High-pressure elastic constants of solid krypton from quasiharmonic lattice-dynamics calculations

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The elastic constants of face-centered-cubic solid krypton in the pressure range 0–8 GPa at 300 K have been calculated from the classical quasiharmonic lattice-dynamics method using several empirical potentials. The calculated equation of state and elastic constants are in excellent agreement with experiments. The theoretical results confirm the observed trend $C_{11}>C_{12}>C_{44}$ derived recently from Brillouin-scattering measurements. Analysis of the mechanical stability conditions show no evidence of structural instability that may lead to a suggested phase transformation above 30 GPa. [S0163-1829(98)03030-6]

I. INTRODUCTION

Recently, the pressure dependence of the three adiabatic elastic constants (C_{11}, C_{12}, C_{44}) of solid krypton have been determined directly by *in situ* Brillouin-scattering spectroscopy up to 8 GPa on a single crystal.[1] The trend, $C_{11}>C_{12}>C_{44}$, is observed over the entire pressure range. This observation differs fundamentally from an earlier paper based on the analysis of the sound velocities, refractive index, and the density where the trend, $C_{11}>C_{44}>C_{12}$, was derived.[2] Furthermore, according to the latter assignment, the deviation from the Cauchy condition,[2,3] $\delta=(C_{44}-C_{12}+2P)/C_{12}$, will be significant at pressures higher than 30 GPa, which might lead to a phase transformation. The assumptions used for the derivation of the elastic constants in the earlier paper have been criticized.[1] The discrepancy between the two sets of elastic constants was attributed to the significant deviation of the ratio of the adiabatic (B_S) to isothermal (B_T) bulk modulus, $\gamma=B_S/B_T$, from unity. In the present paper, the adiabatic elastic constants and isothermal bulk modulus in the pressure range 0–8 GPa of solid krypton are calculated from the quasiharmonic lattice-dynamics method.[4] The theoretical elastic constants are in good agreement with the most recent experimental results.[1] Analysis of the mechanical stability conditions shows solid krypton hydrate is stable at 30 GPa and no structural phase transformation is expected. The organization of this paper is as follows. In the next section, the theoretical background and details on the calculation of the elastic constants are presented, then the results are compared with experimental data and the paper concludes with a discussion of the main results.

II. THEORETICAL AND COMPUTATIONAL DETAILS

Theoretical calculation of the elastic constants of solids under different thermodynamic conditions (T,P) can be approached in a number of ways. The adiabatic elastic constants under pressure can be obtained from the fluctuation of the strain in a constant pressure-constant enthalpy molecular-dynamics calculation.[6] This method has been applied to the calculation of the elastic constants of solid argon employing a Lennard-Jones potential.[7] A drawback of this approach is the large statistical error and very long simulation time required for greater accuracy.[7] An alternative approach is to employ lattice dynamics in the quasiharmonic approximation in which the free energy of a given system (F_{qh}) is calculated by[4,5]

$$F_{\mathrm{qh}}=F_o+F_{\mathrm{vib}},$$

where F_o is the configurational potential energy and F_{vib} is the vibrational contribution. The quasiharmonic approximation is well documented and will not be presented here. Recently, we have derived the necessary equations appropriate for the calculation of the elastic constants for molecular systems.[8] In essence, the appropriate matrix elements of the dynamical matrix are related to the appropriate acoustic sound velocities at the long-wavelength limit For a cubic crystal, the nonvanishing elastic constants are C_{11}, C_{12}, and C_{44}.[9] A detailed comparison of the calculated thermodynamic properties and elastic constants of rare-gas solids, including solid krytpon and using simple Lennard-Jones potentials, have shown that the accuracy of the quasiharmonic lattice-dynamics approximation is comparable to the Monte Carlo method.[10] Moreover, the calculated elastic constants of solid krypton at 115 K and ambient pressure are in good agreement with experimental measurements.[11] Therefore, we expected that the quasiharmonic lattice-dynamics approximation will be valid for the calculation of the elastic properties of solid krypton under external pressure.

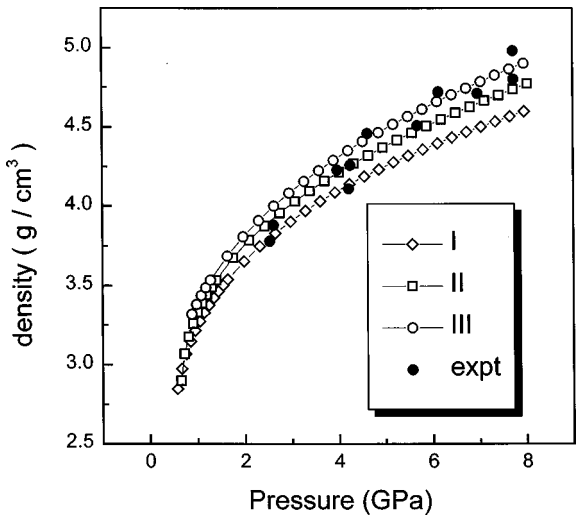

FIG. 1. The equation of state for solid krypton from 1 to 8 GPa.

Quasiharmonic lattice-dynamics calculations were performed with a reference cubic cell consisting of 8 krypton atoms and a lattice constant of 5.4 Å.[12] All calculations were performed at 300 K. The vibrational part of the elastic constant is computed from a uniform sampling of $5\times5\times5$ k points inside the Brillouin zone. Three two-body interatomic Kr-Kr potentials were used. The first potential (I) is a Lennard-Jones (12-6) potential with $\varepsilon/k=175$ K and $\sigma=3.65$ Å.[13] The second potential (II) is a simplified Bobetic-Barker potential[14] without the triplet interaction term. This potential was parametrized by fitting to the zero-temperature lattice constant, Debye temperature, and sublimation energy. A more sophisticated Morse-Spline-van der Waals interatomic potential function (III) derived by Buck *et al.* (case 2 in Table III of Ref. 15) is also used.[15] This potential was obtained from fitting the cross-section data for the Kr+Kr scattering reactions and had been shown to reproduce the second virial coefficient of liquid Kr and the experimental vibrational-level spacings of Kr_2 very well.

III. RESULTS AND DISCUSSION

A. Equation of state

We first examine the adequacy of the various empirical krypton potential models (I, II, and III) in reproducing the structure of face-centered-cubic krypton at high pressure. In Fig. 1, the equation of state (EOS) (pressure vs volume) computed from the three empirical potentials are compared with the room-temperature experimental results obtained from energy-dispersive x-ray diffraction using synchrotron radiation.[14] The agreement between the theoretical and experimental results ranges from highly satisfactory (potentials I and II) to excellent (potential III) over the entire pressure range from 0 to 8 GPa. In the low-pressure region, the predicted densities at 2.53 GPa of 3.80, 3.85, and 3.95 g/cm^3 for potentials I, II, and III, respectively, are in good accord with the observed value of 3.78 g/cm^3. At high pressure, the predicted density at 7.72 GPa of 4.58, 4.74, and 4.88 g/cm^3 for potentials I, II, and III compare favorably with the observed density of 4.80–4.98 g/cm^3. It is apparent that both potentials I and II underestimate the density of solid krypton at the high-pressure end and the accuracy of the simplified Bobetic-Baker potential is somewhat better than the simple Lennard-Jones potential. Potential III is by far the best empirical potential model for predicting the equation of state for solid krypton. Nevertheless, as will be shown later, the results obtained for the elastic constants are not critically dependent on the potential used. The excellent agreement between the calculated and experimental EOS confirms the applicability of the quasiharmonic lattice-dynamics approximation for high-pressure solid krypton.

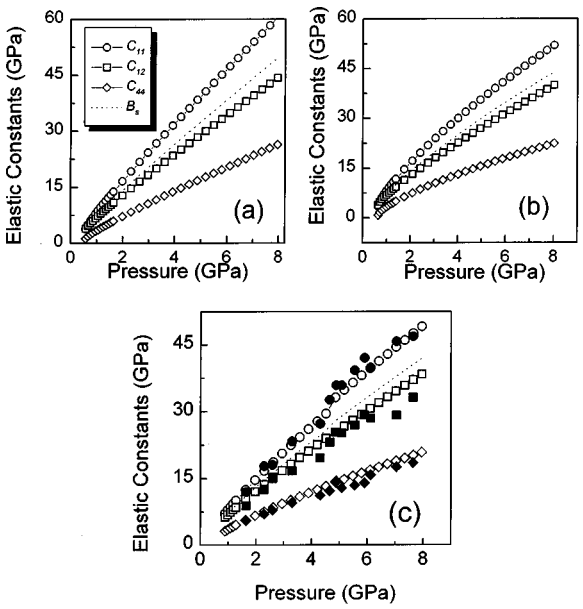

FIG. 2. Elastic constants for solid krypton calculated from several interatomic potentials (see text). (a) Lennard-Jones (potential I); (b) Bobetic (potential II), and (c) Buck (potential III). The solid symbols indicate experimental measurements from Ref. 1.

B. Adiabatic elastic constants

The calculated adiabatic elastic constants C_{11}, C_{12}, and C_{44} from potentials I, II, and III as a function of pressure are shown in Fig. 2. With the exception of potential I, the predicted adiabatic elastic constants from potentials II and III are in excellent agreement with those obtained from the recent Brillouin-scattering experiments over the entire pressure range.[1] The elastic constants calculated from potential I seem to be higher than the corresponding observed values. For example, at 8 GPa, the computed elastic constants of $C_{11}=60.5$ GPa, $C_{12}=44.2$ GPa, $C_{44}=26.4$ GPa are significantly higher than the extrapolated observed values of $C_{11}=52.6$ GPa, $C_{12}=36.2$ GPa, $C_{44}=20.1$ GPa. In contrast, the elastic constants obtained from potential II, $C_{11}=52.0$ GPa, $C_{12}=39.4$ GPa, $C_{44}=22.4$ GPa and those for potential III, $C_{11}=49.0$ GPa, $C_{12}=38.4$ GPa, $C_{44}=20.9$ GPa are in much better agreement with experiment.

The pressure dependence of the elastic constants is almost linear in the range 2–8 GPa. The experimental pressure derivatives of the elastic constants[13] ($\partial C_{ij}/\partial P$) are estimated to be 6.1, 4.1, and 2.4 for C_{11}, C_{12}, and C_{44}, respectively. The corresponding theoretical values are 7.3, 5.3, and 3.2 for potential I, 5.8, 4.5, and 2.5, for potential II, and 5.7, 4.4, and 2.4 for potential III. As expected, the results calculated from

the simplified Bobetic-Baker potential II and the Buck's potential III are superior to those obtained from the simple Lennard-Jones potential I. The adiabatic elastic constants increase monotonically with increasing pressure. At pressures higher than 2 GPa, the following sequence $C_{11}>C_{12}>C_{44}$ is always observed for *all* the potentials used here. The theoretically predicted trend is the same as that reported for a direction-dependent measurement of the acoustic velocities from Brillouin-scattering spectroscopy[1] and at variance with the trend, $C_{11}>C_{44},>C_{12}$, reported in an early study.[2]

It is interesting to examine the importance of the vibrational contributions to adiabatic elastic constants. The vibrations have only a minor effect on C_{44} and C_{12}, and do not seem to affect C_{11}. The elastic constants calculated from potential III without the vibrational components at 300 K and 0.89 GPa are $C_{11}=7.6$ (7.9), $C_{12}=4.7$ (6.8), $C_{44}=4.2$ (3.5) GPa, where the numbers in the parentheses are the correct values. The vibrational effects seems to diminish at higher pressure. This observation is not too surprising since the frequency spectrum of the solid shifts to higher energy with pressure. For example, at 6.1 GPa, $C_{11}=39.5$ (39.7), $C_{12}=28.3$ (30.6), $C_{44}=17.7$ (16.9) GPa.

The discrepancy between the two sets of measurements on the elastic constants of solid krypton has been attributed to a problem associated with the estimation of the envelope of sound velocities in the earlier Brillouin-scattering experiments.[1] One of the critical assumptions made was that the ratio of the adiabatic (B_S) to isothermal (B_T) bulk modulus, $\gamma=B_S/B_T\approx 1$. However, in general, $\gamma>1$ for simple molecular solids and only decreases to 1 at high pressure.[16] The isothermal and adiabatic bulk modulus can be computed directly from quasiharmonic lattice-dynamics calculations. The ratio γ obtained from potential III from 0.8 to 8 GPa is depicted in Fig. 3. As expected, γ deviates significantly from unity at low pressure but decreases rapidly to the theoretical limit at high pressure. The predicted γ is 1.30 at 1 GPa and 1.04 at 6 GPa. The results obtained here fully support the argument presented in the recent paper that the assumption of a constant $\gamma=1$ in the earlier work is not valid.

C. Mechanical instability

The stability of a crystal is determined by Born's stability conditions.[3,8] For a cubic crystal to be stable, the following conditions must be satisfied:

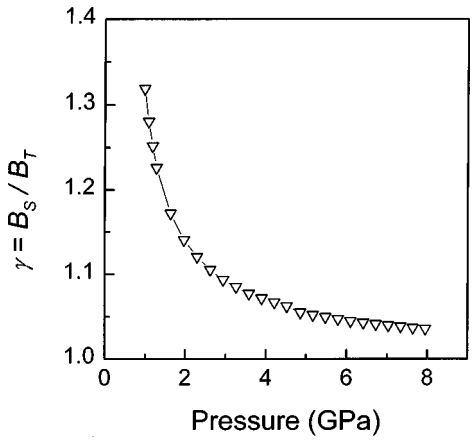

FIG. 3. Calculated ratio (γ) of adiabatic (B_S) and isothermal (B_T) vs pressure.

$$C_{11}-C_{12}>0,$$

$$C_{44}>0.$$

The first stability condition was found to be violated at around 0.6 GPa for potential I and 0.7 GPa for potentials II and III. These calculated critical pressures are very close to the melting point of solid krypton at 0.83 GPa at room temperature. Therefore, the calculated instability probably indicates the onset of a melting transition. The suggestion of a possible structural instability above 30 GPa was also investigated. According to the theoretical results, in the entire pressure range up to 30 GPa the deviation from the Cauchy condition (δ) remains small and the Born's stability conditions are obeyed. Our results, therefore, do not support a possible phase transformation at this pressure.

IV. CONCLUSIONS

Quasiharmonic lattice-dynamics calculations have been employed to determine the elastic constants for solid krypton in the pressure range 0–8 GPa. The theoretical results obtained using the potential proposed by Buck *et al.*[15] are almost in quantitative agreement with the experimental structural and elastic constant data. The theory reproduces the trend, $C_{11}>C_{12}>C_{44}$, reported in the recent Brillouin-scattering measurements.[1] It is shown that the assumption of $\gamma\approx 1$ over the entire pressure range employed in an earlier analysis of the acoustic sound velocities is incorrect.

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