Raman Scattering in Metallic Si and Ge up to 50 GPa

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Optical phonons in metallic high-pressure phases of Si and Ge were studied up to 50 GPa by Raman scattering. Two Raman bands (LO,TO) were observed in the β-tin phase, one of which (LO) becomes soft on approaching the transition to primitive hexagonal. For hcp-Si there is one Raman-active mode (TO), and an additional mode is observed in the stability field of Si-VI. The available theoretical results agree within (10–20)% with the experimental results.

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Phonon spectra of metals are usually investigated by inelastic neutron scattering. For such studies single crystals of rather large size are needed, which makes the application of this method to high pressures rather limited. On the other hand, information on phonons in metals can be obtained by Raman scattering, as was shown for the first time in 1968 by Feldman, Parker, and Ashkin [1]. As a result of the small penetration depth of light in metals, the scattering cross section is rather small, and not many measurements have been reported for Raman scattering. Multichannel detectors have significantly improved measurement sensitivity [2], and make possible the detection of low-intensity Raman signals, for example in metals. The validity of this method will be demonstrated in the present study on Si and Ge, which are known to transform into the metallic state around 10 GPa [3]. For Si the following phase transitions have been found up to 50 GPa [4–7]: cubic diamond to β-tin at $\sim$12 GPa, β-tin to primitive hexagonal (ph) at 13–16 GPa, and ph to intermediate phase Si-VI at $\sim$37 GPa and to hcp at $\sim$42 GPa, Ge transforms into the β-tin structure at 10 GPa and into the ph structure at 75 GPa [8]. Another interesting aspect concerns the involvement of soft phonon modes in some of these phase transitions, as was predicted by theoretical investigations [9–11].

Powdered samples were loaded into a gasketed diamond anvil cell [12] (DAC) together with ruby splinters for pressure determination [13] and a 4:1 methanol:ethanol mixture for the reduction of uniaxial stresses. Raman spectra for Si were excited by the 514-nm and 488-nm lines of an Ar^+ laser while the Ge Raman spectra were excited by the 647-nm line of a Kr^+ laser. Backscattered light was analyzed using a triple spectrograph (Spex, Model 1877) and a liquid-nitrogen-cooled charge-coupled-device multichannel detector (Photometrics, Ltd.).

A group-theoretical analysis of lattice vibrations in the β-tin lattice has been given by Chen [14], and experimental dispersion curves for β-Sn were determined by Rowe [15] and Ivanov *et al.* [16]. At the Γ point of the Brillouin zone (BZ) the optical modes consist of one LO branch and at higher frequencies of a doubly degenerate TO branch, both of which are Raman active. The ph structure with one atom per primitive unit cell has no optical modes. The hcp structure exhibits one doubly degenerate TO branch which is Raman active [1] and one LO branch at higher frequencies.

Raman spectra of Si in the β-tin phase at various pressures are shown in Fig. 1. The TO mode shifts to higher frequencies with increasing pressure (Fig. 2); however, the LO band decreases in frequency and broadens with increasing pressure. At 16.4 GPa, the highest pressure for which Raman spectra of the β-tin phase could be recorded, the intensity of the LO mode has nearly vanished (Fig. 1). A small hysteresis was observed between loading and unloading. The LO mode corresponds to displacements of the face atoms of the β-tin lattice in the c direction, and the freezing-in of this mode, together with slight modifications of the axial ratios, is associated with

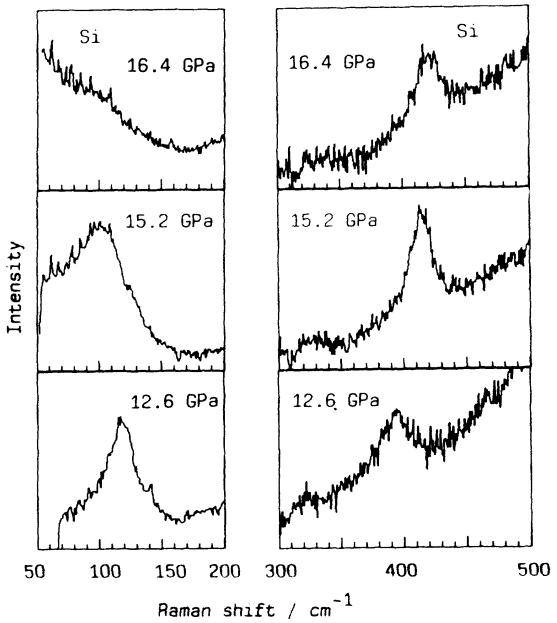

FIG. 1. Raman spectra of Si in the β-tin phase: left-hand panel, LO mode; right-hand panel, TO mode. The power of the laser beam incident on the DAC was 0.4 W. The collection times were 15, 30, and 40 min at 12.6, 15.2, and 16.4 GPa, respectively.

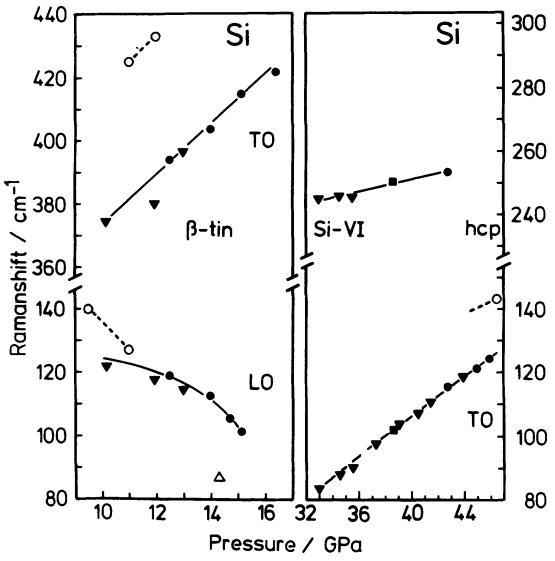

FIG. 2. Pressure shift of Si lattice modes: left-hand panel, β-tin phase; right-hand panel, Si-VI and hcp phases. Present experimental results are denoted by solid symbols: ●, load; ▼, unload; ■, reload. Theoretical results are denoted by open symbols: ○, Ref. [10]; △, Ref. [9]. The solid and dashed lines serve as a guide for the eye.

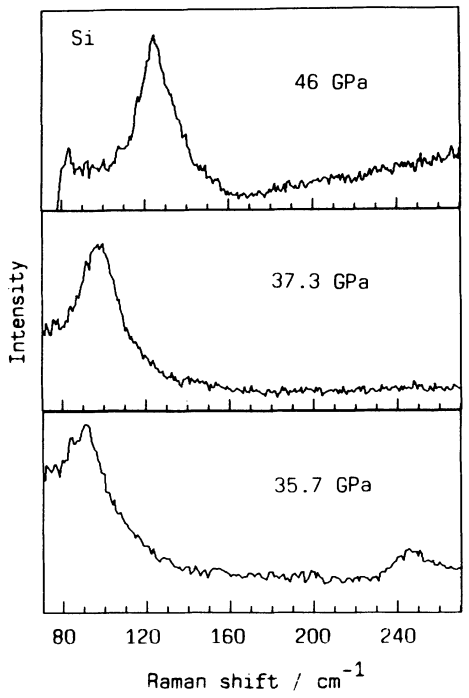

FIG. 3. Raman spectra of Si in the Si-VI and hcp phases. The incident laser-beam power was 0.4 W and collection times were 15 min.

the transition into the ph structure [10].

Raman spectra in the pressure range where Si-VI and hcp-Si are stable are shown in Fig. 3. The TO mode frequency of hcp-Si increases with pressure and was observed for $P \geq 42.8$ GPa on loading and down to 33 GPa on unloading (Fig. 2). In addition, a rather weak peak near 250 cm^{-1} was observed at 42.8 GPa on loading, at $33 \leq P \leq 35.7$ GPa on unloading, and at 38.7 GPa on reloading from 33 GPa (Figs. 2 and 3). This observation shows that at least two Raman modes are characteristic of Si-VI, and that the lower-frequency mode becomes the TO mode of hcp-Si. Slight differences with respect to results from x-ray diffraction studies [7] concerning the stability range of Si-VI and hcp-Si may be due to effects originating from the presence of pressure inhomogeneities [17].

The ph structure can be formed from the hcp structure by sliding every second hexagonal plane by $a/\sqrt{3}$ in the [110] direction. This displacement corresponds to a TO phonon mode at the Γ point in the BZ for a hcp lattice [10]. There is some evidence that the TO mode of hcp-Si is also a characteristic one of Si-VI, and softening of this mode appears to be associated with the transition from Si-VI to ph.

Typical Raman spectra of Ge in the β-tin structure are shown in Fig. 4. As in the case of Si, the TO mode shifts to higher frequencies with increasing pressure. In contrast to Si, the LO mode frequency initially increases slightly with pressure and appears to reach a maximum around 50 GPa (Fig. 5). At higher pressures, on approaching the transition into the ph phase, a negative pressure shift as for Si is expected. This behavior can be noted more clearly from the mode Grüneisen parameter γ_{LO} (compression data of Ref. [5] used in the calculation) which decreases from ≈ 1 at 10 GPa to nearly zero at 50 GPa, whereas values for γ_{TO} range from ≈ 2.4 at 10 GPa to ≈ 1.4 at 50 GPa.

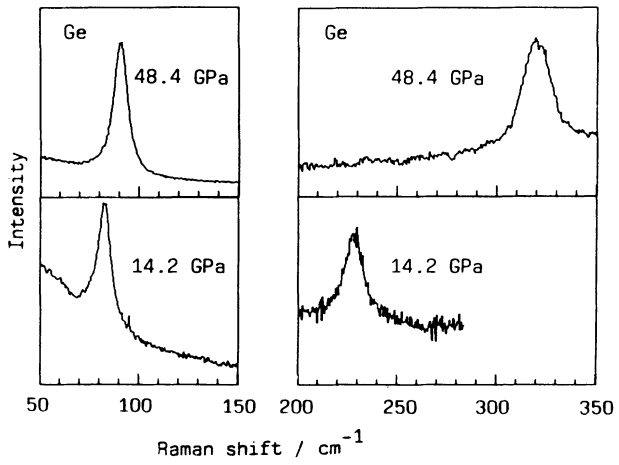

FIG. 4. Raman spectra of Ge in the β-tin phase: left-hand panel, LO mode; right-hand panel, TO mode. The incident laser-beam power was 0.3 W and collection times were 10 min.

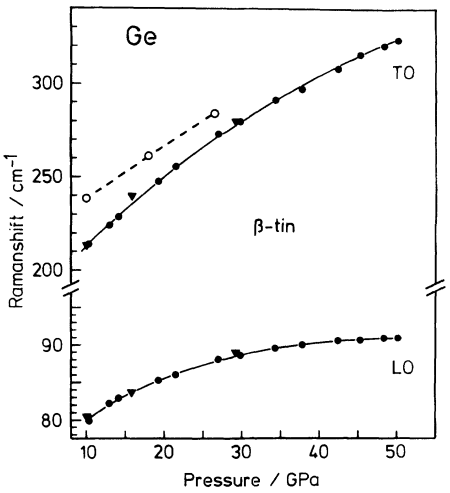

FIG. 5. Pressure shift of Ge lattice modes in the β-tin phase. Present experimental results are denoted by solid symbols: ●, load; ▼, unload. Theoretical results are denoted by open symbols: ○, Ref. [11]. The solid and dashed lines serve as a guide for the eye.

Theoretical results [9–11], shown by open symbols in Figs. 2 and 5, differ from experiment by $\approx 10\%$. In comparing experiment and theory one should take into consideration that the calculations are performed for 0 K whereas the experiments are performed at room temperature. In this context it is interesting to note that a considerable negative temperature shift with increasing laser power was observed for the LO mode in the β-tin structure in a separate run on a Si sample which did not have good thermal contact to the diamond. For the TO mode of the β-tin phase calculated frequencies are available only for the M point of the BZ [10,11], which should be slightly higher than the frequencies for the Γ point according to experimental dispersion curves for β-Sn [15,16]. With these caveats in mind the agreement between theory and experiment appears remarkable.

In conclusion, Raman spectra of metallic high-pressure phases of Si and Ge were recorded up to 50 GPa. The involvement of soft phonon modes in some phase transitions was confirmed. Theoretical predictions are in good agreement with the experimental results. More generally, the present study shows that Raman spectroscopy is an excellent method for the investigation of phonons in metals up to very high pressures, especially with respect to phase transitions and the soft phonon modes involved in them, including systems which are insulators and metallize at higher pressures. In addition, such data provide a stringest test on pseudopotentials, which have been proven to be extremely successful in static structure calculations, in their ability to predict dynamical properties.

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