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## NEW PHASES OF SEMICONDUCTORS AT ULTRAHIGH PRESSURE

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Résumé - Des mesures de diffraction X ont été faites sur Ge, Si, GaP et InAs à très haute pression dans un dispositif à enclumes de diamant. Trois phases de Si ( $\beta$ -Sn, hexagonal simple, hexagonal compact) ont été identifiées, à pression croissante, ainsi qu'une phase cubique centrée à la décompression. InAs se transforme en une phase NaCl sous haute pression, avec une hystérésis lors du retour à la structure blende d'origine. Des expériences sur GaP en milieu quasi-hydrostatique localisent la pression de transition bien au-dessus de 22 GPa en accord avec le travail précédent de Pinceaux, Besson, Rimsky et Weill.

Abstract - X-ray diffraction experiments have been carried out on Ge, Si, GaP, InAs at ultrahigh pressure in the diamond anvil high pressure apparatus. Three phases of Si ( $\beta$ -Sn, simple hexagonal, hcp) have been found on increase of pressure, with bcc phase on release. Only one phase of Ge ( $\beta$ -Sn) has been found to 25 GPa, with tetragonal phase on release. InAs transforms to NaCl phase at high pressure, with some hysteresis in the transformation back to the original zinc-blend phase. Experiments on GaP in a quasi-hydrostatic medium place the transition pressure well above 22 GPa, in agreement with previous work of Pinceaux, Besson, Rimsky, and Weill.

## I - INTRODUCTION

There have been many studies of Group IV elemental and III-V compound semiconductors at high pressure. Jamieson /1/ proposed a simple scaling relationship between the transition pressures for these materials and their band gaps. A more detailed model based on scaling relationships was proposed by Van Vechten /2/. He assumed that the high pressure phase had the tetragonal,  $\beta$ -tin-like structure, and did not distinguish between metallic phases. More recent, *ab initio*, calculations /3-7/ have been capable of distinguishing between different metallic structures.

This paper will address several of the current problems with high pressure behavior of these materials.

## II - InAs

Before proceeding to the more complicated cases of Si and Ge, the relatively simple case of InAs will be considered. Earlier work was obtained only on increase of pressure. The reduced volume versus pressure curve obtained in a recent experiment by us illustrates the hysteresis associated with the cubic (zinc-blend) to cubic (rocksalt) transition with data taken under hydrostatic conditions (Fig. 1). This is the only hysteresis loop obtained for any III-V compound at the present time. These data pose the question of the correct value for  $P_t$ . It must be between  $\sim 3.3 - 8.2$  GPa, and probably between  $\sim 6.4 - 7.2$  GPa. It is to be noted that this probable estimate lies below the value of the onset ( $\sim 7.2$  GPa) on increase of pressure.

## III - GERMANIUM

Yin and Cohen /4,5/ predicted a transition to a  $\beta$ -tin phase at 9.6 GPa, and that no other phase transition would be observed below  $\sim 50$  GPa. Our experiments show that the onset of the transition under quasi-hydrostatic conditions is  $10.6 \pm 0.1$  GPa and completion is at  $11.1 \pm 0.2$  GPa, when the experiment is carried out over periods of hours or days. Compression of the sample in a NaCl medium reduces the onset pressure to  $(9.8 \pm 0.2)$  GPa, and direct compression of a sample in a gasket not only lowers the onset, but smears the I-II coexistence region over a wider pressure range ( $8.1 \pm 0.2 \rightarrow 11.5 \pm 0.5$  GPa). No other phase was found by us on further pressure increase to 26 GPa, and to  $\sim 50$  GPa by Olijnyk et al /8/.

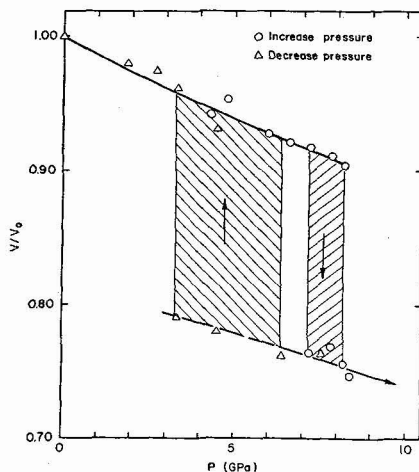


Fig. 1 - Plot of the reduced volume versus pressure for InAs pressurization and release of pressure.

On release of pressure, phase III (tetragonal /9/) is formed. Several experiments were carried out to study this transition, and it was found that the relative yield of phases I and III found at room pressure was dependent not only on the state of stress, but also on the rate at which pressure was released. Our data are not in agreement with those of Qadri et al /10/ and will be reported in detail elsewhere.

## IV - SILICON

Two new high pressure phases of silicon have been observed by us /11/ and Olijnyk et al /8/. The phase sequence observed by us on pressurization is  
 I (cubic, diamond)  $\xrightarrow{11.2 \pm 0.2}$  I+II  $\xrightarrow{12.5 \pm 0.2}$  II (bct,  $\beta$ -tin)  $\xrightarrow{13.2 \pm 0.2}$  (II+V)  $\xrightarrow{16.4 \pm 0.5}$  V  
 (primitive hexagonal)  $\xrightarrow{36 \pm 1}$  V+VII  $\xrightarrow{42 \pm 1}$  VII (hcp) where pressure units are in GPa.  
 On release of pressure, the sequence is reversed with phases II+V coexisting between  $\sim 14.5$ - $11.0$  GPa, and then II+III between  $\sim 10.8$ - $8.5$  GPa, where III is tetragonal.

Experiments carried out by us on the I $\rightarrow$ II $\rightarrow$ V $\rightarrow$ II $\rightarrow$ III sequence below  $\sim 2$  GPa were probably representative of hydrostatic conditions, since results were essentially identical when Argon or 4:1 methanol-ethanol solution was used as the pressure transmitting medium. The result on V $\rightarrow$ VII (using phase notation of Olijnyk et al) was obtained under conditions of higher shear stress, so that the transition pressure, which is in close agreement with the theoretical prediction, may need to be revised.

Powder diffraction patterns from phase V can be indexed on the basis of primitive hexagonal ( $P_6/mmm$  or  $D_{6h}$ ). This is the only case of an element crystallizing in this structure at any pressure. Needs and Martin /7/ have carried out *ab initio* calculations and confirmed that primitive hexagonal Si has a region of stability close to that observed. A detailed account of our measurements and comparison with theory is in preparation.

#### V - GaP

Several earlier studies of the transition in GaP placed the transition pressure at  $\sim 22$  GPa (see Ref. 12 for a review). Pinceaux et al /13/ suggested from optical work that pressurization in a more nearly hydrostatic environment, obtained by rapidly pressurizing 4:1 methanol-ethanol solution, raised the transition pressure to  $\sim 24$  GPa, and that the low pressure phase persisted to  $\sim 26$  GPa.

In-situ x-ray diffraction studies carried out by us /14/ have confirmed the raising of the transition pressure (analogous to the case of Si and Ge) and that the structure is body-centered tetragonal ( $\beta$ -tin analog) /12/, but found no evidence for disproportionation or amorphization of the quenched sample, as suggested by Pinceaux et al /13/. It was found that phase I was recovered at room pressure.

#### VI - A TEST OF VAN VECHTEN'S MODEL

Figure 2 test one of the scaling hypotheses of Van Vechten's model. He assumed a linear relationship between the fractional volume difference between the low pressure ( $\alpha$ ) and high pressure ( $\beta$ ) phases at the transition pressure,  $P_t$ :

$$\frac{V^\alpha(P_t) - V^\beta(P_t)}{V^\alpha(P_t)} = 0.209 - 0.056 f_i$$

where  $f_i$  is the Phillips Ionicity. This equation is represented by the full line in Fig. 2 (experimental data are reviewed in Ref. 15). As noted in this figure, two III-V compounds transform to the NaCl structure (including two II-VI compounds, ZnO, ZnS) while GaAs transforms to an orthorhombic structure /12/. The scaling relationship does not fit the data well.

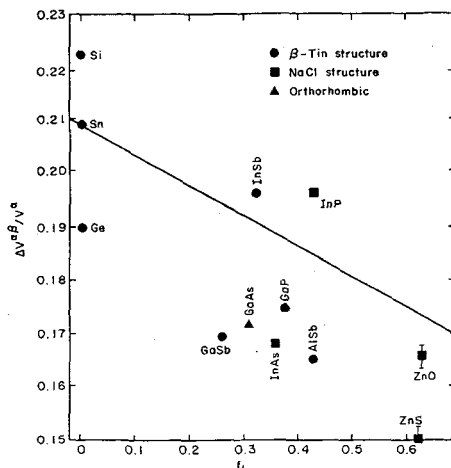


Fig. 2 - Plot of the fractional volume change  $\Delta V^{\alpha\beta}(P_t)/V^\alpha(P_t)$  versus ionicity.

VII - GENERAL COMMENTS CONCERNING HIGH PRESSURE PHASE TRANSITIONS IN SEMICONDUCTORS WITH DIAMOND AND ZINC-BLEND STRUCTURE

Some general conclusions are:

(1) Onset transition pressures are affected by the state of stress. The coexistence region for the two phases is broadened by shear stress.

(2) Onset pressures for the transitions in hydrostatic conditions are higher than thermodynamic, and those recorded with large shear stresses may be lower, so that comparison of experimental and theoretical transition pressures must be made with caution. The meaning of the term pressure in the non-hydrostatic case needs to be considered carefully (see Ref. 16 for example).

(3) Experience shows that compression of samples in a hydrostatic fluid does not guarantee a hydrostatic stress state in the sample. A necessary condition is that the sample particles do not aggregate and form a "bridge" between the anvils.

(4) Details of the transitions depend on the rate of pressurization or depressurization (kinetics). It is conjectured that the correct thermodynamic sequence for Ge and Si is I  $\leftrightarrow$  III  $\leftrightarrow$  II, and that the phase III is not observed on increase of pressure due to kinetic factors.

(5) Simple scaling hypotheses are at best an approximation to observed behavior. However, *ab initio* calculations have improved to the point where reliable predictions need to include phase III for Si and Ge. \*

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\* Note Added in proof : This question was answered at the conference by Prof. M.L. COHEN. Phase III is metastable. The transition sequence II  $\rightarrow$  III on release of pressure is controlled by kinetic factors.