PHYSICAL REVIEW B VOLUME 13, NUMBER 3 1 FEBRUARY 1976

Neutron magnetic form factors of uranium ions*

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(Received 13 August 1975)

The radial $\langle j_i \rangle$ integrals, which contribute to the neutron magnetic form factors, of several uranium ions (U^{3+}, U^{4+}, U^{5+}) are determined from fully relativistic Dirac-Fock wave functions. The expectation values of the r^n operators, $\langle r^n \rangle$, with $n=-3$, 2, 4, and 6 are given for the uranium ions. The possibility of determining the ionization state by magnetic scattering experiments is discussed. The radial $\langle j_i \rangle$ integrals are used to analyze the experimental form factor of US determined by Wedgwood. Satisfactory agreement is found by choosing a $5f^2$ Γ_1 crystal-field ground state with a large internal exchange field inducing ferromagnetism. Contributions to the magnetic scattering from $6d$ electrons are found to be negligible for values of $\sin\theta/\lambda > 0.2$ Å^{-1}.

I. INTRODUCTION

Information about the nature of the $5f$ electrons in the actinides is essential for an understanding of systems formed from elements in this part of the Periodic Table.[1] A key question is whether the $5f$'s are to be treated as localized or itinerant (i.e., by the energy-band method). Although there have been a growing number of experimental and theoretical investigations of these materials, few direct determinations have been made which yield information about the spatial extent of the $5f$ electrons. Neutron magnetic scattering experiments may be used to determine the magnetic form factors of the actinides and thus, through Fourier inversion, detailed information about the spatial distribution of the magnetization density. From such measurements one has a direct means of determining the nature of the $5f$ electrons in these materials, the importance of bonding effects, and, in some cases, the magnitude of the crystalline electric field.

Few neutron magnetic scattering investigations have been performed on actinides.[2-4] The magnetic form factor of US was determined by Wedgwood[2] using polarized neutrons. Single-crystal measurements were also reported by Frazer *et al.*[3] on ionic UO_2. Attempts at interpreting these data from two different systems (US is metallic and UO_2 is an ionic compound) have revealed several problems and have emphasized the need for accurate relativistic $\langle j_i \rangle$ radial integrals with which to formulate even a first approximation.[4] One of the major problems in US is that whereas the bulk magnetization measurements[5] give a moment of 1.55 μ_B/U atom, the neutron results indicate a moment of (1.70 ± 0.03) μ_B/U atom.

In this paper we present free-ion radial integrals of several U ions (3+ to 5+) obtained by means of fully relativistic Dirac-Fock calculations. These radial $\langle j_i \rangle$ integrals show several interesting features which are used to describe the experimental form factor of US. We find that the experimental data are well reproduced using the relativistic $\langle j_i \rangle$ values if one assumes a $5f^2$ Γ_1 ground state with a large internal exchange field inducing a moment of 1.7 μ_B. Comparisons are also made assuming $5f^3$ and $5f^4$ crystal-field states. In the following paper,[6] polarized-neutron measurements of the magnetic form factor of UO_2 in the paramagnetic state are reported; good agreement with theory is obtained with the $\langle j_i \rangle$ integrals of this paper.

II. DIRAC-FOCK EQUATIONS FOR ATOMS

The relativistic counterpart of the Hartree-Fock (HF) method is the Dirac-Fock scheme (DF) in which the one-electron nonrelativistic Hamiltonian is replaced by the Dirac equation. This approximate relativistic Hamiltonian is, of course, not Lorentz invariant because the only electron-electron interaction taken into account is the classical Coulomb repulsion. Nevertheless, it is the only one appropriate for the formulation of the relativistic self-consistent field equations, as has been previously pointed out.[7] After the radial wave functions have been calculated with this Hamiltonian, the relativistic interaction between the electrons may be partially taken into account by including the contribution of the Breit operator as a first-order perturbation correction to the total energy.

The relativistic one-electron wave functions are conveniently expressed in the four-component spinor form

$$\varphi_{nljm} = \begin{pmatrix} r^{-1}P(r)\chi_{ljm} \\ ir^{-1}Q(r)\chi_{-ljm} \end{pmatrix} = \begin{pmatrix} r^{-1}P(r)\chi_{km} \\ ir^{-1}Q(r)\chi_{-km} \end{pmatrix} = \varphi_{nkm}, \tag{1}$$

where the spin angular functions χ_{km} are two-component spinors which are eigenfunctions of the single-particle operators l^2, j^2, j_z, and $k = \beta(\vec{\sigma}' \cdot l + 1)$ with $l(l+1)$, $j(j+1)$, m and k, respectively, as eigenvalues such that

$$j = |k| - \tfrac{1}{2}, \quad l = |k + \tfrac{1}{2}| - \tfrac{1}{2}, \quad \bar{l} = |-k + \tfrac{1}{2}| - \tfrac{1}{2}.$$

We have used the matrices

$$\beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}, \qquad \vec{\sigma}' = \begin{pmatrix} \vec{\sigma} & 0 \\ 0 & \vec{\sigma} \end{pmatrix},$$

where σ_x, σ_y, σ_z, and I are, respectively, the three Pauli matrices and the unit matrix of second order.

The radial functions $P(r)$ and $Q(r)$ are obtained from a minimization of the total energy corresponding to the Hamiltonian

$$\mathcal{H} = \sum_i (-ic\vec{\alpha}_i \cdot \vec{\nabla}_i + \beta_i' c - Z/r_i) + \sum_{i<j} 1/r_{ij}, \tag{2}$$

with the constraint that the wave functions form an orthonormal set; i.e.,

$$\int_0^\infty [P_{nk}(r)\, P_{n'k}(r) + Q_{nk}(r)\, Q_{n'k}(r)]dr = \delta_{nn'},$$

where $\delta_{nn'}$ is the Kronecker δ. For each electron i, the components of $\vec{\alpha}_i$ are the first three Dirac matrices and β_i' is given by

$$\beta' = \beta - \begin{pmatrix} I & 0 \\ 0 & I \end{pmatrix}.$$

The rest-mass energy of the electron (c^2 in a.u.) is subtracted from the Dirac one-electron Hamiltonian. The Breit operator[8]

$$\mathcal{H}_B = \sum_{i<j} \frac{\vec{\alpha}_i \cdot \vec{\alpha}_j}{r_{ij}} + \frac{(\vec{\alpha}_i \cdot \vec{\mathrm{r}}_{ij})(\vec{\alpha} \cdot \vec{\mathrm{r}}_{ij})}{r_{ij}^3} \tag{3}$$

is used as the relativistic interelectronic term and is treated as a first-order perturbation.

As stated, since the Dirac Hamiltonian explicitly includes the spin-orbit interation, the one-electron orbitals are no longer simultaneous eigenfunctions of the orbital ($\vec{\mathrm{l}}$) and spin ($\vec{\mathrm{s}}$) angular momenta, but only eigenfunctions of the total angular momentum $\vec{\mathrm{j}} = \vec{\mathrm{l}} + \vec{\mathrm{s}}$. 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 $\vec{\mathrm{J}} = \vec{\mathrm{L}} + \vec{\mathrm{S}}$ of the system. If, in the relativistic case, we should restrict ourselves to consider a single configuration, this would imply that one is working in the pure *jj* coupling scheme. Even for the heavy ions we consider here such a scheme is not justified since the Coulomb interaction is by no means negligible compared to the spin-orbit interaction.[9]

To overcome this difficulty, the most accurate procedure to determine the wave functions would be to consider total wave functions defined in intermediate coupling. While it is worthwhile to undertake such a calculation for a detailed study in some particular atomic cases, we are dealing here with atoms in a crystal and it would be meaningless to calculate the wave functions for a given term as accurately as we can while ignoring the crystal field. Nevertheless, to be able to compare relativistic with nonrelativistic results we must not depend on different coupling schemes.

In the nonrelativistic case, a useful approximation in HF calculations is the concept of the average energy.[10] In this approximation, the wave functions are calculated not for each (L, S) state but for the center of gravity of all the states belonging to the configurations 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 *LS* configuration; the most natural way to achieve this average is to consider a weighted sum of average *jj* energies, with weights being proportional to the degeneracy of the subconfigurations—an extension which has been proposed independently by several authors.[11,12] Thus for the illustrative case of the $(5f)^2$ configuration we have

$$E_{\mathrm{av}}^{G}(5f^2) = \tfrac{1}{91}[28E_{\mathrm{av}}(5f_{7/2}^2) + 48E_{\mathrm{av}}(5f_{7/2}5f_{5/2}) + 15E_{\mathrm{av}}(5f_{5/2}^2)]. \tag{4}$$

In this expression E_{av} is the average energy for a given *jj* subconfiguration defined as

$$E_{\mathrm{av}} = \sum_n (2J_n + 1)E(J_n) \Big/ \sum_n (2J_n + 1), \tag{5}$$

$E(J_n)$ being the total energy associated with the J_nth state.

The generalization to more than one open shell is straightforward. Given the expression of the total energy E the DF equations are obtained, as in the nonrelativistic case, by varying E with respect to the one-electron radial functions subject to orthonormality constraints. The method of solution[13] and a description of the program[14] have

TABLE I. Expectation values (in a. u.) of $\langle r^n \rangle$ for $n = -3$, 2, 4, and 6 over the $5f^*$ ($j = \frac{5}{2}$), $5f$ ($j = \frac{7}{2}$), and a degeneracy weighted average of $5\bar{f}$ defined in Eq. (7).

	$\langle r^{-3} \rangle$			$\langle r^2 \rangle$			$\langle r^4 \rangle$			$\langle r^6 \rangle$		
Ion	$5f^*$	$5f$	$5\bar{f}$	$5f^*$	$5f$	$5\bar{f}$	$5f^*$	$5f$	$5\bar{f}$	$5f^*$	$5f$	$5\bar{f}$
U^{+3}	5.914	5.417	5.630	2.285	2.392	2.346	10.318	11.347	10.906	83.220	96.307	90.544
U^{+4}	6.528	6.024	6.240	1.999	2.074	2.042	7.310	7.873	7.632	44.781	50.019	47.774
U^{+5}	7.130	6.612	6.834	1.800	1.857	1.833	5.631	5.994	9.838	28.229	30.966	29.793

been given in detail elsewhere and we shall not discuss these points here. All the results we present here have been obtained by using the generalized average just described above and are to be compared with nonrelativistic calculations using the average energy approximation.

III. RADIAL INTEGRALS FOR URANIUM IONS

Mixed configuration Dirac-Fock (MDF) calculations were carried out for several ionization states of uranium in the ground states corresponding to the electron configurations $5f^3$, $5f^2$, and $5f^1$, respectively. The resulting wave functions may then be used to calculate a number of physically interesting quantities, i.e., expectation values of observable operators. Matrix elements of one-electron radial operators, $O_p(r)$, are simply given by the expression

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

where $P(r)$ and $Q(r)$ are, respectively, the large and small components of the relativistic one-electron radial wave functions defined in Eq. (1).

Table I presents our results for the expectation values of the r^n operators, $\langle r^n \rangle$ for some uranium ions; the results for $n = -3$ are needed for estimates of the hyperfine interaction (or of nuclear moment estimates if these are unknown) and the results for $n = 2, 4, 6$ are useful in determining the crystal-field splitting parameters.[15] Table I shows $\langle r^n \rangle$ expectation values over the $5f^*$ ($j = \frac{5}{2}$) and the $5f$ ($j = \frac{7}{2}$) wave functions as obtained from the MDF calculations and a weighted average obtained from their degeneracies by

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

The contraction of the $5f$ radial wave functions with increasing ionization state, as expected from the increased effective nuclear charge, is clearly evident from the values given in Table I. These values of $\langle r^n \rangle$ may be compared with those determined from single determinant (j-j coupling) calculations[15] based on both the Dirac-Fock and Dirac-Fock-Slater (DFS) methods. In the latter scheme the exchange integrals, which are treated exactly in the DF method, are approximated by the Slater $\rho^{1/3}$ free-electron approximation. Our MDF values agree to within a few percent of the DF values derived[15] from Mann's calculations, whereas they differ appreciably from the more approximate DFS values.[15]

We have obtained radial integrals $\langle j_l \rangle$ for the ions studied using the MDF solutions,

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

where κ is the scattering vector and $j_l(\kappa r)$ is the usual spherical Bessel function. In general, one can show that the magnetic form factor can be expressed as

$$f(\vec{\kappa}) = \langle j_0 \rangle + \sum_i c_i \langle j_i \rangle, \tag{9}$$

where the c_i coefficients are defined by the electronic configuration of the magnetic ion and the experimental conditions. One difficulty in the actinides arises from the fact that the spin-orbit and crystal-field interactions are comparable—unlike the case of the rare-earth ions for which the spin orbit is dominant. Thus because of a partial breakdown in the Russell-Sanders coupling the wave functions for the ions in a crystal are not simply expressible in the $|SLJM\rangle$ scheme but instead may be a combination of different J multiplets.[4] These complications may be treated by the tensor-operator method based on the Racah algebra formalism.[16] Various approximate treatments include the assumption that the electron states can be considered as Russell-Sanders configurations (as in the case of the rare earths), and the dipole approximation [valid for low $(\sin\theta)/\lambda$ reflections] that approximates $f(\vec{\kappa})$ by the first two terms of Eq. (9).[16] As examples of the large variation of c_2 possible for the different free ions in their Russell-Saunders ground state configurations, we list in Table II some dipole approximation values of c_2 along with the ordered magnetic moments. The special case of $5f^5(|J| = |S| = \frac{5}{2})$ with L and S oppositely directed leads to some peculiar results, as in the case[17] of Sm^{3+}. This configuration, however, is likely to be greatly affected by mixing with the higher J states (notably $J = \frac{7}{2}$ which lies close by) and this will reduce the effective c_2 coefficient.

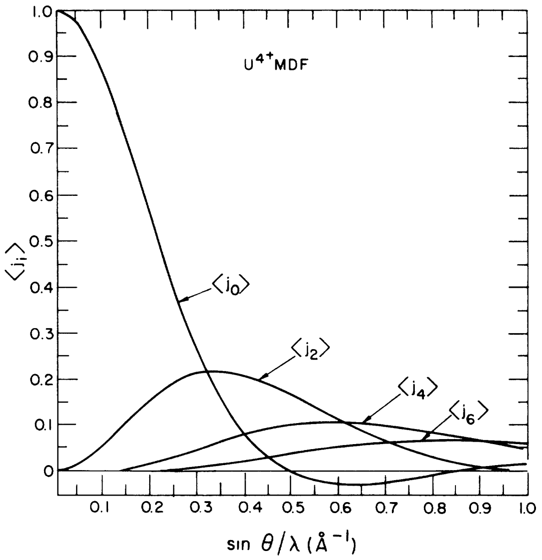

FIG. 1. Radial $\langle j_i\rangle$ integrals obtained with Dirac-Fock solutions for U^{4+}.

The different $\langle j_i\rangle$ functions for U^{4+} plotted in Fig. 1 as a function of $(\sin\theta)/\lambda$ in Å^{-1} show the trends expected: a rapid falloff of $\langle j_0\rangle$ and peaking of $\langle j_i\rangle$ (for $i>0$), but with diminished amplitudes at increasing $(\sin\theta)/\lambda$ values for increasing i. What is unexpected is the large *dominant* contribution of $\langle j_2\rangle$ for $(\sin\theta)/\lambda > 0.5$ Å^{-1} at which the spherical part of the form factor $\langle j_0\rangle$ has gone through zero and has changed sign.

Since the number of $5f$ electrons associated with an actinide ion in a compound is uncertain, we need to determine how sensitive the $\langle j_i\rangle$ radial integrals are to the state of ionization. These results for each of the ions studied are listed in Table III. In this table we list only the configuration average of the individual $\langle j_n\rangle$ obtained for the $5f^*$ and $5f$ radial solutions [cf. Eq. (7)]. For easier comparison we show in Figs. 2–4 the $\langle j_0\rangle$, $\langle j_2\rangle$, and $\langle j_4\rangle$ values for the three U^{n+} ions studied.

TABLE II. Coefficients c_2 of Eq. (9) as given for the various Hunds-rule Russell-Saunders ground states. The ordered moment μ_{sat} is also given.

Number of f electrons	Uranium ionization	Configuration	c_2	μ_{sat}
1	U^{5+}	$^2F_{5/2}$	1.333	2.14
2	U^{4+}	$^3H_4$	1.500	3.20
3	U^{3+}	$^4I_{9/2}$	1.750	3.27
4	U^{2+}	$^5I_4$	2.333	2.40
5		$^6H_{5/2}$	6.000	0.71

TABLE III. Radial $\langle J_l\rangle$ integrals for U^{3+}, U^{4+}, and U^{5+}.

$(\sin\theta)/\lambda$	$\langle j_0\rangle$	$\langle j_2\rangle$	$\langle j_4\rangle$	$\langle j_6\rangle$
		U^{3+}		
0.0	1.0000	0.0	0.0	0.0
0.05	0.9579	0.0167	0.0001	0.0000
0.10	0.8434	0.0600	0.0019	0.0001
0.15	0.6860	0.1140	0.0080	0.0004
0.20	0.5178	0.1628	0.0198	0.0018
0.25	0.36350	0.1963	0.0362	0.0049
0.30	0.23589	0.2117	0.0546	0.0101
0.35	0.13852	0.2108	0.0721	0.0172
0.40	0.06938	0.1978	0.0868	0.0253
0.45	0.0235	0.1771	0.0974	0.0339
0.50	−0.0041	0.1524	0.1037	0.0421
0.60	−0.0234	0.1020	0.1047	0.0554
0.70	−0.0181	0.0595	0.0945	0.0632
0.80	−0.0053	0.0292	0.0785	0.0653
0.90	0.0069	0.0103	0.0608	0.0628
1.00	0.0154	0.0002	0.0442	0.0571
1.10	0.0200	−0.0037	0.0301	0.0496
1.20	0.0212	−0.0039	0.0190	0.0414
1.30	0.0202	−0.0021	0.0108	0.0334
1.40	0.0177	0.0006	0.0051	0.0259
1.50	0.0146	0.0033	0.0016	0.0194
		U^{4+}		
0.0	1.0000	0.0	0.0	0.0
0.05	0.9631	0.0146	0.0001	0.0000
0.10	0.8612	0.0536	0.0014	0.0000
0.15	0.7161	0.1049	0.0061	0.0003
0.20	0.5547	0.1547	0.0158	0.0011
0.25	0.3000	0.1928	0.0304	0.0034
0.30	0.2667	0.2142	0.0482	0.0074
0.35	0.1613	0.2189	0.0666	0.0134
0.40	0.0840	0.2098	0.0832	0.0209
0.45	0.0316	0.1911	0.0963	0.0294
0.50	−0.0008	0.1668	0.1052	0.0382
0.60	−0.0251	0.1139	0.1102	0.0538
0.70	−0.0205	0.0675	0.1019	0.0641
0.80	−0.0066	0.0336	0.0860	0.0683
0.90	0.0071	0.0121	0.0674	0.0670
1.00	0.0168	0.0006	0.0494	0.0619
1.10	0.0220	−0.0040	0.0338	0.0543
1.20	0.0235	−0.0044	0.0214	0.0457
1.30	0.0224	−0.0024	0.0123	0.0371
1.40	0.0197	0.0005	0.0059	0.0289
1.50	0.0163	0.0035	0.0019	0.0218
		U^{5+}		
0.0	1.0000	0.0	0.0	0.0
0.05	0.9668	0.0132	0.0001	0.0000
0.10	0.8740	0.0489	0.0011	0.0000
0.15	0.7390	0.0975	0.0049	0.0001
0.20	0.5845	0.1471	0.0131	0.0008
0.25	0.4314	0.1879	0.0261	0.0024
0.30	0.2952	0.2138	0.0428	0.0056
0.35	0.1839	0.2234	0.0611	0.0106
0.40	0.0999	0.2184	0.0787	0.0174
0.45	0.0412	0.2024	0.0937	0.0256
0.50	0.0037	0.1793	0.1047	0.0344
0.60	−0.0261	0.1253	0.1139	0.0513
0.70	−0.0228	0.0756	0.1081	0.0638
0.80	−0.0081	0.0383	0.0928	0.0701
0.90	0.0070	0.0143	0.0737	0.0704
1.00	0.0179	0.0011	0.0545	0.0660
1.10	0.0239	−0.0043	0.0376	0.0587
1.20	0.0257	−0.0048	0.0240	0.0498
1.30	0.0246	−0.0028	0.0138	0.0406
1.40	0.0217	0.0004	0.0067	0.0319
1.50	0.0180	0.0037	0.0022	0.0241

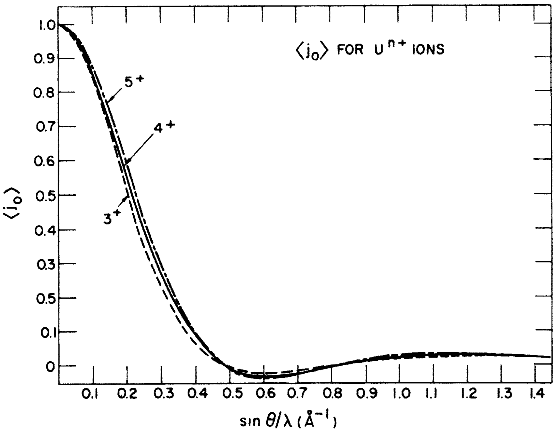

FIG. 2. Comparison of $\langle j_0 \rangle$ values for U^{3+}, U^{4+}, and U^{5+}.

We observe several striking features: the $\langle j_0 \rangle$ values for U^{3+}, U^{4+}, and U^{5+} are remarkably close to each other and cross the zero line at almost the same $(\sin\theta)/\lambda$ value; the $\langle j_2 \rangle$ and $\langle j_4 \rangle$ values are similar for the different ions, with small differences between them in the region beyond their maximum values. Thus we do not expect to be able to distinguish between the different ionization states of uranium on the basis of the radial dependence of the magnetic scattering. On the other hand, the coefficients c_i in Eq. (9) will depend on the crystal-field interaction and may provide a method of distinguishing between different electronic ground states. Unfortunately, over most of the accessible region of $(\sin\theta)/\lambda$ (0.2–0.7 Å^{-1}) the dipole approximation $\langle j_0 \rangle + c_2^{\mathrm{dipole}} \langle j_2 \rangle$ is almost independent of the ionization state. This independence occurs because as the ionization state increases the radial extent of the $5f$ electrons decreases leading to an increase (Figs. 2 and 3) in the $\langle j_i \rangle$ functions; but at the same time the magnitude of c_2 decreases (Table II). For f^1, f^2, and f^3 this effective cancellation is almost complete, but for f^4 the c_2 term is substantially larger and leads to observable effects (cf. Sec. IV).

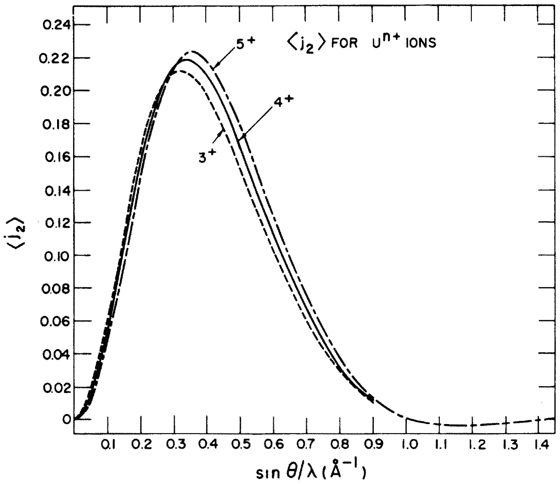

FIG. 3. Comparison of $\langle j_2 \rangle$ values for U^{3+}, U^{4+}, and U^{5+}.

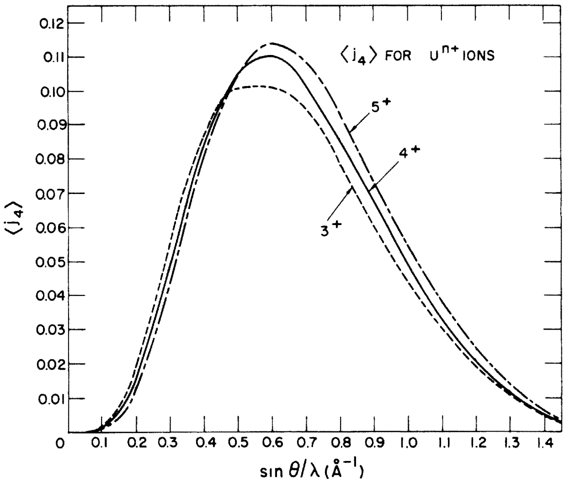

FIG. 4. Comparison of $\langle j_4 \rangle$ values for U^{3+}, U^{4+}, and U^{5+}.

As a crude estimate of the conduction-electron contribution in the case of metals we have calculated the $\langle j_0 \rangle$ radial integral from a $6d$ electron by means of free-ion Dirac-Fock calculations for several U ions containing $6d$ electrons. Figure 5 shows $\langle j_0 \rangle$ for the $6d$ electron determined from the $5f^26d^1$ configuration of U^{3+} together with the $\langle j_0 \rangle$ function for the $5f$ electrons. We see that the $6d$ $\langle j_0 \rangle$ falls off more rapidly as a function of $(\sin\theta)/\lambda$ than does the $5f$ contribution and so gives only a small contribution at the first reflection observed for US (cf. Sec. IV), and essentially a vanishing contribution beyond $(\sin\theta)/\lambda > 0.2$ Å^{-1}. Therefore the $6d$ electrons which may be present in US, do not contribute directly to the form factor, although they probably contribute to the bulk magnetization. The $6d$ band electrons in US are expected to be even less localized than the free-ion result presented and will have an even more rapid falloff with $(\sin\theta)/\lambda$. Estimates have also been made of the $5f$-$6d$ mixing term in the form factor expected from hybridized $5f$ and $6d$ bands. This contribution is found to be small, although their anisotropic contributions at some reflections may be observable.

IV. COMPARISON WITH EXPERIMENT: US

Early experiments by Curry[18] on UN, Frazer *et al.*[3] on UO_2, and Sidhu *et al.*[19] on UP, showed

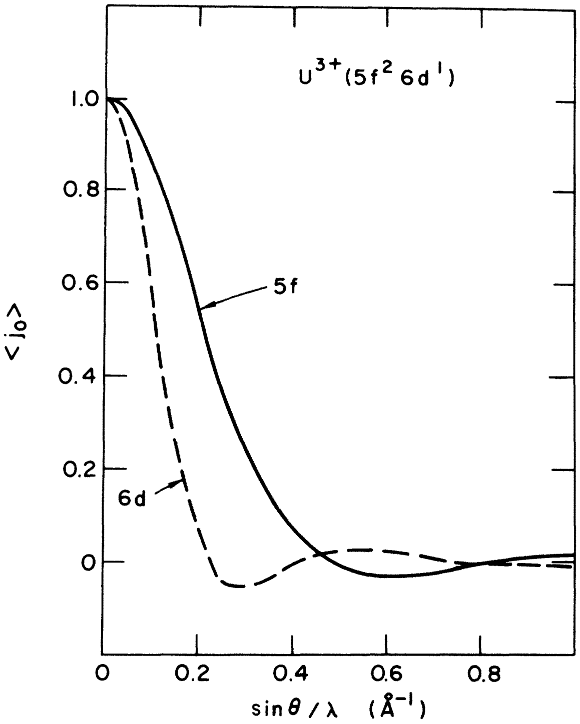

FIG. 5. Comparison of $\langle j_0 \rangle$ for the $5f$ and $6d$ electrons in the configuration U^{3+} ($5f^2$, $6d^1$).

that the unpaired electrons belong to the $5f$ shell. To measure the magnetic cross section more accurately, Wedgwood[2] examined single crystals of ferromagnetic US with polarized neutrons. Accurate magnetic cross sections have not been measured for transuranium ions, primarily because of the lack of single crystals. In this section we reanalyze Wedgwood's data, with the new radial functions. The earlier experimental results[18,19] were not accurate enough to warrant a new analysis with our relativistic $\langle j_l \rangle$ radial functions.

As is well known, an elastic magnetic cross-section measurement determines $\mu f(\vec{\kappa})$ where μ is the magnetic moment and the form factor $f(\vec{\kappa})$ is a function of the scattering vector $\vec{\kappa}$ [$|\kappa| = 4\pi(\sin\theta)/\lambda$]. Since $f(0)=1$ the values of μf extrapolate to μ as $\vec{\kappa} \to 0$. However, neutron measurements are rarely possible at $\vec{\kappa}=0$ so for para- or ferromagnetic materials the value μ is taken from bulk magnetization measurements. For US the magnetization value[5] is 1.55 μ_B/(U atom) but Wedgwood's neutron data suggest a value between 1.67 and 1.72 μ_B. This discrepancy is not fully understood; similar effects in the $3d$ transition metals are commonly viewed as a consequence of conduction-electron polarization. The neutron experiments sense only the *local* moment, whereas the *total* moment (local + diffuse) is measured at $\vec{\kappa}=0$. In analyzing the US data the extrapolation to $\vec{\kappa}=0$ depends on the magnetic form factor and hence on the particular choice of $\langle j_l \rangle$ functions. For models involving f^2 and f^3 configurations we find, in agreement with Wedgwood, that 1.70 μ_B is the best value. For f^4 configurations the best value of μ is somewhat lower ($\sim$1.63 μ_B) but our analysis shows that f^4 is an unlikely configuration. Assuming $\mu = 1.70\ \mu_B$ the experimental form factor f_{obs} is given in Fig. 6.

The magnetic cross section has been calculated with the tensor-operator method.[16,20,21] We have considered models for US that involve f^2, f^3, and f^4 configurations and obey Hund's rule and Russell-Saunders coupling. Chan and Lam[22] have shown that for f^2, f^3, and f^4 configurations the Russell-Saunders state makes up at least 80% of the true ground state, so that the use of a single J manifold is certainly valid until more detailed information on the electronic ground state of US becomes available. In all calculations to be reported the diagonalization is such that $\vec{\mu}_z \| [111]$. Since in the actinides the crystal-field interactions are larger than in the lanthanides, we have made the Lea, Leask, and Wolf[23] (LLW) parameter W sufficiently large to prevent any mixing between the ground and excited states, except in the case of the Γ_1 singlets and the Γ_6 doublet. The Γ_1 singlets are nonmagnetic so that *all* the moment comes from mixing with the excited

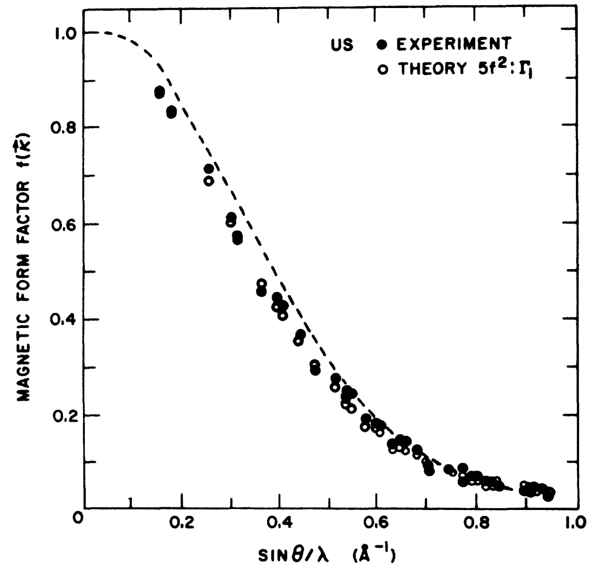

FIG. 6. Magnetic form factor for US. Solid points are from Wedgwood (Ref. 2) using a magnetic moment of 1.70μ_B. Open points are obtained with a $5f^2\ {}^3H_4$, Γ_1 plus exchange model and the $\langle j_l \rangle$ integrals of Fig. 1. The broken line is a smooth curve drawn through the theoretical form factor of the $5f^4\ {}^5I_4$ configuration.

TABLE IV. Wave functions and information used in calculating magnetic cross section of US. The quantities c_2, the coefficient of $\langle j_2 \rangle$ in $f(\kappa)$, and $\langle \Delta f \rangle_{\text{av}}$, the mean deviation between theory and experiment are discussed in the text. Ex in column 2 denotes that the application of an exchange field is necessary to produce the given μ.

Ionic configuration	Crystal-field ground state	Wave functions $\sum a_i \vert M_i$	LLW parameter x	μ (μ_B)	c_2 for $\Theta = \frac{1}{2}\pi$	$\langle \Delta f \rangle_{\text{av}}$
$f^2\ {}^3H_4$	Γ_1 + Ex	$+0.878 \vert 3\rangle - 0.410 \vert 0\rangle - 0.249 \vert -3\rangle$	−0.9	1.70	1.606	0.013
	Γ_5	$+0.721 \vert 4\rangle + 0.678 \vert 1\rangle - 0.135 \vert -2\rangle$	+0.9	2.00	1.671	0.025
$f^3\ {}^4I_{9/2}$	Γ_6 + Ex	$+0.836 \vert \frac{7}{2}\rangle - 0.467 \vert \frac{1}{2}\rangle - 0.287 \vert -\frac{5}{2}\rangle$	−0.8	1.70	1.741	0.039
	$\Gamma_8^{(1)}$	$+0.787 \vert \frac{9}{2}\rangle + 0.610 \vert \frac{3}{2}\rangle - 0.086 \vert -\frac{3}{2}\rangle$	+0.8	1.76	1.857	0.018
	$\Gamma_8^{(2)}$	$-0.617 \vert \frac{9}{2}\rangle + 0.778 \vert \frac{3}{2}\rangle - 0.110 \vert -\frac{3}{2}\rangle$ $+ 0.046 \vert -\frac{9}{2}\rangle$	+0.74	1.88	1.757	0.022
$f^4\ {}^5I_4$	Γ_1 + Ex	$+0.911 \vert 3\rangle - 0.376 \vert 0\rangle - 0.170 \vert -3\rangle$	−1.0	1.44	2.195	0.031
	Γ_5	$+0.720 \vert 4\rangle + 0.680 \vert 1\rangle - 0.136 \vert -2\rangle$	+1.0	1.50	2.303	0.035

states.[24] Similarly, the Γ_6 doublet can support a moment of only 1.33 μ_B and considerable mixing is required to obtain a moment of 1.70 μ_B. The LLW parameter x, which is related to the ratio between the fourth- and sixth-order crystal-field potentials, has been kept to values $|x| \geq 0.7$ to reflect the predominance of the fourth-order interaction. The form factor is essentially independent of x provided $0.75 \leq |x| \leq 1.00$. We list in Table IV the crystal-field ground states for each of the ionic configurations considered, their normalized wave functions (labeled by their magnetic quantum numbers M_i), and the calculated magnetic moments for these states, where

$$\mu = \mu_z = g \sum_i a_i^2 M_i ,$$

and g is the Landé splitting factor. In column 6 we give the coefficient of $\langle j_2 \rangle$ for $\Theta = \frac{1}{2}\pi$, where Θ is the angle between the moment direction and the scattering vector. In the expansion of the form factor given in Eq. (9) the coefficients c_4 and c_6 are usually small and the form factor is especially sensitive to the coefficient c_2 of $\langle j_2 \rangle$. In the last column we give the mean deviation between the calculated and observed form factors,

$$\langle \Delta f \rangle_{\text{av}} = \sum_i [(f_{\text{obs}} - f_{\text{calc}})_i^2 / n]^{1/2} ,$$

where the sum is over all n reflections. For comparison, the value

$$\langle \sigma f_{\text{obs}} \rangle_{\text{av}} = \left(\sum_i \frac{(\sigma f_{\text{obs}})_i^2}{n} \right)^{1/2}$$

is 0.006.

For the f^2 configuration the ground states are Γ_1 plus exchange and Γ_5. The theoretical form factor for the Γ_1 state is shown in Fig. 6 and is clearly in good agreement with experiment.[25] For the Γ_5 ground state more anisotropy is present in the calculated form factor than is observed experimentally. A similar situation occurs for all three f^3 configuration ground states. The best overall agreement for f^3 is obtained with $\Gamma_8^{(1)}$, but the anisotropy predicted by this state is in poor agreement with experiment as shown in Fig. 7. Here we have selected reflections that have the same value of $|\vec{\kappa}|$ and have subtracted the form factors, i.e., $\Delta f = f(\vec{\kappa}_1) - f(\vec{\kappa}_2)$, where $|\vec{\kappa}_1| = |\vec{\kappa}_2|$. Certainly Fig. 7 argues strongly against the $\Gamma_8^{(1)}$ state being correct, in spite of the reasonable

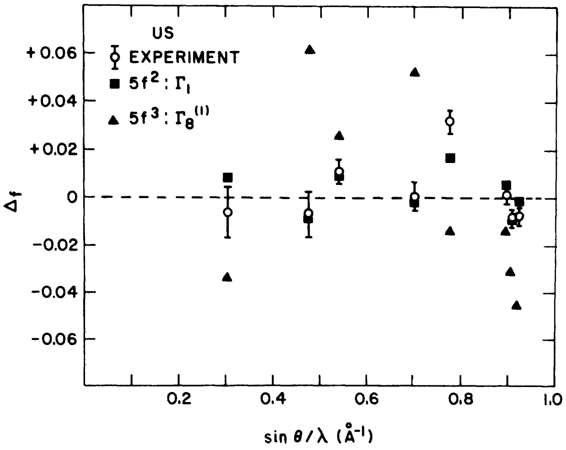

FIG. 7. Illustration of the anisotropy of the form factor in US, and comparison with two of the theoretical models. Each point is derived from the difference in the form factor between two reflections at the same value of $(\sin\theta)/\lambda$.

overall agreement. For the f^4 configuration the values of μ in Table IV are found to be too low. A greater exchange interaction leads to the free-ion state, for which $c_2 = 2.26$. Two strong objections to choosing an f^4 configuration are that the U^{2+} ionization state is unstable, and that the coefficient of $\langle j_2 \rangle$ is sufficiently large to produce a more expanded magnetic form factor than observed. We illustrate this in Fig. 6 with the broken line that lies significantly above f_{obs} for $0.15 < (\sin\theta)/\lambda < 0.45$ Å^{-1}. The agreement between f_{obs} and f_{calc} for both f^4 states may be improved by reducing the value of the experimental magnetic moment, and thus increasing f_{obs} by a constant scale factor. Unfortunately, no uniform scale factor will improve the agreement. For example, a reduction of μ by 5% to 1.62 μ_B leads to agreement in the range 0.35 to 0.5 Å^{-1} but to serious discrepancies at lower angles.

In conclusion, we must emphasize that in the absence of relativistic solid-state calculations for the actinide compounds and information regarding the nature (localized vs itinerant) of the 5*f* electrons, we have given an analysis based on a localized 5*f* crystal-field description.[22] Davis[26] has performed nonrelativistic energy-band calculations which emphasize the band approach and indicate that the 5*f* electrons in compounds such as US possess a reasonable degree of itinerancy. In addition one would expect, just as in the case of the lighter actinide[27] metals, that this would be accompanied by a certain amount of hybridization with the 6*d* and 7*s* band electrons. These effects were considered in Sec. III within the crude free-ion model and estimated to give very small contributions to the magnetic form factor except at $(\sin\theta)/\lambda \simeq 0$. On the other hand, hybridization effects can make significant contributions to the observed magnetic moment. The smaller moment observed in the magnetization measurements compared with the neutron moment is consistent with this mechanism provided there is an antiferromagnetic exchange coupling between 5*f* and 6*d* band electrons. As is shown,[28] interband mixing gives rise to just such a negative exchange interaction which can be dominant over the direct band mixing if the two bands are close together in energy. Whether this mechanism is operative here awaits further extensive investigation.

Our analysis of the results of the polarized-neutron experiments on US suggests that the $5f^2$, Γ_1 plus exchange model is the most appropriate.[25] In recent calculations[6] on UO_2 we have considered the effects of intermediate coupling and *J* mixing on the magnetic form factor. For the f^2, f^3, and f^4 configurations the effects are relatively small, except at large values of $(\sin\theta)/\lambda$, where the anisotropy of the form factor is increased by the inclusion of higher *J* states. We do not believe that such calculations for US would significantly affect the agreement with the $5f^2$ model. Our conclusion, therefore, agrees with Wedgwood and, in addition, we have provided a quantitative fit. In the region $0.5 < (\sin\theta)/\lambda < 0.7$ Å^{-1}, the values of f_{obs} appear to be systematically greater than f_{calc}, suggesting discrepancies between the $\langle j_i \rangle$ functions as derived for the free ion and those in the solid. A serious physical objection to the Γ_1 ground state is that we must understand the origin of the internal exchange field that overcomes the crystal-field interaction separating the Γ_1 and Γ_4 states and causes ferromagnetic ordering at 178 K. However, until more information on these parameters becomes available (for example, through spin-wave measurements) further discussion is unwarranted.

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*Work supported by the U. S. Energy Research and Development Administration and the National Science Foundation.

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