

Short Communications

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The compressibility and structure of selenium. By D. B. SIRDESHMUKH. *Physics Department, Osmania University, Hyderabad, India*

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A critical examination of the existing data on the compressibility of selenium supports an earlier suggestion that the value reported by Bridgman is too large.

The compressibility of hexagonal selenium was measured by Bridgman (see Gschneidner, 1964) and its value at zero pressure is $107.8 \times 10^{-7} \text{ cm}^2.\text{kg}^{-1}$. A controversy regarding the correctness of this value has arisen from the correlation between the compressibility and cohesive energy drawn up by Gschneidner (1964). From the correlation, Gschneidner suggests that Bridgman's value of the compressibility of selenium is higher than the correct value by more than 100%. In the present note the experimental value is examined from a different standpoint.

Recently Knopoff (1965) has developed a method for calculating the compressibility of elements and compounds by combining the finite strain equation of state and the Thomas-Fermi equation of state. We have used this method to compute the compressibility of hexagonal selenium. Calculations are also made for a few other metals chosen randomly. The calculated and experimental values are given in Table 1. Except in the case of selenium, the agreement between calculated and experimental values is fair. We concede that Knopoff's method is approximate and it would be dangerous to give significance to a difference in the calculated and experimental values such as that in the case of Ti. But the difference in the case of selenium seems to be too large and indicates, together with Gschneidner's observation, that Bridgman's value is in error.

Table 1. *Calculated and experimental values of the compressibilities of some metals*

Metal	Compressibility $\times 10^7 \text{ (cm}^2.\text{kg}^{-1}\text{)}$	
	Calculated	Experimental*
Al	15.5	13.6
Ti	14.1	9.3
Mg	37.0	27.7
Zr	11.1	11.77
W	2.5	3.0
Li	124.7	84.8
Se hex.	19.0	107.8
Se α	6.4	

* From Table IV of Gschneidner (1964).

Selenium exists in various phases at room temperature. It has a hexagonal phase (Bradley, 1924), two monoclinic phases (Burbank, 1951; Marsh & Pauling, 1953) and two

cubic phases (Andrievskii, Nabitovich & Kripyakevich, 1959; Andrievskii & Nabitovich, 1960) besides a vitreous phase. However, the cubic phases are not very stable and the Se β monoclinic phase has been shown to be almost the same as the Se α monoclinic phase (Marsh & Pauling, 1953). We have computed the compressibility for Se α also. The value is given in Table 1. This value, again, is much lower than the experimental value. It is extremely difficult to grow single crystals of hexagonal selenium and unless special methods are adopted the melt supercools into the vitreous phase (Gilman, 1963). The amorphous phase often interferes with the crystalline phase. Bradley (1924) attributes the poor quality of the X-ray photographs of hexagonal selenium to the presence of 'a large proportion of amorphous material'. We are therefore led to feel that the high value of the compressibility obtained by Bridgman may be due to the presence of vitreous material in the samples used by him. It is not clear from Bridgman's work whether he was examining the crystallinity of every sample that he used. Our doubt derives support from the recent determination (Vedam, Miller & Roy, 1966) of the elastic constants of completely vitreous selenium. The elastic constants of glassy selenium lead to a compressibility of $104.1 \times 10^{-7} \text{ cm}^2.\text{kg}^{-1}$, which is remarkably close to the value obtained by Bridgman for supposedly non-cubic Se.

It is hoped that the present analysis will serve to emphasize the need for a determination of the compressibility of the various phases of selenium, preferably by the X-ray method.

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