Phonons in Si_{24} at Simultaneous *P, T*

Scientific Achievement

5/2017

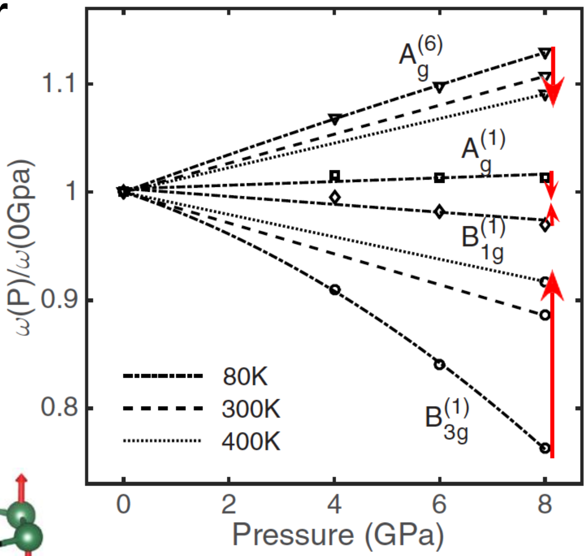
Combined *P,T* caused phonon shifts unexpected from either *P* or *T* alone.

Significance and Impact

Effects of *P* or *T* on phonon thermodynamics are usually assessed separately as "quasiharmonic" or "anharmonic" behavior, and results added.

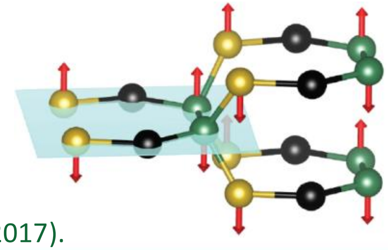
A large term in *P*x*T* was found for Si_{24} for ΔT = 320 K and ΔP = 8 GPa.

Entropy at simultaneously high *P, T* has novel behavior of importance to the Gibbs free energy.



Research Details

- Raman spectra of clathrate-structured Si_{24} were acquired at multiple *P*, *T* from 0-8 GPa and 80-400 K.
- *T* altered Raman shifts with *P* (and *P* altered shifts with *T*). Big differences between phonon modes; B_{3g} modes were most anomalous.
- In short, phonon anharmonicity changed strongly with pressure.



Top right: Fractional frequency shifts of Raman modes with pressure. Red arrows show changes with with increase in T from 80 to 400 K. Bottom left: Displacements of different Si atoms in the B_{3g} mode.

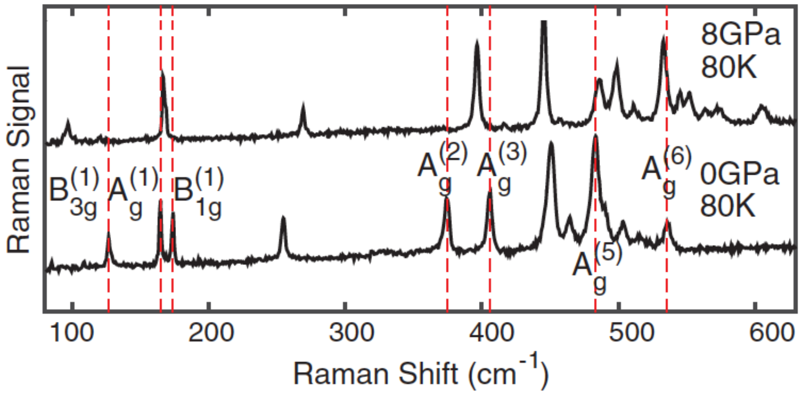
X. Tong, X. Xu, B. Fultz, H. Zhang, T.A. Strobel and D.Y. Kim, "Phonons in Si_{24} at simultaneously elevated temperature and pressure," Phys. Rev. B 95, 094306 (2017).

Backup Slide: Phonons in Si_{24} at Simultaneous *P, T*

Data and analysis

5/2017

Prepared Si_{24} from Na_4Si_{24}. Caltech student did Raman at Strobel's lab at Carnegie. DAC was heated and cooled, with He and Ar pressure media.



Assume $\omega(T, V)$

$$\Delta\omega = \left(\frac{\partial\omega}{\partial T}\right)_V \Delta T + \left(\frac{\partial\omega}{\partial V}\right)_T \Delta V$$

Define Grüneisen parameter, γ anharmonicity, A, and their derivatives

$$\gamma \equiv -\frac{V}{\omega}\left(\frac{\partial\omega}{\partial V}\right)_T \ , \ A \equiv \frac{1}{\omega}\left(\frac{\partial\omega}{\partial T}\right)_V \ , \ g_V \equiv \left(\frac{\partial\gamma}{\partial T}\right)_V \ , \ a_T \equiv V\left(\frac{\partial A}{\partial V}\right)_T$$

Phonon shifts depend on P, T, PT, and P^2. Seven Raman modes were fit, giving results at right.

$$\frac{\Delta\omega_i}{\omega_i} = \left[\frac{\gamma_{i0}}{B}\Delta P\right]_1 + [(A_{i0} - \gamma_{i0}\beta)\Delta T]_2 - \left[\frac{a_{iT}}{B}\Delta T\,\Delta P\right]_3 - \left[\frac{g_{iT}}{2B^2}(\Delta P)^2\right]_4 .$$