the state belonging to the configuration under study. In the relativistic case, it is straightforward to define an average energy for a given jj subconfiguration, but, as mentioned above, we cannot consider only a single jj configuration. This implies that we have to average over the entire configuration; the most natural way to achieve this average is to consider a weighted sum of average jj energies, with weights proportional to the degeneracy of the subconfigurations—an extension which has been proposed independently by several authors.[12,13] Our method of solution[10] and a description of the program[14] have been given in detail elsewhere and we shall not discuss these points here. Our results have been obtained by using this generalized-average-energy procedure and are to be compared with nonrelativistic calculations using the average-energy approximation.

Having obtained mixed-configuration Dirac-Fock (MDF) solutions, the resulting wave functions may be used to calculate a number of physically interesting quantities, i.e., expectation values of observable operators. Matrix elements of one-electron radial operators, $O(r)$, are simply given in terms of $P(r)$ and $Q(r)$ by the expression

$$\langle O(r)\rangle=\int_0^\infty [P^2(r)+Q^2(r)]\,O(r)\,dr . \tag{6}$$

In Table I we present our results for the expectation values of the r^n operators $\langle r^n\rangle$ for Er^{3+}. The results for $n=-3$ are needed for estimates of the hyperfine interaction and the results for $n=2, 4, 6$ are useful in determining crystal-field splitting parameters. Table I shows $\langle r^n\rangle$ expectation values over the 4f^* ($j=\frac{5}{2}$) and the 4f ($j=\frac{7}{2}$) wavefunctions as obtained from the MDF calculations and a weighted average obtained from their degeneracies by

$$\langle r^n\rangle_{\rm av}=\tfrac{6}{14}\langle r^n\rangle_*+\tfrac{8}{14}\langle r^n\rangle . \tag{7}$$

Table I also compares these results with the Freeman-Watson[2] HF solutions obtained earlier. It is clear from this comparison that the indirect relativistic effect on the 4f-shell electrons causes the MDF radial wavefunctions to be expanded spatially relative to the HF values.

We have obtained radial integrals $\langle j_i\rangle$ for Er^{3+} using the MDF solutions,

TABLE I. Comparison between the $\langle r^n\rangle$ values for Er^{3+}, obtained by a MDF calculation, and the nonrelativistic HF results.

	MDF			HF (Ref. 2)
n	$\langle r^n\rangle_*$	$\langle r^n\rangle$	$\langle r^n\rangle_{\rm av}$	$\langle r^n\rangle_{\rm av}$
−3	11.63	11.15	11.36	12.01
2	0.6980	0.7210	0.7111	0.666
4	1.218	1.309	1.270	1.126
6	4.502	5.052	4.816	3.978

TABLE II. Radial integrals $\langle j_i \rangle$ for Er^{3+} obtained by a mixed-configuration DF calculation. The induced-moment form factors have been calculated using Eq. (5).

	MDF					HF
$\sin\theta/\lambda$	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$	$\langle j_6 \rangle$	$f_m(\theta)$	$f_m(\theta)$
0	1	0	0	0	1	1
0.05	0.987 03	0.005 17	0.000 02	0.000 00	0.990 400	
0.1	0.949 58	0.019 83	0.000 24	0.000 00	0.962 506	0.965 385
0.15	0.891 69	0.041 75	0.001 13	0.000 03	0.918 905	
0.2	0.818 93	0.067 92	0.003 16	0.000 14	0.863 204	0.870 719
0.25	0.737 22	0.095 33	0.006 69	0.000 43	0.799 361	
0.3	0.651 93	0.121 44	0.011 79	0.001 04	0.731 091	0.744 615
0.35	0.567 39	0.144 49	0.018 29	0.002 07	0.661 576	
0.4	0.486 68	0.163 45	0.025 85	0.003 61	0.593 225	0.611 644
0.45	0.411 82	0.177 92	0.034 08	0.005 67	0.527 797	
0.5	0.343 93	0.187 90	0.042 55	0.008 23	0.466 413	0.486 244
0.6	0.230 45	0.195 84	0.058 86	0.014 55	0.358 109	0.376 415
0.7	0.145 22	0.191 15	0.072 72	0.021 83	0.269 821	0.285 763
0.8	0.084 04	0.178 10	0.083 11	0.029 32	0.200 135	0.212 593
0.9	0.041 87	0.160 32	0.089 79	0.036 40	0.146 375	0.156 163
1.0	0.014 02	0.140 55	0.093 04	0.042 62	0.105 638	0.113 126

$$\langle j_i \rangle = \int_0^\infty [P^2(r) + Q^2(r)]\, j_i(qr)\, dr , \tag{8}$$

where q is the scattering vector and $j_i(qr)$ is the usual spherical Bessel function. These $\langle j_i \rangle$ values and the magnetic form factor obtained from Eq. (6) are given in Table II, where we also give, for comparison, the form factor calculated using radial integrals obtained by HF calculations.[15] As in the case of Gd^{3+} and Tb^{3+}, it is seen that the form factor of Er^{3+} obtained by using DF radial wave functions decreases with increasing scattering angle faster than that obtained by using HF radial wave functions.

III. EXPERIMENT

In the present experiment a polarized monochromatic beam is diffracted by the crystal oriented for Bragg reflection and subjected to an external magnetic field normal to the scattering plane. The quantity measured is the polarization ratio R, defined as the ratio of the coherent diffracted intensities for the two neutron spin orientations, parallel and antiparallel, respectively, to the applied magnetic field. Under the conditions of the present experiment the ratio of the coherent paramagnetic scattering amplitude $p(\theta)$ to the coherent nuclear scattering amplitude b is given by

$$\frac{p(\theta)}{b} = \frac{\sqrt{R}-1}{\sqrt{R}+1} - \frac{p_d(\theta)}{b} - \frac{p_{so}(\theta)}{b} , \tag{9}$$

where $p_d(\theta)$ and $p_{so}(\theta)$ are the diamagnetic[16] and neutron-spin–neutron-orbit[17] scattering amplitudes, respectively. The diamagnetic term arises from the interaction of the magnetic moment of the neutron with the field-induced diamagnetic moment and the spin-orbit term is due to the neutron-spin–neutron-orbit interaction in the Coulomb field of the ion. Both the diamagnetic and spin-orbit contributions to the coherent scattering amplitude of Er are small in comparisons with the paramagnetic contribution: for the (100) reflection the diamagnetic and spin-oribt contributions amount to approximately one part per thousand and five parts per ten thousand, respectively, of the measured scattering amplitude. Thus the experimental data, corrected for the negligibly small diamagnetic and spin-orbit contributions, provide the paramagnetic scattering amplitude $p(\theta)$, which can be compared with the theoretical calculations.

For intensity reasons the experiments were performed using single crystals. The single crystals have been grown by the strain-anneal technique[18] from high-purity material (better than 99.9 at. %) prepared at the Ames Laboratory. The following impurities (in ppm) by weight of Er metal were detected: H (2), N (5), O (43), C (40), F (50), Si (100), Ca (90), Ni (30), Ho (< 100), Yb (< 50). Four single crystals were used in the present experiment: two slices 2 and 1 mm thick, respectively, a pillar with dimensions $1\times1\times6$ mm, and a large 7-mm-thick crystal.

The measured polarization ratios obtained with single crystals must be corrected for secondary extinction effects. To minimize this problem the mosaic spread of the two slices and the pillar were increased gradually by successive compressions. After each compression the mosaic spread of the crystals was assessed by measuring the full width at half maximum (FWHM) of their rocking curves, using a monochromatic neutron beam obtained by Bragg reflection from a perfect Ge crystal. These crystals were compressed until their FWHM

increased from a few minutes of arc to approximately 17 minutes of arc. The secondary extinction problem has been systematically examined, for the pillar, by measuring the integrated reflectivities of the (100), (200), (300), (400), (002), (004), (006), (008), (101), and (202) nuclear reflections at room temperature. The measured integrated reflectivities, corrected for absorption, were consistent with negligible secondary extinction and a Debye-Waller correction corresponding to a Debye temperature of 181 ± 5 K and were checked by two independent measurements. The integrated reflectivities of the nuclear reflections were compared at liquid-N_2 and liquid-He temperatures. The Debye temperature obtained for these measurements agreed, to within experimental precision, with that obtained from the room-temperature measurements. In addition, the ordered-state magnetic form factor was measured at liquid-He temperature and found to be in good agreement with previous measurements.[19] In order to determine that secondary extinction effects did not affect the present experiments, the polarization ratios of all but the outermost nuclear reflections were measured using four different crystals: a composite cystal consisting of the 2- and 1-mm slices cemented together with Duco Cement (measured FWHM $\simeq 26'$), the 2-mm-thick slice, the 1-mm-thick slice, and the pillar. The polarization ratios obtained in these measurements were found to agree to within experimental precision. The 7-mm-thick crystal has not been deformed (measured FWHM $\simeq 6'$) and it was used only to improve the statistical precision of the polarization ratios of the (008) and (207) reflections. The polarization ratios of these reflections, as measured with the 7-mm-thick crystal, were found to agree to within experimental precision with those obtained using the 2-mm-thick slice.

Renninger-type[20] experiments were performed to ascertain whether the measured polarization ratios were contaminated by simultaneous Bragg scattering. With the counter and crystal positions optimized for a particular reflection the crystal was rotated about the scattering vector. It was concluded that the inner reflections, of particular interest in the present experiments, were not affected by simultaneous Bragg scattering, since no change in the polarization ratios was observed upon rotation of the crystal.

The measurements, with a 22-kOe magnetic field on the sample, were performed using a highly polarized neutron beam at the Ames Laboratory Research Reactor. The neutron wavelength λ was 1.05 Å with a $\frac{1}{2}\lambda$ contamination of approximately 0.6%. The temperature of the sample mounted in the 1-in. gap of a conventional electromagnet, as measured by a thermocouple, was found to be approximately 300 K. In order to avoid correcting the polarization ratios for the drifting of the diffraction peak intensity the neutron spin was flipped 20 times/sec and the neutrons of the two spin states were counted in two separate scalers.

The static susceptibilities were determined by measurements[6] on crystals cut from the same ingot as the pillar crystal used in the present experiment. At 300 K, $\chi_{\parallel} = \frac{1}{3254}$ emu/g and $\chi_{\perp} = \frac{1}{3669}$ emu/g for $\vec{H} \parallel \vec{c}$ and $\vec{H} \perp \vec{c}$, respectively; the corresponding values of $p(0)/b$ are 0.068 61 and 0.060 85, respectively. These values were calculated using Eq. (4) and $b = 0.80 \times 10^{-12}$ cm.

IV. ANALYSIS AND DISCUSSION OF RESULTS

The angular dependence of the coherent paramagnetic scattering amplitude of erbium at 300 K was measured with the external magnetic field of 22 kOe both perpendicular and parallel to the c axis of the crystal. The polarization ratios of 29 reflections were determined, 20 with the field perpendicular and the rest with the field parallel to the c axis of the crystal. The ratios $p(\theta)/b$, obtained from the measured polarization ratios are summarized in Figs. 1 and 2.

Assuming the validity of Eq. (1) let us compare the calculated free-ion form factor with the experimental data at large scattering angles. The normalization constant needed for this comparison can be obtained by a least-squares fit to the data at large scattering angles (in our case $\sin\theta/\lambda \gtrsim 0.35$ Å^{-1}), where the conduction-electron contribution to the magnetic scattering amplitude is expected to be negligibly small. In Fig. 1 the theoretical free-ion 4f-electron form factors cal-

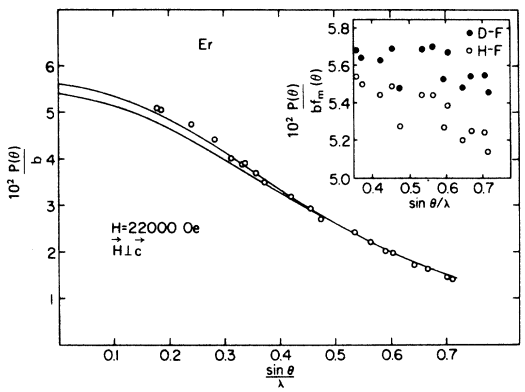

FIG. 1. Comparison of the coherent paramagnetic scattering amplitude for $\vec{H} \perp \vec{c}$ with DF and HF calculations of the magnetic form factor of erbium. The normalization factor for the theoretical curves has been obtained by least-squares fitting to the large-angle ($\sin\theta/\lambda \gtrsim 0.35$) experimental data. The better fit to the large-scattering-angle data of the DF calculation is illustrated in the inset, where we plot the ratios of the measured p/b values to the calculated DF and HF form factors.

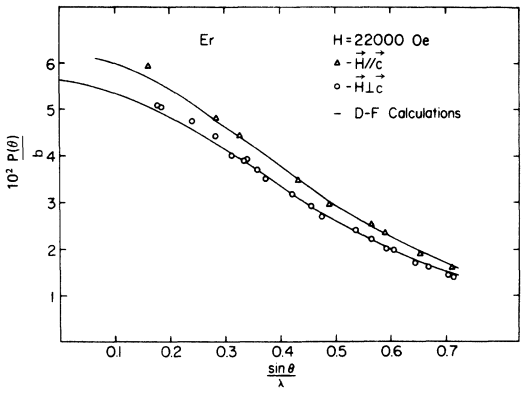

FIG. 2. Comparison of the coherent paramagnetic scattering amplitudes for $\vec{H} \parallel \vec{c}$ and $\vec{H} \perp \vec{c}$ with DF calculations of the magnetic form factor of erbium. The normalization factor for the theoretical curves has been obtained by least-squares fitting to the large-angle ($\sin\theta/\lambda \gtrsim 0.35$) experimental data.

culated using DF and HF radial wave functions given in Table II are compared with the experimental data obtained with the magnetic field applied perpendicularly to the c axis of the crystal. It is seen from Fig. 1 that for $\sin\theta/\lambda \gtrsim 0.5$ Å^{-1} the DF calculations are in substantially better agreement with the experimental data than the HF calculations. A more striking illustration of this is given in the inset of Fig. 1, where we plotted $[p(\theta)/b]/f_m(\theta)$ for both the DF and HF form factors. From Fig. 2 the DF form factor is seen to be also in good agreement with the experimental data obtained with the field applied parallel to the c axis of the crystal. Thus the $4f$-electron form factor of the Er^{3+} ion, calculated using DF radial wave functions, is in quite good agreement with the measured form factor for the metal. The large difference between the magnetic scattering amplitudes obtained for the two directions of the external magnetic field is due to the magnetic anisotropy of erbium. The ratio of the zero-angle magnetic scattering amplitudes for $\vec{H} \parallel \vec{c}$ and $\vec{H} \perp \vec{c}$, obtained by extrapolation, is 1.124 ± 0.011. This value, which is, of course, the ratio of the $4f$-electron susceptibilities for $\vec{H} \parallel \vec{c}$ and $\vec{H} \perp \vec{c}$, respectively, is in excellent agreement with the ratio 1.127 obtained from the measured static susceptibilities. This result is not surprising, since any conduction-electron polarization is expected to be proportional to the induced localized moment.

It is seen that although the agreement between the experimental data and the free-ion DF calculations of the $4f$-electron form factor is quite satisfactory (Fig. 2), the experimental points at small scattering angles are systematically higher than the theoretical curves. These differences are larger than the experimental errors and are larger than the average standard deviation of these curves from the experimental points at large scattering angles. The deviations of the experimental points from the DF theoretical curves are, of course, very sensitive to any small changes in the values of the localized form factor used in the analysis. Let us then consider the approximations used in the evaluation of the localized form factor. This form factor has been calculated using Eq. (5), which has been derived by considering the coupling of the magnetic moment of the neutron to the spin and convection electronic current of the atom. The convection part of the electronic current has been assumed to be that associated with the kinetic energy term of the atomic Hamiltonian, which is an excellent approximation for light atoms. However, in a heavy atom such as Er the convection current associated with the spin-orbit and mass-velocity correction terms could be of some importance. The contribution of these terms to the magnetic scattering amplitude can be easily evaluated.[8] The effect of these terms on the calculated form factor for the Er^{3+} ion has been found[21] to be small—of the order of a few parts per thousand at large scattering angles ($\sin\theta/\lambda \sim 1.0$). Although these relativistic effects are in the right direction, they are too small to account for the deviations observed at small scattering angles in the present experiment. On the other hand, the accuracy of the DF radial wave functions used in the evaluation of the magnetic form factor cannot be as easily ascertained. The DF radial wave functions have been calculated using the mixed-configuration approximation. The effect of this approximation on the radial wave functions, assessed by performing a multiconfigurational self-consistent-field calculation, shows that the error introduced by this approximation is small in comparison with the uncertainties introduced by assuming that the calculated form factor for the Er^{3+} ion correctly describes the localized part of the form factor in the metal. Finally, by making this latter assumption, one neglects effects such as screening of the nuclear charge by the conduction electrons, interband mixing, and core polarization effects, which could affect the theoretical localized magnetic form factor. Harmon and Freeman[5] examined these effects in some detail in their study of Gd metal and concluded that these effects cannot fully account for the small-scattering-angle deviations observed in Gd.[1]

In view of this discussion, it appears reasonable to assume that the DF-calculated form factor for the Er^{3+} ion is an adequate approximation for the localized part of the magnetic form factor. Two facts support this assumption. First, the devia-

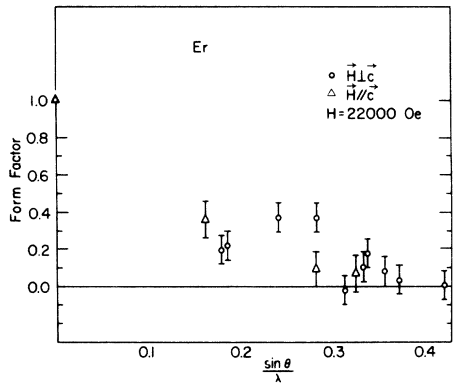

FIG. 3. Angular dependence of the conduction-electron contribution to the coherent paramagnetic scattering amplitude of erbium.

tions of the experimental points from the theoretical curves (Fig. 2) are of the same order of magnitude as those observed in Gd.[1] Second, the ratio of the localized susceptibilities obtained by the neutron-diffraction measurements is in good agreement with the ratio of the measured static susceptibilities; i.e., the additional moment observed in the static-susceptibility measurements is approximately proportional to the localized moment, in agreement with the assumption that this additional moment is due to the polarization of the conduction band.

The angular dependence of the conduction-electron contribution to the coherent scattering amplitude given in Fig. 3 is obtained by subtracting from the experimental values of Fig. 2 the $4f$ contribution given by the DF calculations. The observed angular distribution is quite different from an atomic $5d$ or $6s$ atomic form factor[3]; it exhibits an oscillatory character which shows the unusual, but interesting, feature of remaining positive for all the significant reflections ($\sin\theta/\lambda < 0.3$) shown in Fig. 3. In the absence of energy-band determinations of the conduction-electron magnetization density for Er, a detailed comparison of the experimental data with theory is not possible at present. The magnetization density of neither ferromagnetic[5] nor paramagnetic[22] Gd metal yields an oscillatory form factor. Recently, a detailed APW calculation for paramagnetic Sc by Gupta and Freeman[23] gave a magnetic form factor with an angular dependence which is qualitatively similar to that obtained by us here, and in very good agreement with the measurements of Koehler *et al.*[24] on Sc metal. Gupta and Freeman[23] found their theoretical APW magnetization density to be greatly expanded spatially relative to that expected from a free-ion–atom $3d$ density. They attributed the unusual angular dependence to the asphericity of the spin density and to interference effects, through the Fourier transform, between the inner and outer parts of the radial density. The qualitative similarity between their observations for Sc and ours for Er is consistent with the assumption that the small-angle contribution to the magnetic scattering amplitude is due to the polarization of the conduction band, since it is well known that the conduction-band structure of the heavy-rare-earth metals is similar to that of the hcp $3d$ transition metals.[25]

In conclusion, this combined experimental and theoretical study has revealed that some challenging information about the distribution and nature of the conduction electrons is contained in the neutron magnetic scattering data. Clearly, further theoretical and experimental work is necessary to elucidate the problem. Lutetium is an attractive candidate for a systematic study, since in this metal the $4f$ electrons form a closed shell. Measurements of the induced-moment form factor of Lu, as well as band-theoretical calculations, are presently in progress.

ACKNOWLEDGMENTS

The authors are grateful to B. N. Harmon, H. W. Deckman, and R. P. Gupta for many useful discussions during the course of this work.

*Work supported by the U. S. Energy Research and Development Administration under Grant No. W-7405-eng-82, and by the NSF.

[1]R. M. Moon, W. C. Koehler, J. W. Cable, and H. R. Child, Phys. Rev. B 5, 997 (1972); see also W. C. Koehler, R. M. Moon, J. W. Cable, and H. R. Child, J. Phys. 32, 296 (1971); R. M. Moon, W. C. Koehler, J. W. Cable, and H. R. Child, J. Appl. Phys. 42, 1303 (1971); R. M. Moon and W. C. Koehler, Phys. Rev. Lett. 27, 407 (1971).

[2]A. J. Freeman and R. E. Watson, Phys. Rev. 127, 2058 (1962).

[3]A. J. Freeman and J. P. Desclaux, Int. J. Magn. 3, 311 (1972).

[4]G. H. Lander, T. O. Brun, J. P. Desclaux, and A. J. Freeman, Phys. Rev. B 8, 3237 (1973).

[5]B. N. Harmon and A. J. Freeman, Phys. Rev. B 10, 1979 (1974).

[6]F. H. Spedding and W. J. Gray (unpublished).

[7]M. Habenschuss, C. Stassis, S. K. Sinha, H. W. Deckman, and F. H. Spedding, Phys. Rev. B 10, 1020 (1974).

[8]C. Stassis and H. W. Deckman, Phys. Rev. B 12, 1885 (1975).

[9]R. I. Karaziya, Ya. I. Vizbaraite, Z. B. Rudzikas, and A. P. Jucys, *Talitsy dlya rascheta matrichnykn zlementov operatorov atomnykh velichin* (Acad. Nauk Lit. SSR, Inst. Fiz. Mat., Moscow, 1967).

[10]J. P. Desclaux and N. Bessis, Phys. Rev. A 2, 1623 (1970).

[11]J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960), Vol. 2, Chap. 17.
[12]D. F. Mayers, J. Phys. (Paris) 315, C4-221 (1970).
[13]J. P. Desclaux, C. M. Moser, and G. Verhaegen, J. Phys. B 4, 296 (1971).
[14]J. P. Desclaux, Comp. Phys. Commun. 9, 31 (1975).
[15]M. Blume, A. J. Freeman, and R. E. Watson, J. Chem. Phys. 37, 1245 (1962); 41, 1878 (1964).
[16]C. Stassis, Phys. Rev. Lett. 24, 1415 (1970).
[17]J. Schwinger, Phys. Rev. 73, 407 (1948).
[18]H. E. Nigh, J. Appl. Phys. 34, 3323 (1963).
[19]J. W. Cable, E. O. Wollan, W. C. Koehler, and M. K. Wilkinson, Phys. Rev. 140, A1896 (1965); W. C. Koehler and E. O. Wollan, Phys. Rev. 92, 1380 (1953).
[20]M. Renninger, Z. Phys. 106, 141 (1937); R. M. Moon and C. G. Shull, Acta Crystallogr. 17, 805 (1964).
[21]The authors wish to thank Dr. B. N. Harmon and H. W. Deckman, who performed these calculations.
[22]B. N. Harmon (private communication).
[23]R. P. Gupta and A. J. Freeman (private communication).
[24]W. C. Koehler (private communication).
[25]A. J. Freeman, in *Magnetic Properties of Rare Earth Metals*, edited by R. J. Elliott (Plenum, New York, 1972).