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PHASE TRANSITIONS IN Si, Ge AND Sn UNDER PRESSURE

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Abstract - Si, Ge and Sn have been studied by energy dispersive X-ray diffraction up to 50 GPa. Si shows first the well known transition from diamond to \( \beta \)-Sn structure around 11 GPa. It transforms to a primitive hexagonal structure (Si-V) around 15 GPa, to an intermediate phase Si-VI around 35 GPa and finally to hcp (Si-VII) around 40 GPa. Ge stays stable in the structure \( \beta \)-Sn up to 54 GPa. The well known \( \beta \)-Sn high pressure modification of Sn at first shows a continuous increase in c/a from 0.91 to 0.94, but around 35 GPa, a transition to bcc.

It is well known that the group IV B elements show a change from openly packed covalent to denser packed metallic structures with increasing atomic number: carbon crystallizes in the hexagonal layered structure of graphite with coordination number (CN) 3, as well as in the metastable cubic diamond (cd) structure (CN=4), which is also the stable form for Si and Ge at ambient pressure. The cd phase of Sn(\( \alpha \)-Sn) transforms to a denser metallic phase (\( \beta \)-tin structure) with 6 nearest neighbours just below room temperature at normal pressure, while Pb is known to crystallize in the cubic closed packed (fcc) structure.

This tendency to higher coordinated structures has also been observed for the individual elements under compression. It was shown by Jamieson /1/ that Si and Ge transform to the metallic \( \beta \)-tin structure above 10 GPa and Sn is found in a body centered tetragonal structure (c/a = 0.91, CN = 8) above 9.5 GPa /2/. We have extended the structural investigations of the latter three elements into the 50 GPa regime by energy dispersive X-ray diffraction. A conventional X-ray source with a conical slit system /3/ was used and in the case of Sn and Si additional work was done in HASYLAB with synchrotron radiation /4/. The pressure was determined by the ruby fluorescence method with \( d \lambda / d p = 3.65 \) GPa/A /5/. The 4 : 1 methanol : ethanol mixture was used as pressure transmitting medium.

Si is stable in the \( \beta \)-tin phase only over a small pressure range and transforms to a primitive hexagonal (ph) cell (CN=8), Si-V, around 15 GPa /6,7/. Two further phase transitions to Si-VI and Si-VII occur around 35 GPa and 40 GPa, respectively /6/. While Si-VII crystallizes in the hcp structure (CN=12) with c/a = 1.69, we were not able to arrive at a definite structural assignment for Si-VI, because the diffraction patterns between 35 GPa and 40 GPa obviously consist of a phase mixture of Si-V, Si-VI and Si-VII.

The high pressure behaviour of Ge is much simpler. Ge remains in the \( \beta \)-tin structure up to the highest pressure of 54 GPa.
Sn shows under compression in its high pressure bct phase at first a continuous approach towards a bcc structure as shown in fig. 1a by the increase of c/a from 0.91 to 0.95 between 10 and 50 GPa. However, new lines develop in between the bct doublets (fig. 2) above 35 GPa, and with further compression the bct peaks lose on intensity. A bcc indexing fits all the new lines. Around 56 GPa the predominant lines correspond to the bcc phase, but some reminiscent bct lines indicate that even at this pressure the transition to bcc has not been completed. The pressure dependence of the lattice parameters of bct and bcc Sn (fig. 1b) clearly shows the first order nature of this transition. Fig. 1c reproduces the pressure dependence of the reduced volume v/v₀.

Fig. 1 – Pressure dependence of
a) the c/a ratio of Sn-III (bct)
b) the lattice parameters of Sn-III (bct) and Sn-IV (bcc)
c) the reduced volume v/v₀

Fig. 2 – X-ray diffraction patterns for Sn at various pressures. The thick lines point to diffraction peaks of the bcc phase while thinner refer to peaks of the bct phase. g denotes gasket reflections.
Table 1 compares the experimental values for the transition pressures and volumes at room temperature with theoretical values for 0 K. For Si and Ge, the agreement between experiment and theory is very good, while for Sn there is qualitative agreement in the lower compression range and an hcp phase comes out to be more stable at 0 K as compared to the observed bcc phase at room temperature. However, a bcc phase is commonly observed at high temperatures and, therefore, we cannot exclude the existence of a hcp phase for Sn at lower temperatures.

<table>
<thead>
<tr>
<th></th>
<th>CD → β-TIN</th>
<th>β-TIN → PH</th>
<th>PH → Si-VI</th>
<th>Si-VI → HCP</th>
<th>THEORY(Exp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>A 0.93 (0.92)</td>
<td>B 0.68 (0.69)</td>
<td>C 0.56 (0.54)</td>
<td>v/v₀</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.9 (11.5)</td>
<td>14.3 (15)</td>
<td>41 (40)</td>
<td>P[GPA]</td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>A 0.895 (0.89)</td>
<td></td>
<td></td>
<td>v/v₀</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.6 (10)</td>
<td></td>
<td></td>
<td>P[GPA]</td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>D 0.73 (0.88)</td>
<td>E 0.70 (0.88)</td>
<td>0.68</td>
<td>v/v₀</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(9.5)</td>
<td>(35)</td>
<td>40</td>
<td>P[GPA]</td>
<td></td>
</tr>
</tbody>
</table>

A) Ref. 8
B) Ref. 9
C) Ref. 10
D) Ref. 11
E) Estimated from the experimental room temperature EOS

Table 1 - Comparison of experimental values for transition pressures and volumes at room temperature with theoretical 0 K values. The experimental values are expressed in parenthesis.

For Si the structural sequence results in a systematic increase in CN from 4 to 12 which corresponds to a closer packing of the atoms and a weakening of the directional covalent bonds. One can assume therefore that Si ultimately has turned into a simple metal in the hcp phase. The extended range of stability for the β-tin phase in Ge shows on the other hand that one has to be careful with simple analogies between lighter and heavier elements in one group of the periodic table. Apparently the inner d-shells in Ge and Sn lead to different behaviour in comparison with Si /8,9/.

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