

## High-pressure structural investigation of cesium above 10 GPa

K. Takemura\* and K. Syassen

*Physikalisches Institut, Universität Düsseldorf, D-4000 Düsseldorf 1, Federal Republic of Germany*

(Received 3 December 1984)

High-pressure x-ray powder diffraction studies of the phase Cs V have been performed between 9.6 and 26.5 GPa at room temperature. The observed diffraction patterns are interpreted equally well by three slightly different structures:  $P4_2/mbc$ ,  $Z=8$ ;  $Pnma$ ,  $Z=4$ ;  $Pbcm$ ,  $Z=4$ . The proposed structures have in common a sixfold coordination, which suggests a considerable degree of directional bonding in Cs V.

### I. INTRODUCTION

The outer  $s$  electrons in the heavy alkali metals undergo a transfer into  $d$ -like states at high pressures, because initially unoccupied  $d$  states are lowered through the Fermi level. The high-pressure behavior of cesium has been studied extensively, because the electron transfer proceeds with a series of phase changes at relatively low pressures.<sup>1-4</sup> Some of the phenomena related to the electronic transition are (in order of increasing pressure): the drastic change of the optical properties in the bcc (Cs I, 0–2.3 GPa) and fcc (Cs II, 2.3–4.1 GPa) phases,<sup>5</sup> the anomalously large compressibility of Cs II,<sup>6</sup> a pronounced melting point maximum near 2.4 GPa,<sup>7</sup> the 13% isostructural volume collapse (Cs II→Cs III) near 4.1 GPa,<sup>3</sup> the 10% decrease in atomic radius at the 4.2-GPa transition to the eightfold-coordinated tetragonal phase Cs IV,<sup>4</sup> and, finally, the large increase in electrical resistance<sup>2</sup> and the occurrence of superconductivity<sup>8</sup> in the vicinity of the Cs IV→Cs V transition near 10 GPa. At this pressure, Cs is compressed to 27% of its normal volume.

Energy-band calculations have provided insight into some details of the gradual occupation of  $d$  states at reduced volume.<sup>9-11</sup> More recently, theoretical investigations<sup>12-15</sup> have focused on the relation between electronic structure and phase stability under pressure. In accordance with a previous suggestion based on optical reflectivity measurements,<sup>5</sup> Skriver<sup>15</sup> finds that the bcc-fcc transition is primarily driven by the degree of  $s$ - $d$  transfer, which is in contrast to earlier interpretations in terms of a core-repulsion effect only (see, e.g., Ref. 16). The isostructural volume collapse near 4.1 GPa has been explained by an interplay between the Fermi-surface topological transition (lowering of the  $X_3$  pocket with mainly  $d$  character through the Fermi level) and an anomalous decrease of the macroscopic Grüneisen parameter.<sup>12,13</sup> This prediction is supported by experimental measurements of the Grüneisen parameter.<sup>17</sup> The calculated stability region of Cs IV (Ref. 14) relative to more densely packed structures is in excellent agreement with experiment. The occurrence of new close-packed structures is predicted at relative volumes  $V/V_0 < 0.25$ .<sup>14</sup>

Band-structure calculations for an assumed fcc structure<sup>9-11</sup> and for the “Cs IV” structure<sup>14</sup> show that the  $6s$ - $5d$  transition continues at volumes corresponding to

the stability of Cs IV. However, the calculated “ $d$  occupation number” has already reached a value near 0.8 at a relative volume  $V/V_0=0.27$  (10 GPa). At pressures above 10 GPa, where the phase Cs V becomes stable, one apparently approaches the unique state of a monovalent elemental metal with one outer electron of mainly  $d$  character. For this reason and in view of the recent theoretical attempts to explain the crystal structure systematics of a large group of elemental metals in terms of the number of  $d$  electrons in the conduction band,<sup>14,15,18</sup> a structure determination of the phase Cs V is of particular interest.

We have performed x-ray investigations of Cs V between 9.6 and 26.5 GPa. Based on powder diffraction data, three slightly different structures are proposed. A characteristic feature of all three structures is a distorted sixfold coordination, which suggests a considerable degree of directional bonding. A preliminary account of the present work was given elsewhere.<sup>19</sup>

### II. EXPERIMENTAL PROCEDURE

Cs metal of 99.95% nominal purity was injected under silicone oil or under dry argon atmosphere into the gasket hole of a diamond-anvil high-pressure cell. Powder x-ray diffraction patterns were taken in the angle-dispersive mode using Mo  $K\alpha$  radiation and either a position-sensitive detector or a conventional scintillation counter. Pressures were determined from the red shift of the ruby  $R_1$  fluorescence line using a conversion factor of 3.65 Å/GPa.<sup>20</sup> There was no noticeable difference in the qual-

TABLE I. Observed  $d$  values (in Å) and relative peak intensities of Cs V at 18 GPa. Values marked by asterisks are less accurate due to overlap with a neighboring reflection.

$d$	$I$	$d$	$I$
3.256	15	1.628	7
2.899*	32*	1.569	23
2.816	100	1.516	25
2.584	24	1.457	16
2.301	31	1.415	18
2.126	6	1.288	8
2.027	29	1.211	7
1.766	11		

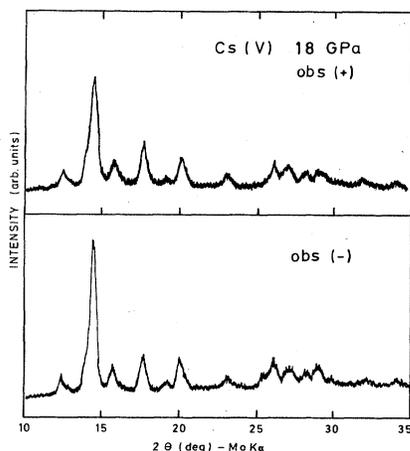


FIG. 1. X-ray diffraction patterns of Cs V at 18 GPa taken for positive and negative scattering angle.

ity of the diffraction patterns for runs with and without silicone oil pressure medium.

### III. EXPERIMENTAL RESULTS

A typical diffraction pattern of Cs V at 18 GPa is shown in Fig. 1. One notices differences in peak intensities of equivalent reflections for positive and negative scattering angles, which arise from an inhomogeneous intensity distribution within Debye-Scherrer rings due to recrystallization at the IV-V phase boundary. The experimental errors of peak intensities are estimated to be roughly  $\pm 15\%$ . The observed  $d$  values and intensities are summarized in Table I.

Indexing of the patterns was performed with the program IDX, which was successfully used in the structure analysis of Cs IV. This indexing procedure and the searching method for space groups is briefly described elsewhere.<sup>21</sup> In addition, the indexing program DICVOL developed by Louër and Vargas<sup>22</sup> has been used for cross-checking purposes.

Among cubic, tetragonal, hexagonal, orthorhombic, and

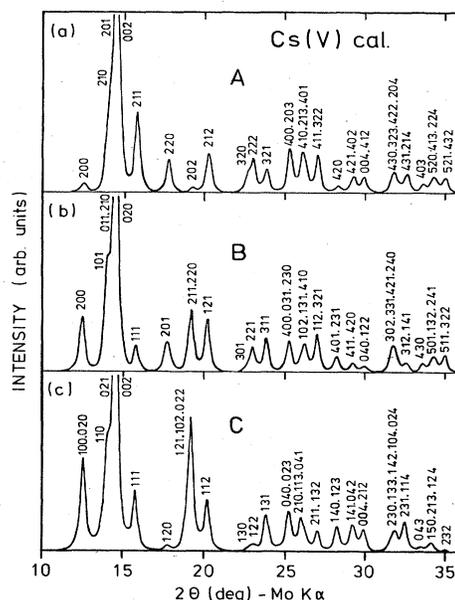


FIG. 2. Calculated intensity profiles for Cs V at 18 GPa based on the corresponding structures A, B, and C shown in Fig. 3.

monoclinic systems (the search in the monoclinic system was limited to  $Z \leq 4$ ), two unit cells give reflections which explain the observed  $d$  spacings within the experimental error of  $\pm 0.3\%$  and which show some systematic extinctions. One unit cell is tetragonal, the other is orthorhombic. From the extinction rules, we find one possible space group for the tetragonal cell and two space groups for the orthorhombic cell.

Calculated diffraction patterns for each structure (denoted A, B, and C) are shown in Fig. 2. The corresponding structures are shown in Fig. 3. The atomic positional parameters are determined to give a best fit to the averaged intensity profile. Since the experimental error in observed peak intensities is rather large, it is not possible to discriminate between the three structures. In fact, the reliability factor defined by  $R = \sum |I_{\text{obs}} - I_{\text{cal}}| / \sum I_{\text{obs}}$ ,

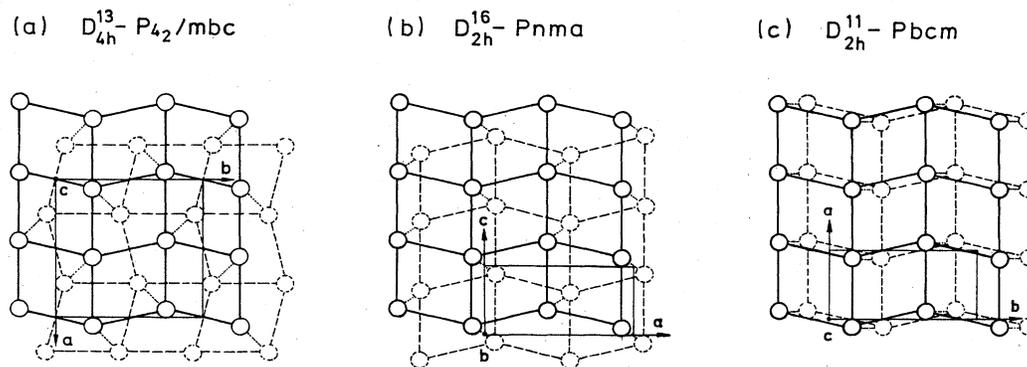


FIG. 3. Proposed structures for Cs V. The figure shows the projection of atomic positions onto (a) the tetragonal  $aa$  plane, (b) the orthorhombic  $ac$  plane, and (c) the orthorhombic  $ab$  plane for structures A, B, and C, respectively. Thin solid lines represent the unit cell. Atoms drawn by dashed circles locate half a lattice constant below those drawn by closed circles.

where  $I_{\text{obs}}$  and  $I_{\text{cal}}$  denote observed and calculated intensities, is as large as 30% for each structure.

Structure *A* is tetragonal with eight atoms in the unit cell. The lattice parameters at 18 GPa are  $a = 6.506 \pm 0.004$  Å and  $c = 5.627 \pm 0.005$  Å. The space group is  $D_{4h}^{13}$  ( $P4_2/mbc$ ) and atoms locate at  $8h$  sites. From the systematic extinction of  $hkl$  reflections with  $h, k = 2n + 1$ , the atomic positional parameter  $y$  was determined to be  $\frac{1}{4}$ . A least-squares fit to the observed average intensity profile yields  $x = 0.073 \pm 0.009$ .

Structure *B* has a unit cell which is half of that of structure *A*. Thus the lattice parameters are  $a = 6.506 \pm 0.004$  Å,  $b = 5.627 \pm 0.005$  Å, and  $c = 3.253 \pm 0.002$  Å. The space group is  $D_{2h}^{16}$  ( $Pnma$ ). Four atoms occupy  $4c$  sites. The atomic positional parameters are  $x = -0.070 \pm 0.024$  and  $z = 0.125 \pm 0.018$ . The atomic arrangement in the  $ac$  plane is almost the same as that in the  $aa$  plane of the corresponding tetragonal structure *A*.

Structure *C* is another possible arrangement of atoms in the same orthorhombic unit cell as for structure *B*. The space group is  $D_{2h}^{11}$  ( $Pbcm$ ) and four atoms locate at  $4d$  sites. The atomic positional parameters are  $x = -0.125 \pm 0.018$  and  $y = 0.150 \pm 0.014$ . The arrangement of atoms in the  $ab$  plane is again nearly the same as that found in structures *A* and *B*.<sup>23</sup>

#### IV. DISCUSSION

An obvious difference between the three proposed structures *A*, *B*, and *C* is the way of stacking of a "distorted square lattice" along the tetragonal  $c$  axis. In structure *A*, subsequent lattice planes (which may also be viewed as distorted hexagonal layers) are rotated 90° around the  $c$  axis, whereas in *B* and *C* it is basically a 180° and 0° rotation, respectively. Also, an appropriate translation of the second layer in structure *B* within the layer plane results in structure *C*. The coordination of Cs atoms is nearly the same for all three structures. Each Cs atom has *only six* neighboring atoms, four in the plane and two in adjacent planes, the latter two at nearest-neighbor distances of 3.25, 3.08, and 3.10 Å for structures *A*, *B*, and *C*, respectively, at 18 GPa. Uncertainties in atomic positional parameters cause errors of approximately  $\pm 0.05$  Å in nearest-neighbor distances.

We have performed model calculations for more complicated stacking sequences of the "distorted square layers," e.g., doubling of the axis perpendicular to the layers. None of the layer stackings tested gives better agreement with the experimental data as compared with the original *A*, *B*, and *C* structures.

Since there remains an ambiguity with regard to the exact layer stacking in Cs V, the remainder of the discussion will only focus on those features, which are common to all three proposed structures. These are the sixfold coordination, the similar "in plane" structure and the low symmetry. Some similarities to structures of other elemental metals will be pointed out.

The pressure-volume curve and pressure-atomic-radius relation are shown in Fig. 4. Atomic radii are defined as half of the nearest interatomic distance and corrected to eightfold coordination. The changes both in volume and

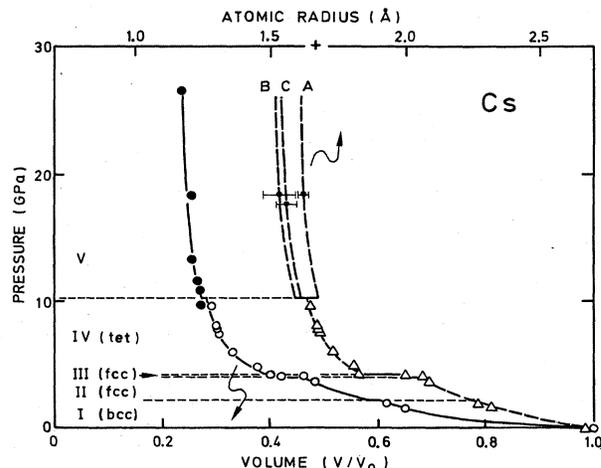


FIG. 4. Pressure as a function of relative volume (solid curve) and pressure-atomic radius relation (dashed curves). Data for phases I, II, III, and IV (open circles and open triangles) are from Refs. 3 and 4. Solid circles are from present work. The pressure-volume relation is common to the three proposed structures *A*, *B*, and *C*. Curves are a guide for the eye. The ionic radius of Cs at normal conditions is indicated by a cross on the abscissa for atomic radii.

in atomic radius are small at the IV-V transition, which would account for the coexistence of both phases in a pressure range from 9.6 to 10.8 GPa. The transition pressure is thus given as  $P_t = 10.2 \pm 0.6$  GPa. We note that above 7 GPa the molar volume of Cs becomes less than the volume of the neighboring rare-gas element Xe.<sup>24</sup> Furthermore, the atomic radius of Cs V is close to the ionic radius of Cs at normal pressure (1.67 Å). If we neglect the compression of the ion core, the ionic and atomic radii are nearly identical at 10 GPa. We may thus infer from experiment that a large amount of  $6s$  electrons is transferred to the spatially more localized  $5d$  states, which have a radial extent not much larger than  $5p$  core states.

The sequence of coordination numbers in Cs under pressure is 8 (bcc)—12 (fcc)—8 (Cs IV)—6 (Cs V). The reduction in coordination number can be interpreted in terms of increasing covalency. As was shown by Louie and Cohen<sup>10</sup> in their electron density plots for fcc Cs at reduced volume, the  $s-d$  transfer results in a redistribution of charge in a way typical for a partly covalent character of the bonds.

The increase in covalent bonding suggests an explanation of the Cs V structure based on directional bonds constructed from atomic hybridized orbitals. As discussed before, energy-band calculations for fcc Cs (Refs. 9–11) and for the phase Cs IV (Ref. 14) indicate that the  $s-d$  transfer is almost completed at 10 GPa. This is in agreement with our above reasoning based on the comparison of ionic and atomic radii. If we assume a pure  $d$  character of the outer electron of Cs, we could probably expect perpendicularly oriented, sixfold-coordinated bonding resulting in an octahedral arrangement of atoms or at least a centrosymmetric nearest-neighbor configuration. The

observed structures can be viewed as a heavy distortion of an octahedral coordination. It is difficult to see how  $s$ - $d$  hybridization can account for the low symmetry, because both  $s$  and  $d$  orbitals are of the *gerade* type. Within the local bonding picture we are therefore left with the conclusion, that either  $p$ - $d$  or  $f$ - $d$  hybridization has to be considered in explaining the bond directions.

Energy-band theory<sup>14</sup> does not support a significant degree of  $f$ - $d$  hybridization. Wittig<sup>8</sup> proposes a small amount of  $4f$  admixture in Cs in order to explain that superconducting behavior is found in Cs near 10 GPa, but not in Rb up to 20 GPa. This argument could, however, be made more convincing, if the behavior of Cs near 10 GPa would rather be compared with that of Rb around 40 GPa, where also Rb is expected to approach the completion of the  $s$ - $d$  transition.<sup>14</sup>

In this context we mention some similarities and differences between the Cs V structure and the  $\alpha$ -uranium structure.<sup>25</sup> The  $\alpha$ -U type structure is assigned to high-pressure phases of early lanthanides [ $\alpha'$ -Ce,<sup>26</sup> Pr IV (Ref. 27)] and some actinides [Am IV,<sup>28</sup> Bk III,<sup>29</sup> and Cf IV (Ref. 29)]. The occurrence of this structure seems to be related to the participation of itinerant  $f$  electrons ( $4f$  or  $5f$ ) in bonding. The  $f$ -electron bonding is believed to account for the exotic fourfold coordination and the short bond length (2.7–2.9 Å). The Cs V structure, especially (C), shows some similarity to the  $\alpha$ -U structure: the axial ratios  $b/a$  and  $c/a$  are almost the same as the corresponding ratios of  $\alpha$ -U, and, if the atomic positional parameter  $x$  of Cs V (C) becomes  $\frac{1}{4}$ , the  $\alpha$ -U structure is realized. However, there are also two distinct differences between these two structures: the shortest interatomic distance of 3.10 Å in Cs V (C) is larger than the typical  $4f$  bond length [2.90 Å in  $\alpha'$ -Ce at 5.8 GPa (Ref. 26) and 2.69 Å in Pr IV at 23.3 GPa (Ref. 27)], and the coordination number of Cs V is definitely larger compared with  $\alpha$ -U.

These differences in structural properties between  $\alpha$ -U and Cs V suggest that an admixture of  $f$  character to the occupied conduction band states is not important for the bonding properties of Cs V. Therefore,  $p$ - $d$  hybridization must be considered to be the predominant effect in determining the bonding directions. The effect of  $p$ - $d$  hybridization in Cs has been investigated in the recent theoretical work by McMahan<sup>14</sup> with the result that it has a strong

effect on structural energy differences at relative volumes  $V/V_0 < 0.25$ , which roughly corresponds to the onset of the stability region of Cs V.

The sixfold coordination of Cs V is reminiscent of the  $\beta$ -Sn structure, which has been interpreted in terms of mixing between  $p$  and  $d$  orbitals.<sup>30</sup> Actually, the structure of Cs V, especially (B), can be viewed as a distortion from the  $\beta$ -Sn structure. If the atomic positional parameter  $x$  becomes zero and the  $b$  axis becomes equal to the  $a$  axis, the  $\beta$ -Sn structure is obtained. The structure of Cs V has, therefore, lower symmetry than  $\beta$ -Sn just as in the case of the above comparison with the  $\alpha$ -U structure.

Finally, there appears to be no obvious physical argument which favors one of the three structures proposed for Cs V. The significant core repulsion in these open lattices, as evidenced by the comparison of atomic and ionic radii and supported by McMahan's calculations,<sup>14</sup> could possibly rule out structures B and C having smaller nearest-neighbor distances compared with structure A. On the other hand, without detailed calculations, it is not clear to which extent the larger core repulsion could be balanced by a larger  $d$ -band width and therefore a larger bonding contribution of the valence electrons.

In conclusion, the x-ray investigation of Cs V has resulted in proposing three possible crystal structures for this phase. The structures only differ in the packing arrangement of almost identical distorted square lattices. The structures have in common an approximately sixfold coordination, which suggests a considerable degree of directional bonding. Total-energy calculations using a method suitable for dealing with open lattices might be helpful in deciding which of the proposed three structures is the most likely one. An experimental approach will be the attempt to grow a single crystal of Cs V within a diamond-anvil cell and to perform single-crystal x-ray diffraction studies.

#### ACKNOWLEDGMENTS

During this work we have enjoyed discussions with J. Akella. The authors are grateful to D. Louër for providing the indexing program DICVOL and for some test runs. One of us (K.T.) would like to thank the Alexander von Humboldt Foundation for support.

\*Present address: Physics Laboratory, College of General Education, Nagoya City University, Nagoya 467, Japan.

<sup>1</sup>P. W. Bridgman, *Collected Experimental Papers* (Harvard University Press, Cambridge, 1964).

<sup>2</sup>R. A. Stager and H. G. Drickamer, *Phys. Rev. Lett.* **12**, 19 (1964).

<sup>3</sup>H. T. Hall, L. Merrill, and J. D. Barnett, *Science* **146**, 1297 (1964).

<sup>4</sup>K. Takemura, S. Minomura, and O. Shimomura, *Phys. Rev. Lett.* **49**, 1772 (1982).

<sup>5</sup>H. Tups, K. Takemura, and K. Syassen, *Phys. Rev. Lett.* **49**,

1776 (1982).

<sup>6</sup>D. B. McWhan, G. Parisot, and D. Bloch, *J. Phys. F* **4**, L69 (1974).

<sup>7</sup>G. C. Kennedy, A. Jayaraman, and R. C. Newton, *Phys. Rev.* **126**, 1363 (1962); A. Jayaraman, R. C. Newton, and J. M. McDonough, *ibid.* **159**, 527 (1967).

<sup>8</sup>J. Wittig, *Phys. Rev. Lett.* **24**, 812 (1970); J. Wittig, in *Proceedings of the IVth Conference on Superconductivity in d- and f-Band Metals*, edited by W. Buckel and W. Weber (Kernforschungszentrum Karlsruhe, Karlsruhe, 1982).

<sup>9</sup>J. Yamashita and S. Asano, *J. Phys. Soc. Jpn.* **29**, 264 (1970).

- <sup>10</sup>S. G. Louie and M. L. Cohen, *Phys. Rev. B* **10**, 3237 (1974).
- <sup>11</sup>A. K. McMahan, *Phys. Rev. B* **17**, 1521 (1978).
- <sup>12</sup>D. Glötzl and A. K. McMahan, *Phys. Rev. B* **20**, 3210 (1979).
- <sup>13</sup>L. Dagens and C. Lopez-Rios, *J. Phys. F* **9**, 2195 (1979).
- <sup>14</sup>A. K. McMahan, *Phys. Rev. B* **29**, 5982 (1984).
- <sup>15</sup>H. L. Skriver, *Phys. Rev. B* **31**, 1909 (1985).
- <sup>16</sup>T. M. Eremenko and E. V. Zaroquentsev, *Solid State Commun.* **30**, 785 (1979).
- <sup>17</sup>R. Boehler and M. Ross, *Phys. Rev. B* **29**, 3673 (1984).
- <sup>18</sup>See, e.g., J. C. Duthie and D. G. Pettifor, *Phys. Rev. Lett.* **38**, 564 (1977); H. L. Skriver, *ibid.* **49**, 1768 (1982); J. A. Moriarty and A. K. McMahan, *ibid.* **48**, 809 (1982); see also Ref. 15.
- <sup>19</sup>K. Takemura and K. Syassen, in *Solid State Physics under Pressure*, edited by S. Minomura (Reidel, Dordrecht, 1985), p. 127.
- <sup>20</sup>G. J. Piermarini, S. Block, J. D. Barnett, and R. A. Forman, *J. Appl. Phys.* **46**, 2774 (1975).
- <sup>21</sup>K. Takemura, *High Temp. High Pressures* **16**, 559 (1984).
- <sup>22</sup>D. Louër and R. Vargas, *J. Appl. Crystallogr.* **15**, 542 (1982).
- <sup>23</sup>The space groups assigned to structures *B* and *C* have higher symmetry than those given in Ref. 19.
- <sup>24</sup>K. Syassen and W. B. Holzapfel, *Phys. Rev. B* **18**, 5826 (1978).
- <sup>25</sup>Although the diffraction patterns look strikingly similar to a pattern calculated for the  $\alpha$ -U type structure, the observed spectra can not be explained by this structure. For instance, the fifth peak at  $2\theta=17.77^\circ$ , which is neither an impurity line nor a gasket line, does not correspond to any reflection allowed in  $\alpha$ -U.
- <sup>26</sup>W. H. Zachariasen and F. H. Ellinger, *Acta Crystallogr. Sect. A* **33**, 155 (1977).
- <sup>27</sup>G. S. Smith and J. Akella, *J. Appl. Phys.* **53**, 9212 (1982); W. A. Grosshans, Y. K. Vohra, and W. B. Holzapfel, *J. Phys. F* **13**, L147 (1983).
- <sup>28</sup>R. B. Roof, R. G. Haire, D. Schiferl, L. A. Schwalbe, E. A. Kmetko, and J. L. Smith, *Science* **207**, 1353 (1980).
- <sup>29</sup>U. Benedict, J. R. Peterson, R. G. Haire, and C. Dufour, *J. Phys. F* **14**, L43 (1984).
- <sup>30</sup>H. Krebs, *Grundzüge der anorganischen Kristallchemie* (Enke Verlag, Stuttgart, 1968), p. 154.