

Stability of silicon carbide at high pressures

A. F. Goncharov, E. V. Yakovenko, and S. M. Stishov

Institute of Crystallography, Academy of Sciences of the USSR

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The effect of high pressures on the phonon spectrum of SiC along the Λ direction has been studied by Raman scattering and through the use of the universality of the dispersion curves of the SiC polymorphs. The frequency of the TA vibrations has been found to decrease at the boundary of the Brillouin zone, indicating an approaching instability of the lattice. It is suggested that a structural phase transition occurs in SiC at $P > 1.5$ Mbar.

Covalent tetrahedral crystals are known to be unstable when compressed. They undergo a transition to a denser, metallic phase at comparatively low pressures, on the order of 100 kbar. Diamond is an obvious exception to the general rule, remaining totally stable at extremely high pressures, up to several megabars.

According to the theory of Ref. 1, the unusually wide stability range of diamond stems from the absence of p electrons from the ion core of the carbon. If this is true, a “hybrid” material such as silicon carbide should exhibit some sort of intermediate behavior. Recent studies of the lattice dynamics of cubic SiC at high pressures have shown² that the Grüneisen parameter of the $LTO(\Gamma)$ phonons decreases upon compression. This decrease may indicate an approaching instability of the lattice, caused (as in the case of other tetrahedral crystals) by a weakening of noncentral interatomic interactions.³ A final resolution of this question, however, will have to await a study of the behavior of TA phonons near the boundary of the Brillouin zone.⁴

It was shown in Ref. 5 that phonon dispersion curves for SiC can be constructed from data on first-order Raman scattering for several polymorphs.¹⁾ This method of plotting dispersion curves is based on the idea that as the number of atomic layers in the unit cell increases by a factor of N , the size of the Brillouin zone in the axial direction decreases, also by a factor of N , giving rise to additional phonons which are active in Raman scattering at the center of the zone. These additional phonons actually correspond to phonons with $q \neq 0$ in the so-called standard large zone.

The latter circumstance which makes it possible to observe the evolution of the phonon spectrum of SiC at high pressures by the diamond-anvil technique.

In this letter we are reporting a study of the 6H and 15R polymorphs, which contain 6 and 15, respectively, double atomic layers per lattice period (the space groups are $P6_3mc$ and $R3m$).

The experiments were carried out in a diamond cell filled with compressed helium. The samples were single-crystal platelets with dimensions of $60 \times 40 \times 15 \mu\text{m}$. The pressure was determined from the ruby scale⁶ within a random error of 0.05 GPa.

The lattice constants of SiC-15R were determined from the angular positions of the (110) and (0015) reflections in a hexagonal apparatus, within errors of 0.06% for the constant a and 0.08% for c .

The Raman spectra were measured with the help of a triple spectrometer with

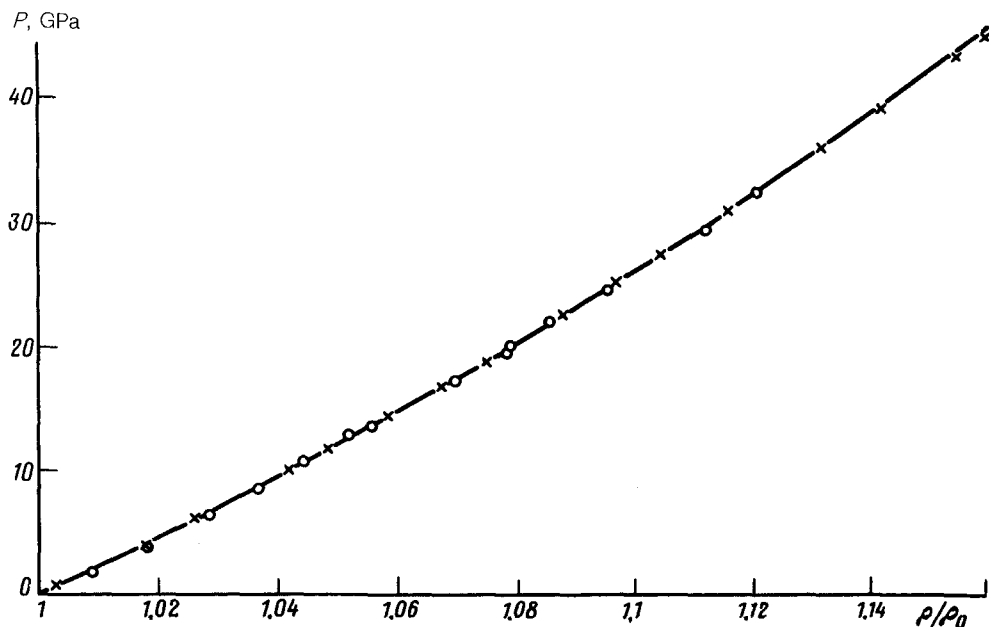


FIG. 1. Pressure versus the density for SiC-3C and SiC-15R. \times —3C; \circ —15R. Solid line) Least-squares fit by the approximating function $P = A(\rho/\rho_0 - 1) + B(\rho/\rho_0 - 1)^2$. The bulk modulus is found to be $K_0 = 224 \pm 3$, and its derivative with respect to the pressure is found to be $K'_0 = 4.3 \pm 0.3$.

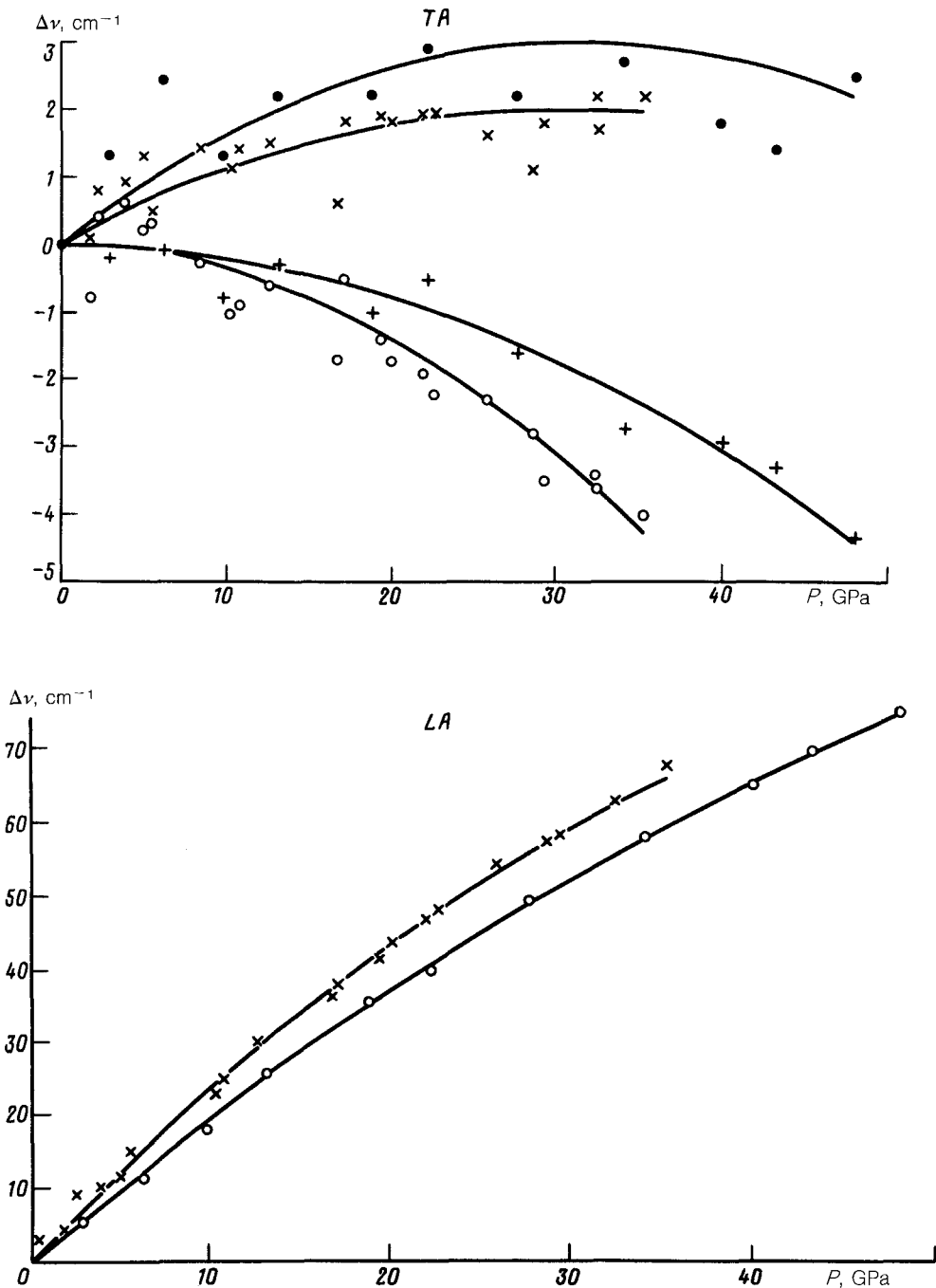


FIG. 2. Shift of the phonon frequencies versus the pressure. Top: TA vibrations. ●— $q = 0.33$; ×— $q = 0.4$; +— $q = 0.67$; ○— $q = 0.8$. Bottom: LA vibrations. ○— $q = 0.67$; ×— $q = 0.8$. The solid lines are least-squares fits by the approximating function $y = y_0 + Ax + Bx^2$.

multichannel recording. This spectrometer consisted of a monochromator filter, a Jobin Yvon THR-1000 spectrograph-monochromator, and an OSMA optical multi-channel analyzer.

All the measurements were carried out at room temperature.

Figure 1 shows the experimental equation of state and the elastic constants of SiC-15R, along with corresponding data on cubic SiC (Ref. 2). The equations of state of these substances are seen to be the same, within our experimental error. Note also that the compression of SiC-15R is isotropic.

The phonon frequencies were classified in accordance with the standard large zone. This approach makes it possible to determine the position of each Raman frequency on the composite dispersion curve.⁵ Figures 2a and 2b show the acoustic frequencies versus the pressure for the two polymorphs. The optical frequencies are shifted upward by the pressure, as are the *LA* frequencies.

The softening of the *TA* mode which we observe near the zone boundary is characteristic of covalent tetrahedral crystals and agrees with the decrease found previously² in the Grüneisen parameter $\gamma_{LTO}(\Gamma)$ in diamond-like SiC under pressure. This result actually shows that the behavior of SiC at high pressures is similar to that of silicon and that we should expect to see a structural phase transition associated with a lattice instability.

On the other hand, the decrease in the frequency of the *TA(L)* phonons in SiC occurs far more slowly than in Si ($\Delta\omega \sim 1.6\%$ with $\Delta\rho \sim 13\%$ in SiC and $\Delta\omega \sim 13\%$ with $\Delta\rho \sim 13\%$ in Si; Ref. 4).

To estimate the phase-transition pressure, we use the sum rule for lattice vibrations which was found by Brout⁷ and which was extended to covalent systems by

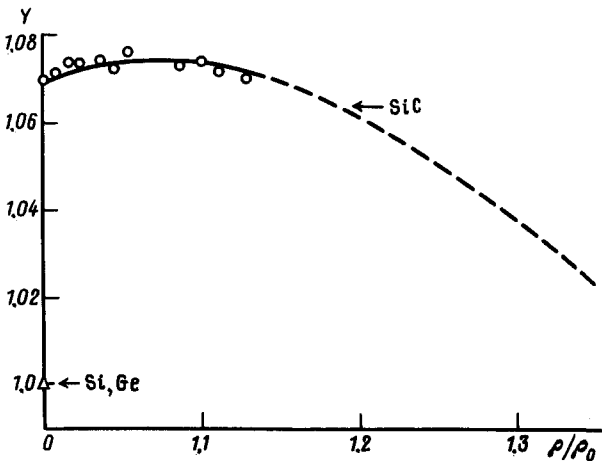


FIG. 3. The value of y at $q = 0.8$ (see the text proper) as a function of the degree of compression. ○—Experimental values; solid line—least-squares fit; dashed line—extrapolation to high compression; △—data on Ge and Si from Refs. 8 and 9.

Rosenstock.⁸ According to Ref. 8, a deviation of the quantity

$$y = \sum_i \omega_i^2(q) / \sum_i \omega_i^2(q=0)$$

from unity with $q \neq 0$ means that the crystal contains nonelectrostatic forces, which are acting between the atoms of the same ("trace-variable forces"). The most important of these forces in the case at hand are the noncentral interactions of a covalent nature which determine the stiffness of the lattice with respect to $TA(L)$ vibrations.

Figure 3 shows the results calculated from the expression above for $q = 0.8$ (by way of comparison, the corresponding value of y for diamond is ~ 1.15 , while that for germanium and silicon is^{8,9} ~ 1.0 , at $q = 1.0$ and at atmospheric pressure).

It can be seen from Fig. 3 that the compression of SiC weakens the noncentral interactions, which become negligible at a compression of 40%. That figure corresponds to a pressure of 150 GPa, according to our equation of state. This quantity may be taken as a lower limit on the transition pressure; it looks completely reasonable. The actual value of the transition pressure would apparently not differ from this value by more than a few tens of gigapascals, by analogy with germanium and silicon.

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¹⁾ In the SiC polymorphs, the atoms of one species are in a close-packing arrangement, differing from each other only in the order of alternation and in the number of atomic layers in the unit cell. The polymorphs have many physical properties in common; in particular, the phonon spectrum in the axial direction is universal.

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