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X-Ray Diffraction Study of Electronic Transitions in Cesium under High Pressure

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The crystal structure of the high-pressure phase of cesium (IV) was determined to be a tetragonal lattice with $Z = 4$. The space group is $D_{4h}{}^{19}$-$I4_1/amd$ and the lattice parameters are $a = 3.349$ Å and $c = 12.487$ Å at 8.0 GPa. From the structure it is deduced that the atomic radius of cesium decreases dramatically at the III-IV transition, which suggests a discontinuous s-d electronic transition.

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Cesium is well known to show many polymorphic transitions under pressure. The crystal structure of Cs, whic is bcc at normal pressure, changes to fcc (Cs II) at 2.3 GPa and to another fcc (Cs III) at 4.2 GPa.[1] The transition from Cs II to Cs III is a rare case of isomorphic transitions. It goes further to Cs IV at 4.3 GPa[1,2] and Cs V at about 10 GPa.[3,4] The characteristic behavior of Cs under pressure is interpreted in terms of s-d electronic transition. At normal pressure, the conduction band of Cs is almost of s character, but the lowest $5d$ band including the X_1 state already touches the Fermi level. As pressure is increased, the $5d$ subbands near the X point go down relative to the $6s$ band near the Γ point.[5,6] As the X_1 subband has the same symmetry as the $6s$ band, there occurs hybridization between the two bands. The movement of the X_1 subband downwards in energy with pressure facilitates the electron transfer from the $6s$ band to the more localized $5d$ band. This causes the unusually soft bulk modulus in the low-pressure region (phases I and II).[7] On the other hand, the isostructural II-III transition is related to the higher energy $5d$ states of X_3 symmetry.[6] These states do not have the right symmetry to hybridize with the $6s$ band and therefore the X_3 subband abruptly shifts down through the Fermi level with increasing pressure. Recent relativistic calculation of pressure isotherms of Cs shows that the isostructural transition does not occur at $T = 0$ and that the thermal effect plays an important role in the transition at room temperature.[8] This calculation well accounts for the disappearance of the II-III transition at low temperature[9] and the dramatic fall of melting temperature with pressure of Cs II.[10]

Band calculations[5] suggest that the electronic transition continues to take place to about 10 GPa. Therefore it is important to establish the crystal structure of phase IV, to gain an understanding of the nature of the s-d transition. The structure determination of Cs IV has been tried by Hall, Merrill, and Barnett[1] and by Inoue[11] using the x-ray diffraction technique and by McWhan, Bloch, and Parisot using the neutron diffraction technique.[12] Their results were, however, not sufficient to determine the structure. We have carried out high-pressure powder x-ray diffraction analysis on Cs IV utilizing a diamond-anvil cell[13] and an x-ray position-sensitive detector.[14]

Cesium with purity of 99.95% was obtained from Wakoh Pure Chemicals, Ind. Ltd. As Cs is a very reactive material, a lot of attention was paid to handling. The inside of the diamond cell was filled with dehydrated silicone oil, and the molten Cs in a syringe was injected into the gasket hole. The color of Cs thus enclosed in the gasket hole was golden. The formation of Cs oxide was not detected in x-ray photographs. Pressure was determined by the ruby fluorescence technique.[15] The pressure distribution in the sample was estimated to be less than 0.5 GPa at 8.0 GPa, judging from the broadening of the ruby line.

X-ray diffraction photographs of compressed Cs were taken to check the homogeneous distribu-

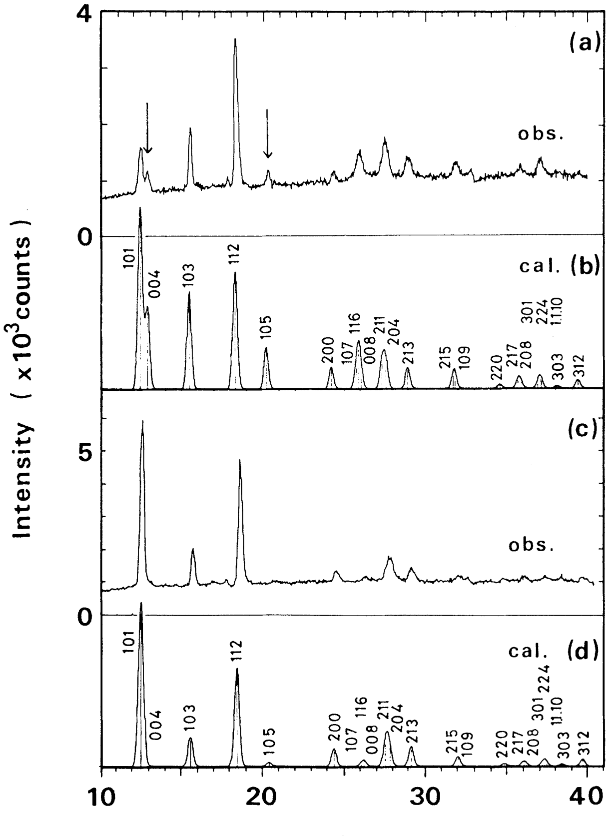

FIG. 1. Diffraction profiles of Cs IV: (a) observed at 7.3 GPa in the course of decreasing pressure, (b) calculated without taking the preferred orientation into account, (c) observed at 8.0 GPa in the course of increasing pressure, and (d) calculated with the preferred orientation taken into account.

TABLE I. Observed and calculated d values of Cs IV at 8.0 GPa. Note that the $00l$ and $10l$ reflections with large value of l disappear in the observed pattern.

$h\ k\ l$	d_{obs}	d_{calc}	$h\ k\ l$	d_{obs}	d_{calc}
1 0 1	3.246	3.235	2 1 3	1.411	1.409
0 0 4	⋯	3.122	2 1 5	1.284	1.284
1 0 3	2.612	2.609	1 0 9	⋯	1.282
1 1 2	2.215	2.214	2 2 0	1.186	1.184
1 0 5	⋯	2.002	2 1 7	1.143	1.147
2 0 0	1.672	1.675	2 0 8		1.142
1 0 7	⋯	1.574	3 0 1	1.110	1.112
1 1 6	1.565	1.563	2 2 4		1.107
0 0 8	⋯	1.561	1 1 10		1.105
2 1 1	1.482	1.487	3 0 3	1.082	1.078
2 0 4		1.476	3 1 2	⋯	1.044

tion of intensity of the Debye-Scherrer rings. The photograph taken at low pressures (phase I) showed a spotty pattern, indicating large crystallites. The crystallites were not broken effectively by repeating the phase change between II and III or between III and IV. However, a powder photograph with good quality was obtained when the pressure was directly raised to about 8.0 GPa (phase IV). X-ray diffraction profiles were measured for several samples with the ISSP-XPSD system which employed a fine-focused Mo x-ray tube and a position-sensitive detector.[14] A typical measuring time for a pattern was 24 h in the scattering angle range of 40°. All measurements were done at room temperature.

X-ray diffraction patterns of Cs were taken up to 16.0 GPa. A typical pattern of Cs IV taken in the course of increasing pressure is shown in Fig. 1(c). Cs IV transforms reversibly to Cs V at about 10 GPa. Figure 1(a) shows the pattern of Cs IV in the course of decreasing pressure from 10 GPa and above. Two peaks at $2\theta = 12.9°$ and $20.3°$ (marked by arrows) are newly observed in the latter pattern, while the other peak positions coincide with those in the former. The indexing was done for six dominant peaks which were common to both patterns [Figs. 1(a) and 1(c)], on the basis of the method developed by Aoki, Shimomura, and Minomura.[16] Among the cubic, tetragonal, hexagonal, and orthorhombic systems, only a tetragonal lattice with $Z = 4$ and axial ratio, c/a, of 3.729 gives a reasonable set of indices which satisfy the extinction rule: $h+k+l=2n$, $2k+l=2n+1$ or $4n$. The space group with this extintion rule is uniquely determined as $D_{4h}{}^{19}$-$I4_1/amd$. Four atoms occupy the special positions ($4a$ site) $(0,0,0)$, $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, $(0,\frac{1}{2},\frac{1}{4})$, $(\frac{1}{2},0,\frac{3}{4})$. The observed and calculated d values are listed in Table I. The calculated diffraction profile for this structure is shown in Fig. 1(b). The overall feature is in good agreement with the observed one and the peaks at $2\theta = 12.9°$ and $20.3°$ can be indexed as 004 and 105, respectively [Fig. 1(a)]. In Fig. 1(c), two peaks (004 and 105) are missing and the peaks with indices of $00l$ and $10l$ with large values of l seem to have weaker intensities than those in Fig. 1(b). This suggests the possibility of preferred orientation in the pattern of Fig. 1(c). Under nonhydrostatic pressure, it is probable that one crystallographic axis tends to lie along the direction of uniaxial stress which will be coincident with the x-ray beam in the case of the present diamond-anvil cell. In Fig. 1(d), the calculated diffraction profile is shown, on the assumption that the crystallites have preferred

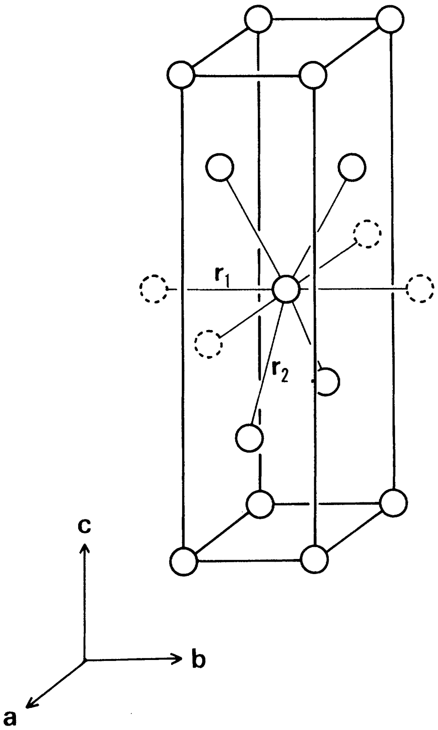

FIG. 2. Unit cell of Cs IV. The atoms drawn with dashed lines are located at the body centers of neighboring unit cells. r_1 and r_2 denote the first- and second-nearest-neighbor distances, respectively.

orientations along the c axis. The intensities agree well with those of Fig. 1(c). This analysis supports the proposition that the Cs IV belongs to the space group D_{4h}^{19}-$I4_1/amd$.

The crystal structure of Cs IV is shown in Fig. 2. The lattice parameters at 8.0 GPa are $a = 3.349 \pm 0.006$ Å and $c = 12.487 \pm 0.030$ Å. The interatomic distances of the first (four) and second (four) nearest neighbors are calculated as $r_1 = 3.349$ Å and $r_2 = 3.542$ Å. The difference between r_1 and r_2 is only 6%. The Cs atom in phase IV is, therefore, considered to have coordination eight. The variation of lattice parameters was measured in the pressure range of 4.6 to 9.6 GPa. The axial ratio, c/a, was found to be constant throughout this pressure range. The variation of relative volume, V/V_0, with pressure, calculated from the lattice parameters, is shown in Fig. 3 by circles and a solid line. The data by Hall, Merrill, and Barnett from x-ray diffraction experiments[1] are also plotted. Hall, Merrill, and Barnett assumed an fcc lattice for Cs IV and calculated the volume using one reflection line. In Fig. 3, their data for Cs IV are corrected under the assumption of a tetragonal lattice with the same c/a ratio as that obtained in the present work.

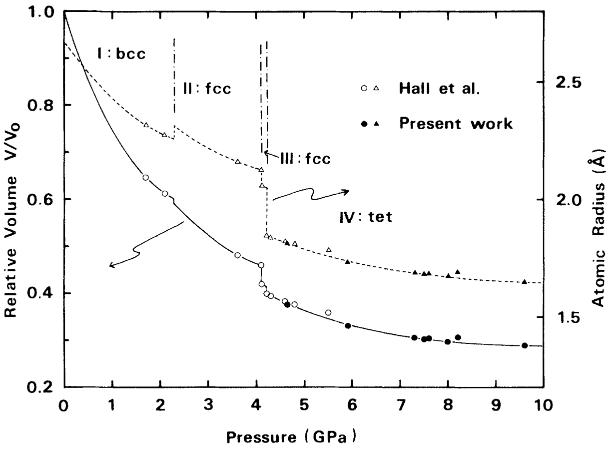

FIG. 3. Variation of relative volume (circles) and atomic radius (triangles) of Cs with pressure. Closed symbols are the present results and open symbols are those by Hall, Merrill, and Barnett (Ref. 1).

The crystal structure of Cs IV is not a close-packed one. The transition from a close-packed structure (fcc) to a non-close-packed structure at high pressure strongly suggests a decrease in the atomic radius of Cs. The variation of atomic radius of Cs with pressure is shown in Fig. 3 by triangles and a dashed line. The volume change and the change of atomic radius at each phase transition are also listed in Table II. Here, the atomic radius is defined as half of the nearest-neighbor distance, with the assumption of a spherical shape for the Cs atom in each phase. In the low-pressure region (phases I and II), the continuous transfer of electrons from the 6s band to the X_1 subband causes a smooth decrease in the atomic radius. The slight increase in the atomic radius (2%) at the I-II transition is due to

TABLE II. Transition pressure, relative volume, volume change, atomic radius, and change of atomic radius at the phase transitions of cesium under pressure. The data for phases I, II, and III are quoted from Ref. 1. The lattice constant at normal pressure is taken as $a_0 = 6.178$ Å.

Phase	P_t(GPa)	V/V_0	$\Delta V/V$(%)	r(Å)	$\Delta r/r$(%)
I→II	2.3	0.601	−1.0	2.258	+2.3
II→III	4.2	0.460	−9.1	2.124	−3.1
III→IV	4.3	0.418	−4.3	2.058	−10.2

the increase in coordination number. On the other hand, the contraction of atomic radius at the III-IV transition is as large as 10%. Band calculations show that after the X_3 subband goes down below the Fermi level, the electrons in the s band abruptly transfer to the X_3 subband, which leads to a large contraction of atomic radius. Therefore, we suggest that the III-IV transition is caused by the sudden movement of the X_3 subband below the Fermi level. The decrease in atomic radius in phase IV more than compensates for the non-close-packed structure of Cs IV.

The bulk modulus of phase II is smaller than that of phase I near the transition pressure and this is explained as a consequence of the continuous s-d electronic transition related to the X_1 subband. On the other hand, the bulk modulus of phase IV is larger than that of phase II. According to the calculation by Glötzel and McMahan,[8] the number of d-like density of states increases rapidly when the X_3 subband moves below the Fermi level. This means a large progress of the s-d transition, and Cs is no longer soft as in phases I and II. The continuous part of the s-d transition, however, will continue still in phase IV until the 6s band completely goes above the Fermi level. The II-III transition is confirmed not to exist at low temperatures both experimentally[9] and theoretically.[8] Moreover, the range of stability of phase III is very narrow (~0.1 GPa). These facts, combined with the large shrinkage of atomic radius at the III-IV transition, suggest that the discontinuous s-d transition related to the X_3 subband mainly occurs at the III-IV transition, and not at the II-III transition.

Cs IV transforms to Cs V at about 10 GPa. Superconductivity has been found in this phase.[4] The diffraction pattern of Cs V is more complicated than that of Cs IV. Structure analysis on this phase is now in progress.

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