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Tin at high pressure: An energy-dispersive x-ray-diffraction study to 120 GPa

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The high-pressure phases of tin have been studied by energy-dispersive x-ray diffraction to 120±10 GPa at room temperature in a diamond-anvil cell. The body-centered cubic structure, evolving from the body-centered tetragonal structure at 45±5 GPa, is found to be stable to the highest pressure of 120 GPa. Along with previously published data, the present results complete the equation of state of tin to 120 GPa at room temperature. The stability of the bcc phase is discussed in the broader perspective of the pressure behavior of the other Goup-IVA elements and the isoelectronic III-V compound InSb.

Substantial progress in understanding the high-pressure structural behavior of solids has been made since the advance of high-pressure generation capability, the development of the diamond anvil cell,[1,2] and the availability of high-brilliance synchrotron-radiation sources.[3,4] In the framework of a systematic study of the behavior of the Group-IVA elements C, Si, Ge, Sn, and Pb and their related isoelectronic compounds under very large compression, this paper presents a study of the structural stability against pressure of tin.

Tin was first studied by Jayaraman *et al.*,[5] who determined the high-temperature–high-pressure phase boundaries. Early indications of a phase transition at 10 GPa at room temperature were observed by electrical resistivity measurements.[6] In the first x-ray-diffraction study at high pressure by Jamieson,[7] the structural phase above 10 GPa was indexed as bcc with a 5% relative volume change at the transition. Subsequent experiments showed that the structure was body-centered tetragonal with an axial ratio c/a of ∼0.91.[8] Liu and Liu[9] showed that the axial ratio indeed increased to unity with increasing pressure; it has the bcc crystalline form at 44±2 GPa.[10,9]

In order to investigate the stability of the bcc structure and the possibility of a transformation to a denser, close-packed structure upon compression, we have undertaken an x-ray-diffraction study of tin to the 100-GPa range. Earlier works, in a similar pressure range, demonstrated that silicon transforms to hcp and, eventually, to fcc close-packed forms.[11] Similarly, germanium, at large enough pressure, should energetically favor hcp, a transformation yet to be recorded.[12] And, at the bottom end of the Group-IVA elements, lead is already fcc at ambient conditions and transforms to hcp upon compression.[13] In addition, it is worth noting that a qualitative scaling based on the insulator-to-metallic transition critical pressure which, in fact, decreases as the atomic number increases, permits one to hypothesize that tin should adopt a close-packed form at "reasonably" large pressure. Furthermore, hcp Sn has been theoretically calculated to be the stable structure at high pressure (above 30 GPa) by Hafner using the pseudopotential method.[14]

The tin sample was studied by energy-dispersive x-ray diffraction using a white beam of the Cornell High Energy Synchrotron Source (CHESS), collimated to a nominal diameter of ∼20 μm. A detailed account of the experimental technique is to be found elsewhere.[3,4] High-purity tin powder (99.99%), supplied by Research Organic/Inorganic Chemical Corporation, was loaded without a pressure medium in a sample hole with an area of ∼500 μm^2 and ∼40 μm thick formed by drilling a pre-indented T301 stainless-steel gasket. High pressures were generated in a diamond anvil cell using diamonds with 300 μm culets, 100 μm flats, and 5° bevels. Pressures were measured by the ruby fluorescence technique[1] using the nonhydrostatic calibration established by Bell *et al.* to 180 GPa.[15]

An energy-dispersive x-ray-diffraction spectrum, recorded at 112±5 GPa at room temperature, is shown in Fig. 1. Spectra taken at different pressures were all equally good. Diffraction lines from the gasket, which has a hcp structure, were present at all pressures but did not interfere with the sample lines and were easily identified. All the sample diffraction lines, seven or eight, indexed well to a body-centered cubic unit cell. Table I gives the calculated and observed *d* spacings at 112 GPa. Intensity ratios of the diffraction lines agree qualitatively with those predicted.

It is worth noting that at 52.1±0.2 GPa (the lowest pressure for which a diffraction pattern of tin was recorded in the present study), tin is pure bcc. No reminiscence of the body-centered tetragonal, the structure from which bcc evolves, was observed. This is in contrast with earlier results obtained by Olijnyk and Holzapfel[10] and Liu and Liu[9] where the two solid phases were observed to coexist from 40.5 to 56 GPa and from 46.5 to 53.4 GPa, respectively. As a possible explanation, we invoke the fact that, for the cited studies, the x-ray beam collimation was not sufficiently small to overcome sample structural inhomogeneities resulting from the possible presence of pressure gradients. It should also be pointed out that both data sets show another inconsistency. The experimental equations of state cross at a pressure near 20 GPa, at room temperature, resulting in an undercompression below and an overcompression above 20 GPa of the data of Olijnyk and Holzapfel with respect to the data of Liu and Liu. As far as we could tell, the only major experimental

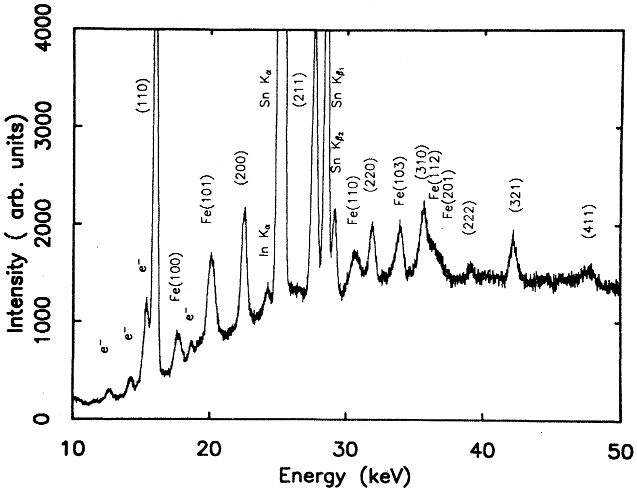

FIG. 1. Energy-dispersive x-ray-diffraction spectrum of tin at 112±2 GPa. The eight sample diffraction lines are labeled according to a bcc (hkl) indexing. Fe(hkl) lines are from the stainless-steel gasket in the hcp structure. e^- denotes an escape peak from the intrinsic Ge detector. The fluorescence peak at 24.2 keV was identified as K_α of indium present in tiny amounts in the sample.

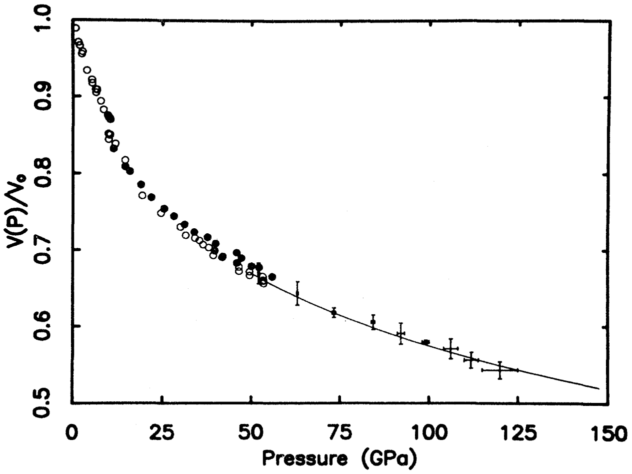

FIG. 2. Equation of state of tin to 120±5 GPa. $V_0=27.07$ Å^3/atom (Ref. 9). Data are from three different high-pressure studies: error bars, present work; ○, Liu and Liu (Ref. 9); and ●, Olijnyk and Holzapfel (Ref. 10) (three data points in the β-Sn phase are not shown in this figure). The present data are fitted to a Birch first-order equation with $B_0=76.6$ GPa and $B_0'=4.04$ (solid line).

difference was the use of ice as a pressure medium in the latter study. It is known that ice is not a hydrostatic pressure medium above 18 GPa (Ref. 16) and therefore can support a pressure gradient. Using the ruby fluorescence of a small localized crystal would result in an inaccurate estimation of the pressure corresponding to the region sampled by x rays. This may explain the discrepancy between the two studies. It should be noted that the pressure condition encountered in this study was similar to the one used by Olijnyk and Holzapfel.[10]

Tin keeps the body-centered-cubic structure to the highest pressure reached in the present experiment, 120±5 GPa. The relative volume change as a function of pressure is shown in Fig. 2. The volume at atmospheric pressure, V_0, is that of the β-tin structure: 27.07 Å^3.[9] Data obtained in the present study are presented along with earlier data. Data points in the bcc phase can be fitted to a Birch first-order equation with $B_0=76.4$ GPa and $B_0'=4.04$. With a compression of 0.54 achieved at 120 GPa, tin is still somewhat compressible, an indication that the solid has not reached a high level of compactness. Because all our V-P data points were taken in the bcc phase of tin, we could not confirm the slight relative change of volume at the bct-bcc transition as published data[10,9] seemed to indicate.

TABLE I. Observed and calculated d spacings and x-ray-diffraction integrated intensities for bcc tin at 112±2 GPa. The weak (411) line was omitted in the calculation. Intensities are normalized to $I(110)$ in both cases. A sample thickness of 20 μm was assumed for the intensity calculations.

(hkl)	d_{obs} (Å)	d_{calc} (Å)	I_{obs}	I_{calc}
110	2.199	2.199	100	100
200	1.560	1.555	39	28
211	1.269	1.270	95	55
220	1.100	1.100	20	4
310	0.985	0.984	24	5
222	0.897	0.898	3	1
321	0.831	0.831	16	1

A theoretical investigation of the high-pressure structural stability has been performed by Hafner.[14] Among the different structures studied [diamond, β tin, fct (including bct), and hcp], the hcp structure has been shown to be more stable over the tetragonal phase at high pressure. Although the evaluation of the critical compression significantly depends upon the screening function used to perform the pseudopotential-based minimum-energy calculation, Hafner estimated the tetragonal-to-hcp transition to take place at an atomic radius ~3 a.u. With an ideal c/a ratio and a value of the room-pressure volume of 27.07 Å^3/atom, this yields $V/V_0=0.68$. Based on the experimental equation of state presented in Fig. 2, tin still has the bct structure at $V/V_0=0.68$ (pressure ~30 GPa). It should be emphasized though that, even for the lower-pressure structures, the experimental[10] and the calculated[14] critical atomic radii do not come to a close agreement. Nevertheless, tin is expected to transform to a close-packed structure at sufficiently high compression. In comparison with Si, Ge, and Pb, the hexagonal close-packed structure is likely to be a stable phase at high pressure. Moreover, it is interesting to compare the pressure behavior of the III-V isoelectronic compound, indium antimonide, to tin.

Energy-dispersive x-ray-diffraction results, obtained recently,[17] showed that InSb, similarly to tin, adopts the bcc form at high pressure namely at 25.5±0.5 GPa$\leq P \geq$30.5±0.5 GPa. At 30.5±0.5 GPa, the observed relative volume was 0.60. Pure bcc InSb was observed to 66±1 GPa, the maximum pressure studied, at which V/V_0 was decreased to 0.51.

It is interesting to point out that the high-pressure structural-phase-transition sequence in tin, β-Sn→bct→bcc, is different from that observed in Si and Ge. Both Si and Ge show the diamond→β Sn→primitive hexagonal→"intermediate" structure sequence with increasing pressure.[11,12] Furthermore, Si eventually transforms to a hexagonal close-packed and then to a face-centered-cubic structure.

To summarize, tin was observed in the body-centered cubic structure to 120±5 GPa with $V/V_0=0.52$ by energy-dispersive x-ray diffraction. It is suggested that first-principles total-energy calculations be reexamined for the possible existence of close-packed structures for tin at very high pressures.

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