X-ray Diffraction Studies on Tin at High Pressure and High Temperature

Abstract. *Tin at a pressure of 39 kb and at 314°C has tetragonal symmetry with an atom at each point of a body-centered tetragonal lattice. The unit cell dimensions are* a *equal to 3.81 Å,* c *equal to 3.48 Å, and c/a = 0.91. The melting curve of tin was observed up to 45 kb and the boundary line between the tin I and tin II phases was observed to 70 kb by x-ray diffraction techniques.*

The fusion curve of tin[1] indicated a phase transition with a triple point at 34 kb (corrected to the volume scale) and 318°C. The resistance measurements in this region failed to establish the phase line (the boundary line between tine I and tin II) extending from the triple point, and it was suggested that other techniques would be necessary for its determination.

Kennedy and Newton by means of differential thermal analysis succeeded in finding and following this phase line to 50 kb[2]. Stager, Balchan, and Drickamer[3] detected a small rise in the resistance curve of tin at 113 to 115 kb, which they correlated to an extrapolation of the tin I-II phase line described by Kennedy and Newton. Stager *et al.* suggested a cubic structure for the tin II phase. The crystal structure of the tin II phase was postulated to be face-centered cubic (fcc) by Kaufman,[4] and Jamieson has indicated that a body-centered cubic (bcc) phase exists at the 113- to 115- kb transition reported by Drickamer.[5]

By means of a tetrahedral, high pressure and high temperature, x-ray diffraction apparatus, we have obtained the standard Debye-Scherrer pattern for tin II at 39 kb and 308°C (data were obtained from an overnight experiment in which the temperature fluctuated between 308° and 320°C). The data (Table 1) indicate a simple body-centered tetragonal (bct) structure with two atoms per unit cell located at 000 and ½ ½ ½, Unit-cell parameters are: a = 3.81 Å, c = 3.48 Å, and c/a = 0.91. A calculation of the volume yields a compression ($\Delta V/V_0$) of 0.65 relative to 1 bar at 25°C.

The tin I structure is tetragonal with four atoms per unit cell located at 000, ½ 0 ¼ , ½ ½ ½, and 0 ½ ¾. A possible (nonreconstructive) mechanism for the tin I-II transition involving a
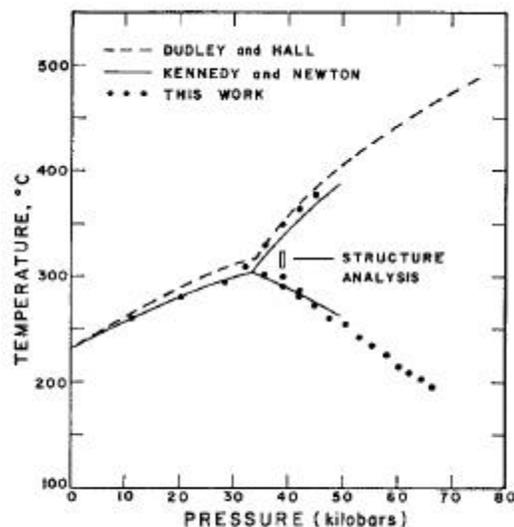

Fig. 1. Phase diagram for tin.

simple shifting of atoms in the tin I structure has been considered from the standpoint of lattice vibrations.[6] According to Musgrave,[6] the atoms will be located at the lattice points of a bct lattice if one selects appropriate vibrational modes of the tin I structure and considers the position of the atoms at the moment of maximum displacement. At this moment the atoms would have eight nearest neighbors. Musgrave then assumes that the more symmetrical bcc structure forms immediately from the bct structure.

Table 1. X-ray diffraction data for tin II at 39 kb and 308° to 320°C. The observed interplanar spacing corresponding to the indexes *hkl* is $d_{exp.}$. The corresponding calculated spacing, $d_{calc.}$, is based on a bct lattice with a = 3.811 Å, c = 3.483 Å, and c/a = 0.914. the calculated intensity, $I_{calc.}$, includes multiplicity, structure, and Lorentz polarization factors but does not include absorption or temperature factors $I_{exp.}$ Is the observed, integrated intensity of the diffracted x-ray beam.

hkl	$d_{calc.}$	$d_{exp.}$	$I_{calc.}$	$I_{exp.}$
110	2.688	2.695	58	50
101	2.571	2.571	100	100
200	1.915	1.906	26	40
002	1.747	1.741	7	9
211	1.534	1.531	38	30
112	1.463	1.463	17	4
220	1.341	1.347	7	4

The "virtual" bct structure would have lattice parameters of $a = 4.12$ Å and $c = 3.18$ Å, with $c/a = 0.77$ at 1 bar and 25°C. Our measurements indicate an incomplete movement of this virtual bct lattice toward the bcc lattice (the bcc lattice may be considered as a bct lattice with $c/a = 1.00$). Apparently at 39 kb and 314°C the bonds between second nearest neighbors located along the c axis are sufficiently important to prevent the complete movement to the bcc structure, as suggested by Musgrave.

In addition to the above elucidation of the tin II structure, we have used x-ray diffraction techniques to determine the phase diagram for tin. The melting curve was followed to 45 kb and the tin I-II phase boundary to 70 kb. Melting was followed to the triple point by observing the (200) and (101) lines of the tin I x-ray pattern as temperature was slowly increased at a fixed pressure. The temperature at which these lines disappeared into the background was taken to be the melting point. This temperature was reproducible to $\pm 4°$. Temperature was measured by a thermocouple located within an electrically heated graphite furnace used to heat the tin. The tin was centrally located within the furnace, and was surrounded by polyethylene. The x-ray beam was directed axially through the furnace. Melting beyond the triple point was similarly detected by observing the (110) and (101) lines of the tin II pattern.

The phase boundary between the tin I-II was determined by the disappearance of the (200) and (101) lines of tin I and the appearance of the (110) and (101) lines of tin II. During temperature excursions of one particular sample, the presence of a small single crystal properly oriented for Bragg diffraction became evident in the form of a sharp, high-intensity peak. This peak, in a matter of seconds, would repeatedly disappear or reappear as the transition temperature was traversed. The rapidity of the transformation and the retention of the crystal orientation after passing to tin II and returning to tin I provide strong evidence for the nonreconstructive nature of this transition. It was possible to detect the occurrence of this transition with $\pm 2°C$. A comparison of our determination of the tin phase diagram with that of Dudley and Hall and that of Kennedy and Newton is shown in Fig. 1.[7]

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References and Notes

[1] J. D. Dudley and H. T. Hall, *Phys. Rev.* **118**, 1211 (1960).

[2] G. C. Kennedy and R. C. Newton, in *Solids Under Pressure*, W. Paul and D. M. Warschauer, Eds. (McGraw-Hill, New York, 1963), p. 163.

[3] R. A. Stager, A. S. Balchan, H. G. Drickamer

[4] L. Kaufman, in *Solids Under Pressure*, W. Paul and D. M. Warschauer, Eds. (McGraw-Hill, New York, 1963), p. 303.

[5] J. C. Jamieson, Geol. Soc. Am., meeting, Houston (November 1962), abstr.

[6] M. J. P. Musgrave, *Phys. Chem. Solids* **24**, 557 (1963).

[7] Supported by U.S. Army Research Office, Durham.

25 July 1963