High Pressure Polymorphism in Cesium

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Abstract. A new polymorph of cesium, existing over the narrow pressure range from about 42.2 to 42.7 kilobars at room temperature, has been discovered. Its crystal structure is face-centered-cubic with a = 5.800 ± 0.007 Å at 42.5 kb and 27°C. Cesium-II, which exists over the pressure range 23.7 to 42.2 kb, is also face-centered-cubic with a = 5.984 ± 0.011 Å at 41 kb and 27°C. An improved resistance-pressure curve and x-ray compressibility measurements for Cs are also given.

By displacement and electrical resistance measurements Bridgman[1] discovered several pressure-induced transitions in cesium metal. Volume transitions were reported to occur at about 23 kb with relative volumes v/v_0 of 0.6284 and 0.6224 (uncompressed Cs being 1.0000) and at about 45 kb with relative volumes of 0.498 and 0.442. We have obtained the relative volumes at 45 kb by interpolation from Bridgman's data. Bridgman gives data as compressions and also as volumes (relative volumes). The compressions at 23 kb given by Bridgman have been converted to relative volumes by subtracting his compression values from unity.

Bridgman found a resistance transition at about 23 kb and identified it with the corresponding volume transition. He also found a sharp resistance cusp at about 55 kb. Bridgman presented arguments for and against this transition's being identified with the volume transition at 45 kb without coming to any conclusion. Kennedy and LaMori[2] proposed that Bridgman's resistance cusp was caused by the same transition responsible for the large volume decrease at 45 kb and that the pressure given for Bridgman's resistance transition was 10 kb too high. They determined (by piston displacement) the pressures required to obtain the two volume transitions in Cs as 22.6 ± 0.6 kb and 41.8 ± 1.0 kb, respectively. However, volume changes occurring at the transitions were not reported.

Kennedy, Jayaraman, and Newton[3] determined the fusion curve and stability regions for Cs phases to 50 kb. Bundy[4] measured the electrical resistance of Cs in the belt apparatus and, after correcting Bridgman's data to the "new" pressure scale, obtained essentially the same curve. Stager and Drickamer[5] also measured the electrical resistance of Cs in a supported flat anvil device. They discovered a new transition starting at about 175 kb (sharp resistance rise of about 200 percent) and observed Bridgman's 45 kb cusp to occur at apparent pressure ranging from 20 to 70 kb. Hall[6] measured the electrical resistance of Cs as a function of pressure, using the cusp as a pressure calibration point for the Belt apparatus, and obtained a curve considerably different from the other curves that have been reported, the sweeping cusp being replaced by one resembling a spike.

Table 1. X-ray diffraction data for face-centered-cubic Cs II at 27°C and 41 kb. Average a (with average deviation from the mean) = 5.984 ± 0.011 Å; v/v_0 = 0.455. The calculated intensities (*I*) include multiplicity, structure, and Lorentz polarization factors, but do not include absorption of temperature factors.

hkl	d	a	I_{exp}*	I_{calc}
111	3.456	5.986	318†	100
200	2.996	5.991	51	51
220	2.105	5.953	42	41
311	1.808	5.997	54	55
222	1.727	5.982	16	16
400	1.499	5.998	vw‡	7
331	1.375	5.993	22	23
420	1.335	5.972	16	20

* Integrated intensity. † The (III) line exhibited an unusually high intensity. The observed relative intensities are based on (200) = 51. ‡ Very weak.

A resistance curve has also been determined in the tetrahedral press which has excellent

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resolution. This device clearly shows a spike, with an essentially flat top, 0.5 kb wide (Fig. 1). For comparison, Bridgman's original curve is also given. The present determination was made by four-lead resistance measurement techniques on Cs metal contained in a polyethylene tube (approximately 0.63 cm long X 0.050 cm inside diameter X 0.076 cm outside diameter) embedded in a silver chloride slug, which in turn, was centered within a pyrophyllite tetrahedron. The temperature was 25°C. Readings were taken with increasing pressure for the curve shown. The flat-topped spike clearly indicates the presence of a formerly unsuspected phase. We will call this phase Cs III and, for the present, label the phase (or phases) just to the right of the spike "Cs IV." A calibration[7] for the tetrahedral press with the fixed transition points Bi I-II, 25.3 kb; Tl I-II, 37.0 kb; Ba I-II, 59.0 kb, gives the Cs transition points (from the resistance curve) as follows: Cs I-II, 23.7 kb; Cs II-III, 42.2 kb; Cs III-"IV", 42.7 kb.

An interesting feature was disclosed on investigating the resistance curve over the temperature range of 24 to 31°C. On cycles of increasing pressure, the curve is identical with that shown in Fig. 1. Also, on reducing pressure the resistance curve faithfully retraces the characteristics of the forward curve (with attendant hysteresis due to pyrophyllite), clearly showing the spike and other features as long as

the temperature is above 26.0° ± 0.4°C. However, at temperatures below 26.0° ± 0.4°C, on cycles of decreasing pressure, the Cs III phase is by-passed; "Cs IV" apparently transforms directly to Cs II since the spike is not present.

Table 2. X-ray diffraction data for face-centered-cubic Cs III at 27°C and 42.5 kb. Average a (with average deviation from the mean) = 5.800 ± 0.007 Å; v/v_0 = 0.414.

hkl	d	a	I_{exp}*	I_{calc}
111	3.345	5.804	100	100
200	2.898	5.796	41	51
220	2.055	5.812	24	41
311	1.746	5.791	32	55
222	1.673	5.795	12	16

Bardeen[8] suggested that the 23 kb Cs I-II transition is a change from the normal body-centered to a face-centered form resulting from the non-electrostatic interaction energy of the ions. We have examined the Debye-Scherrer pattern for Cs II, making use of the tetrahedral x-ray diffraction press,[9] and confirm this hypothesis. Data for Cs II at 27°C and 41 kb are given in Table 1. The average lattice parameter is 5.984 ± 0.011 Å average deviation from the mean. Bridgman gives a relative volume of about 0.50 for Cs II at 42 kb compared to 0.455 found in this study. We observed this higher compressibility in several separate experiments.
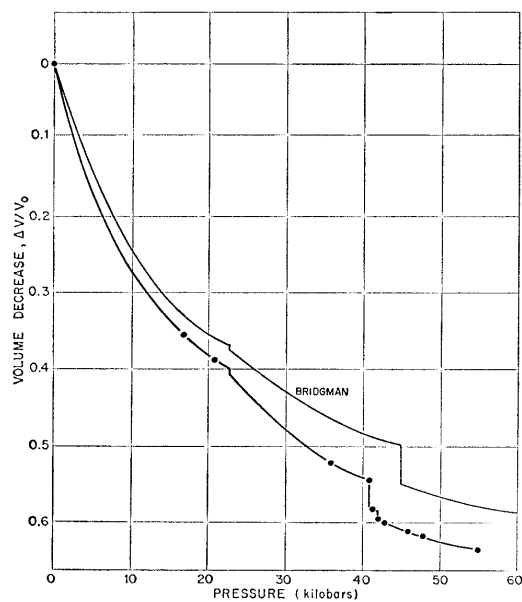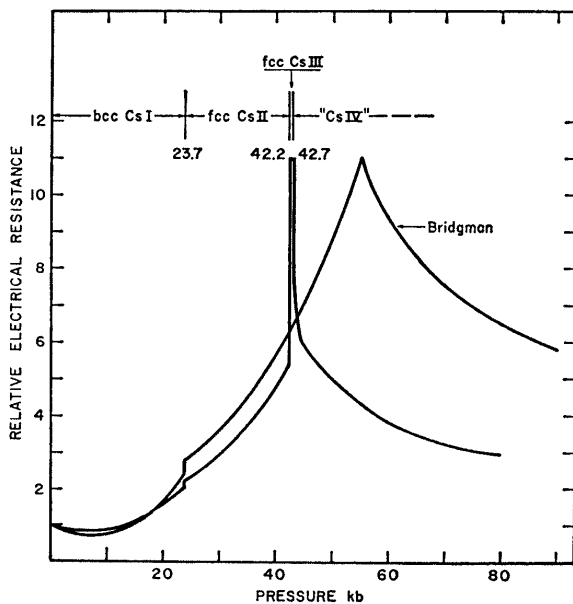

Fig. 1 (left). Relative electrical resistance of cesium metal as a function of pressure, *fcc*, face-centered-cubic; *bcc*, body-centered-cubic.
Fig. 2 (right). The compression of cesium. Lower curve shows x-ray diffraction results. Upper curve gives results obtained by Bridgman by volume displacement methods.

We have also obtained the Debye-Scherrer pattern of Cs III. The electrical resistance of the Cs sample was monitored simultaneously with the taking of the various x-ray diffraction measurements. This made it possible to "sit on top of" the narrow resistance spike while the Cs III x-ray diffraction pattern was being recorded. These simultaneous measurements show that the resistance changes accompany the various phase changes (in Fig. 1) and confirm Kennedy's proposal that Bridgman's "55 kb" resistance transition and "45 kb" volume transition are the same—except for the complicating factor of the additional phase disclosed in this work. The Cs III is face-centered-cubic with an average lattice parameter $a = 5.800 \pm 0.007$ Å at 27°C and 42.5 kb. The relative volume is 0.414; the volume decrease at the Cs II-III transition is about 9.0 percent (Table 2).

Bridgman realized that there was something unusual about the 45 kb volume transition, for, in the abstract of his paper "New Results at Pressures up to 100,000 kg/cm^2," he wrote, "The most interesting result is a reversible volume discontinuity in caesium near 50,000 of about 12 percent. The explanation of this is not clear, since already, below 50,000, caesium has assumed the close-packed arrangement. It probably means some deep-seated arrangement within the atom"[10]. Sternheimer[11] attributed this volume discontinuity to a shift of valence electrons from the $6s$ band to the empty $5d$ band and presented calculations to support this explanation. Ham,[12] on the basis of more recent calculations on the band structure of the alkali metals, has criticized Sternheimer's work. Alekseev and Arkhipov[13] have also analyzed this "electronic" transition. A face-centered-cubic to face-centered-cubic transition is known to occur in only one other substance: namely, the element cerium.[14] The transition in cerium takes place at about 7 kb at room temperature.

We have also taken Debye-Scherrer patterns of "Cs IV" but have not been able to index them satisfactorily. Some lines can be indexed as hexagonal with a certain c axis repeat distance. Other lines can also be indexed as hexagonal with the same value of the parameter a but with a different c axis repeat. There are some lines that could be attributed to face-centered-cubic packing (the Cs-III pattern, however, has completely disappeared and no lines can be attributed to it). The patterns suggest the possibility of stacking fault or "double c-axis" structures similar to those existing in the rare earths or, alternatively, suggest a mixture of

phases resulting from a "disproportionation" of the Cs III. Such a mixture of phases could conceivably have a lower free energy than a single phase. Rate considerations might also favor the formation of a mixture of solid phases rather than a single phase on passing from the Cs II to "Cs IV" region. Assuming "Cs IV" to be approximately close-packed, and considering only one diffraction line that could be attributed to a face-centered-cubic structure, we have calculated relative compressions for "Cs IV" at pressures between 43 and 55 kb at 27°C.

These compressions are included in Fig. 2 which gives the compressibility of Cs as we have measured it by x-ray diffraction techniques. For comparison, the results Bridgman obtained by volume displacement methods are also shown. With the above assumption, v/v_0 for "Cs IV" at the Cs-III-"IV" transition is calculated to be 0.404. This corresponds to a volume decrease of about 2.4 percent. This, when added to the 9.0 percent decrease occurring at the Cs II-III transition, gives an overall change of about 11.4 percent which agrees well with the value determined by Bridgman.

In our most successful procedure for preparing these specimens, so difficult to handle, for simultaneous diffraction-resistance measurements, use was made of a two-piece polyethylene cell. The two mating parts were designed to form a rectangular cavity of dimensions approximately 0.16 X 0.24 X 0.015 cm. At each end of the 0.24-cm wide portion of the cell were tiny reservoirs for Cs. A fine, pointed, copper wire was pushed through the polyethylene in each reservoir area to make contact with the Cs for the resistance measurements. Liquid Cs was injected into the cell with a small hypodermic needle. The outside dimensions of the polyethylene cell were 0.48 X 0.24 cm. This cell was centered in a 2.54 cm (on edge) tetrahedron composed of boron-filled, phenol-formaldehyde resin. The corresponding triangular anvil faces were 1.90 cm on a side. The press was used with the x-ray tube in position "B." the primary beam of x-rays was directed perpendicularly to the 0.015-cm thick Cs specimen.

We experienced difficulty because of the presence of relatively large crystals in all the Cs phases. This is undesirable in powder diffraction work. Various schemes, such as cycling through the various phase changes, were sometimes successful in breaking up the large crystals. In the main, however, samples not containing some large crystals were only obtained by chance.

This made it necessary to prepare and run many samples in order to obtain usable patterns.

The Cs[15] comes in contact with polyethylene and with copper during the experiments. There seems to be no evidence of contamination that would affect the results. Diffraction patterns taken before and after an experiment, both taken at low pressure, give the same result.

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References and Notes

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