

isothermal compressibility.⁷ This is characteristic of nearly all well-behaved solids in the absence of phase transitions, and indicates that Eq. (1) is a reliable interpolation formula below 150 kbar.

A correction for the irreversible heating occurring in shock compression must be made to the shock Hugoniot in order to find the normal isotherm at high pressures. The conventional method⁸ was used in which the thermal pressure of the solid due to shock heating is given by a Mie-Grüneisen equation of state.⁷ The thermal pressure is proportional to the Grüneisen coefficient, $\gamma_G = V(\partial P/\partial E)_V$, which is found from the Dugdale-MacDonald formula.⁸ According to this formula, γ_G equals 2.12 at normal conditions, whereas the thermodynamic value determined from handbook thermal data⁹ and the above bulk sound velocity is 2.37. This disagreement is typical of shock data for metallic elements. Although the calculated isothermal pressure for iodine in Fig. 1 is thus somewhat uncertain, its large displacement from the x-ray-determined isotherm ($\sim 40\%$) is an order of magnitude larger than typical offsets of shock and static data^{3,4} ($\sim 5\%$). It is furthermore surprising that the x-ray isotherm lies above the Hugoniot, since the normal thermal pressure correction is always negative.

After communicating with Drickamer and confirming this discrepancy, we considered ways of resolving the disagreement. A possible cause of the differing compressibilities could have been the high temperatures produced by shock compression. For instance, at 45 kbar the calculated shock heating is 340°C. The fact that solid iodine is a very anisotropic, weakly bound molecular crystal suggests that a high-temperature phase transition to a higher density phase may have taken place in the shock experiments.

It was decided that a convenient starting point for investigating this possibility would be a conventional static P - V measurement with an available piston-displacement apparatus.¹⁰ Such data had not been previously published, although Bridgman¹¹ had reported evidence of a phase transition with a 2% volume change in the vicinity of 15 kbar. An end-loaded press capable of volume measurements up to 40 kbar was used to obtain data shown in the right portion of Fig. 1.

⁷ E. Grüneisen, *Handbuch der Physik* (Julius Springer-Verlag, Berlin, 1926), Vol. 10, p. 1.

⁸ M. H. Rice, R. G. McQueen, and J. M. Walsh, *Solid State Phys.* 6, 1 (1958).

⁹ *American Institute of Physics Handbook*, D. E. Gray, Ed. (McGraw-Hill Book Co., New York, 1963), 2nd ed. Sec. 4.

¹⁰ D. R. Stephens, *J. Phys. Chem. Solids* 25, 423 (1964).

¹¹ P. W. Bridgman, *Collected Experimental Papers* (Harvard Univ. Press, Cambridge, Mass., 1964), Article No. 113.

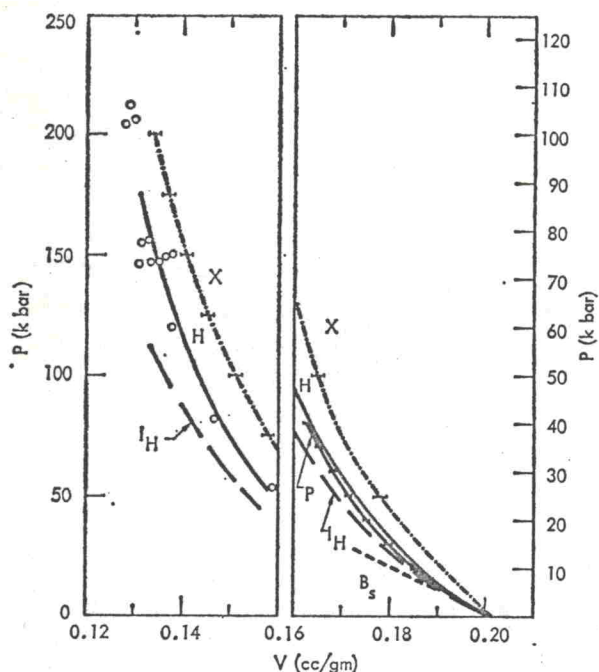


FIG. 1. Compressibility data of solid iodine. Pressure scales on right and left ordinate scales refer to right- and left-half of graph, respectively. Letters refer to different types of data as follows: X—x-ray compression; H—shock Hugoniot; P—piston displacement; I_H —normal isotherm calculated from shock data; B_s —slope of normal adiabat according to acoustic data.

With such a press, phase transitions with 0.5% or less volume change are generally detected. The line P in Fig. 1 represents the average of four runs, two each with the iodine in lead and gold capsules to check the effects of possible reactivity with the capsules. The brackets indicate the spread of the P - V data among the four runs (~ 0.001 cc/g).

The static volume displacement was found to vary continuously over the whole pressure range as indicated in Fig. 1, and thus shows no evidence of the transition reported by Bridgman.¹¹ These volume changes are substantially in agreement with the shock isotherm I_H at low pressure, indicating also that a phase transition does not occur upon shock compression of iodine. We thus conclude that the compressibility of solid iodine given by shock data is correct and much larger than indicated by x-ray data up to 200 kbar.

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