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High Pressure Scale as Determined by X-ray Diffraction Techniques up to Approximately 100 kbar

by

H. Tracy Hall
Brigham Young University
Provo, Utah, 84601

POST BRIDGMAN PRESSURE-SCALE MUDDLE

I suppose as much blame can be placed on me as on anyone for the pressure-scale muddle of the emerging post-Bridgman era. No doubt the first Ba transition observed outside of Bridgman's laboratory was observed in February of 1954 in my Belt apparatus. While, due to secrecy, these results with the Belt were not published until six years later, I had managed to circumvent the Belt secrecy by the invention of the Tetrahedral Press. The published calibration for this apparatus (anvil load vs. pressure) used fixed points of 25, 44, 54, and 78 kbars (Bridgman's resistance points) for Bi, Tl, Cs, and Ba transitions. (Note: Previous work expressed in kg/cm^2 and atmospheres has been converted to kilobars in this paper). This precedent was followed by others until George C. Kennedy, at the June 1960 International High Pressure Conference held at Bolton Landing, Lake George, New York, conveyed the unsettling news that Bridgman's "resistance fixed points" were too high and should be lowered to Bridgman's "corresponding volume fixed points".

Kennedy's insight ran ahead of the experimental evidence. In hindsight one might possibly say Bridgman recognized that certain of his resistance points corresponded to lower volume points. However, a rereading of the crucial paper "The Resistance of 72 Elements, Alloys and Compounds to 100,000 kg/cm^2"[1] Will impress the reader that Bridgman was certain that the pressures given for his electrical resistance transitions were correct.

IDENTITY OF RESISTANCE AND VOLUME TRANSITIONS ESTABLISHED

In view of the Nobel Laureate's 50 years of accomplishment in the field, it would have been imprudent to challenge Bridgman's results without some definitive experiments. A definitive experiment would be one in which the volume transition and the electrical resistance transition were simultaneously observed in the same sample specimen. The shapes of the resistance curves in the regions of the fixed points (for example in Tl, Cs, Ba, etc.) are very characteristic and if these were found to occur simultaneously with the volume transition, a one-to-one correspondence between the transitions; i.e., an identity would be established.

The first one-to-one correspondence to be established at pressures beyond 30 kbar was in the instance of Ba. This work took place in the Brigham Young University high pressure laboratory at Provo. A tetrahedral x-ray diffraction press was employed for this purpose[2] 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[(2,3)]. As this was done, the characteristic electrical resistance pattern described by Bridgman[4] with an abrupt increase in electrical resistance at 70 kbar (Bridgman's resistance value) was found.

A new x-ray diffraction pattern appeared simultaneously with the crossing of this resistance discontinuity. Compressions determined 3 kbar above and 10 kbar below the discontinuity by x-ray

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[1] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 81, 167-251 (1952).
[2] J. D. Barnett, and H. T. Hall, Rev. Sci. Instr. 35, 175-182 (1964).
[3] J. D. Barnett, Roy B. Bennion, H. T. Hall, Science 141, 534-535 (1963).
[4] Reference No. 1 pp. 198 and 199.

diffraction were each only 4% higher than those determined from Bridgman's data[5]. (Bridgman determined his volume transition to occur at 59 kbar). The x-ray determined change in compression at the transition was the same as found by Bridgman. In addition, the overall Ba compressibility curve determined by x-ray matched a corresponding curve plotted from Bridgman's compression data quite well if a value of 59 kbar were selected for the Ba transition pressure. This furnished compelling evidence that the 79 kbar resistance and 59 kbar volume transitions were one and the same and that the correct transition pressure was about 59 kbar.

In addition to establishing the identity of the resistance and volume transitions, the x-ray work indicated the 59 kbar transition to be from the normal body centered cubic symmetry to a hexagonal close packed symmetry with cell parameters of a = 3. 90 Å, c = 6.15 Å and c/a = 1.58 at about 3 kbar above the transition pressure.

Even though the above research constituted the first experimental evidence that the electrical resistance transition pressures should be lowered, most high pressure researchers had already at a much earlier date assumed the identity of Bridgman's 44, 54, and 79 kbar resistance transitions with his 40, 44, and 59 kbar volume transitions in Tl, Cs, and Ba respectively. Also, they assumed the volume transitions to give the approximately correct pressure values. This decision may have been influenced by P. W. Bridgman himself. It has been reported that at a Gordon Conference on High Pressure held shortly after the Bolton Landing Conference, Bridgman indicated that the pressures of discontinuities in the resistance as given in his 1952 paper were not suitable to use as fixed reference points for pressure calibration. There are no written reports of Gordon Conference proceedings and I did not attend that particular conference, consequently my information on this point is only hearsay.

Irregardless, subsequent high pressure x-ray diffraction work has established resistance-volume change correspondences for transitions in Tl, Cs, Yb, Bi and other metals that have been used as pressure fixed points. In all instances it has been necessary to decrease the transition pressure of Bridgman's electrical resistance transitions.

ESTABLISHMENT OF CONTINUOUS PRESSURE SCALE BY X-RAY

After the one-to-one correspondence between the resistance and volume transitions had been established, one could focus attention on the problem of obtaining better values for the fixed points. Of particular interest, in this connection, are the Bi III-V and Ba I-II transitions which Bridgman had established (by volume change) to occur at 88 and 59 kbar respectively.

It would be very useful to have some type of pressure calibrant that would give continuous readings. Fixed points might then be compared to this. Such a calibrant might be based on the atomic separation of the atoms of a simple substance, said separation being determined by x-ray diffraction techniques. A simple substance for which the compression can be predicted with some degree of certainty is NaCl. Jeffery, Barnett, Vanfleet and Hall using the previously mentioned tetrahedral x-ray diffraction press and an equation of state developed by D. L. Decker used this approach[6]. In this work Bi or Ba metal was imbedded in polycrystalline NaCl and the transitions were detected by the electrical resistance change of the metal while the lattice parameter of the adjacent NaCl was simultaneously measured by x-ray diffraction. The Ba I-II and Bi III-V transformations at room temperature were assigned values of 53.3 ± 1.2 kbar and 73.8 ± 1.3 kbar, respectively, corresponding to NaCl linear compression values of $\Delta a/a$ = 0.0510 and 0.0637. These values were 9.4 and 16.2% smaller than Bridgman's volume values and were, at first, treated with reserve and skepticism. However, recent personal communications from other laboratories give similar values. They are listed below together with the BYU values. All x-ray values have been corrected to Decker's improved equation of state of NaCl[7].

Laboratory	Method Used	Ba I -II, kb	Bi III-V, kb
B. Y. U.	X-ray tet. press	54.4 ± 1.2	75.6 ± 1.3
aNaval Res. Lab.	"		75.0
bWestinghouse	"		
cNagoya U.	Bridgman Anvils		76 ± 4

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[5] P. W. Bridgman, Phys. Rev. 60, 351-354 (1941).
[6] R. N. Jeffery, J. D. Barnett, H. B. Vanfleet, H. T. Hall, J. App. Phys. 37, 3172-3180 (1966).
[7] D. L. Decker, Brigham Young University, Unpublished, 1968.

dU. C. L. A.	Piston-cylinder, vol.	55.0 ± 0.5	77.5 ± 1.0
eSignal Corps. Ft. Mammouth	Manganin gage	56.3	

Courtesy of a) Perry Ahlers, b) A. Taylor, c) H. Mii, d) G. C. Kennedy e) H. Vanfleet.

The B. Y. U. Naval Res. Lab., Westinghouse, and Nagoya U. values all depend on Decker's equation of state for NaCl. At this juncture, the agreement among the above parties has been narrowed to about ± 3%. There is a Russian determination of the Ba and Bi transitions in a free piston gage for which no experimental details are supplied of 58.5 and 89.3 kbar ± 1%[8]. This appears to be the only holdout for Bridgman's pressure values at the present time.

The work of Kennedy and his colleagues at U.C.L.A. and of Zeto and colleagues at Fort Mammouth is commendable in that they are using non-x-ray approaches to pressure scale problems. Full confidence in a pressure scale will only be achieved when data from several different approaches are in agreement. Kennedy is attempting to push the pressure limit of piston-cylinder apparatus toward 100 kbar and measure volume changes by piston displacement. Vanfleet and Zeto are utilizing a manganin wire gage immersed in a true liquid within a large pyrophyllite cubic pressure cell. The manganin gage is accurately calibrated to the Hg and Bi I-II transitions, fit by a quadratic equation, and extrapolated to higher pressures.

IMPROVED X-RAY DIFFRACTION PRESSES

The tetrahedral x-ray diffraction press in use at BYU was designed years ago. Eight years of experience with this press have amply indicated improvements that could be made, particularly if the objective is to establish a pressure scale. Incidentally duplicates of the BYU press constructed by McCartney Manufacturing Co. are installed at Commissariat a 1'Energie Atomique, Paris, and also at the Iron and Steel Institute of Tohoku University, Sendai, Japan. The design of these presses was completed before the invention of Anvil Guide[9]. Correct anvil position and sample location with respect to the x-ray beam are, therefore, more difficult to achieve than in presses equipped with anvil guide.

I have designed a tetrahedral press with anvil guide for use with x-ray diffraction. Two devices of this design have been built by McCartney Manufacturing. One is located at the Westinghouse Monroeville, Pennsylvania Laboratory; the other at the U.S. Bureau of Mines Laboratory, Albany, Oregon.

Years of experience at BYU with tetrahedral and cubic presses show that tetrahedral presses can achieve the highest pressures with the least anvil breakage. Pressures of 120 kbar on Decker's volume scale have been obtained with ¼ inch (6.3 mm) on edge triangular faced tetrahedral anvils.

Because of its higher pressure capabilities, I would choose the tetrahedral press over the cubic press in any new design for x-ray diffraction work. A new design for pressure scale work should be built with increased ruggedness and with the highest possible precision. The stretching of the tie-bar frame under load introduces correction factors in former tetrahedral x-ray presses because x-ray tube, goniometer track, etc. are attached to different parts of the frame. This could be eliminated in new presses based on the Ram-In-Tie-Bar type equipped with Sure-Guide[10]. In such a press, all the x-ray equipment could be mechanically connected to the Sure-Guide which remains in fixed position with respect to the exact center of the press under any load. Such a press, specifically designed with pressure scale research in mind, could be built for about $50,000 (exclusive of x-ray diffraction equipment).

IMPROVEMENT OF SOLID PRESSURE MEDIA

In addition to excellent prospects for the improvement of high pressure diffraction apparatus to provide more precise and accurate measurements relating to the pressure scale, there are good prospects for improving solid pressure transmitting media. It is known that the media surrounding a wire of a fixed point calibrant (such as Bi) influences the pressure required for onset and completion of a transition and also influences the hysteresis connected with the reverse transition. For example, Davidson and Lee[11] using a

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[8] L. F. Vereshchagin, E. V. Zuhova, I. P. Buimova, K. P. Burdena, Dokl. Akad. Nauk SSSR, 169, 74 (1966).
[9] H. T. Hall, Rev, Sci. Instr. 33, 1278-1280 (1962).
[10] H. T. Hall, Rev. Phys. Chem. Japan 37, 63-71 (1967).
[11] T. E. Davidson and A. P. Lee, Trans. Met. Soc. AIME, 230, 1035 (1964).

liquid media have measured a hysteresis of from 0.55 to 0.90 kbar for the Bi I-II transition. On the other hand, Jeffery, Barnett, Hall, and Vanfleet(6) measure an average hysteresis of 5.3 kbar for a cylindrical 0.010 inch diameter wire and of 2.8 kbar for a 0.002 inch thick flat strip surrounded by NaCl. Keep in mind that the pressures in the latter work were determined from atomic spacings in the NaCl immediately adjacent to the Bi wire or strip. Various explanations have been offered as to why transition sluggishness and hysteresis are always greater in solid media. Regardless of the explanations, the large hysteresis is undesirable. Ideally, both the NaCl and the Bi wire should be immersed in a true hydrostatic fluid in the x-ray work. For the most part, this is impractical. However, it should be possible to obtain a closer experimental approximation to the ideal situation than that of a Bi wire embedded in polycrystalline NaCl. For example NaCl powder could be mixed with an excess of powdered material which possessed a lower coefficient of shear friction than NaCl. This mixture could then serve as the matrix for embedding the Bi or other wire. The material admixed with the NaCl must, of course, be sufficiently transparent to x-rays and meet other requirements pertinent to the experiment at hand. At 25 kbar, shear friction measurements with rotating Bridgman Anvils show NaCl powder to have a friction coefficient of 0.12, Boron nitride powder and graphite powder have coefficients of 0.07 and 0.04 respectively. Mica sheet has a coefficient of .07. In powdered form, mica would have an even smaller coefficient. The coefficient for powdered polyethylene is not known but should be lower than that for NaCl. The friction coefficient for NH4F has not been measured but extrusion experiments at high pressure indicate it to be very low. If a search were conducted, no doubt a great many materials would be found with shear friction coefficients well below that of NaCl.

While solid pressure transmitting substances offer many practical advantages in all types of high pressure experiments, there still seem to be some unknown if not mysterious factors connected with their use. Additional research in this area is certainly needed.