Large Orbital-Moment Contribution to 5*f* Band Magnetism

M. S. S. Brooks
Commission of the European Communities, Joint Research Center, Karlsruhe Establishment, European Institute for Transuranium Elements, D-7500 Karlsruhe, Federal Republic of Germany

and

P. J. Kelly[a]
Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart 80, Federal Republic of Germany
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It is calculated that spin-orbit coupling induces a predominant orbital magnetic moment ($-1.5\mu_B$) antiparallel to the spin moment ($1.0\mu_B$) in the spin-polarized energy bands of UN. The shape of the magnetic form factor, pressure dependence of the moment, and presence of large magnetic anisotropy then become compatible with itinerant-electron theory.

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The first actinide metal with an ordered ground-state moment is curium, and the elemental actinide metals provide no examples of itinerant-electron magnetism, ordering and *f*-electron localization occurring almost simultaneously in the middle of the series.[1] The cohesive and magnetic properties of compounds of the light actinides remain puzzling.[2] The dependence of their lattice parameters upon *f* occupation number is quite different from that of the corresponding rare-earth compounds, and suggests that the *f* electrons participate in the chemical bond.[3] Most studies of the magnetism of these compounds treat the *f* electrons as localized or moderately delocalized.[4] There is, however, a relationship between the existence of an ordered moment and the magnitude of the lattice parameter[5] which suggests that the *f* electrons are itinerant in those compounds with small lattice parameters —in particular, UC and UN.

We have therefore made linear-muffin-tin-orbital (LMTO) energy-band calculations in the atomic-sphere approximation[6] (ASA) for UC and UN, with self-consistent charge densities constructed in the local-spin-density approximation[7,8] (LSDA), and use of the modified Pauli equation[6] from which spin-orbit splitting is omitted. The lattice parameters and bulk moduli were evaluated from the calculated zero-temperature equations of state[9] (Table I). The calculated partial *f*-electronic pressure at the equilibrium lattice parameter is about – 40 GPa in either compound —comparable to the *f* pressure in uranium metal[1] but containing about equal contributions from metallic *f*-*f* bonding and hybridization (hopping) between uranium *f* and anion *p* states.

TABLE I. Measured and calculated properties of UC and UN.

	UC	UN
Measured lattice parameter (Å)	4.95	4.89
Calculated lattice parameter (Å)	4.86	4.82
Measured bulk modulus (GPa)	159	193
Calculated bulk modulus (GPa)	168	214
Stoner product IN	0.52	1.8
Measured moment[a] μ_B	•••	0.75
Calculated ferromagnetic spin moment (μ_B)	•••	0.99
Calculated antiferromagnetic spin moment (μ_B)	•••	1.04
Calculated ferromagnetic total moment (μ_B)	•••	0.50
$d\ln m^z/d\ln V$, experiment[b]	•••	19
$d\ln m_s{}^z/d\ln V$, theory, ferromagnetic	•••	0.5
$d\ln m_s{}^z/d\ln V$, theory, antiferromagnetic	•••	4.1
$d\ln m^z/d\ln V$, theory, ferromagnetic total	•••	6.0
Calculated g factor	•••	−1.1

[a]Ref. 10. [b]Ref. 12.

UC is paramagnetic and UN is a type-I antiferromagnet with a sublattice moment of $0.75\mu_B$.[10] In our self-consistent spin-polarized band calculations a ferromagnetic ground-state moment fails to develop in UC, whereas both ferromagnetic and antiferromagnetic moments develop in UN (Table I). Although the energy-band structures of UN in the ferromagnetic and antiferromagnetic ground states are quite different, the radial distributions of spin density are almost identical—closely resembling the corresponding partial f charge density. The calculated moment is about 30% larger than the measured moment, but both are much less than a saturated moment of more than $2.5\mu_B$ that would have been obtained if only spin-up f states were populated. It would therefore be tempting to attribute the discrepancy to inaccuracies in LSDA or the energy-band calculations, especially since the present results describe other ground-state properties very well and are consistent with the photoemission experiments of Reihl *et al.*[11] However, the apparent agreement between theory and experiment turns out to be dangerously deceptive.

Convincing experimental evidence that UN is an itinerant-electron antiferromagnet has been collected by Fournier *et al.*,[12] who found that the magnitude of the sublattice moment and the Néel temperature have the same pressure dependence.[13] Although our calculated moment decreases far more rapidly under pressure for an antiferromagnetic than for a ferromagnetic ground state, the decrease is less rapid than is measured[14] by a factor of 4–5 (Table I). In contrast to the discrepancy in the magnitude of the moment, the anomaly is too large to be attributed merely to a lack of accuracy.

The second discrepancy occurs when the magnetic form factor is studied. In the dipole approximation,[15] the normalized form factor of the spin density is given by

$$F(Q) = 8\pi\mu_B \int dr\, j_0(Qr) r^2 s^z(r)/m_s{}^z = \langle j_0 \rangle_s \qquad (1)$$

in terms of the scattering vector $Q = (\sin\theta)/\lambda$, spherical Bessel functions j_0, spin density s^z, and spin moment $m_s{}^z$, with the integral taken over atomic spheres. The calculated form factors of the spin densities of the actinide-nitride series[16] are shown in Fig. 1. The calculated form factors for the ferromagnetic and antiferromagnetic ground states of UN are essentially identical. The spread of the form factors between UN and AmN represents the extent to which the form factor is changed by actinide contraction.

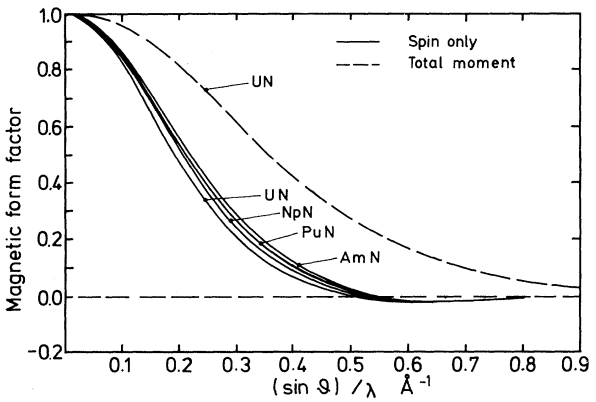

FIG. 1. Form factors of the spin densities of the actinide nitrides. The experimental magnetic form factor is virtually identical to the calculated magnetic form factor of UN with an orbital moment (dashed line).

We have verified, by comparing with calculated free-atom form factors, that the difference made by the formation of bonding charge is even smaller. However, the measured magnetic form factor[10] is the dashed line labeled "total moment" in Fig. 1. The discrepancy between theory and experiment is so large here that it must be caused by an error in principle.

We have found that the origin of these discrepancies is the combination of large spin-orbit splitting ($\simeq 0.7$ eV for U) and small f bandwidths ($\simeq 2.5$ eV) in UN and possibly several other actinide compounds, which produces a phenomenon unique to $5f$ magnetism. When the spin-orbit coupling Hamiltonian, $\xi l \cdot s$, is added to the Hamiltonian matrix[6] of the *spin-polarized* band-structure problem an orbital-moment density is induced.[17] The spherical average of the total moment density in the ASA sphere of type t (in the present case t is U or N) is the sum of spin and orbital contributions:

$$m_t{}^z(r) = \mu_B[l_t{}^z(r) + 2s_t{}^z(r)]. \qquad (2)$$

The orbital angular momentum density is calculated in practice from[18]

$$l_t{}^z(r) = (1/4\pi)\sum_{l,m}\sum_s \int^{E_F} N_{tlms}(E) m \times \varphi^2{}_{tls}(E,r)\,dE. \qquad (3)$$

Here l and m are the orbital and azimuthal quantum numbers, s is the spin index, and N_{tlms} and φ_{tl} are the corresponding state densities and atomic-sphere wave functions,[6] respectively. The total moment, $m^z = m_s{}^z + m_l{}^z$, is obtained in ASA by integrating the moment density, (2),

over the tth atomic sphere and summing over spheres. It is straightforward in principle, but complicated in practice, to calculate the orbital moment *ab initio* from (3).[19] We have done so for the *ferromagnetic* ground state of UN,[20] assuming that the difference between the spin-up and spin-down potentials is a function of the spin, but not orbital-moment, density—i.e., that LSDA remains unchanged in the presence of an orbital moment. The calculations were iterated to self-consistency with spin-orbit coupling in the LMTO Hamiltonian matrix.

At a lattice parameter of 5.03 Å we calculate a total moment of $-0.73\mu_B$, consisting of a spin component of $1.1\mu_B$ and a *predominant* orbital component of $-1.83\mu_B$. The conduction (non-f) electron polarization is only $0.03\mu_B$ in UN, contains a negligible orbital contribution, and was found to be *antiparallel* to the total moment.[21] At a lattice parameter of 4.78 Å the calculated total moment is $-0.26\mu_B$, with an orbital component of $-1.01\mu_B$ and a spin component of $0.75\mu_B$. Thus the volume dependence of the moment is principally due to the rapid quenching of the induced orbital component with increasing bandwidth. The total moment, calculated by interpolation onto the experimental equilibrium lattice parameter, is $0.5\mu_B$ (Table I). The magnetic form factor given by

$$F(Q) = [\langle j_0 \rangle_s m_s^z + \langle j_0 + j_2 \rangle_l m_l^z]/m^z \qquad (4)$$

replaces (1) where $\langle \ldots \rangle_i$ refers to the radial integrals in (1) with the appropriate density. The calculated magnetic form factor of UN, obtained from (4), is now the dashed line in Fig. 2 and the second anomaly is resolved. It is the dependence of $\langle j_2 \rangle$, arising from the shape of the orbital *magnetization* density,[22] upon the scattering vector that is responsible for the unmistakable tail in the form factor.

Our calculations demonstrate that f bands in light actinide compounds fulfill the conditions for very large (in comparison with other itinerant-electron systems) orbital moments to be stable in the LSDA ground state. Several important consequences follow immediately. The presence of an orbital moment has been used as evidence for localized magnetism,[23] since the orbital moment is almost totally quenched in normal itinerant-electron magnets. More careful analysis will be required before localized and itinerant $5f$ magnetism can be distinguished. Moreover, the energy bands depend strongly upon the direction of the moment in itinerant $5f$ systems [we calculate the energy difference between the (100) and (111) *ferromagnetic* ground states of UN to be 7×10^{10}ergs/cm^3] and other experimental evidence normally used to identify localized magnetism—the presence of large magnetic anisotropy or energy gaps in the magnetic excitation spectra of ferromagnets—also becomes ambiguous.

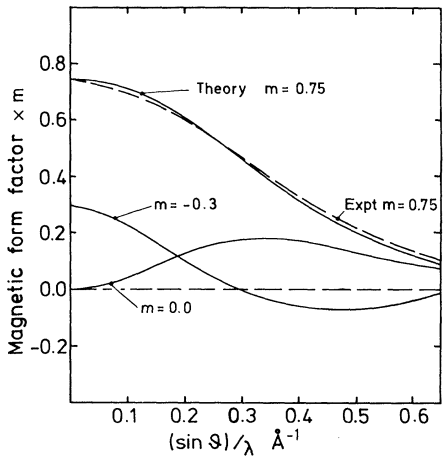

FIG. 2. Calculated magnetic form factors of UN for different values of the total moment as the orbital component is quenched under pressure. The total moment should go through zero since the orbital and spin contributions are antiparallel and, at ambient pressure, the orbital component is larger.

Since pressure quenches the orbital component of the moment more rapidly than the spin component, the total moment, magnetic form factor, and magnetic anisotropy should be strongly pressure dependent. We have plotted the calculated form factors for UN under pressure in Fig. 2. At ambient pressure the total moment is $0.75\mu_B$, but passes through zero[24] as the pressure is increased. When the total moment is zero the magnetization density[22]—which scatters the neutrons at $Q \neq 0$—remains finite (although its integral and scattering at $Q = 0$ vanish). At higher pressures the total moment is *parallel* to the predominant *spin* moment and the form factor falls off very rapidly. Similar pressure dependence of the moment, magnetic anisotropy, and magnetic form factor of ferromagnetic actinide compounds should be observable if their f electrons are itinerant.

[a]Present address: IBM Thomas J. Watson Research Center, Yorktown Heights, N.Y. 10598.

[1]H. L. Skriver, O. K. Anderson, and B. Johansson, Phys. Rev. Lett. 44, 1230 (1978).

[2]See, e.g., the collection of papers in *The Physics of the Actinides and Related 4f Materials*, edited by P. Wachter [Physica (Utrecht) 102B (1980)].

[3]M. S. S. Brooks and D. Glötzel, Physica (Utrecht) 102B, 51 (1980).

[4]See, e.g., S. K. Chan, J. Phys. Chem. Solids 32, 1111 (1971); B. R. Cooper, J. Magn. Magn. Mater. 29, 230 (1982).

[5]H. H. Hill, in *Plutonium 1970*, edited by W. M. Miner (Metallurgical Society of AIME, New York, 1970), p. 2.

[6]O. K. Andersen, Phys. Rev. B 12, 3060 (1975).

[7]W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

[8]U. von Barth and L. Hedin, J. Phys. C 5, 1629 (1972).

[9]D. G. Pettifor, Commun. Phys. 1, 141 (1976).

[10]N. A. Curry, Proc. Phys. Soc., London 86, 1193 (1965).

[11]B. Reihl, G. Hollinger, and F. J. Himpsel, J. Magn. Magn. Mater. 29, 303 (1982). Spin-polarized calculations for antiferromagnetic UN have also been made by J. Kübler (unpublished) who obtains very good agreement with the photoemission experiments.

[12]J. M. Fournier, J. Beille, A. Boeuf, and A. Wedgwood, Physica (Utrecht) 102B, 282 (1980).

[13]P. A. Fedders and P. C. Martin, Phys. Rev. 143, 245 (1966).

[14]The measured pressure dependence of the moment in UN, Ref. 12, is also given by $d\ln m/dP = -10$ Mbar^{-1}, i.e., some 20 times larger than in iron.

[15]See, e.g., W. Marshall and S. W. Lovesey, *Theory of Thermal Neutron Scattering* (Oxford Univ. Press, Oxford, 1971).

[16]M. S. S. Brooks, J. Magn. Magn. Mater. 29, 257 (1982).

[17]M. Singh, J. Callaway, and C. S. Wang, Phys. Rev. B 14, 1214 (1976).

[18]The first term of Eq. (2.29) of Ref. 17 is evaluated in ASA where tail cancellation simplifies Eq. (2.27). Other contributions to Eq. (2.15) are small for narrow $5f$ bands. We find that the orbital moment is due almost entirely to the $5f$ electrons and all other partial contributions may be neglected.

[19]The major complications are that (1) the size of the irreducible zone is increased [see A. P. Cracknell, Phys. Rev. B 1, 1261 (1970)]; (2) since spin-up and spin-down states are coupled by the spin-orbit Hamiltonian, the size of all matrices is doubled; (3) all of the partial N_{lms}, rather than just the partial N_{ls}, state densities must be computed to calculate the orbital-moment density.

[20]The matrix of the band-structure problem for an antiferromagnet is twice as large again but we expect qualitatively similar results.

[21]As is deduced by comparing neutron scattering and magnetization measurements; e.g., F. A. Wedgwood, J. Phys. C 5, 2427 (1972).

[22]O. Steinsvoll, G. Shirane, R. Nathans, M. Blume, H. A. Alperin, and J. Pickart, Phys. Rev. 161, 499 (1967).

[23]See, e.g., G. H. Lander, in *Rare Earths and Actinides 1977*, edited by W. D. Corner and B. K. Tanner (Institute of Physics, Bristol, 1977), p. 173.

[24]This may at first seem strange, but unlike the theory for localized systems the Wigner-Eckart theorem is not used in the energy-band calculations. At a general point in the zone no symmetry remains and, in LSDA, the splitting depends only upon the spin density. The net spin is therefore the order parameter.