

## Complex Crystal Structure of Cesium-III

M. I. McMahon, R. J. Nelmes, and S. Rekhı

*Department of Physics and Astronomy and Centre for Science at Extreme Conditions, The University of Edinburgh, Mayfield Road, Edinburgh EH9 3JZ, United Kingdom*

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The structure of Cs-III, stable between 4.2 and 4.3 GPa at room temperature, has been determined from single-crystal x-ray diffraction data. Rather than the simple fcc structure previously reported [Hall *et al.*, *Science* **146**, 1297 (1964)], the data yield a complex new type of elemental structure which is orthorhombic (space group  $C222_1$ ) with 84 atoms in the unit cell. No evidence could be found for the fcc form reported previously, even in a further experiment, conducted under conditions close to those used by Hall *et al.*, which also yielded the 84-atom structure.

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The high-pressure behavior of cesium has long attracted special attention because of its rich and unusual phase transition sequence [1]. Cs-I is body-centered cubic (bcc) and transforms to the face-centered cubic (fcc) Cs-II phase at 2.3 GPa [1]. Cs-III exists over only a very narrow pressure range of 0.05 GPa between  $\sim 4.2$  and  $\sim 4.3$  GPa [2]. It was reported to have the same fcc structure as Cs-II but with 9% greater density [2], making Cs one of only two elements, with Ce, known to have an isostructural phase transition under pressure [1]. At  $\sim 4.3$  GPa, Cs-III transforms to the non-close-packed tetragonal Cs-IV [3], which in turn transforms to orthorhombic Cs-V at  $\sim 12$  GPa [4] and to double hexagonal close packed Cs-VI at  $\sim 70$  GPa [5].

The very high compressibility of Cs below 10 GPa [6]; the apparent existence of an isostructural phase transition [2]; the (unusual) decrease in coordination with increasing pressure, from 12 in Cs-II and Cs-III to 8 in Cs-IV [3]; and unusual melting [7,8], resistivity [8–10], and optical [11] properties are all thought to arise from a pressure-driven  $s \rightarrow d$  transition, in which conduction electrons are transferred from the 6s to the 5d band. Because this electronic transfer and the resulting complex behavior occur at relatively modest pressures, Cs has been studied extensively and has become a model system for understanding such phenomena.

Earlier computational studies appeared to support the existence of the fcc  $\rightarrow$  fcc transition [12,13]. However, recent preliminary diffraction studies have reported large  $d$  spacings of 7.5 and 35 Å, and suggested that Cs-III has a more complex structure “with a large-period supercell” [4]. Furthermore, recent detailed *ab initio* computational studies have variously concluded that Cs-III cannot have the fcc structure [14,15], that fcc Cs-III is stable only at significantly greater densities than are observed [16], and that fcc Cs-III will become unstable against a soft phonon that may give rise to a superstructure prior to the transition to Cs-IV [17]. In this Letter we report a single-crystal diffraction study of Cs-III using laboratory and synchrotron x-ray sources.

Experiments were done with high-purity (99.996%) Cs samples obtained from the Aldrich Chemical Company, us-

ing Merrill-Bassett diamond-anvil pressure cells (DACs) with tungsten gaskets. The Cs was loaded without a pressure-transmitting medium, in an oxygen- and water-free atmosphere ( $<1$  ppm  $O_2$  and  $<1$  ppm  $H_2O$ ), to prevent contamination. A small ruby sphere was enclosed with the sample for pressure measurement [18].

Initial diffraction patterns were obtained on station 9.1 at SRS, Daresbury Laboratory, using angle-dispersive techniques with an image-plate area detector [19]. Data from Cs-I and Cs-II on pressure increase showed that all samples recrystallized readily in both phases to give image-plate patterns consisting of only one or two very intense Bragg reflections. Takemura *et al.* [3] reported the same behavior, and that these crystallites could not be readily broken up by cycling samples through the II-III and III-IV phase transitions, thus making reliable powder-diffraction studies impossible with the small sample volume of a DAC. However, the preliminary work reported by Schwarz *et al.* [4] and the ease with which Cs recrystallizes suggested the use of single-crystal techniques, as already applied successfully to Cs-II [20].

On pressure increase, Cs-III was first observed close to 4.2 GPa, with the appearance of single-crystal reflections in addition to those obtained from Cs-II. We attempted to obtain single-phase samples of Cs-III by increasing the pressure slightly after the initial appearance of Cs-III, but this always caused the sample to transform to Cs-IV. Single-phase samples were successfully obtained if, instead, the sample was simply left for  $\sim 24$  h after the peaks from Cs-III first appeared.

Single-crystal diffraction data were collected both on our laboratory Bruker D8 diffractometer equipped with an APEX CCD detector and a Mo ( $\lambda = 0.71$  Å) x-ray tube, and also on a Bruker Platform diffractometer equipped with a SMART 1K CCD detector on station 9.8 at SRS, using a wavelength of 0.4815 Å [21]. The data were collected in a series of scans about the crystal rotation axis  $\omega$ . On the laboratory (synchrotron) source, the scans were each over  $0.3^\circ$  ( $0.1^\circ$ ) in  $\omega$ , with exposures of 30 s (1 s) per frame, collected first with the stationary detector covering 0 to  $56^\circ$  ( $42^\circ$ ) in  $2\theta$  and then covering 0 to  $-56^\circ$  ( $-42^\circ$ ) in

2 $\theta$ . On both diffractometers, the SMART, RLATT, GEMINI, SAINTPLUS program suites [22] were used for indexing, integration, and data reduction. *Ab initio* structure solution was performed using SHELXS-86 [23], SIR-92 [24], and SIR-97 [25] direct methods packages, and structure refinement was performed using SHELXL-97 [26]. All structure solving and refinement was performed via the WinGX interface [27].

Part of the diffraction pattern from one sample is shown in Fig. 1. Split peaks, as marked in the image, showed the sample to comprise a number of closely aligned crystallites, and it was subsequently found to be unsuitable for data collection. But it is clear from this diffraction pattern that Cs-III does not have the fcc structure. The spacing between the rows of spots corresponds to a direct space dimension of about 7.5 Å, and the spacings along the rows of spots to a dimension of about 35 Å, as reported by Schwarz *et al.* [4].

Further attempts to grow a higher quality single crystal of Cs-III were rewarded by a sample that gave sharply defined, single spots on the image plate. Data collection on the laboratory APEX system revealed the sample to comprise two single crystals, as shown in Fig. 2, with reflection widths of  $\omega \sim 1.0^\circ$ . Indexing of the reflections

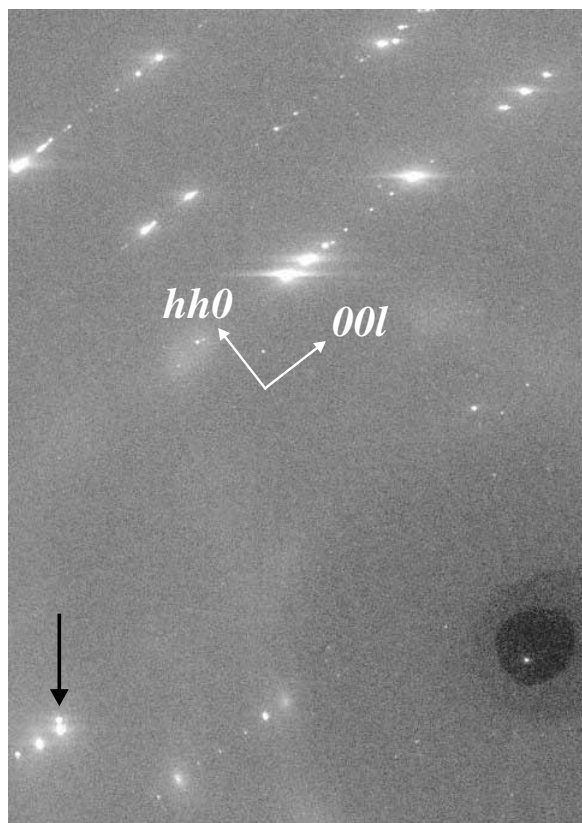


FIG. 1. Part of an image-plate diffraction pattern collected from a sample of Cs-III at  $\sim 4.2$  GPa. The principal directions in the plane of the image are  $[00l]$  and  $[hh0]$  as marked. The vertical black arrow marks an example of a split reflection. The left-to-right streaks from the strongest reflections are due to saturation of the image plate.

of both crystals showed that they could all be indexed on an orthorhombic unit cell with dimensions  $a = 9.28$  Å,  $b = 13.32$  Å, and  $c = 34.25$  Å. In a subsequent study of the same sample on station 9.8 at the SRS, Daresbury, data were collected from the larger of the two crystals to obtain better measurements of the many weak reflections.

The different orientations of the two crystals, shown in Fig. 2, and the shorter wavelength used in the synchrotron study enabled a wide range of reflections to be observed. This was particularly important for space group determination, where the systematic absences allowed the space group to be determined uniquely as  $C222_1$ . From the previously published densities of Cs-II and Cs-IV [2,3], the unit cell of volume 4234 Å<sup>3</sup> must contain a minimum of 78 atoms and a maximum of 90. However, in space group  $C222_1$  the number of atoms must be a multiple of 4, which reduces the possible values to 80, 84, or 88.

*Ab initio* structure solution was performed using direct methods both on the in-house diffraction data obtained from each single crystal and on the diffraction data collected from one of them at the synchrotron. In all three cases, the same 84-atom structure was found to give the best fit. And structure solution using different direct-methods software—SHELXS-96, SIR-92, and SIR-97 [23–25]—all gave the same result. In the following discussion, we describe the results obtained from the synchrotron study.

After removing those reflections affected by Bragg reflections from the diamonds, and powder lines from the tungsten gasket and beryllium backing discs of the DAC, a total of 1968 reflections were collected to a resolution of 0.9 Å. These were averaged to give 1166 unique reflections, of which 795 had  $F > 4\sigma(F)$ . The final fit to the structure, which included anisotropic atomic displacement (thermal motion) parameters, gave  $R_1 = 11.11\%$  for the 795 unique data with  $F > 4\sigma(F)$  and a goodness of fit  $\chi^2$  of 1.198. The largest residual density in the Fourier

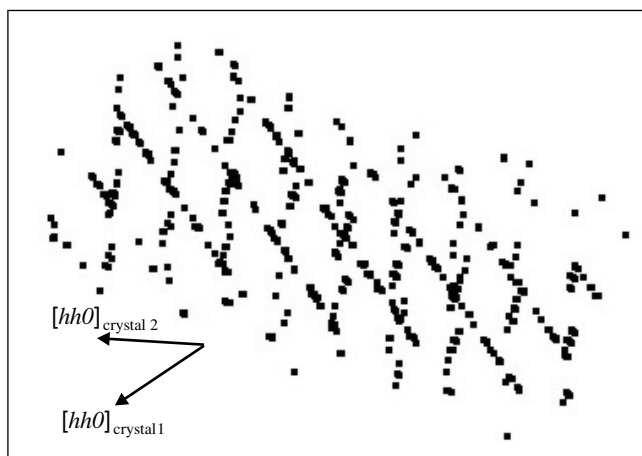


FIG. 2. Reciprocal space plot showing the locations of the strongest observed reflections from a sample of Cs-III at 4.3 GPa. The  $[hh0]$  directions for the two Cs-III crystals are marked.

difference map was  $1.44 e^-/\text{\AA}^3$ . In comparison, deletion of one of the Cs atoms in the refinement resulted in a difference peak of  $\sim 24 e^-/\text{\AA}^3$ . This confirms that no atoms have been omitted by the 84-atom solution.

The refined atomic coordinates obtained from the synchrotron data at 4.3 GPa are given in Table I. The lattice parameters were determined as  $a = 9.2718(1) \text{\AA}$ ,  $b = 13.3013(3) \text{\AA}$ , and  $c = 34.2025(7) \text{\AA}$ , slightly smaller than those determined in the laboratory-based study and indicative of a slightly higher pressure of about 4.3 GPa. The atomic volume of Cs-III at this pressure is then  $50.21 \text{\AA}^3/\text{atom}$ , some 3% larger than the value of  $48.78 \text{\AA}^3/\text{atom}$  determined by Hall *et al.* [2] on the basis of an fcc structure. The resulting reduced volume ( $V/V_0$ ) of Cs-III is 0.426(1) [28], compared to 0.400 for Cs-IV at 4.2 GPa [29], and 0.455 in Cs-II at 4.1 GPa [2]. The volume changes ( $\Delta V/V$ ) at the Cs-II  $\rightarrow$  Cs-III and Cs-III  $\rightarrow$  Cs-IV transitions are then 6.4(1)% and 6.1(1)%, respectively, compared to the values of 9.0% and 3.4% obtained assuming an fcc structure for Cs-III [2].

The orthorhombic structure of Cs-III is shown projected down the  $a$ ,  $b$ , and  $c$  axes in Fig. 3. This is a remarkably complex new type of elemental structure. The atoms lie on  $a$ - $c$  sheets buckled with a periodicity of  $a/2$  along  $a$  and  $c/5$  along  $c$ . Viewed along the  $b$  axis, the atom centers lie on a “close-packed” array of cylinders, which lie in ten  $a$ - $b$  layers along  $c$  and reflect the  $a/2$  and  $c/5$  periodicities already noted. And the cylinder axes vary a little in their  $x$  coordinates with a periodicity of  $c$  along the  $c$  axis. It can also be seen in the projection down  $a$  that the density of atoms in each  $a$ - $c$  sheet is modulated along the  $c$  axis with a periodicity of  $c$ , being greatest in the vicinity of the two Cs3 atoms marked and at the symmetry-related positions in the other sheets. The atoms are not close packed, in contrast to the fcc structure previously found [2], and the structure is considerably more complex than the superstructure proposed in Ref. [17]. The nearest-neighbor distances in Cs-IV just above the transition, and in Cs-II just

below it, are 3.7  $\text{\AA}$  and 4.2  $\text{\AA}$ , respectively [2,3]. The number of interatomic distances for each atom in the ranges  $<3.7 \text{\AA}$ ,  $3.7\text{--}4.2 \text{\AA}$ , and  $4.2\text{--}4.4 \text{\AA}$  is given in Table I [30]. Each atom is surrounded by 8–11 others at distances between 3.6 and 4.4  $\text{\AA}$ , with the majority being in the range 3.7–4.2  $\text{\AA}$ . The average coordination of the Cs-III structure is then close to 10, intermediate between that of Cs-II (12-coordinated) and Cs-IV (4 + 4-coordinated).

The shortest (single) Cs-Cs distance of 3.62  $\text{\AA}$  is found between atom Cs3 and one of its symmetry equivalents. This is the only nearest-neighbor distance below 3.7  $\text{\AA}$ . As the corresponding atomic radius of 1.81  $\text{\AA}$  is slightly smaller than the atomic radius of 1.84  $\text{\AA}$  in Cs-IV at 4.2 GPa [3], this may suggest a slight inaccuracy in the determined position of atom Cs3. However, it is also the case that Cs3 has only eightfold coordination and is in the region of higher density of atoms visible in the  $a$ - $c$  sheets, as marked in Fig. 3 and already discussed: it may indeed have an unusually close approach to its nearest neighbors.

It seems certain that the samples of Schwarz *et al.* [4] had this same structure. They reported exactly the same spacings as are seen in Fig. 1. (In fact the spacing giving 7.5  $\text{\AA}$  is not a true  $d$  spacing; it is between adjacent  $[hhl]$  lines in reciprocal space and this does not correspond to a spacing of any reciprocal lattice planes.) By contrast the relationship of our results to those reported by Hall *et al.* [2] appear still to remain uncertain. We cannot find any convincing correspondence between Hall *et al.*'s  $d$  spacings and those of our structure. Hall *et al.* show a very good fit to fcc  $d$  spacings, and even obtain reasonable reflection intensities. They collected their data with a considerably larger sample volume with a tetrahedral press which would have applied more uniform stress to the sample. Furthermore, they collected their data at 27  $^\circ\text{C}$ , some 9  $^\circ\text{C}$  above our “room” temperature. To test the possible effects of these differences, we have loaded a sample of Cs into a Paris-Edinburgh pressure cell—which is known to give quite hydrostatic conditions [31], at least as uniform as the

TABLE I. Refined atomic coordinates of Cs-III at 4.3 GPa in space group  $C222_1$ . Cs1 occupies a fourfold  $4b$  site, and Cs2–Cs11 occupy eightfold  $8c$  sites. The refined lattice parameters are  $a = 9.2718(1) \text{\AA}$ ,  $b = 13.3013(3) \text{\AA}$ , and  $c = 34.2025(7) \text{\AA}$ . The number of nearest-neighbor interatomic distances in the ranges (i)  $<3.7 \text{\AA}$ , (ii)  $3.7\text{--}4.2 \text{\AA}$ , and (iii)  $4.2\text{--}4.4 \text{\AA}$  are given for each atom.

	Atomic coordinates ( $\times 10^4$ )			Number of bond lengths		
	$x$	$y$	$z$	(i)	(ii)	(iii)
Cs1	0	3288(13)	2500	0	8	2
Cs2	2091(12)	6027(10)	2589(2)	0	9	1
Cs3	1116(13)	8727(14)	2935(3)	1	7	0
Cs4	9649(10)	6552(10)	3552(3)	0	8	2
Cs5	5499(10)	6366(10)	3374(2)	0	9	1
Cs6	3425(12)	8736(13)	3830(3)	0	8	0
Cs7	7381(9)	9156(10)	3507(3)	0	9	1
Cs8	7231(9)	5851(8)	4526(2)	0	8	3
Cs9	759(10)	3703(10)	4746(2)	0	7	3
Cs10	3136(10)	6204(10)	4329(2)	0	6	5
Cs11	4791(10)	3320(9)	4482(3)	0	8	3

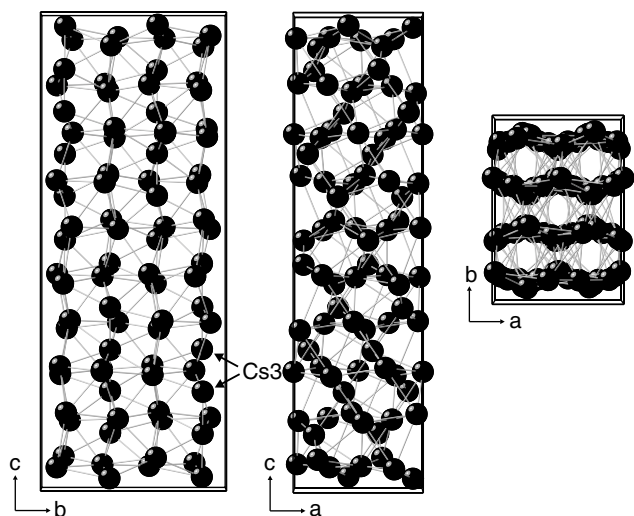


FIG. 3. Crystal structure of Cs-III as viewed down the  $a$ ,  $b$ , and  $c$  axes of the orthorhombic  $C222_1$  unit cell. Bonds are shown between atoms whose interatomic spacing is between 3.6 and 4.4 Å. The labeled Cs3 atoms are discussed in the text.

type of press used by Hall *et al.*—and compressed it at the same temperature of 27 °C as was used by Hall *et al.* Neutron diffraction data collected on the PEARL beam line at the ISIS Facility showed the same structure as our x-ray studies. This strongly suggests that Hall *et al.*'s findings did not arise from any obvious difference in experimental conditions. Moreover, our samples crystallized slowly into high quality single crystals, which suggests an equilibrium process, and extensive recent calculations show that the fcc structure is not stable at the observed density of the Cs-III phase [14–16], or is close to dynamic instability [17]. We thus conclude that the complex orthorhombic structure reported here is the equilibrium form of Cs-III, but cannot completely rule out the possibility that Hall *et al.* [2] found another or intermediate fcc form. It would now be extremely interesting to carry out calculations of the orthorhombic structure to resolve this issue.

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