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High Pressure X-ray Diffraction Studies on Barium

Abstract. Simultaneous x-ray diffraction and electrical resistance measurements on barium establish, with certainty, that Bridgman's 78-kb resistance transition in identical with his59-kb volume transition. During this transition, the body-centered cubic structure changes to hexagonal-close packed. Lattice parameters for the latter structure at 62 kb (volume scale) are: a = 3.90 Å, c = 6.15 Å, and c/a = 1.58. Compression ($\Delta V/V_0$) at 62 kb is 0.359 ± 0.005 compared to 0.345 previously reported by Bridgman. Below the transition, at 49 kb, compression is 0.300 ± 0.005 compared to Bridgman's 0.288. Bridgman's 17-kb volume transition was not detected by x-ray diffraction.

In addition to the intrinsic interest of determining the crystallographic nature of pressure-induced phase changes previously reported to occur in barium (by displacement and electrical resistance measurements), x-ray measurements are important because the 59-kb transition is used as a fixed-pressure calibration point. In 1942, Bridgman published compressions of Ba to 100 kb and reported two volume discontinuities.[1] The first of these was said to occur at 17 kb with compressions ($\Delta V/V_0$) of 0.135 and 0.141. The second was reported to occur at 59 kb with compressions of 0.318 and 0.337.

In 1952, Bridgman published a curve of the relative electrical resistance of Ba to 100 kb[2]. There was a sharp resistance discontinuity occurring at 78 kb (which Bridgman suggested might be associated with the 59-kb volume discontinuity observed 10 years earlier). He also reported evidence of a small electrical resistance discontinuity related to the 17-kb volume change.

During the early development of ultra-high pressure, high-temperature apparatus, researchers assumed 78 kb to be the correct value for the Ba resistance transition and used it as a fixed-pressure reference point. This was comfortable because this value, along with Bridgman's values for electrical resistance transitions in Tl (44 kb) and Cs (54 kb), gave a straight-line relationship between applied load and chamber pressure. This "old" pressure scale was unquestioned until Kennedy[3] suggested that Bridgman's resistance transitions in Tl, Cs, and Ba were all too high and that these transitions were actually identical with Bridgman's volume transitions reported to occur at about 25-percent lower pressure. Very shortly thereafter, researchers generally accepted the identity of the resistance and volume transitions, and adopted a "new" pressure scale which accepted pressure values based on the volume transitions (37, 42, and 59 kb in Tl, Cs, and Ba, respectively).

We have now been able to establish with certainty the fact that Bridgman's 78-kb electrical resistance transition and his 59-kb volume transition occur at the same pressure. This has been made possible by the development of a tetrahedral, x-ray diffraction, high-pressure, high-temperature press at Brigham Young University. This apparatus is equipped with a modified x-ray diffractometer and both strip-chart and printout recording devices. With this equipment, the electrical resistance of Ba foil was monitored (at room temperature) simultaneously with the monitoring of its Debye-Scherrer diffraction pattern as pressure was slowly increased. A new diffraction pattern appeared simultaneously with the crossing of the resistance discontinuity. This was observed in five separate and independent experiments. The new pattern indicates transformation to a hexagonal close-packed structure. Diffraction data at 62 kb (new scale) for the new structure are presented in Table 1. At 62 kb the values for the lattice parameters *a* and *c* are 3.90 Å and 6.15 Å, respectively. The *c/a* ratio is 1.58 which is within the normal range for hexagonal close-packed metals.

Table 1. Diffraction data for Ba with hexagonal close-packed structure at 62 kb

hkl	$d_{calc.}$*	$d_{exp.}$	$l_{calc.}$	$l_{exp.}$†
100	3.379	3.376	24	32
002	3.077	3.074	25	38
101	2.962	2.963	100	100
102	2.275	2.264	17	14
110	1.950	1.954	22	23
103	1.754	1.748	23	17
200	1.688		4	
112	1.647	1.646	7	11‡
201	1.628	1.627	19	20‡
004	1.539	1.533	4	5
202	1.481		5	
104	1.400	1.395	4	2
203	1.305	1.305	9	3

210	1.277		3	
211	1.250	1.250	16	5

* Calculated for a = 3.901 Å and c = 6.154 Å; c/a = 1.578. † Integrated intensity. ‡ Incompletely resolved lines.

Bridgman's compression for Ba at 62 kb is 0.345 compared to our x-ray value of 0.359 ± 0.005. Below the transition, at 49 kb, Bridgman's compression is 0.288; ours is 0.300 ± 0.005. In both instances our measurements indicate 4 percent greater compression than Bridgman's, but they confirm his volume transition and its magnitude.

Diffraction measurements at pressures up to the 59-kb transition (at room temperature) indicate only the presence of the normal body-centered cubic structure. We observed no discontinuity in *d* values in the vicinity of 17 kb. This casts serious doubt on the existence of a transition at this point.[4]

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References and Notes

[1] P. W. Bridgman, *Proc. Am Acad. Arts. Sci*. **74**, 425 (1942).
[2] -------, *ibid*. **81**, 165 (1952).
[3] G. C. Kennedy, in *Progress in Very High Pressure Research*, F. P. Bundy *et al*., Eds. (Wiley, New York, 1961), pp. 304-311.
[4] Supported by the U.S. Army Research Office, Durham, N.C. The Ba used in our experiments was obtained from A. D. Mackay, Inc., New York City, and was stated to be 99.5 percent pure. One of us (H.T.H.) is an Alfred P. Sloan research fellow.

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