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The Refinement of α-USe_2, Twinning in a $SrBr_2$-Type Structure

HORST P. BECK AND WILMA DAUSCH

Institut für Anorganische Chemie der Universität, Egerlandstr. 1, 8520 Erlangen, West Germany

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The refinement of α-USe_2 is reported. It crystallizes with a $SrBr_2$-type structure (space group $P4/n$; $a = 1070.0$ pm, $c = 660.0$ pm). It is shown that this high-temperature form is not necessarily restricted to nonstoichiometric compositions and that other descriptions in a space group with higher symmetry and varying U to chalcogen ratios may be due to the fact that the merohedral twinning of this compound was not recognized. The size of the twin domains can be influenced by equilibrating the crystals at elevated temperatures. The small size of crystals grown at very high temperatures leads to pseudoextinctions simulating a higher symmetry. © 1989 Academic Press, Inc.

Introduction

Several authors have studied different modifications of the disulfides and diselenides of uranium. At high temperatures the tetragonal forms α-US_2 (*1–6*) and α-USe_2 (*2–4, 7*) are found to form. They were mostly characterized by powder diffraction patterns, and there is considerable scatter in the lattice constants reported, which is taken as an indication of varying nonstoichiometric compositions (*2–4*). It was even believed (*3*) that the β–α transition is not a polymorphic one, but one due to chalcogen loss, and that the α-forms will only be stable with a uranium-to-chalcogen ratio of about 1 : 1.88. We, too, are convinced that these uranium chalcogenides show considerable nonstoichiometry, the range of which will vary with the crystal structure. However, we will show in this paper that the transition really is polymorphic, the tetragonal form being stable at a stoichiometric composition also.

The first single-crystal study on an α-form was reported by Mooney Slater (*6*), who derived $I4/mcm$ as the space group from powder data and proposed U positions by evaluating the intensities of *hk*0 reflections recorded with an integrating Weissenberg camera. In 1984, finally, Noël and Le Marouille (*8*) reported single-crystal investigations of phases for which they give the compositions α-$US_{1.82}$ and α-$USe_{1.82}$. The uranium atoms are found in the positions 8f and 4c of the space group $P4/ncc$; however, a satisfactory refinement is only achieved by reducing the occupancy of the latter position to 75% (giving $U_{1.1}S_2$), and even then the thermal parameters for these atoms remain very large with a pronounced anisotropy. The large U_{33} values were taken as the result of a high mobility of these cations along [001].

Some results of this structure refinement seemed unsatisfactory to us, especially those which define the composition of the crystals. Partial occupancy may well occur

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in such systems and an enhanced mobility will be reflected in the thermal parameters, but the findings will not lead to such a conclusion unambiguously. They may also be interpreted as an indication of an even lower occupancy of this site (giving perhaps stoichiometric dichalcogenides), which could not be resolved due to the high correlation of the thermal and occupancy parameters during the refinement procedures and/or because of a wrong space group symmetry. Finally, the close correspondence of these structures with those of the dibromides of Sr (*9*) and Eu (*10*), which have the space group symmetry *P*4/*n*, has led us to reinvestigate the structure of α-USe_2 in the course of our studies on the crystal chemistry of actinide dichalcogenides (*11, 12*).

Experimental Procedures

USe_2 was prepared in two steps. Stoichiometric amounts of U powder (cleaned according to (*13*)) and Se were reacted in evacuated silica tubes by slowly (100°C/day) increasing the temperature to 500°C, then to 800°C within 2 days, firing at this temperature for 2–3 days, and slowly cooling to room temperature. The crude product was then transferred to new silica tubes (10–12 cm long) for a chemical transport reaction under vacuum at about 940°C using small amounts of UBr_4 or mixtures of UBr_4 and Br_2 as a transporting agent. The amount of transporting agent and the U : Se ratio defines the velocity of transport and the type of products. With U : Se = 1 : 2.1 and UBr_4/Br_2 we found crystals of β-USe_2, USe_3, and of an unidentified phase (with lattice constants a = 1087.0 pm, b = 876.2 pm, c = 1394.3 pm, β = 101.71°, *A*-type cell) in the region of the tube between 830 and 730°C within 12 hr. With U : Se = 1 : 2 and only UBr_4 no transport was observed within 20 hr at the same temperature conditions, but the raw material was recrystallized in the 940°C region to crystals of α-USe_2 up to 1 mm in size. USe_2 in the high-temperature zone always crystallized in the α-form, material transported to lower temperatures in the β-form. The crystals of α-USe_2 often showed interpenetrating individuals as macroscopic evidence of twinning.

We chose an apparently nontwinned specimen with well-defined faces, which could be indexed and measured for an accurate absorption correction (μ = 566.8 cm^{-1}) and enclosed it in a silica capillary. Buerger photographs were taken with Mo$K\bar{\alpha}$ radiation, those showing the $0kl$ and the $h\bar{h}l$ reflections were exposed up to 119 hr to check for weak violations of the extinction rules. The cell constants (a = 1070.7 pm, c = 660.0 pm) and the intensities were determined with a Philips PW 1100 diffractometer using Ag$K\bar{\alpha}$ radiation (whole sphere in the range 2° < θ < 16°, hkl and $\bar{h}\bar{k}\bar{l}$ in the range 16° < θ < 20°; 3715 reflections measured, of which 2735 were observed, with 365 symmetrically independent reflections).

This *same* crystal was then equilibrated at 500°C in the capillary containing USe_2 powder at the other end, which was kept at higher temperatures (about 600°C) to ensure that the composition of the crystal did not change due to loss of Se by evaporation. The same Buerger photographs as before were taken with exposure times up to 63 hr and the intensities were measured in the range 2° < θ < 23° in the hkl, $\bar{h}\bar{k}l$, $h\bar{k}\bar{l}$, and $\bar{h}k\bar{l}$ regions of reciprocal space; 4478 reflections were measured, of which 3864 were observed, with 946 symmetrically independent reflections.

The usual corrections were applied and the intensities were corrected for absorption using the program SHELX 76 (*14*). Details of the refinement procedure are reported below.

TABLE I

POSITIONAL AND THERMAL PARAMETERS IN COMPARISON

Compound	Atom	x	y	z	Multiplicity	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}[a]
α-USe$_2$ refined in *P*4/*ncc* after (*8*)	U(1)	0.59536(5)	0.40464(5)	0.25	0.50	130(2)	130(2)	208(2)	16(3)	11(4)	11(4)
	U(2)	0.25	0.25	0.8635(5)	0.186	118(3)	118(3)	659(11)	0	0	0
	Se(1)	0.0405(2)	0.3379(1)	0.1194(3)	1.00	155(6)	132(6)	232(6)	−5(5)	−18(7)	−4(6)
	[Se(1)′	0.4595	0.3379	0.6194]^b							
	Se(2)	0.25	0.75	0.0	0.25	138(6)	138(6)	194(11)	0	0	0
	[Se(2)′	0.25	0.75	0.50]^b							
α-USe$_2$ at high temperatures refined in *P*4/*ncc*	U(1)	0.5941(1)	0.4059(1)	0.25	0.50	213(7)	213(7)	229(9)	24(7)	12(5)	12(5)
	U(2)	0.25	0.25	0.8565(2)	0.137(3)	187(18)	187(18)	355(30)	0	0	0
	Se(1)	0.0409(3)	0.3380(3)	0.1174(5)	1.00	224(18)	198(17)	248(17)	−23(13)	−23(14)	−6(14)
	[Se(1)′	0.4591	0.3380	0.6174]^b							
	Se(2)	0.25	0.75	0.0	0.25	204(20)	204(20)	314(36)	0	0	0
	[Se(2)′	0.25	0.75	0.50]^b							
α-USe$_2$ equilibrated at low temperature refinements as twin in *P*4/*n*	U(1)	0.59201(14)	0.40398(14)	0.24977(25)	1.00	244(7)	254(8)	250(4)	14(4)	15(6)	9(6)
	U(2)	0.25	0.25	0.85809(42)	0.249(2)	206(7)	206(7)	344(13)	0	0	0
	Se(1)	0.04123(44)	0.33812(44)	0.11300(54)	1.00	275(22)	239(20)	243(24)	−24(18)	−14(16)	25(17)
	Se(2)	0.46042(46)	0.33855(46)	0.61912(62)	1.00	283(22)	266(21)	303(26)	−8(19)	33(19)	7(18)
	Se(3)	0.25	0.75	0.0	0.25	267(20)	267(20)	201(30)	0	0	0
	Se(4)	0.25	0.75	0.50	0.25	257(20)	257(20)	296(34)	0	0	0
SrBr$_2$ after (*17*)[c]	Sr(1)	0.5856	0.3955	0.2476							
	Sr(2)	0.25	0.25	0.8483							
	Br(1)	0.0428	0.3388	0.0963							
	Br(2)	0.4590	0.3469	0.6258							
	Br(3)	0.25	0.75	0.0							
	Br(4)	0.25	0.75	0.50							

[a] U_{ij} are given in square picometers.

[b] These symmetrically equivalent positions are given for comparison with the values of the sites, which are independent in *P*4/*n*.

[c] For better comparison some symmetrically equivalent atoms other than those published are chosen to define the asymmetric unit and the numbering of Br(1) and Br(2) is interchanged.

Results and Discussion

The α-Form at Higher Temperatures

The first set of precession photographs taken with the crystal grown at 940°C showed the typical extinction rules for the space group *P*4/*ncc* even after very long exposure times. However, some 0*kl* reflections, which should be extinct, showed counting rates slightly higher than those of the background when they were scanned very slowly, especially in comparison with the counting rates of extinct *hk*0 reflections.

We started the refinement using the SHELX 76 program with the coordinates given in (*8*), assuming the space group *P*4/*ncc*. The refinement converged to R = 0.075 with a 55% occupancy of the 4c position for U(2) in contrast with 74% found by Noël and Le Marouille (*8*). The second parameter set in Table I gives the results of this refinement.

The stoichiometric composition calculated from the new occupancy parameter is now USe$_{1.96}$. We still find a strong thermal anisotropy for the U(2)-type atoms, but it is markedly reduced in comparison with the values given in (*8*) ($U_{11} : U_{33}$ = 1 : 2 vs 1 : 6.5). The data were corrected very carefully for absorption (R_{int} for merging : 0.034), but the R value of refinement is not satisfactory. This could indicate that the model used for refinement was not consistent with the microscopic domain structure of the real crystal. The deviations in stoichiometry showed up as artifacts of the mathematics when the refinement was repeated with another model and with the second data set taken after equilibrating the crystal at lower temperatures.

The α-Form at Lower Temperatures

The second set of precession photographs clearly showed $0kl$ and hhl reflections with $l = 2n + 1$; $hk0$ reflections were extinct for $h + k = 2n + 1$. The prolonged treatment of the crystal at 500°C had changed the space group to $P4/n$. U(1) is now in a general position, and the 4c position of the former space group $P4/ncc$ is split into two independent 2c positions, which were related by a $[00\frac{1}{2}]$ translation in the higher symmetry case. Occupation of only one of these 2c sites (U(2)) would result in a stoichiometric USe_2 compound. The refinement of the structure with the second data set was at first unsatisfactory. Occupation of only one 2c site—no matter which—resulted in R values of 0.18 and large, very anisotropic thermal parameters for this U(2) cation. A 50% occupancy of both sites reduced the R value (0.13), but gave thermal parameters for these atoms which were too small. At this stage of the investigation it was helpful to remember some problems encountered during the determination of the structures of $SrBr_2$ and $EuBr_2$, and this finally led to a better model for the refinement of the α-phase.

A Comparison with the $SrBr_2$-Type Structure

The solution of the structure of the isotypic dibromides of Sm, Eu, and Sr is a case study for some problems encountered in the determination of structures with low Laue symmetry. From powder data, Sass *et al.* (*15*) had derived a structure model for $SrBr_2$ in the space group $P4/n$ just as the one given above with a 50% occupancy of the two 2c sites. Single-crystal investigations by Eick *et al.* (*9, 16*) on $SrBr_2$ and independently by one of us on $EuBr_2$ (*10*) clearly showed that only one of the twofold positions is occupied. Eick published the parameter $z = 0.848$ for Sr(2); for $EuBr_2$ we found Eu(2) in $z = 0.356$. In their paper Smeggil and Eick (*9*) discussed the possibility of partial occupancy of a second 2c site at $z \cong 0.35$ due to a certain mobility of this cation at higher temperatures (see, however, remarks under Discussion of the Structure). They even believed that the type of cation (Sm, Eu, Sr) determines, which site is occupied.

It can be shown, however, that the two seemingly different parameter sets, for $SrBr_2$ and $EuBr_2$, respectively, describe the same structure (*10*). Hirshfeld (*17*) has derived sets of transformations, against which the unit cells and all coordinates of equivalent positions are invariant with the help of the so-called Cheshire groups. The Cheshire group of $P4/n$ is $P4/mmm$, and it has the smaller unit cell $(\frac{1}{2}a_1 - \frac{1}{2}a_2) \times (\frac{1}{2}a_1 + \frac{1}{2}a_2) \times (\frac{1}{2}c)$. Discussing the relations between the Cheshire group and its subgroup $P4/n$, we find that there are eight different, but equivalent, parameter sets, by which any structure with space group $P4/n$ may be described. Four of them are referred to different origins in the $P4/n$ cell (000, $\frac{1}{2}\frac{1}{2}0$, $00\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$), which reflects the fact that we need four Cheshire group cells to cover the space of the $SrBr_2$ unit cell. The second four sets are derived from the first four by applying a transformation, which represents a symmetry element lost in going from $P4/mmm$ to this subgroup, the diagonal mirror plane, or, better, the diagonal twofold axis to keep the right-handedness of the coordinate system. In the course of a structure determination which inversion center is chosen as origin will be irrelevant, since only the sign of F will change, and different parameter sets are immediately recognized as based on different origins. However, the combination of an origin shift together with some symmetry transformation may well obscure the relationship between two parameter sets. The $SrBr_2$-type structure has a high pseudosymmetry, in so far as the anion lattice together with the Sr(1) positions almost fulfill the symmetry conditions of the higher symmetric space group. The appropriate change of origin together with the application of a diagonal twofold axis will therefore give only minute changes in the values for the positional parameters of these atoms. Only the z parameter of Sr(2) changes perceptibly from z to $z + \frac{1}{2}$. Our parameters for $EuBr_2$ and Eick's for $SrBr_2$ therefore describe the same structural arrangement. Which parameter set we arrive at during the structure determination depends on the arbitrary choice of the a_1, a_2-axes, i.e., on the indexing *hkl* or *khl* of a given reflection. This makes a difference only in the case of low Laue symmetry, where *hkl* and *khl* reflections have different intensities. Similar effects are to be expected in the other low-symmetry crystal classes, where problems will always arise, when only powder data are available.

In the case of α-USe_2, however, both 2c positions seem to be occupied as a result of the refinement procedure, and this could mean that "the X-ray beam sees" the $SrBr_2$-type structure in two orientations simultaneously because of merohedral twinning, where reflections of one "individual" coincide perfectly with those of the other one. The anions and the U(1) form an almost perfect lattice throughout the whole crystal due to the pseudosymmetry mentioned before. The domain structure results virtually only by the distribution of the U(2) atoms in the quadratic antiprismatic voids, which are lined up along $\frac{1}{4}\frac{1}{4}z$ and $\frac{3}{4}\frac{3}{4}z$. Within a twin domain these voids are filled and empty alternatively along [001], at the domain boundary two may be filled or empty in sequence. The distinction from antiphase domains is hard to see.

The same seems to be true for α-US_2 and perhaps more or less for all substances having this structure. However, the amount of twinning or the domain sizes depend on the conditions of growth of the crystals.

The Refinement Regarding Twinning

Our "α-phase at high temperature" is made up of very small domains, in which virtually only the U(2) atoms would contribute to the intensity of the otherwise extinct *0kl* and *hhl* reflections. The fact that "extinctions" should depend on domain sizes is at first puzzling. Beams diffracted from different twin domains should not interfere, but add up in intensity. The occurrence of additional extinctions can therefore never be due to equal volume elements of domains containing the structure in different orientations. In our case the "crystallite sizes" are so small, i.e., the periodicity is so poor, that the reflections are broadened and their intensity is too weak to be detected. We find only slightly higher counting rates in diffuse regions (see above)—we may call these "pseudoextinctions." Perhaps stronger disorder fluctuations prevent the growth of larger domains at higher temperatures; the domains have evidently grown when we equilibrated the crystal at lower temperatures, and now the structure refinement with this better model showed α-USe_2 to be a normal $SrBr_2$-type arrangement.

Defining the twin operation in matrix form ($h' = hM$; $M = (010/100/00\bar{1})$) we could refine the structure using a modified version (*18*) of Busing's SFLS program (*19*), in which intensities of overlapping reflections are calculated as $I_c\ (hkl/h'k'l') = (1 - \alpha)I(hkl) + \alpha I(h'k'l')$. The α can be refined as an additional parameter and $(1 - \alpha):\alpha$ defines the ratio of the volumes of the different domains. The refinement converged to a reliability index $R_w = 0.053$

using $1/\sigma^2$ as weighting scheme. The α is refined to 0.53; the ratio of the volumes of the two domains is 1 : 1.14. The final parameters are given in Table I.

The refinement of an occupancy parameter shows the 2c position to be fully occupied; the crystal has a stoichiometric composition. The thermal anisotropy of U(2) is no longer unusual; the ratio $U_{11} : U_{33}$ reflects the normal mobility of a cation in quadratic antiprismatic coordination.

A close inspection of the F_o/F_c table revealed that the observed structure factors of the $0kl$ reflections, which should be extinct in the space group $P4/ncc$, are all smaller than the calculated ones by 10–25%. It seems that many of the twin domains are still too small to contribute perceptibly to the intensity of these reflections and this explains the "high" R value, which could surely be reduced by equilibrating the crystal for even longer times.

Conclusions

It is not the aim of this paper to prove that uranium dichalcogenides are always stoichiometric and that they show no ion mobility, which could be traced in the anisotropy of the thermal motion. However, we point out that the evaluation of diffraction data may lead to such conclusions, which may be erroneous for a given crystal, when its domain structure is not taken into account.

TABLE II

INTERATOMIC DISTANCES IN α-USe$_2$ (IN pm)

U(1)–Se(3)	288.0		U(2)–Se(2)	290.8	4×
–Se(4)	288.1		–Se(1)	295.2	4×
–Se(2)	290.1				
–Se(1)	290.7				
–Se(1)	292.3				
–Se(2)	294.2				
–Se(1)	309.2				
–Se(2)	313.3				
Se(1)–U(1)	290.7		Se(2)–U(1)	290.1	
–U(1)	292.3		–U(2)	290.8	
–U(2)	295.2		–U(1)	294.2	
–U(1)	309.2		–U(1)	313.3	
Se(3)–U(1)	288.0	4×	Se(4)–U(1)	288.1	4×

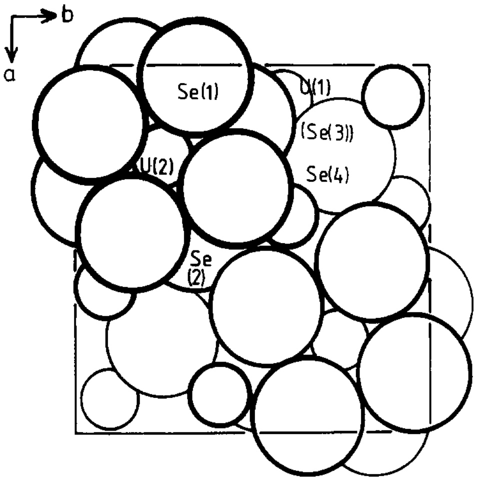

FIG. 1. Projection of the α-USe$_2$ structure along [001].

Discussion of the Structure

Figure 1 shows the α-USe$_2$ structure in a view along c. We see quadratic antiprisms made up of Se(1) and Se(2) sharing common quadratic faces to form chains in the [001] direction. These polyhedra are alternatively empty or filled by the U(2)-type atoms, which are slightly displaced along [001] from the center of gravity of the eight surrounding anions giving shorter U–Se(2) distances. This can be explained by Pauling's electrostatic valence rule, since the effective coordination number of Se(2) is smaller than that of Se(1) (see Table II). The coordination of the U(1)-type cations can be described as a distorted quadratic antiprism (coordination number [7 + 1]), and four such distorted ones surround the nearly ideal one around U(2). These

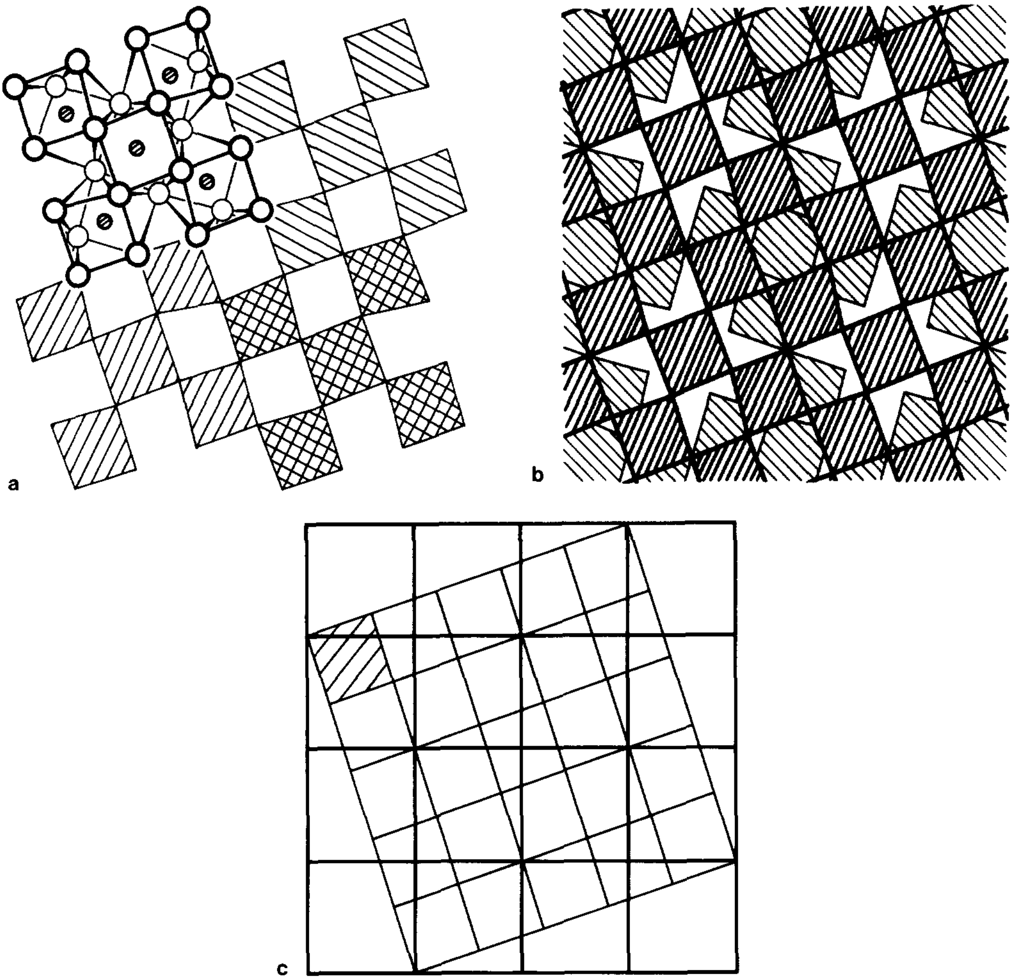

FIG. 2. (a) A schematic representation of the arrangement of "ideal" and distorted antiprisms in one layer. (The "4 + 1" group is emphasized.) (b) Two successive layers of antiprisms viewed along *c*. (c) The relation of the pseudocubic subcell to the tetragonal cell of the $SrBr_2$-type structure (large grid).

(4 + 1)-units are connected in slightly wavy layers to form a chessboard-like pattern (Fig. 2a), and succesive layers of this kind are displaced one against another to reduce electrostatic repulsion between the cations, so that empty and filled quadratic antiprisms alternate also in the direction of projection. The schematic representation of the structure in Fig. 2b shows the close relation of this structure type to the fluorite structure. We find an fcc-type arrangement of cation coordination polyhedra in both structures, antiprisms in the former and cubes in the latter.

Neglecting the small distortions we could define the (4 + 1)-unit mentioned above as a smaller unit cell of an fcc-type arrangement. Fig. 2c shows the relation of this subcell to the $SrBr_2$ cell. The two lattices coincide only in every fifth point of the subcell lattice and in every second of the other one. The relation of the lattice constants is $1:\sqrt{5}/\sqrt{2}$, which is comparable with the tetragonal c/a ratio; the relation to a cubic structure is evident. The combination of tetragonal antiprisms sharing faces in an fcc-type arrangement is only possible by distorting four out of five of them. The resulting superstructure has the same orientation and modulation characteristics as are found in the structure of the ordered alloy $MoNi_4$ (space group *P*4/*n*!) (*20*), where the composition gives the same ratio of different building units for a close-packed arrangement.

It is known that the anion lattice of $SrBr_2$-type compounds is more or less disordered at elevated temperatures ($SrBr_2$ shows anionic conduction and hardly any cation mobility (*21*); this could be true for the uranium dichalcogenides as well) and that transition into a fluorite-type arrangement is possible at temperatures just below the melting point. The growth of crystals with a $SrBr_2$-type structure will therefore be influenced by the strong tendency to create a fluorite-type ion distribution. The polydomain structure discussed in this paper will result from the symmetry reduction in minimal steps due to displacements and ordering of the ions according to the "short-range needs" of the individual ions during crystallization, and this process may well nucleate in different orientations in different parts of the growing crystal. By the way, the ordered $MoNi_4$ alloy also shows a complex domain structure of twins and antiphase domains, which can be understood on the basis of group–subgroup relations between the ordered and the disordered phase (*22*).

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