Pressure Induced Frequency Shifts of Transverse Acoustic Phonons in Germanium to 9.7 GPa

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(Received 15 October 1996)

A complete set of transverse acoustic phonon frequencies of Ge has been measured at pressures up to 9.7 GPa by inelastic neutron scattering and studied by *ab initio* calculations using density functional perturbation theory. At the X and L points, the pressure dependence of the phonon frequency ω in the cubic structure is shown to be that of a classical soft mode with ω^2 strictly linear in pressure P. This finding is in contrast with previous interpretations that associated the pressure dependence of the zone boundary modes with the occurrence of the first order transition at $\sim$10 GPa and represented the pressure dependence of its frequencies by a polynomial in P. [S0031-9007(97)03824-6]

PACS numbers: 63.20.Dj, 61.12.Ex, 62.50.+p

The transverse acoustic phonons of cubic semiconductors show characteristic features, which have been extensively discussed in the past: (1) Their dispersion curves are low in energy and become flat away from the zone center, although the corresponding sound velocities are rather high. (2) Experimentally, these modes show negative Grüneisen parameters $\gamma_j(q) = -\partial \ln \omega_j(q)/\partial \ln V$ (j, mode; q, wave vector; ω, frequency; V, volume) at zone boundary points (X and L) [1]. This behavior explains the negative thermal expansion coefficient at low temperatures [2] but was also associated with their high pressure phase transitions from fourfold to higher coordination [3]. Whereas various theoretical approaches have succeeded in correctly reproducing the ambient pressure dispersion curves [4], the situation is far from being settled concerning their pressure dependence. This is due mainly to the lack of experimental data. Until very recently, inelastic neutron scattering, the only technique which is able to provide phonon energies over the entire zone, could not be performed at the high pressures required to measure shifts with sufficient precision. Recent progress in high pressure and neutron scattering techniques have lifted these limitations [5,6]. Single crystal samples of several 10 mm^3 may be compressed up to 10 GPa and phonon dispersion curves determined on triple axis neutron spectrometers.

This technique has been applied to the study of the pressure dependence of the dispersion curves of transverse acoustic (TA) phonon modes of germanium up to its transition pressure at $\sim$10 GPa. Germanium was chosen due to its excellent neutron scattering properties. However, since the characteristic features of the phonon dispersion curves of germanium are common to most tetrahedrally bonded semiconductors, our results will also apply to the lattice dynamics of most of these systems.

Single crystals of 25 mm^3 volume were compressed up to 9.7 GPa [7] in three different runs with the Paris-Edinburgh cell [9] using lead as the pressure transmitting medium as previously described [5]. The crystals were recovered undamaged after the experiments. The neutron scattering measurements were performed at the 2T1 triple-axis spectrometer of the Orphée reactor (Laboratoire Léon Brillouin, Saclay, France) using horizontally and vertically focusing monochromator and analyzer crystals [6]. Constant-Q scans were recorded at 300 K with a fixed final energy of 14.7 meV (3.55 THz) in the energy-loss mode. Figure 1 shows typical scans at reduced wave vectors (0.2 0 0) ($\xi = 0.2$) and (1.0 0 0) ($\xi = 1.0$) across the Δ_5 mode at ambient and maximal pressures. The fitted peak positions show standard errors of $\pm 0.5\%$ for most of the points reported here. The ambient pressure frequencies before and after compression were found to be identical within these errors. They are approximately 2% higher than those measured at 80 K by Nilsson and Nelin [10]. Differences of this order are commonly found under such experimental conditions (small samples, open collimation), but this will not affect the values of the pressure coefficients.

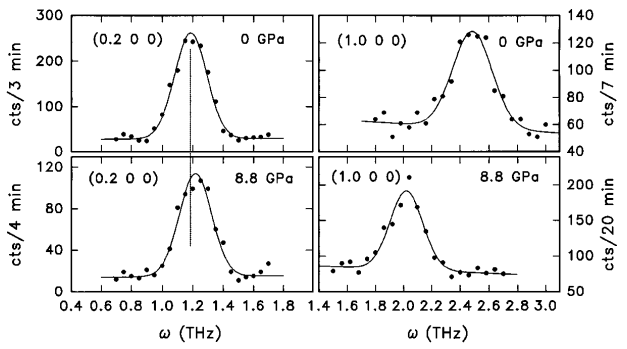

FIG. 1. Raw data of constant Q scans across the Δ_5 mode along [100] at $\zeta = 0.2$ and $\zeta = 1.0$ (X point) at ambient pressure and 8.8 GPa. The solid line is a least squares fit to a Gaussian, including a linear background.

Scans were performed across the Δ, Σ, and Λ branches along the [100], [110], and [111] directions, respectively. Data were collected at 0, 5.3, 8.8 GPa for Δ_5, at 0, 5.4, and 8.7 GPa for Σ_3, at 0, 5.8, 8.0 and 9.7 GPa for Σ_4, and at 0, 5.2, 7.6, and 9.3 GPa for Λ_3. In addition, the Σ_4 mode was investigated at 0 and 2.3 GPa for $\xi = 0.8$ and $\xi = 1.0$ (point X). Figure 2 shows the frequency variations of the Δ_5 and Σ_4 modes for small and large wave vectors. For phonons close to Γ, frequencies initially increase with pressure, in agreement with ultrasonic results [12]. The data reveal, however, a pronounced nonlinearity in the frequency shifts, which leads to a decrease of most frequencies at high pressures. This primarily affects the Σ_4 and Λ_3 modes, to a lesser extent the Δ_5, and least of all the Σ_3 frequencies. In fact, the Σ_4 phonon frequencies decrease phonon beyond 6 GPa for all wave vectors (see Fig. 2) and the Λ_3 beyond 8 GPa. For the Δ_5 mode, the same effect is observed only for $\xi > 0.3$, and for Σ_3 only for $\xi > 0.6$.

Figure 3 illustrates the mode Grüneisen parameters obtained from the frequency shifts to ~5 GPa and also shows other experimental data presently available. For small wave vectors our results agree reasonably well with the ultrasonic measurements, and our value for $\gamma_{\mathrm{TA}}(X)$ is in good agreement with published Raman data [13]. In contrast, the decrease of the TA(L) frequency is at least twice as large as indicated by previous tunneling spectroscopy measurements [14]. Figure 3 shows that the measured values for $\gamma_{\mathrm{TA}}(X)$ and $\gamma_{\mathrm{TA}}(L)$ of Ge are equal within the experimental uncertainty, a situation which is also found in Si, GaAs, GaP, InP, ZnSe, and ZnTe [15].

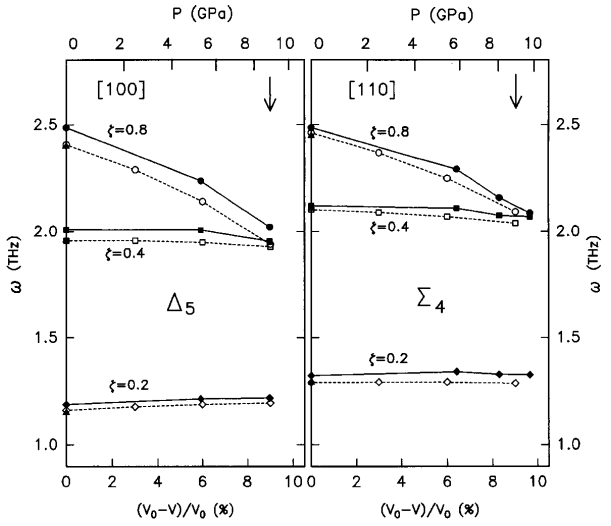

FIG. 2. Frequency as a function of pressure P and relative volume change $(V_0 - V)/V_0$ for the Δ_5 modes (see also Fig. 1) and Σ_4 modes at different wave vectors. Lines are guides to the eye through experimental (solid dots) and calculated (open dots) values. The triangles represent published [10] ambient pressure frequencies. The arrows indicate the thermodynamic transition pressure to the β-tin phase [11].

The pressure dependence of the phonon dispersion of germanium was also investigated by *ab initio* calculations using density functional theory. Our calculations were performed in the framework of the local density approximation using the plane wave pseudopotential method. The analytical forms of the exchange-correlation energy and the potential were taken from Ref. [16]. Soft norm-conserving pseudopotentials were generated for germanium using the scheme proposed by Troullier and Martins [17]. Different pseudopotentials were constructed for different values of the angular momentum of the electrons ($l = 0, 1, 2$) in order to reproduce the correct tails for the atomic wave functions, energy levels, and excitation energies for a number of electronic configurations of the single atom. The sums over electronic eigenstates in the Brillouin zone (BZ) were performed using 28 Chadi-Cohen special points in the irreducible wedge [18]. The dimension of the plane-wave basis set at a given $\mathbf{q}$ point in the first BZ was fixed through the condition $(\mathbf{q} + \mathbf{G})^2 \leq E_{\mathrm{cut}}$, where $\mathbf{G}$ is a reciprocal lattice vector and E_{cut} is the kinetic energy cutoff.

The dynamical properties within the harmonic approximation, i.e., the phonon frequencies and eigenvectors, were determined using self-consistent density functional perturbation theory (DFPT) [19]. Within DFPT, the atomic displacements from their equilibrium positions are considered as a static perturbation acting on the valence electrons. A detailed description of DFPT and of its application to the lattice dynamics of covalent semiconductors is given in Refs. [19] and [20]. A set of five dynamical matrices was obtained along the high-symmetry directions [100], [110], and [111], and the phonon eigenvectors and phonon dispersion curves along these directions were determined via a one-dimensional deconvolution.

For the calculation of the static and dynamical properties at the equilibrium volume, $E_{\mathrm{cut}} = 18$ Ry was used in

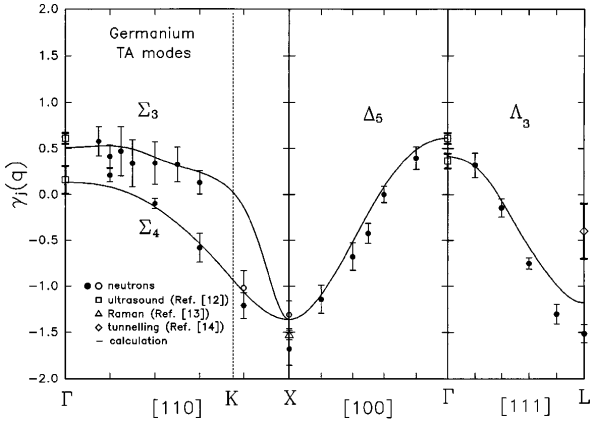

FIG. 3. Mode Grüneisen parameters of germanium. Solid and open dots are values derived from measured frequency variations to ~5 and 2.3 GPa, respectively.

order to ensure convergence of the calculated phonon frequencies to within 2 cm^{-1} (0.06 THz). In order to avoid spurious effects related to the change of the dimension of the basis set for each of the different crystal volumes (under pressure), the kinetic energy cutoff was chosen in such a way that the number of plane waves per atom is fixed. More details will be published elsewhere [21].

The results of these calculations are included in Figs. 2 and 3. The calculated frequencies for ambient pressure fit with the experimental values within ~2%, and the nonlinear volume dependence of the phonon frequencies is reproduced. The zero pressure Grüneisen parameters, as extracted from the calculated frequencies, are plotted in Fig. 3. The calculated value for $\gamma_{TA}(X) = -1.36$ is in excellent agreement with our experimental results (1.31 ± 0.15). For $\gamma_{TA}(L)$ the theoretical value is -1.18, which is ~20% smaller than the neutron result (-1.52 ± 0.1). We note, however, that these calculations give Grüneisen parameters at zero pressure, whereas the measurements average over a finite pressure range of ~5 GPa in most cases. In fact, if $\gamma_{TA}(L)$ is evaluated from the calculated frequencies at 0 and 5.2 GPa (i.e., in the same way as the experimental $\gamma_{TA}(L)$ was determined), a value of -1.56 is obtained. This clearly shows that there is no discrepancy between theoretical and experimental findings. Our calculations also provide data on the pressure dependence of the optical mode of Ge [21] which fit to less than 1% with recent measurements by Ulrich *et al.* [22].

The excellent agreement between calculated and measured data at all wave vectors and pressures thus validates the calculations to a high degree of accuracy. Thus, the theory can be taken as reliable in reproducing the behavior of cubic Ge even beyond 10 GPa, whether the structure is actually stable or not. This allows, in particular, the study of the pressure dependences of the TA(X) and TA(L) modes well beyond 10 GPa, which is not possible experimentally due to the transition to the β-tin phase. Up to the present, the limited pressure range has not allowed the real $\omega(P)$ relationship to be determined, and the pressure dependence of these modes has been described so far with an empirical $\omega = \omega_0 + aP + bP^2$ law (where a and b are fitting parameters) with no physical justification. Such an analysis was applied to a wide range of tetrahedrally bonded semiconductors, such as Si [1], Ge (Ref. [13] with $b = 0$), GaP [1], GaAs [23], and also to the chalcopyrites $CuGaS_2$ [24,25] and $AgGaS_2$ [24]. The TA(X) mode in the diamond and zinc-blende structures correspond to the Γ_5 frequency in chalcopyrite.

Figure 4 shows the results of the calculations up to $P_0 = 25$ GPa, where the TA(X) frequency is seen to drop to zero at $(V_0 - V)/V_0 = 18\%$ [7], whereas the TA(L) energy has decreased to 40% of its ambient pressure value. The dependence of these modes on pressure is found to be extremely simple: The squared frequencies are strictly linear in P. Such behavior is predicted in the Landau theory of soft mode transitions for either temperature or pressure as the relevant variable [26]. Whereas softening of modes as a function of temperature has been studied in many compounds, examples of pressure induced mode softening with $\omega^2 \sim (P_0 - P)$ are much fewer. Such soft mode behavior has been established, to our knowledge, only for zone center phonons of ionic crystals, clearly in the ferroelectric SbSI [26] and possibly in $PbTiO_3$ [27]. We believe that our finding in Ge is quite general for tetrahedrally bonded semiconductors, even for ionic compounds. Preliminary calculations on GaAs do show ω^2_{TA} to be quasilinear in P at the X and L points, and the predicted frequencies compare well (within 1%) with two-phonon Raman scattering results up to 7.2 GPa [23].

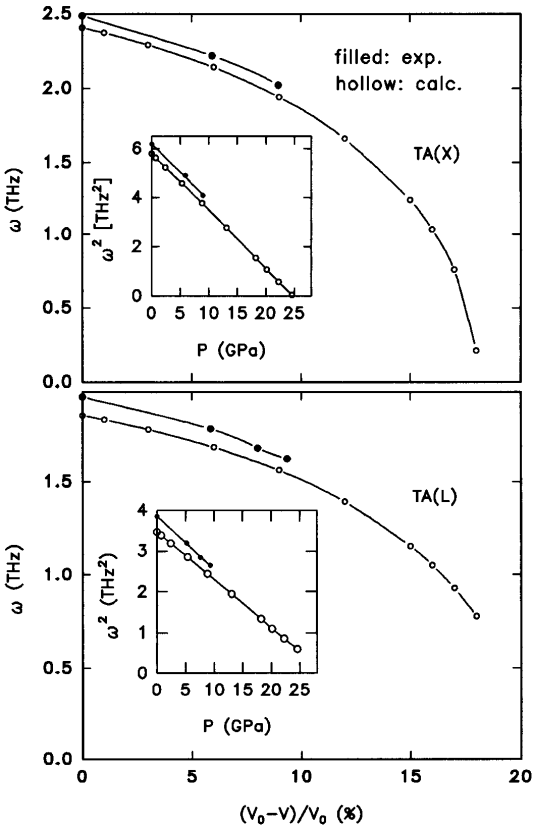

FIG. 4. Main figures: TA(X) (top) and TA(L) (bottom) frequencies as a function of volume change. Insets: squared frequencies as a function of pressure. Solid and open dots represent experimental and calculated values, respectively.

By symmetry, the decrease of the TA(X) or TA(L) frequency cannot induce the first order phase transition to the β-tin phase at 10 GPa and is hence not directly related to it. Instead, it seems to be associated with a second order transition at higher pressures, which is hidden by the first order transition to the β-tin phase: The diamond lattice tends to become unstable with respect to this type of shear all over its domain of existence with no pretransitional effects occurring close to the first order transition. Moreover, our theory clearly predicts that the *ad hoc* description $\omega = \omega_0 + aP + bP^2$ is artificial, and

the agreement of our theory with the available data up to 9.7 GPa supports this.

Finally, we want to remark that a displacive transition mechanism from the diamond to the β-tin structure in Ge involves the acoustic Σ_4 mode at long wavelengths (zone center). Such a mechanism was actually proposed for the archetypal α-β transition in Sn at 286 K. In Ge, the pressure coefficient of the Σ_4 branch at Γ is indeed negative at the thermodynamic transition pressure [11], as previously shown by ultrasonic measurements [28], but no anomalous behavior occurs either in this mode or in any other mode over the entire Brillouin zone. Since the restoring forces which govern the lattice dynamics have an electronic origin, this implies that no redistribution of the charge density occurs, as a pretransitional effect, close to the phase transition [29]. This is confirmed directly by the evolution of the charge density which comes out of the present calculations [21].

The authors would like to acknowledge support by the French Commissariat à L'Energie Atomique and the European Community through a fixed contribution contract supporting one of us (S. K.). Computer time was granted by the Hochleistungsrechenzentrum Jülich.

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