Cs(VI): A New High-Pressure Polymorph of Cesium above 72 GPa

K. Takemura and O. Shimomura
National Institute for Research in Inorganic Materials, Tsukuba, Ibaraki 305, Japan

H. Fujihisa
Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

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A new structural phase transition in cesium has been found around 72 GPa using high-pressure powder x-ray-diffraction techniques with a diamond-anvil cell and an imaging plate. The crystal structure of the high-pressure phase Cs(VI) is either hexagonal close packed or double hexagonal close packed. The transition from the open-packed Cs(V) structure to the close-packed Cs(VI) structure implies significant influence of the 5*p* core repulsion to the cohesion of Cs(VI), as well as a possible occurrence of the 5*p*-5*d* overlap.

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The pressure-induced *s*-*d* electronic transitions in heavy alkali metals (potassium, rubidium, and cesium) have been extensively studied both experimentally[1-5] and theoretically.[6,7] Cesium, the heaviest alkali metal, shows the electronic transition at relatively low pressures, and has been the subject of great interest. In brief, the energy levels of the 6*s* conduction band of cesium move up relative to the initially unfilled 5*d* band under pressure, and the conduction electrons are transferred from the 6*s* to the 5*d* band. The *s*-*d* electronic transition in cesium starts just above the atmospheric pressure and terminates around 10–15 GPa.[7] Cesium has five phases in this pressure range. The crystal structures variously reflect the changes in the electronic structure as summarized below.

The bcc-fcc (I-II) transition is related to the degree of the *s*-*d* transfer, as shown by Tups, Takemura, and Syassen[2] in the comparison of the reflection spectra of Cs and Rb. The fcc-fcc (II-III) isostructural transition at 4.2 GPa has been explained by the abrupt increase in the *d*-like density of states at the Fermi energy, induced by the drop of the nearly pure 5*d* states below the Fermi level.[6] Cs(III) transforms to (IV) at 4.3 GPa. The crystal structure of Cs(IV) is open packed. It is tetragonal with four atoms in a unit cell.[1] The structure can be viewed as a tetragonal distortion of the diamond structure (the axial ratio $c/a = 3.73$), resulting in an *eightfold* coordination. The atomic radius decreases dramatically at the (III) to (IV) transition, which has been interpreted as accelerated progress of the *s*-*d* transition.[1] The crystal structure of Cs(V) above 10 GPa has not yet been solved unambiguously, but seems apparently open packed. Takemura and Syassen proposed three structural models; one is tetragonal, the other two are orthorhombic.[5] The three structures are very similar to one another with characteristic atomic arrangement of *sixfold* coordination. The bonding in Cs(IV) and (V) are therefore highly directional, possibly caused by the unique 5*d* (or 5*d*-5*p* hybridized) monovalent electronic states with minor or virtually no *s* electron.

In comparison with the progress in understanding the *s*-*d* transition in cesium, little is known about changes in the electronic structure *after* the *s*-*d* transition. McMahan has calculated the stability of several crystal structures for cesium above the *s*-*d* transition.[7] He concluded that the repulsion of the 5*p* core electrons plays an important role in this pressure range, and found hcp to be the most stable structure followed by a transition to bcc at very high pressures. Unfortunately, the real Cs(V) structure was not included in his calculation. The purpose of the present high-pressure powder x-ray-diffraction experiments is to study the stability of the Cs(V) structure at high pressures and to look for new phase transitions, which may be related to changes in the electronic structure after the *s*-*d* transition.

High-pressure powder x-ray-diffraction experiments have been done with the use of a diamond-anvil cell combined with a synchrotron-radiation source and an imaging plate (IP).[8] The diamond anvil was single beveled with a center flat of 100 μm diam, bevel angle of 2°, and a culet diameter of 300 μm. The gasket made of Udimet 700 alloy was preindented to a thickness of 41 μm, and a hole of 40 μm diam was drilled at the center. Cesium metal (99.95%) obtained from Rare Metallic Co. Ltd. was loaded in the hole of the gasket under silicone oil without pressure medium. Pressure was determined with the ruby fluorescence method based on the pressure scale given in Ref. 9. Powder x-ray-diffraction patterns were obtained in the angle-dispersive mode. The monochromatized x rays ($E = 18.00$ keV) on the beam line 6B from the bending magnet at the Photon Factory, KEK (2.5 GeV, 300 mA) were collimated with a pinhole of 80 μm diam. The diffracted x rays were recorded on the IP. A typical exposure time to take a pattern was 6 h. The two-dimensional intensity data on the IP were rearranged as a function of the scattering angle 2θ and were reduced to integrated one-dimensional data with an improved signal-to-noise ratio.[10] All experiments were done at room temperature.

Diffraction patterns taken at pressures between 10 and

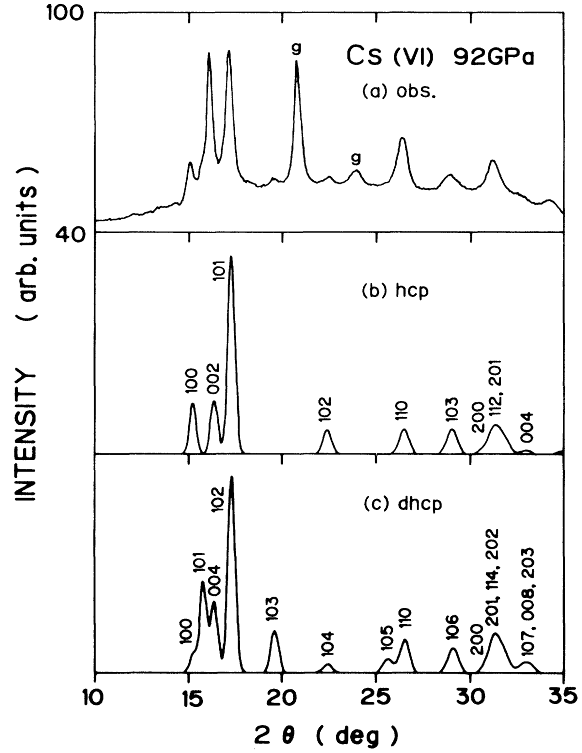

FIG. 1. Powder x-ray-diffraction patterns of Cs(VI) at 92 GPa: (a) observed pattern, (b) calculated pattern for hcp, and (c) calculated pattern for dhcp. The x-ray energy was 18.00 keV. The peaks marked *g* in (a) denote the gasket lines. Constant background is subtracted in (a).

70 GPa were identical to the previous data of Cs(V),[5] but of better quality.[11] A notable change in the pattern was first observed when pressure was raised to 74 ± 3 GPa, indicating a structural phase transition to a new high-pressure phase Cs(VI). Figure 1(a) shows the observed diffraction pattern of cesium at 92 ± 4 GPa, the highest pressure attained in the present experiments. There were no reflections at scattering angles lower than 10° ($d \gtrsim 4$ Å) indicating that the unit cell is small. The observed pattern can be explained by either a hexagonal-close-packed (hcp) or a double hexagonal-close-packed (dhcp) structure. Figures 1(b) and 1(c) show simulated diffraction patterns based on the respective structures. Since some diffraction peaks of Cs(V) still coexisted with those of Cs(VI), it was not possible to differentiate between two structures.[12] The difference between the two structures, however, does not alter the essential bonding properties of Cs(VI), which will be discussed later. It should also be noted that other closed-packed structures with different layer stacking such as the Sm-type or the triple hexagonal-close-packed structures can safely be excluded from the possibilities, since those structures give additional diffraction lines which are not present in the observed pattern. Table I compares the observed and calculated lattice spacings and diffraction intensities for Cs(VI) at 92 GPa. The lattice parameters for hcp were determined to be $a = 3.011 \pm 0.007$ Å and $c = 4.855 \pm 0.016$ Å with the axial ratio $c/a = 1.612 \pm 0.009$. The calculated molar volume 11.48 ± 0.06 cm^3/mole yields the relative volume of $V/V_0 = 0.162 \pm 0.001$ at 92 GPa, where V_0 denotes the

TABLE I. Observed and calculated lattice spacings and diffraction intensities for Cs(VI) at 92 ± 4 GPa.

Observed		Calculated (hcp)[a]			Calculated (dhcp)[a]		
d_{obs} (Å)	I_{obs}	*hkl*	d_{cal} (Å)	I_{cal}	*hkl*	d_{cal} (Å)	I_{cal}
2.626(4)	25	100	2.608	24.0	100	2.608	8.0
2.519(4)	19	···	···	···	101	2.518	43.5
2.453(3)[b]	76	002	2.427	26.1	004	2.427	34.8
2.305(2)	100	101	2.297	100.0	102	2.297	100.0
2.030(3)	4	···	···	···	103	2.031	23.0
1.767(1)	5	102	1.777	15.0	104	1.777	5.0
···	···	···	···	···	105	1.557	9.6
1.507(1)	49	110	1.506	17.0	110	1.506	22.6
1.378(3)	22	103	1.375	18.3	106	1.375	18.2
···	···	200	1.304	2.5	200	1.304	0.8
···	···	···	···	···	201	1.292	4.8
1.278(1)	33	112	1.279	18.4	114	1.279	24.5
···	···	201	1.259	13.0	202	1.259	12.9
···	···	···	···	···	107	1.225	3.9
···	···	004	1.214	2.5	008	1.214	3.3
···	···	···	···	···	203	1.209	3.7
···	···	202	1.149	2.9	204	1.149	1.0

[a] Calculations are done for an hcp lattice with $a = 3.011$ Å and $c = 4.855$ Å ($c/a = 1.612$) and for an equivalent dhcp lattice.

[b] This is probably the strongest peak [(201) and (002) of the structural model "*A*"] of Cs(V) (Ref. 5).

volume at atmospheric pressure. On decreasing pressure from 92 to 46 GPa, the diffraction pattern of Cs(VI) was still unchanged except for the peak shift due to the volume expansion. The reverse transition to Cs(V) started around 40 and was complete at 36 GPa. The large hysteresis of the transition makes it difficult to estimate the equilibrium transition pressure from the present experiments alone. We tentatively give the forward transition pressure P_t as 72 ± 2 GPa. The relative change in volume at the transition is $\Delta V/V_t = 5\%$. The atomic radii defined by half the nearest interatomic distance show no change at the transition, if corrected for the coordination number. Figure 2 shows the equation of state (EOS) of cesium to 92 GPa. One notices the rapid stiffening of the EOS after the Cs(IV) to (V) transition, which is probably related to the termination of the 6*s* to 5*d* electronic transition. A detailed description of the structural data and the bulk moduli of Cs(IV), (V), and (VI) will be reported elsewhere.[13]

The phase transition from Cs(V) to (VI) can be interpreted basically in terms of the competition between the 5*d* directional bonding and the 5*p* core repulsion. According to the calculation by McMahan,[7] the repulsion of the 5*p* core electrons might play a predominant role in determining the EOS and the crystal structure after the termination of the *s*-*d* transition around 10–15 GPa. He predicted hcp to be the most stable structure under this condition. On the contrary, the actual Cs(V) structure was not hcp but open packed. The discrepancy could be attributed to the still predominant 5*d* attraction in Cs(V). The heavily distorted sixfold coordination of Cs(V) has been explained by its 5*d* (or 5*d*-5*p* hybridized) character of the conduction electrons.[5] Eventually at high pressures, however, the 5*p* core repulsion should overcome the 5*d* bonding, resulting in a phase transition to a close-packed structure. The present finding of the close-packed Cs(VI) structure (either hcp or dhcp) is in good agreement with this trend.

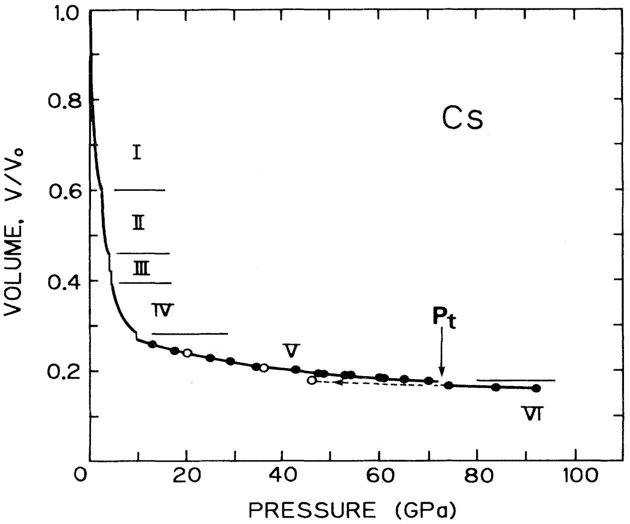

FIG. 2. The equation of state of cesium to 92 GPa. The present results are shown by solid circles (on increasing pressure) and open circles (on decreasing pressure). The other data are from Refs. 1, 4, and 5. The curves are fits by the Birch equation of state, except that for Cs(VI), which is a guide to the eye. The horizontal bars indicate the approximate boundaries between each phase.

It is now of great interest to discuss to what extent the 5*p*-5*d* overlap occurs in Cs(VI). As shown in Ref. 7, the 5*p* core band of cesium becomes broader under sufficiently high pressure and is expected to overlap with the 5*d* conduction band. This 5*p*-5*d* overlap, or the pressure ionization of the 5*p* core electrons, is calculated to occur in cesium around the relative volume of 0.13 and pressure of 150–200 GPa, if no hybridization is assumed. In the real system, the pressure ionization may proceed rather gradually with pressure because of the 5*p*-5*d* hybridization. In this regard, a sizable 5*p*-5*d* overlap is well expected in Cs(VI) ($V/V_0 \leq 0.17$). Even in Cs(V) the 5*p*-5*d* overlap may start, since the 5*d* band width in the open-packed Cs(V) structure should be wider than that of the close-packed structures treated in Ref. 7, leading to 5*p*-5*d* overlap at still larger volume.

If the 5*p*-5*d* overlap occurs in Cs(VI), its electronic state ($5p^{6-x}5d^{1+x}$) may be comparable with those of the metallic xenon ($5p^{6-x}5d^{x}$) and the metallic iodine ($5p^{5}$). Xenon has been shown to become metallic above 150 GPa.[14] Its metallic character originates from the closure of the indirect 5*p*-5*d* gap. Iodine is a monatomic metal above 21 GPa,[15] with the $\frac{5}{6}$ filled 5*p* conduction band.[16] At sufficiently high pressures, the energy levels of the 5*d* band will be lowered and iodine is expected to become a 5*p*5*d* metal ($5p^{5-x}5d^{x}$). Figure 3 shows the change in the molar volumes of these neighboring elements as a function of pressure. The molar volumes

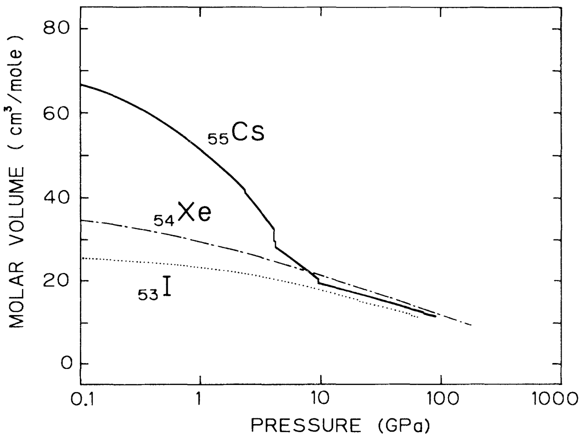

FIG. 3. Molar volumes of iodine, xenon, and cesium as a function of pressure on a logarithmic scale. The data of xenon of iodine are from Refs. 14 and 15, respectively.

agree with each other above about 10 GPa,[17] which is well understood, if the EOS of these elements are commonly determined by the $5p$ electrons. Above 150 GPa, where all these elements are metallic, the crystal structures are equally close packed: hcp for metallic xenon,[14] fcc for metallic iodine,[15] and hcp (or dhcp) for cesium, if the phase (VI) still persists. The similarities in the electronic structures, volumes, and crystal structures strongly suggest that these three elements, I, Xe, and Cs, would form a new class of metals at high pressures, to be called the $5p5d$ metals. Ross and McMahan have pointed out the systematics of the s-d and p-d electronic transition in these elements.[18] Consequently, it is quite natural to expect them to have similar properties in their metallic states. Obviously, further experimental and theoretical works are necessary to verify these arguments. X-ray-diffraction experiments at higher pressures are necessary to obtain a single phase of Cs(VI) and to unambiguously solve the crystal structure. The reflection spectra will be helpful in investigating the electronic structure of Cs(VI) and in making comparisons with the metallic Xe and iodine. The x-ray-absorption spectra may provide alternative information. Detailed energy-band calculations should be supplied for the better understanding of the properties of Cs(VI) and related $5p5d$ metals.

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[11] Recently, new structural models for Cs(IV) and (V) have been proposed [L. Pauling, Proc. Natl. Acad. Sci. U.S.A., **86**, 1431 (1989)]. Our new diffraction data of both phases, however, do not support his models, since the reflections which should appear at low scattering angles in his models were not observed.

[12] The peak (103) of dhcp, which clearly distinguishes dhcp from hcp, coincides with the peak (211) of Cs(V) [the structural model "A" (Ref. 5)]. On the other hand, the weak shoulder ($2\theta = 15.72°$, $d = 2.519$ Å) in Fig. 1(a) can be indexed only to the (101) reflection of dhcp (see Table I). The large deviation ($\sim 0.7\%$) of the first peak ($d_{\text{obs}} = 2.626$ Å) from the calculated one cannot be accounted for by the coexistence of Cs(V) alone. Further experimental studies at higher pressures are necessary to obtain a single phase of Cs(VI) and to solve the crystal structure unambiguously.

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