Decentralized Unpaired Electrons and Valence Bonding in Chromium Uranium Trisulphide‡

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A valence-bond approach using bidirectional orbitals is employed in a discussion of the uranium bonding in $CrUS_3$. The unpaired outermost-bound uranium electron density recently discovered in this new semiconducting material is identified with a d_{z^2} uranium orbital extending through and beyond the uranium valence electrons. The f character employed in bond formation by uranium is estimated to be 20—30%.

THE recent discovery by Wolfers *et al.*[1] of significant spin density located >2 Å distant from any atom is of considerable theoretical interest, especially since the materials are apparently semi-conducting anisotropic antiferromagnets and represent a growing class of compounds including $CrUS_3$, VUS_3, $CrUSe_3$, $CoUS_3$, $NiUS_3$,[2] and $CrThS_3$. The first three compounds have been shown[1] *via* neutron diffraction techniques to have decentralized unpaired uranium electrons.

In order to provide a basis for understanding these new materials, all prepared for the first time by Professor H. Noel of Rennes, we treat the chemical bonding from the combined approaches of Pauling's metallic radii[3] and the bidirectional orbital approximation[4] (BOA). The first method permits an estimate of bond orders from the observed interatomic distances, and from the second method one obtains a distribution of the orbitals employed in bonding. Particular attention is given to the bonding of uranium and its use of f orbitals. The net result is a picture in general agreement with the magnetic data and the identification of the decentralized electron density with an extended $6d_{z^2}$ uranium orbital. The decentralization or the extendedness of this electron is such that its two centres of unpaired density were found *via* neutron diffraction to be >2.0 Å away from the uranium nucleus. Since the uranium valence electrons have a smaller radius (1.5—1.7 Å) the unpaired electron is hence an example of a 'supra-valence' electron in the sense of being beyond or outside the valence electrons but still being primarily bound to the uranium nucleus. However, prior to discussing the above approaches and their results, it is desirable to consider some details of the known crystalline and magnetic structure[1] of $CrUS_3$. This compound shows the largest decentralization known to date and magnetically is strongly anisotropic.

RESULTS AND DISCUSSION

Structure.—The prototype material $CrUS_3$ crystallizes[1] in an orthorhombic space group, *Pnam*, in a structure related to cementite where, however, Cr is at an octahedral site vacant in cementite. Uranium is located in a somewhat distorted right prism of sulphurs, with two of the rectangular faces capped with additional, more distant, sulphur neighbours. The nearest U–U interactions are at 4.32 Å. The relations of prisms along the a axis may be described by noting that there are two kinds of sulphurs (I, 4c site; II, 8d site), with the second kind forming a pleated ladder-like arrangement in the a direction. These sulphurs, S(II), constitute one of the three rectangular prism faces of the US_6 prisms. The prisms alternate on each side as they progress up the ladder and have common top and bottom edges [rungs of the S(II) ladder]. The type I sulphurs, in pairs, constitute the third prism edge and are located, like U (4c site), on the mirror plane containing the a and b axes and bisecting the ladder and its prisms. In the b direction these ladders are one unit-cell edge apart and are joined by the S(I) pairs such that prisms of adjacent ladders share corners. Chromium, at the 4a site inversion centre, relates adjacent ladders in the c direction while bonding them *via* the S(I) atoms. Chromium also forms four bonds with S(II) atoms linking parallel ladders in the a direction. Therefore, S(I) has a metal co-ordination of four (2Cr, 3U) since it bonds one U of the adjacent ladder in the c direction, thereby capping a U prism face.

The analysis[1] of the neutron-diffraction data showed that Cr was antiferromagnetically aligned along the a axis while the uranium moment was in the crystallographic mirror plane at $c/4$. While this magnetic arrangement was in general agreement with the data, refinement was not possible with a localized unpaired electron distribution. Other models considered in the refinement include unpaired electron density (1) at the sulphur site, (2) along the U–S bond axis, (3) in the prism plane perpendicular to the prism axis containing the U atom, and (4) along the prism axis. Only the last decentralized electron distribution refined to a reasonable R factor of 0.059. This distribution is illustrated in Figure 1.

Metallic Radii.—In the application of Pauling's metallic radii[3,4] to $CrUS_3$ the principal uncertainty involved is the single-bond radius for U which is expected

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[1] P. Wolfers, G. Fillion, M. Bacmann, and H. Noel, *J. de Physique*, 1976, **37**, 57.

[2] H. Noel, personal communication.

[3] L. Pauling, in 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, 1960, pp. 403—436.

[4] F. L. Carter in 'Density of States,' ed. L. Bennett, N.B.S. Special Publ. No. 323, 1970, p. 358.

to vary with both valence and hybridization. The assumption made was that the U–S bonds of the idealized prism (see below) had a bond order of 0.5, in keeping with the filled half-bond consideration of BOA theory and the semi-conducting character of these materials. This gave uranium an $R(1)$ of 1.578 Å compared with Pauling's value of 1.426 Å for a valence of six. The results of Table 1 are calculated then from the known interatomic distances and the assumption that the sulphur octet is filled with shared or unshared electron pairs. This latter assumption gives rise to the sulphur formal charges and subsequently to those of the metal atoms by reason of cell neutrality. The effective charges differ from the formal charges by reason of bond polarizability, which is proportional to bond order times ionicity (ionicity to be calculated from electronegativity differences). Since the Cr has octahedral co-ordination (distorted), the 3.54 unshared electrons locate themselves in three d_{xy}-type orbitals to give 2.46 unpaired electrons (while 2.42 are observed at 4.2 K and 2.10 at 60 K). The total observed moment associated with U is 2.58 electrons at 60 K and 3.00 electrons at 4.2 K, compared with 2.46 estimated here. By adjusting the single-bond radius of U, agreement between the estimated moment for U and either of the experimental values can be made perfect without other substantial changes; however, in view of the experimental uncertainties, the filled half-bond assumption above seems less *ad hoc*. The existence of a larger effective sulphur charge on the 8d site is supported by a slight splitting of the S($2p$) ESCA line.[5] However, this result is uncertain as a mild oxygen contamination of the sample surface was present.

TABLE 1

Metallic radii results for CrUS$_3$

	Valence	Formal charge	Effective charge	Unpaired electrons	Obs. μ_B
Cr (4a)	2.44	0.02	0.45	2.46	2.42
U (4c)	3.39	0.15	1.02	2.46	2.29 (+0.71) (delocalized)
S(I) (4c)	2.27	0.27	−0.29	0.0	0.0
S(II) (8d)	1.78	−0.22	−0.59	0.0	0.0

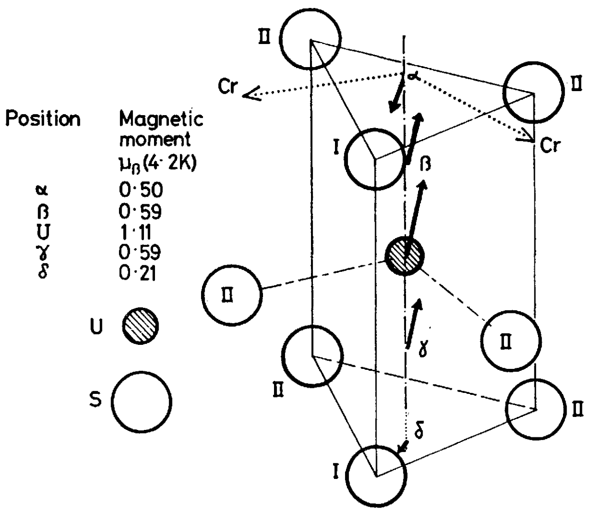

FIGURE 1 The US$_6$ prism with two capping sulphurs. All the magnetic vectors are in the mirror plane at $c/4$. The unpaired electron density at position α is close to two chromiums (2.62 Å), but the position δ is appreciably further (3.33 Å) from its four Cr neighbours (Figure adapted from Wolfers *et al.*[1])

Bidirectional Orbitals.—In the BOA method, hybrid valence-bond orbitals are sought such that the electron density is concentrated into two primary directions for bond formation in those directions with two atoms. Further, one seeks a basis set such that all the neighbours are simultaneously bonded and equivalent neighbours are treated in an equivalent manner. In the treatment here it is implicitly assumed that the radial parts of the s, p, d, and f orbitals have a similar extension in space and that the measure of goodness of bond formation is the extension of the angular parts of the hybrid orbital in the direction of the bond, *i.e.*, Pauling's concept of strength, S, is used.[3] The assumption of radial equivalence is probably more justified in the case of uranium and its neighbouring actinoids than in any other part of the Periodic Table because the relativistic contraction of the $7s$ orbital and $7p$ orbitals results in increased shielding and extension of the $6d$ and $5f$ orbitals.[6] Moreover, the delicate balance between these orbitals is further sensitized by a splitting of, for example, the $5f$ orbitals into those which are radially extended for bond formation and those which are contracted for localized f electrons. Such a splitting has been recently discussed for the $3d$ orbitals of the first transition metals by Pauling and Keaveny,[7] and considered previously by other workers, including Craig *et al.*[8] and Carter.[4] The assumption that the strength, S, of the orbital is a measure of its goodness undoubtedly overestimates f character, since the long narrow extension of the f orbital lobes does not have proportional overlap integrals with bonded neighbours. It is likely then that the results given here overestimate the f-orbital contribution when this contribution is high.

The co-ordination of the U atom is idealized here as being located in a symmetric right prism (height = 3.723, base edge = 3.532Å) with two of its rectangular

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[5] H. Noel, J. Verbist, and E. Thiebaut, personal communication.

[6] J. P. Desclaux, 'Atom. Data Nucl. Data Tables,' 1973, vol. **12**, pp. 311—406.

[7] L. Pauling and I. Keaveny, in 'Wave Mechanics. The First Fifty Years,' ed. W. C. Price, Butterworths, London, 1973, p. 88.

[8] P. D. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 1954, 332.

faces capped. Three bidirectional orbitals of the same hybridization are employed to bond the six sulphur atoms, and the fourth orthogonal orbital of good strength is sought for bonding the two capping sulphurs in the basal plane. The simplest mathematical representation of the orbitals considered is indicated by equations (1)—(3), while Figure 2 illustrates their angular distributions. The Cf1 and Gf2 orbitals are most suitable

$$\mathrm{Cf1} = D\,.\,p_z + F\,.\,d_{xz} + J\,.\,f_{z(5z^2-3r^2)} \qquad (1)$$

$$\mathrm{Cf2} = B\,.\,p_x + F\,.\,d_{xz} + K\,.\,f_{x(5z^2-r^2)} \qquad (2)$$

$$\mathrm{Gf2} = A\,.\,s + B\,.\,p_x + I\,.\,d_{z^2} + K\,.\,f_{x(5z^2-r^2)} \qquad (3)$$

for bonding between neighbours where the included angle is large, such as those across the rectangular prism face; Cf2 has an included angle of <90° and can be used by U to bond two sulphurs in the vertical plane. The orthogonality conditions for the Cf1 and Gf2 orbitals under three-fold symmetry were indicated earlier[9] but that for the Gf2 orbital [equation (4)] is repeated correctly here together with that for the Cf2 orbital [equation (5)]. The orbital Gf2 is rotated out of the xz plane about

$$\mathrm{Gf2}: \quad [3I^2 + (5K^2/4)]\sin^4\beta - \sin^2\beta\,.\,I^2 + \tfrac{8}{9} = 4(B^2 + K^2)/3 \qquad (4)$$

$$\mathrm{Cf2}: \quad 3B^2 + (9K^2/8) = (3F^2/2) + (15K^2/16) = 1 \qquad (5)$$

$$\mathrm{Basal}: \quad A\,.\,a = (2 - \sin^2\beta)I\,.\,\frac{i}{4} + 15^{\frac{1}{2}}\sin^2\beta\,.\,K\,.\,\frac{k}{16} \qquad (6)$$

$$\mathrm{Gf2}: \quad B\,.\,b = 3\sin^2\beta\,.\,H\,.\,\frac{i}{4} + (4 - 5\sin^2\beta)\,.\,K\,.\,\frac{k}{16} \qquad (7)$$

the x axis by the angle β in positioning it for bond formation with the two sulphurs at the opposite corners of a prism face. The other four sulphurs are bonded by equivalent orbitals rotated by 120 and 240° about the z (prism) axis from the first orbital. The two capping sulphurs in the basal plane have an included angle of 125.9° at U and hence can be bonded by either a single Cf1 or Gf2 orbital. However, it is interesting that for the basal Cf1 orbital f character is excluded by orthogonality conditions in the case of Cf1 prism orbitals and appears to be only a few percent at most when Gf2 orbitals are used to bond the prism sulphurs. Accordingly, Gf2 orbitals are used in both these cases. The orthogonality conditions for the basal-plane Gf2 orbital for the Gf2 prism are indicated by equations (6) and (7)

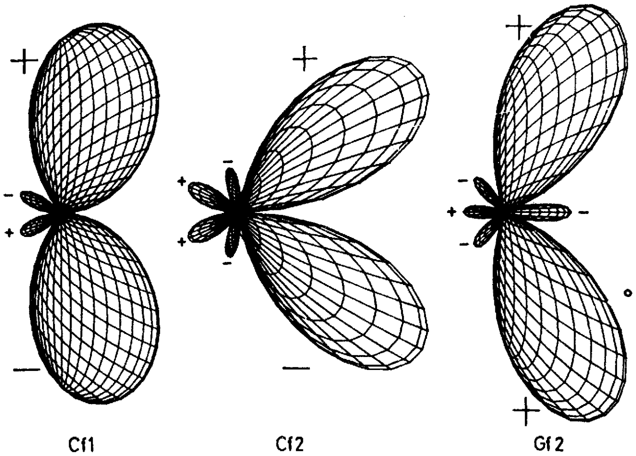

FIGURE 2 Proposed uranium orbitals (angular part only) for bonding the prism sulphur atoms under three-fold symmetry, showing excellent concentration of electron density into two lobes directed toward two sulphur atoms. The orbital strengths and angles for these orbitals are indicated at the top of Table 2

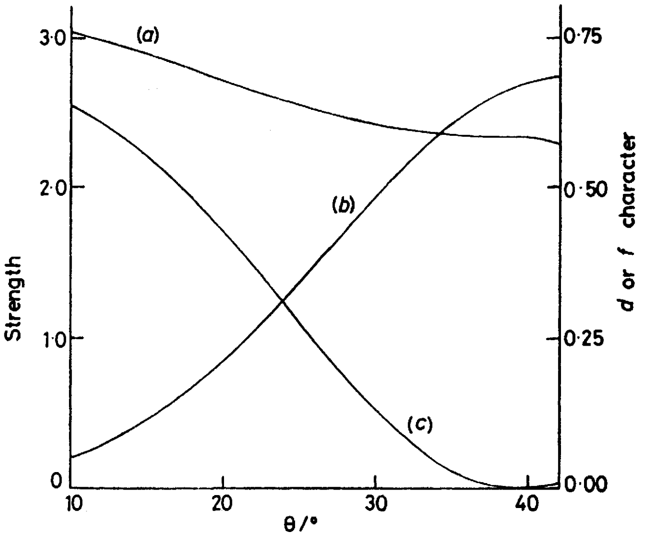

FIGURE 3 Maximum possible strength (a) of the Cf1 orbital as a function of θ = (180 — bond angle)/2 where the ' bond angle ' is that between the two main lobes. (b) and (c), d and f character respectively

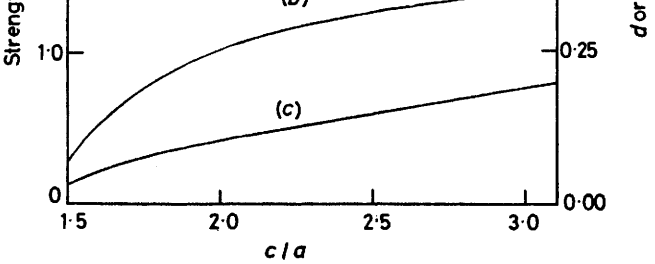

FIGURE 4 Maximum strength of Cf1 orbitals under the restrictions of a right prism. The average d plus f character is considerably reduced compared to the unrestricted case of Figure 3. Details as in Figure 3

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[9] F. L. Carter, T. L. Francavilla, and R. A. Hein, *Proc. 11th Rare Earth Res. Conf.*, Traverse City, Michigan, 1974, p. 36.

where the lower case coefficients are for the basal orbital.

Additional restraints are put on the orbital coefficients by the requirement that the strength, S, is maximized as a function of θ where the included bond angle $= 180° - 2\theta$. Figures 3 and 5 show the maximum strength and the d and f character for both the Cf1 and Gf2 orbitals as a function of θ (no other restraints) and Figures 4 and 6 give data as a function of c/a under the geometric restraints of a right prism. For comparison, we note that as c/a varies from 1.5 to 3.1, θ decreases from 24.8 to 17.4°. For the ideal US_6 prism, $c/a = 2.107$, $\theta = 21.7°$, and $\beta = 43.5°$. A comparison of the figures for the same orbital type shows that the f character is strongly decreased and that the d character is generally decreased under the three-fold symmetry restraints. However, in all cases, the strengths are still excellent with the Gf2 orbital being more adaptable. The Cf1 orbital, in the three-fold symmetry, cannot be used for $c/a < 1.414$, or $\beta > 54.74°$.

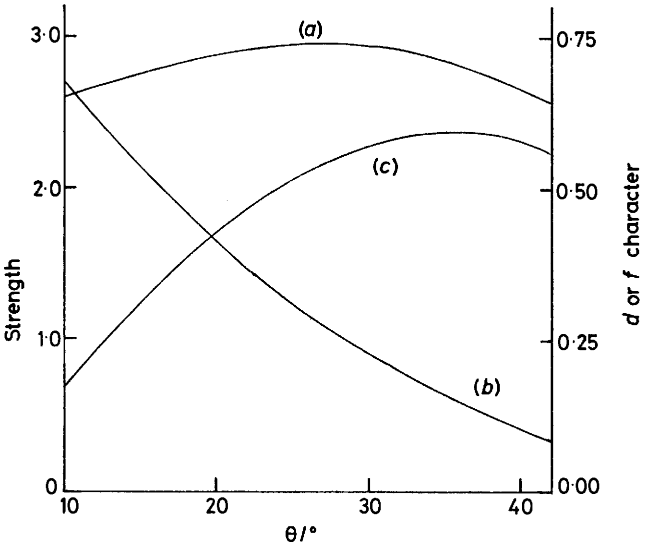

FIGURE 5 Maximum strength (a) and related d (b) and f character (c) of Gf2 orbitals as a function of θ

TABLE 2

Uranium bonding-orbital occupation

	Type[a]	Cf1	G′f2	Cf2	G′f2	Gf2	G′f2	
	Strength	2.50	2.94	2.95	2.96	2.89	2.77	
	$\beta/°$	43.5	90.0	0.0	90.0	43.5	90.0	
	$\theta/°$	21.7	27.0	47.9	27.0	21.7	27.0	
								Average
s[b]	A	0.04		0.05		0.73		0.27
p_x	B	0.49		0.01		0.15		0.22
p_y	C	0.44		0.00		0.06		0.17
p_z	D	0.97		0.53		0.00		0.50
d_{xy}	E	0.19		0.00		0.08		0.09
d_{xz}	F	0.21		0.61		0.35		0.39
d_{yz}	G	0.21		0.61		0.35		0.39
$d_{x^2-y^2}$	H	0.26		0.17		0.10		0.18
d_{z^2}	I	0.02		0.06		0.09		0.06
$f_{z(5z^2-3r^2)}$	J	0.01		0.47		0.00		0.16
$f_{x(5z^2-r^2)}$	K	0.09		0.00		0.12		0.07
$f_{y(5z^2-r^2)}$	L	0.08		0.00		0.11		0.06
$f_{z(x^2-y^2)}$	M	0.08		0.40		0.40		0.29
f_{xyz}	N	0.08		0.40		0.40		0.29
$f_{x(x^2-3y^2)}$	P	0.14		0.05		0.41		0.20
$f_{y(3x^2-y^2)}$	Q	0.02		0.00		0.00		0.01
	Valence	3.35		3.36		3.35		3.35

[a] The G′f2 orbitals are in the basal plane bonding the capping sulphurs. [b] Quenched orbital notation of Eisenstein.

The principal result of this paper is indicated in Table 2, which shows the total occupation of the orbitals in electrons for all the three models of prism bonding, *i.e.* using Cf1, Cf2, and Gf2 orbitals and a U valence of 3.35. The atomic f-orbital notation is that of Eisenstein.[10] Table 2 also shows the average atomic-orbital occupation assuming that the best wavefunction resonates equally among the three types of bonding models. This is equivalent to writing $r^2 = s^2 = t^2 = 1/3$, where the total wavefunction ψ is symbolically written as in (8)

$$\psi = r(\mathrm{Cf1}) + s(\mathrm{Cf2}) + t(\mathrm{Gf2}) \qquad (8)$$

where $r^2 + s^2 + t^2 = 1$.

The assumption that the best wavefunction resonates equally among the Cf1, Cf2, and Gf2 models is justified on the near equivalence of the strengths of the orbitals listed at the top of Table 2. Since uranium is surrounded by an imperfect trigonal prism, it is clear that no single model will by itself be adequate for the U–S prism bonds because Cf1 and Cf2 are antisymmetric with respect to a 180° rotation and Gf2 is purely symmetric (Figure 2). Further, we note that mixing among these three models will increase net overlap *via* their crossterms and also improve electron correlation.

In considering the results of Table 2, however, it is desirable to keep in mind that (1) these models were obtained by maximizing orbital strength, which probably overestimates f character, and (2) the relativistic contraction for the 7s electron decreases its availability, especially if d and f electrons which normally shield it

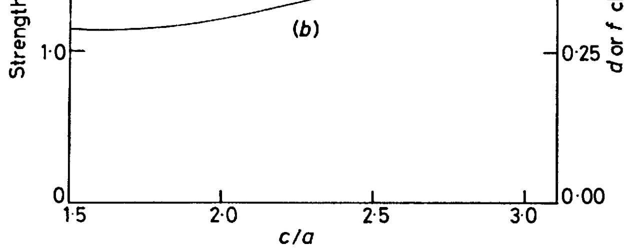

FIGURE 6 Maximum strength (a) of Gf2 orbitals under the restrictions of a right prism. Here again, the d plus f character is reduced significantly compared with the unrestricted case of Figure 5 but the strength remains high. Details as in Figure 3

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[10] J. C. Eisenstein, *J. Chem. Phys.*, 1956, **25**, 142.

are employed in bonding. Both these considerations suggest that the *d*-bonding character in Table 2 should be enhanced somewhat. However, beyond this latter caveat, it should be emphasized that in this BOA valence-bond approach the geometric and orthonormal restrictions [equations (4)—(7)] of concentrating electron density along bond directions are more important than the exact details of the relative weighting of *p*-, *d*-, and *f*-orbital strengths.

On a percentage basis, we note that average bond formation by U in the prototype compound is estimated here at 8.1% 7*s*, 26.6% 7*p*, 33.1% 6*d*, and 32.2% 5*f*. From ESCA results obtained by Verbist *et al.*[11] on both uranium oxides and metals, and from preliminary results on these materials,[5] we know that the *f*-electron orbital energies are within 2 eV of the Fermi edge,* even though atomic relativistic calculations in general show them to be several eV deeper (for example, see Desclaux[6]). If the *f* electrons are so near the Fermi surface then it is not surprising that they play an important role in the bonding, as suggested by this work.

From the results shown in Table 2 (average column) one may also estimate which orbitals are suitable for localized unpaired electrons. It will then be shown that the results of assuming $r^2 = s^2 = t^2 = 1/3$ are, in fact, quite general ones over much of the allowed *s*–*t* parameter space. In general, localized unpaired electrons may be expected to have contracted radial-orbital *f* character as has been found using positron annihilation by Rozenfeld *et al.*[12] for U_3As_4, a covalently bonded semiconductor roughly equivalent to $CrUS_3$. From Table 2 the order of availability of *f* orbitals for local electrons is $f_{y(3x^2-y^2)}$, $f_{y(5z^2-r^2)}$, and $f_{x(5z^2-r^2)}$. The latter two orbitals may be associated with the *L* values ± 1, while the first orbital ($L = \pm 3$) should be strongly quenched by the high bonding *f* character of the $f_{x(x^2-3y^2)}$ orbital. The next orbital of *d* or *f* character with lowest utilization is the d_{z^2} orbital. This then suggests the following distribution of the 2.5—3 unpaired observed electrons: one electron occupies the $f_{y(3x^2-y^2)}$ orbital, the second occupies a combination of the $f_{x(5z^2-r^2)}$ and $f_{y(5z^2-r^2)}$ orbitals, and the third electron, partly due to repulsion with the second electron and partly due to repulsion with *f* bonding electrons, occupies an extended d_{z^2} orbital. The last orbital is probably hybridized with few percent *f* or *p* character as a result of the crystalline asymmetry and the use of d_{z^2} character (6%) in bonding.

In consideration of the radial extension of the outer uranium orbitals, it is important to remember that the 5*f* and 6*d* orbitals will be strongly shielded by the inner parts of the 6*s*, 6*p*, and 7*s* electrons due to the relativistic contraction of those orbitals near the nucleus. One effect of these extra relativistic shielding effects is to put the 5*f*, 6*d*, 7*s*, and 7*p* electrons in a more delicate balance both with respect to their intershielding and repulsion effects and with respect to bond formation. The involvement of *f* orbitals in bond formation leads to a splitting of the *f* orbitals with regard to their radial extension such that local *f* orbitals are additionally contracted and bonding *f* orbitals are extended. The radial extension of the *d* orbitals is also split, but now the bonding *d* orbitals are smaller in radial extension than the non-bonding d_{z^2} orbital containing the unpaired outer electron. This supra-valence electron in the d_{z^2} orbital is then shielded by the local *f* orbitals and partly shielded and repulsed by the *f*, *d*, *s*, and *p* hybrid bonding electrons. The resulting overall picture of unpaired electron density is in reasonable agreement with the neutron-diffraction results of Figure 1, *i.e.* one electron at the U site [$f_{x(5z^2-r^2)}$ and $f_{y(5z^2-r^2)}$], one electron somewhat spatially separated from the first at the β, γ site [$f_{y(3x^2-y^2)}$], and the third fractional electron, of different spin direction and at a greater distance, unsymmetrically distributed between the α and δ sites (mostly d_{z^2}).

Finally we have to show that the above distribution for unpaired uranium electrons is generally true and not just an artifact of the special condition $r^2 = s^2 = t^2 = 1/3$. By retaining the individual bond-orbital occupation constant in the Cf1, Cf2, and Gf2 models, as in Table 2, and varying *s* and *t* over all the allowable parameter space subject to $r^2 + s^2 + t^2 = 1$, we find that the same orbitals for unpaired electrons are least occupied in the same order for 26% of *s*–*t* parameter space. Furthermore, they are least occupied (by bonding electrons) in any order over 46% of *s*–*t* parameter space and are among the four least-occupied orbitals over 90% of parameter space. Accordingly, we have indicated that the suggested distribution for the unpaired uranium electrons is rather insensitive to the exact proportions of the *r*, *s*, and *t* parameters and hence has a general validity.

In summary then, we have introduced strong *f* character into the BOA approach for the bonding of uranium in $CrUS_3$ and estimate *f*-orbital character as being 20—30%. In consideration of the location of unpaired electrons, we have proposed a bonding scheme which is in good agreement with the observed results of Wolfers *et al.*[1]

[7/2286 *Received, 29th December*, 1977]

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* Throughout this paper: 1 eV $\approx 1.60 \times 10^{-19}$ J.

[11] J. Verbist, J. Riga, J. J. Pireau, and R. Caudano, *Proc. Internat. Conf. Electron Spectroscopy*, eds. R. Caudano and J. Verbist, North-Holland, Amsterdam and London, 1975, p. 193.

[12] B. Rozenfeld, E. Debowska, and Z. Henkie, *J. Solid State Chem.*, 1976, **17**, 101.