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X-Ray Diffraction Studies on Tin to 100 Kilobars*

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The high-pressure equilibrium phase diagram of tin is investigated, and the crystal structure of Sn II at 98 kbar and 25°C is shown to be body-centered tetragonal with $a=3.70$ Å, $c=3.37$ Å, $c/a=0.91$, and with two atoms per unit cell. The linear compressibility of white tin is given at 25°C up to the high-pressure transformation at 92 kbar, and the latent heat of the transformation is measured as 225 cal/g-atom.

THE crystal structure of white tin with its tetrahedral coordination in a tetragonal unit cell represents an interesting example of directional bonding, and considerable interest has recently been shown in the vibrational modes of the lattice[1–3] and the atomic force constants[4] for this rather unique material. Somewhat related to these studies is the investigation of the polymorphic phase transitions induced by either temperature or pressure, since the mechanisms for such transitions might be explained by vibrational instabilities or anomalous changes in atomic force constants. The measurements reported here were made in order to clarify and elucidate some aspects of the high-pressure phase diagram for Sn and to obtain room-temperature linear compressibility data on Sn I (white tin) up to the high-pressure (Sn I–Sn II)transition.

A. HIGH-PRESSURE PHASE DIAGRAM

The measurement of a cusp in the melting curve at approximately 33 kbar and 310°C by Dudley and Hall[5] in 1960 was the first indication of the existence of a high-pressure polymorph. Efforts by them to detect the phase line emanating from the cusp by monitoring electrical resistance failed. Kennedy and Newton,[6] using a differential thermal analysis technique, confirmed the cusp and established the phase line with a negative slope of approximately 2.5°C/kbar. Stager, Balchan, and Drickamer[7] measured a discontinuity in resistance at a reported pressure of 113 to 115 kbar and 25°C in reasonable agreement with the extrapolated phase line of Kennedy and Newton. Stager, Balchan, and Drickamer, as well as Kaufman,[8] speculated that the transformation was to a cubic phase, and thermodynamic calculations seemed to give strength to this assumption. Jamieson,[9]

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from x-ray diffraction data, reported a structure determination of body-centered-cubic (bcc) for Sn in the region of 130 kbar and 25°C. Barnett, Bennion, and Hall[10] working in this laboratory reported a structure determination of body-centered-tetragonal (bct) ($c/a=0.91$) for Sn at 39 kbar and 314°C in apparent contradiction to the work of Jamieson. Jamieson[9] later reported observing the bct structure at pressures in excess of 120 kbar at 25°C.

A correlation of these data implied the existence of either a new phase line on the phase diagram or a continuous variation of the c/a ratio of the tetragonal lattice from 0.91 to 1.00 as one moves to higher pressures along the Sn I–Sn II phase line. Such a variation would be of great interest.

During the past year the pressure capabilities of the high-temperature, high-pressure, tetrahedral x-ray diffraction apparatus[11] have been extended to approximately 120 kbar by utilizing smaller anvils with wedge-shaped gaskets.[12] Using this apparatus the structure of Sn in the region above the transition at room temperature was determined to be simple bct with a c/a ratio of 0.91, which, within experimental error, is the identical structure previously observed at 39 kbar and 314°C, in direct contradiction with Jamieson's work. The x-ray powder data for one determination of the new structure are given in Table I. Three independent determinations were made, and agreement on lattice parameters was better than 0.2% when corrected to the same pressure. No diffraction lines were observed which could not be indexed, and no evidence of a cubic phase could be found. This result implies the existence of a single phase line connecting the melting curve and the room-temperature transition as originally assumed by Stager, Balchan, and Drickamer. As further support for this conclusion, the Sn I–Sn II phase line was followed from about 48 kbar and 250°C to the room-temperature transition point by observing the Sn I (200) and (101) lines disappear and appear alternately with the Sn II (101) and (110) lines as the phase line was repeatedly traversed. As an additional indication, while at a pressure above the room-temperature transition point, the temperature was increased slowly to a nominal 500°C. No change was observed in the dominant features of the x-ray pattern.

TABLE I. X-ray diffraction data for Sn II at 98 kbar and 25°C indexed as a simple body-centered tetragonal lattice.[a]

hkl	d_{cal}	d_{exp}	I_{cal}	I_{exp}
101	2.491	2.492	100	100
110	2.614	2.616	58	54
200	1.848	1.849	26	17
002	1.685	1.681	7	7
121	1.484	1.484	38	34
112	1.416	1.416	17	12
220	1.307	1.309	7	9
202	1.245	1.244	12	8

[a] $a=3.70\pm0.01$ Å; $c=3.37\pm0.01$ Å; $c/a=0.911$.

In view of these results and the fact that Jamieson observed the bct structure at much higher pressures, we propose the simple diagram of Fig. 1 as the equilibrium phase diagram of Sn with no other phase lines existing in the pressure–temperature region of 1 bar to 100 kbar and 25° to 500°C. The measurements of Jamieson might be due to preferential orientation of the sample crystallites in his uniaxial (Bridgman anvil) apparatus. If the transformation mechanism is that described by Musgrave,[13] the preferred orientation in the Sn I phase previous to the transformation reported by Jamieson[9] might give rise to an altered c/a ratio in Sn II due to the anisotropic stress distribution produced during the transformation. It is also possible that a stress-stabilized bcc phase might exist, due to stresses caused by this same preferential orientation. Such a phenomenon would be interesting and significant in and of itself. Preferred orientation and shear stress is greatly minimized in a tetrahedral apparatus due to the three-dimensional character of the applied force. Furthermore, the Sn powder used in the present experiment was intimately mixed with micron-sized polyethylene powder in a volume ratio of one to four to assure more uniform pressure distribution among the individual particles. Evidence of the random crystallite orientation in the tetrahedral apparatus is found in the good agreement of the calculated and measured relative line intensities in both the Sn I and Sn II diffraction patterns.

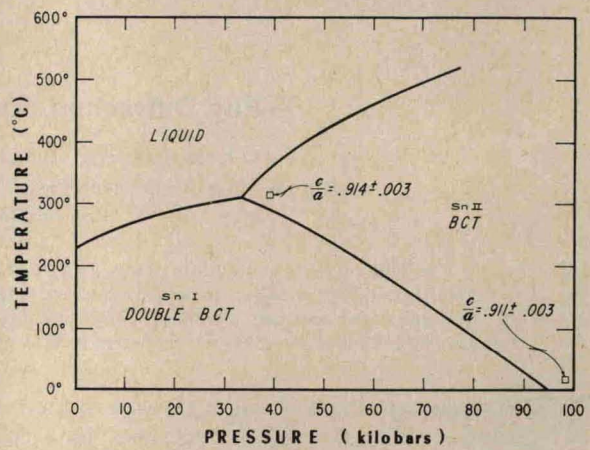


FIG. 1. Phase diagram of Sn to 100 kbar showing points where bct structure determinations have been made.

In Fig. 1 the phase line is drawn to a point at 92 kbar and 25°C, a pressure value lower than that previously reported. A determination of this pressure was made utilizing a sodium chloride internal standard intimately

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mixed with the Sn. A measurement of the lattice parameter of sodium chloride by x-ray means determined the pressure by reference to the compressibility data theoretically determined by Decker[14] for this purpose. This lowering of the pressure value assigned to the Sn transition at room temperature is consistent with measurements of other fixed calibration points made in this laboratory[15] by the same technique and represents a significant decrease in the values assigned to these high pressure transitions.

B. COMPRESSIBILITY DATA

The lattice parameters of Sn I at pressures just below the transition and the linear compressibility in the two crystallographic directions at that point have bearing on the stability of the lattice, the mechanism for the transformation, and the latent heat of the transformation. Datum points obtained for the linear compression of Sn I as measured by x-ray techniques are shown in Fig. 2 for pressures up to the transition at 92 kbar and 25°C. The last datum point shown at 94 kbar was obtained when a sizable portion of the sample had transformed. The Sn I–II and II–I transitions are somewhat sluggish at room temperature but are very rapid at temperatures above 150°C. At the higher temperature the I–II transition line should represent true equilibrium. Near room temperature the line may deviate from true equilibrium by as much as ±3 kbar, the approximate region of indifference.

The solid curves are second-order polynomial equations in which the linear coefficient was taken from the elastic constants data of Rayne and Chandrasekhar,[3] thus establishing the initial slope. Their data agreed well with the initial slope of Bridgman's single-crystal linear compressibility data to 30 kbar[16] shown as solid circles in Fig. 2. The quadratic coefficient was determined by a least-square fit to the high-pressure data given herein. The average deviation of the datum points from these curves is less than the 0.2% probable error estimated for an x-ray volume measurement in our apparatus on a material such as Sn. The expressions for the linear compressions (where the pressure P is given in bars) are

$$\Delta a/a = 5.80\times10^{-7}P - 1.15\pm0.20\times10^{-12}P^2,$$

and

$$\Delta c/c = 6.63\times10^{-7}P - 1.20\pm0.20\times10^{-12}P^2.$$

It is interesting to note that the c/a ratio of Sn I changes by less than 0.1% from 1 bar to 90 kbar, and

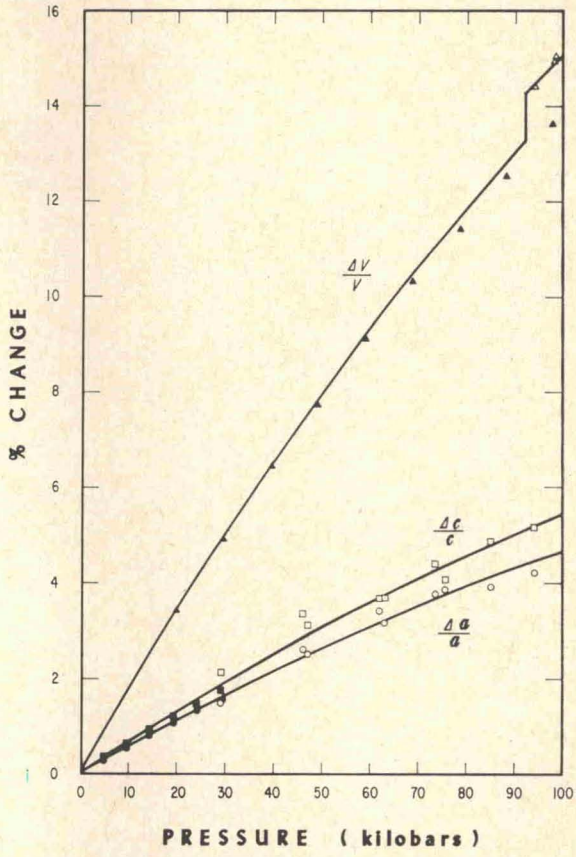


FIG. 2. Linear and volume compressions for Sn (at 25°C) to 100 kbar compared with Bridgman's data. ○ measured a-axis compressions; □ measured c-axis compressions; ● Bridgman's a-axis compressions, Ref. 16; ■ Bridgman's c-axis compressions, Ref. 16; ▲ Bridgman's volume compressions, Ref. 17; △ measured volume compressions for Sn II phase. The solid lines are quadratic expansions using initial slopes from elastic constants data as discussed in text.

the c/a ratio of Sn II changes by less than 0.5% between 40 and 100 kbar. The small change in this particular parameter implies a strong influence in both structures of the next-nearest atomic coordination atom, which is in the c direction. The volume compression curve shown in Fig. 2 is obtained analytically from the linear compression equations. Bridgman's[17] 100-kbar volume compression data are shown for comparison as solid triangles. Agreement here is consistent with the accuracy of the pressure calibration used in each case.

From Fig. 1 we obtain a slope of −170 bars/°C for the Sn I–Sn II phase line at room temperature and at 92 kbar and a volume compression of 1.1±0.2% at the transition from Fig. 2. Using these data the Clapeyron equation yields a latent heat of 225 cal/g-atom at 25°C and 92 kbar with an estimated accuracy of ±45 cal/g-atom.

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