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Electronic Structure of Uranium Chalcogenides: Contribution of a Crystal Data Analysis

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The uranium oxidation state in chalcogenides is shown to be correlated to the mean uranium–chalcogen distances, which vary as the uranium ion size in the crystal lattice. Reference values for U^{3+}–X and U^{4+}–X distances are proposed, taking into account the bond length shortening due to covalency effects. Interpolated values of the mean effective uranium valency as derived from such a correlation, particularly 3.5, 3.36, 3.18 in US, USe, and UTe, are consistent with other previous studies.

Introduction

The electronic structure of neutral uranium is |Rn|, $5f^3$ $6d^1$ $7s^2$. In ionic or ionocovalent compounds, such as the halides and oxyhalides, this element is known to exhibit four valence states: U^{3+}, U^{4+}, U^{5+}, U^{6+}, which corresponds to a progressive participation, from $5f^3$ to $5f^0$, of all the $5f$ electrons to the bonding (*1*). The oxidation state of uranium is not so easily assessed in most of the compounds having metallic or semiconducting type conductivities, such as intermetallic alloys, the pnictides and compounds which we are dealing with: the chalcogenides (*2*). The large spatial extension of the $5f$ wave function, which implies a high sensitivity of the $5f$ electrons to the crystalline environments, and the energetic quasi-degeneracy of the $5f$ and $6d$ electronic states, generate rather complex magnetic and electronic behavior. Thus, magnetic susceptibility and neutron experiments which are current methods to determine the valence state of $3d$ and rare-earth (RE) ions, are rather inadequate for this purpose in uranium compounds (*3–6*). In metallic systems, theoretical models developed for RE where the $4f$ electrons remain strongly localized, or for $3d$ electrons with itinerant character, do not apply well to the $5f$ electrons which are supposed to be in an intermediate situation (*2*).

In this paper, we show from a compilation of the available crystal data of uranium chalcogenides that reliable values of the $5f$ electron number may be derived from its correlations with the uranium ion size in the crystal lattice.

Bond Length and Valency

It is well known that the valence electron number strongly affects the ionic size; alternatively ionic size considerations may help in determining the valence state of an element. Such an analysis is particularly suitable in the RE family. The ionic radii differ-

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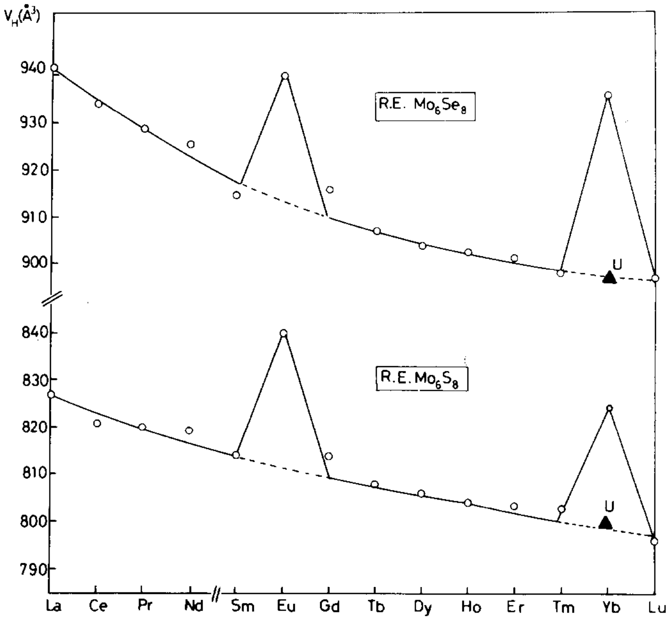

FIG. 1. Unit cell volumes of ternary (RE, U) molybdenum chalcogenides.

ences are approximately equal to 0.20 Å between Sm^{2+} and Sm^{3+}, and 0.16 Å between Yb^{2+} and Yb^{3+} (*7*). Thus, unit cell volume anomalies in the regular lanthanide contraction are indicative of divalent or intermediate valent states for the corresponding elements (*8*) (Fig. 1).

The actinides (*An*) ions sizes are also largely dependent on the valence, 5*f*, electron population, and the ionic radii of U^{3+} is known to be about 0.12 Å higher than that of U^{4+} (*7, 9*). The An^{n+} ionic radii, derived from interatomic distances in halides, decrease also regularly with increasing atomic number. This contraction (Fig. 2) is also observable from bond length variations in isomorphous series of oxides. These ionic or iono-covalent compounds have empty conduction bands and hence localized 5*f* electrons, so the *An* valency is there equal to the number of electrons transfered on the anions. The reduction of americium (and other actinides) from the 4+ to the 3+ states was reported to induce an increase of the americium-oxygen distance by about 0.15 Å independently of the coordination number (*10*), so that a departure from the 4+ state among the actinide oxides could also be easily detected from unit-cell volume or bond length anomalies within the series.

Figure 1 displays the *An*–*X*(*X* = S, Se, Te) bond length variation in *An*X. Clearly the assignment of the uranium electronic state is not as straightforward as in the previous cases. Thorium is a typically tetravalent element, but americium is known to have a RE-like behavior in chalcogenides (*11*), and so to be trivalent. Thus, continuous reference values for the pure 3+ or 4+ states are not available in the chalcogenides.

Furthermore, covalency effects which shorten the bonds, increase with decreasing the anion electronegativity, so that the uranium ionic radii tabulated in the literature and calculated from ionic compounds are not valid as absolute values in chalcogenides, in which the concept of crystal radii, or more simply the mean values of U–*X* distances, or bond length, have to be considered (*12*). In oxides, uranium valency and bond lengths relationships have been used as a method of predicting uranium–oxygen distances when the coordination numbers and the uranium oxidation state have established values (*13*). Owing to the larger spatial extent of the 5*f* wave function than the 4*f*'s, the covalency effects are far more important in uranium than in RE compounds. As an example, the U^{3+} ion size is equivalent to that of La^{3+} in halides (*7, 14*), but to that of Pr^{3+} or Nd^{3+} in the oxyhalides UOY (Y = Cl, Br, I) (*15, 16*) where oxygen introduces some degree of covalency. Such a shift of the *An* crystal radii with respect to the RE's when the ligand electronegativity decreases, was also noticed in the case of americium (*17*). Yet, within the actinide series, covalency effects are expected to be much more important with the first elements up to Pu than in americium and elements beyond, as a result of the localization of the 5*f* states in the latter (*18*). We postulate that a shorter Pu–*X* than Am–*X* distance in the NaCl-type compounds, is probably due to the covalency effect reduction from Pu to Am, both elements being in the trivalent state.

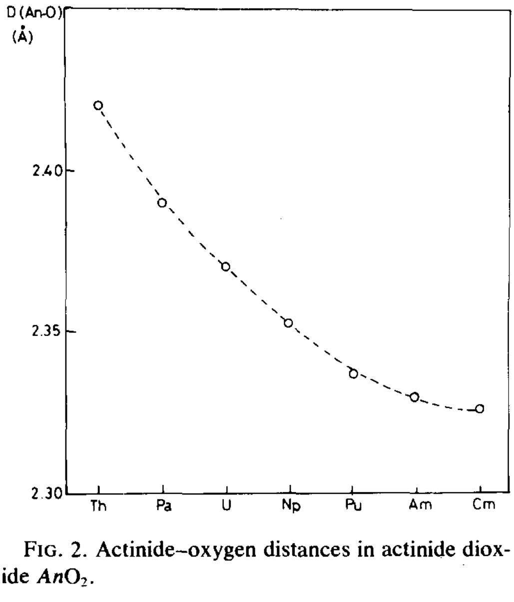

FIG. 2. Actinide–oxygen distances in actinide dioxide AnO_2.

Besides a U–*X* covalent bonding character, the uranium monochalcogenides US, USe, and UTe exhibit a metallic type conductivity, and in such compounds, the uranium effective valency is equal to the total number of electrons transfered in the bonding and in the conducting bands. The magnitude of the latter contribution is, in fact, the unresolved problem. The previous attempts at deriving uranium valency from U–*X* distances considerations, were based on the absolute values of U^{3+} and U^{4+} ionic radii as a reference (*3, 19*), which give misleading indications of the uranium oxidation state in these compounds.

Uranium–Chalcogen Distances and Reference Values for U^{3+}–X and U^{4+}–X

Many ternary uranium chalcogenides have been synthesized in the past years, and an increasing number of accurate uranium to chalcogen distances is known from single crystal X-ray diffraction studies. Figure 2 displays the mean U–*X* distances as calculated from the available experimental data, for uranium with six-, seven-, and eightfold coordination. Higher coordination occurs only in nonconducting compounds where the chalcogen-to-uranium ratio is higher than or equal to 2, such as β-US_2, U_2S_5. Uranium is assumed there to be tetravalent, on account of the existence of chalcogen–chalcogen double bonds in the latter compound, which is thus a polysulfide (*20*).

Previous studies revealed uranium to be in an inhomogeneous mixed valent state in the binaries U_3S_5 and U_3Se_5: the static ionic distribution of uranium over two crystallographic sites was evidenced by crystallochemical considerations (*21–23*) and supported by low temperature magnetic susceptibility results (*24*). The isostructural neptunium sulfide Np_3S_5 was shown to exhibit the same mixed valence behavior, by Mössbauer spectroscopy (*25*).

A lot of informations concerning the U^{3+} and U^{4+} crystal radii may be extracted from the reported data on U_3X_5 and the ternary compounds prepared by selective substitutions on the U^{3+} and U^{4+} crystallographic sites: the unit-cell volume of U_3S_5 is higher than that of UPu_2S_5 (*21*) and equivalent to that of USm_2S_5 (*24*) so that the U^{3+} crystal radius is higher than that of Pu^{3+}, as expected from the actinide contraction, and equivalent to that of Sm^{3+} in chalcogenides. This latter assessment was also deduced from crystal structure calculations (*26*) and is consistent with the increase of the covalency effect from the halides to the chalcogenides.

Half of trivalent uranium in $U^{4+}U_2^{3+}Se_5$ can be oxidized to the tetravalent state on substitution of the other half by a divalent alkaline earth or lead (*27*). The charge balance is $2\ U^{3+} = Pb^{2+} + U^{4+}$, and the decrease of the mean U–Se distance corresponding to this oxidation process of uranium without changing its point symmetry is equal to 0.11 Å (*27*). This value is settled as being the crystal radius difference between U^{3+} and U^{4+} in chalcogenides.

TABLE I

REFERENCE VALUES FOR THE U^{4+}–X AND U^{3+}–X DISTANCES (Å)

	d (U^{n+}–S)		d (U^{n+}–Se)		d (U^{n+}–Te)	
Coordination	4+	3+	4+	3+	4+	3+
6	2.69 2.69^a	2.80	2.80	2.91	2.99	3.10
7	2.75 2.75^a	2.86 2.83^a	2.88	2.99		
8	2.82 2.83^a	2.93 2.91^a	2.97	3.08		

^{a} Values calculated from Ref. (*12*).

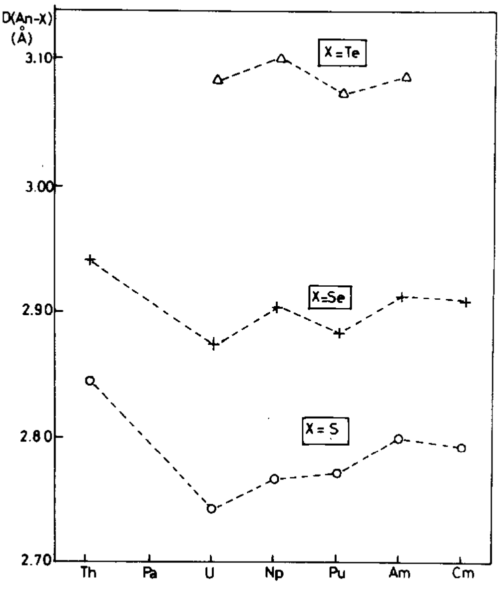

FIG. 3. Actinide–chalcogen distances in the NaCl-type compounds *An*–*X*.

Moreover, rare earths and actinides occupy also the same crystallographic position in ternary molybdenum chalcogenides of the (*An*, RE)Mo_6X_8 type (Chevrel phases) (*28*, *29*). From cell volume considerations (Fig. 1), we can conclude that the U^{4+} crystal radius is equivalent to that of the heaviest lanthanides, the closest being the interpolated radius of Yb^{3+}. In a sixfold coordination, this leads to a U^{4+}–S distance equal to Yb^{3+}–S $\simeq$ 2.69 Å (interpolated value from NaCl-type compounds) which is also the bond length calculated in $BaUS_3$ by neutron diffraction powder profile refinement (*30*).

The characteristic U^{4+}–X distances in 7 and 8 coordinations are deduced from nonconducting ternary compounds where we assume, from chemical considerations, uranium to be in a pure tetravalent state. All the reference values are gathered in Table I, together with U–S distances extracted from a tabulation of crystal radii in sulfides by Shannon (*12*). An excellent agreement between the two sets of values is noticeable for the tetravalent state. Our proposed U^{3+} crystal radius is slightly higher by about

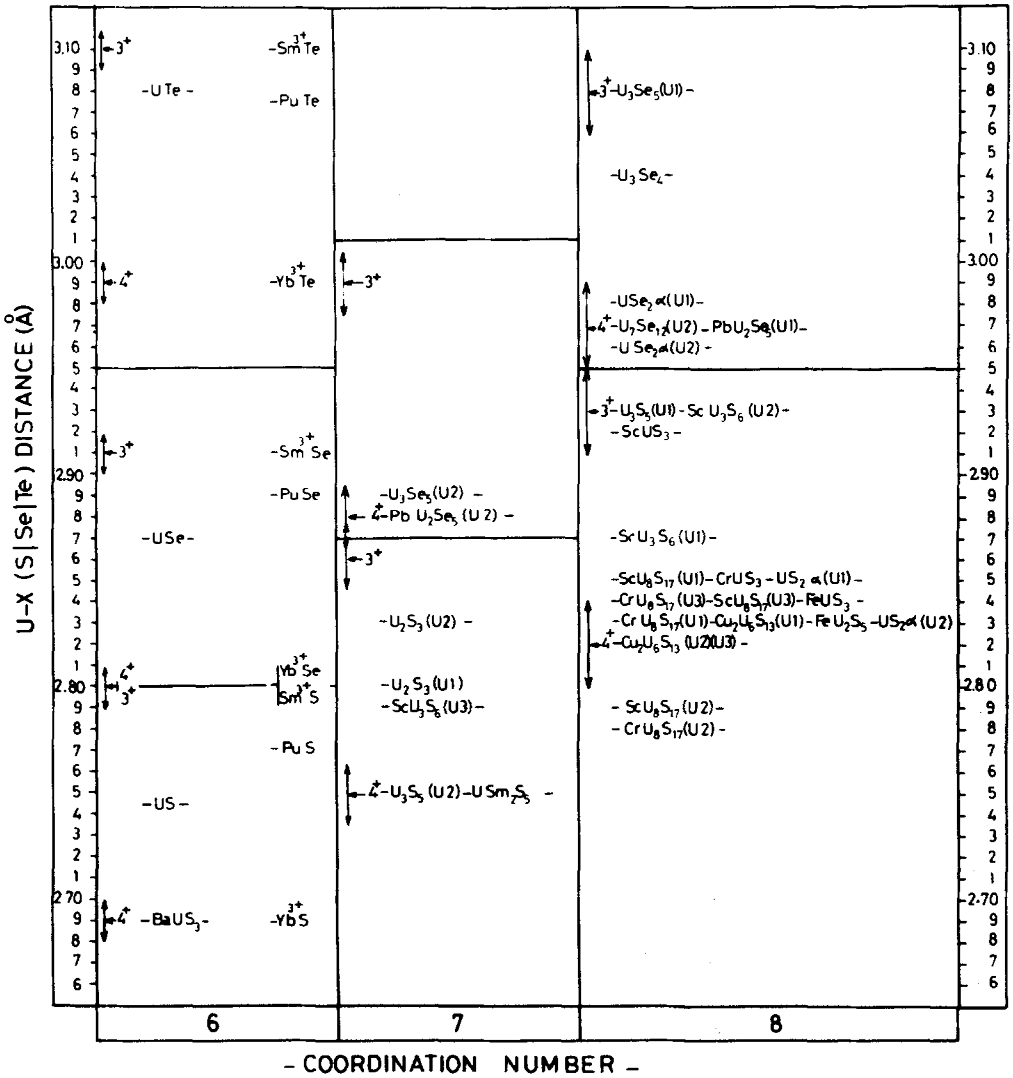

FIG. 4. Plot of the mean uranium to chalcogen distances in binary and ternary uranium chalcogenides.

0.02–0.03 Å. The reference U^{3+}–X and U^{4+}–X distances thus obtained are plotted as horizontal arrows in Fig. 1, together, in sixfold coordination, with the Yb^{3+}–X, Pu^{3+}–X and Sm^{3+}–X which serve as markers. Uncertainties resulting from polyhedron distortions are estimated not to be higher than ±0.01 and ±0.02 Å for 6 to 8 coordinations, and are visualized by vertical double arrows on the plot.

Electronic Structure of the NaCl-Type Uranium Chalcogenides

In order to explain the unusual electronic and magnetic properties of the uranium monochalcogenides, a nonintegral 5*f* electron number with 5*f*–6*d* hybridization was proposed as an alternative solution to localized $5f^2$ or $5f^3$ configurations (*5*). Convergence toward such a fractional 5*f* electron occupancy, or intermediate valence model, merges from the observations of phonon anomalies in inelastic neutron scattering experiments (*31, 32*) from density of states calculations (*33*), reflectivity (*34*), and photoemission studies (*35, 36*). Our results corroborate quite well a band picture which arises from these studies: a $5f^{3-\delta}$ configuration in resonance with the $6d$ conduction band. As a first approximation, from a linear interpolation scheme within the bond length scale, the effective uranium valency can be estimated to be 3.5, 3.36, and 3.18 in US, USe, and UTe, respectively. As these values represent the total number of electrons delocalized in the bonding and conducting bands, we can assume δ values to be equal to, or to vary as 0.5, 0.36 and 0.18. This corresponds to an increasing localization of the $5f$ electrons from the sulfide to the telluride (i.e., a tendency for uranium to become trivalent) in fair agreement with previous studies, and particularly from X = S to Se and Te:

—The increase of the uranium magnetic moment (*3, 6*) originating from localized $5f$ electrons;

—The decrease of the $5f$–$6d$ bandwidth and indications as to a decrease of the number of electrons in the conduction band (*34, 35*);

—A shift of the $5f$ states relative to the Fermi level in UTe, corresponding to a tendency to localization of the $5f$ electrons (*36*);

—Assignments of the trivalent rather than tetravalent state for uranium in UTe to interpret neutron (*37*) and resonant photoemission experiments (*38*).

Other Binary Uranium Chalcogenides

The crystal structures of U_2X_3 and U_3X_4 type compounds have not yet been refined from single crystal data (39). Although the corresponding U–X distances, plotted on Fig. 2, have to be considered as approximate, they are indicative of intermediate valency for uranium in these compounds too. This is to be related to the fact that the X/U ratio is lower than 2, and that they are probably semi-metallic conductors (*40*). The electronic structure of uranium in these compounds should then be described similarly as in the monochalcogenides.

α-US_2 and α-USe_2 exhibit nonstoichiometry as a result of an incomplete filling of the U(2) crystallographic site (*41*). The existence of empty sites is expected to have a minor effect on U(2)–X distances for high occupancy factors (>.75), and U(2) is so assumed to be tetravalent. The rather high value of U(1)–S is suggestive of the departure of U(1) from a pure $5f^2$ state.

Ternary Uranium Chalcogenides

Uranium has a eightfold coordination in majority of the ternary compounds, mainly sulfides, investigated so far. Their electrical properties are not known but owing to their generally grey–black aspect, they are probably semiconductors. Expecting thus a charge localization on the anions and the cations, the uranium valency may be obtained from a simple charge balance calculation. The spread of the U–X distances in Fig. 2 is quite consistent with such analysis: uranium is postulated to be tetravalent in $FeUS_3$ (*42*) but trivalent in the isostructural compound $ScUS_3$ (*43*) as a result of the substitution of divalent Fe^{2+} by the typically trivalent scandium Sc^{3+}. A similar electron transfer is observable in the CrU_8S_{17}-type compounds (*44, 45*), where substitution of Cr^{2+} by Sc^{3+} is concomitant with an increase of the U(1) crystal radius. In these compounds, the anomalously low value of the U(2) crystal radius is suggestive of a U(2)–$5f$ electron occupancy lower than $5f^2$.

The uranium crystal radius in the chromium uranium sulfide $CrUS_3$ is larger than that corresponding to a pure U^{4+} state. Interaction of the 3*d* transition metal with uranium was found to induce in this compound unusual magnetic and electronic properties (*46–48*): a significant spin density, up to 2 Å away from the uranium nucleus, was evidenced by neutron diffraction. The decentralized moments, antiparallel to the main 5*f* contribution, were attributed to polarized 6*d* electrons which may originate from some 3*d*–6*d* electron transfer (*49*). It is worth mentioning that a 6*d*-magnetic moment was found in the thorium vicinity, in the isostructural compound $CrThS_3$ (*49*). Antiparallel coupling of 5*f* and 6*d* magnetic moments was also shown to occur in the monochalcogenides US, USe, and UTe, by electron spin polarization studies in photoemission experiments (*50, 51*). These results highlight the important role of 6*d* electrons, and thus of the respective 5*f* and 6*d*-band electron fillings, in determining the physical properties of actinide materials.

Conclusion

Self-consistent correlations have been found to occur in uranium chalcogenides between the uranium valency and its crystal radius. So, as for rare earth compounds, bond length analysis appears to be a very convenient way to get a first insight in the electronic structure of uranium chalcogenides, an even more, to approach the number of localized 5*f* valence electrons. The U^{4+}–X and U^{3+}–X distances proposed as a reference for the pure valence states, are subject to further refinements when more single crystal data will become available, and very few are known so far for uranium tellurides.

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