

Raman scattering in hcp rare gas solids under pressure

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We present Raman measurements of hcp rare gas solids (RGSs) at megabar pressures together with lattice dynamics calculations. The E_{2g} phonon was measured in Xe up to metallization near 135 GPa and in Ar up to 58 GPa. A comparative analysis of first-principles and semiempirical calculations shows that three-body forces contribute to the energetics at low pressures and that at volume compressions greater than ~ 2.6 higher-order many-body forces become important. The distinct behavior of He under pressure relative to that of the rest of the RGS family is discussed.

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I. INTRODUCTION

Among cryocrystals only quantum crystals—solid helium, J -even solid hydrogens (p -H₂, o -D₂), and HD—crystallize in the hexagonal close-packed (hcp) structure at ambient or low pressure. The heavier or classical rare gas solids (RGSs)—Ne, Ar, Kr, and Xe—crystallize in the face-centered cubic (fcc) structure. Diamond-anvil-cell studies have shown that the hcp phase can be formed stably and metastably in Xe,¹ Kr,² and Ar,³ with the fcc and hcp phases coexisting over a broad range of pressures. X-ray diffraction measurements have shown that hcp Kr and Xe appear below 4 GPa;^{2,4} the hcp phase in Ar has been observed at 47 GPa.³ The hcp/fcc ratios then tend to increase with pressure until the transition is complete.^{2,3} Estimated pressures for the equilibrium fcc-hcp transition in Ar and Kr are 310 (Ref. 3) and 170 GPa,² respectively. In Xe at room temperature the hcp/fcc ratio reaches unity at 70 ± 5 GPa.^{2,4,5} In addition, the hcp phase of Xe becomes metallic around 140 GPa^{6–8} and is predicted to be superconducting at higher pressure.⁹

Unlike fcc, the hcp structure has optical branches in the phonon spectrum. At the center of the Brillouin zone, one of the branches, an LO mode, is polarized along the c axis. The doubly degenerate TO mode (symmetry E_{2g}) is polarized within the hexagonal planes and is Raman active. It corresponds to the out-of-phase shear motions of the layers of atoms in the two orthogonal directions in the ab plane. The study of the pressure effects in the lattice vibrations of RGS can be very helpful to improve the current understanding of their electronic and structural properties. However, as yet, little has been done in this matter and the available experimental studies are constrained to relative low pressures. There are low-pressure neutron data up to 0.5 GPa¹⁰ and Raman-scattering data up to 1 GPa¹¹ for the E_{2g} phonons in solid He. Recently, Raman spectra for solid Xe up to 41 GPa were published,¹² but no data exist for other hcp RGS. Here we report the first Raman measurements for solid hcp Ar and Xe at megabar pressures and compare the results with theoretical calculations and previous experiments.

II. EXPERIMENTAL DETAILS AND THEORETICAL CALCULATION METHODS

Though not widely used for RGS, Raman scattering complements x-ray diffraction^{1–4,8} by providing direct information on vibrational dynamics and details of intermolecular interactions. First-order Raman scattering is allowed in the hcp RGS but the intensity of this Raman excitation is very low because of the lack of substantial electron density between atoms (the electronic density of RGS atoms is located spherically around the nuclei). Thus, Raman experiments (especially in diamond cells with the small samples that can be probed) require highly refined experimental methods. In our experiments we used Raman systems with high optical throughput as described elsewhere.¹³ The spectra were excited with the 514.5 and 488 nm lines of Ar-ion lasers. In order to decrease stray light, we used a 135° scattering geometry. High-purity Xe and Ar were loaded cryogenically and at room temperature at 0.2 GPa, respectively, in the 50–100 μm gasket holes of rhenium gaskets in diamond-anvil cells. Very low-fluorescence synthetic type II(a) diamonds were used as anvils.

We have performed density-functional theory (DFT) calculations of the Raman frequencies in Xe and Ar. To further understand the systematics in the hcp RGS family we also performed calculations for He. For Ar and Xe we used the Vienna *ab initio* simulation package (VASP).¹⁴ For He the full-potential linear muffin-tin orbital (FP-LMTO) code¹⁵ was used. Both codes are all-electron full-potential methods widely used for high-pressure calculations. The generalized gradient approximation (GGA) has been used for all considered systems. All the DFT calculations were done for $T = 0$ K disregarding zero-point vibrations.

In addition to the DFT calculations, which do not properly treat van der Waals interactions (very important at low compressions^{16,17}), we also performed semiempirical calculations for He, Ar, Kr, and Xe. This approach provides insights in terms of potentials of the interatomic interactions. In these calculations we used a many-body interatomic po-

tential U_{tot} having pair (U_{p}) and triple (U_{tr}) forces ($U_{\text{tot}} = U_{\text{p}} + U_{\text{tr}}$) and two types of pair potentials. The best available pair potentials for rare gas solids are the Aziz pair potentials (He),¹⁸ (Ar and Kr),¹⁹ and (Xe),²⁰ which reproduce a variety of experimental gas phase data, as well as zero-temperature, zero-pressure properties of the solid phase. However, the pure pair potential does not describe properly the properties of the solid-state phase and many-body corrections should be taken into account. At modest pressures the main correction comes from the three-body dispersion interaction. At high pressures the many-body exchange effects should be taken into account. The Aziz pair potential is known to overestimate the pressure for a given volume, as the repulsion is too strong at short distances and should be softened by adding the three-body exchange correction term. Here we restrict ourselves to the three-particle interaction, which consists of three-body dispersion (Axilrod-Teller) and exchange terms. For all RGSs the latter was used in a Slater-Kirkwood form.^{21,22}

There has been many attempts to propose effective pair potentials which would have the same softening effect as attractive many-body forces.^{23–25} For compressed solid Kr and Xe the short-range behavior of the Aziz potentials was corrected by Kim *et al.*²⁴ with a two-term polynomial correcting term. The resulting pressure-volume equations of state (EOSs) were in good agreement with experiment to the highest available experimental pressures. The same approach has been successfully used by Hemley *et al.*²⁵ modifying the Silvera-Goldman potential for H_2 and D_2 ,²⁶ with a similar short-range correcting term. At the same time, the effects of these corrections on the properties other than EOS need to be examined. For example, a significant softening of the E_{2g} phonon was found using the corrected potential for hcp H_2 and D_2 .²⁷ We checked the accuracy of this effective pair potential for the lattice dynamics in the present work.

In the semiempirical calculations we also restrict ourselves to $T=0$ K. The zero-point energy was taken into account using an Einstein approximation. For the heavier RGS, this approximation is valid for the whole pressure range under study, but for He we excluded from consideration the small pressure range (~ 0.1 GPa) where quantum-crystal effects play a decisive role. All calculations were done for the ideal ratio $c/a = \sqrt{8/3}$. High-pressure x-ray studies of He give $c/a = 1.630 \pm 0.005$.²⁸ Measurements for the heavier RGS^{1–3,29} show that c/a remains nearly constant and close to the ideal value on compression. Our calculations show that the deviation of the axial ratio from ideal remains small (of the order of 10^{-3}) up to the highest experimental pressures for all hcp RGS (detailed results will be published elsewhere). The EOSs calculated previously with the same model for all the RGS are in excellent agreement with experiment.²²

III. RESULTS AND DISCUSSION

We report the first Raman spectrum of hcp Xe (Fig. 1) over a broad range of pressures up to metallization. As the metallization transition is approached (at 135 GPa), the E_{2g} peak broadens markedly suggesting an increase on the electron-phonon interaction.

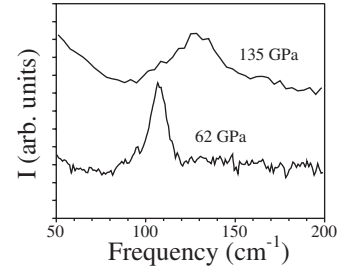


FIG. 1. Raman spectra of hcp Xe at selected pressures.

Experimental and theoretical pressure dependencies of E_{2g} phonon frequencies for hcp Xe and Ar are presented in Fig. 2. At low compressions the semiempirical calculations agree with experiment somewhat better than DFT: for Ar at 30 GPa the root-mean-square deviations from experiment are 8.2 and 11.5 cm^{-1} , respectively. However for DFT the deviations decrease with rising pressure, while for the semiempirical calculations they increase and between 55 and 60 GPa (volume compression of ~ 2.6) the differences become negligible. For Xe the DFT Raman frequencies are in good agreement with experiment throughout the whole studied range (60–135 GPa); the comparison made in a previous Raman study to 40 GPa¹² showed that good agreement extended down to 20 GPa but at lower pressures the experimental and theoretical results diverged. The curves obtained for the many-body semiempirical potential agree with experiment from the lowest pressures up to ~ 75 GPa (volume compression of ~ 2.7). At higher pressures as metallization is approached the frequencies are progressively overestimated due to the neglect of still higher-order many-body contributions. The effective pair potential, on the other hand, gives rather poor description of the Raman frequencies (Fig. 2, dotted curves): for both Xe and Ar they are strongly underestimated at low and intermediate pressures and overestimated at high pressures.³⁰ The curves obtained for the pure pair Aziz potentials lie very close to that obtained for the

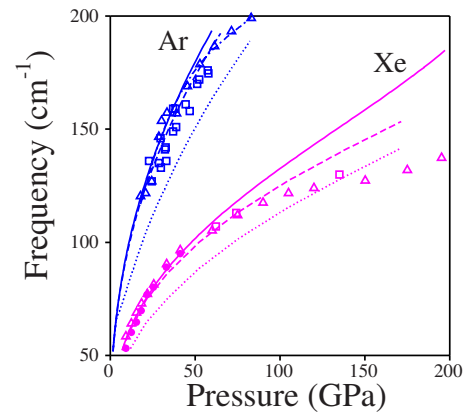


FIG. 2. (Color online) Experimental and calculated Raman frequencies as a function of pressure for hcp Ar and Xe. Experiment: present work (empty squares); full circles (Ref. 12). Semiempirical calculations: many-body potentials (solid lines); pair potentials (dashed lines); and effective pair potentials (dotted lines). DFT calculations (empty triangles); the dot-dash line through the empty triangles for Ar serves as a guide for the eyes.

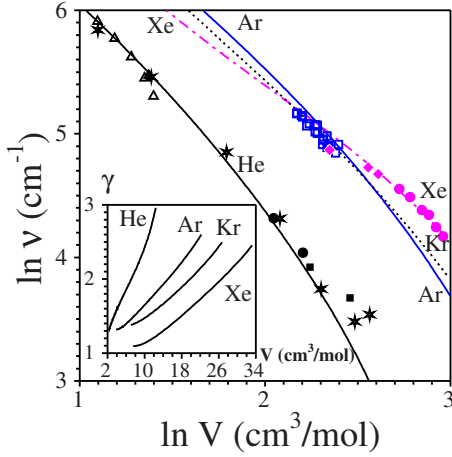


FIG. 3. (Color online) Raman frequencies of hcp RGS as a function of volume. Semiempirical many-body calculations: Ar (solid line), Kr (dotted line), and Xe (dot-dash line). Experiment: present work—Ar (empty squares); Xe (full diamonds), full circles—Ref. 12. He: semiempirical many-body calculations (solid black curve); DFT calculations (asterisks); experiment: Raman data [full black circles;¹¹ neutron data [full black squares¹⁰]; open triangles (calculated using C_{44} data from Ref. 28)]. Inset: Grüneisen parameter as a function of volume.

many-body potentials, suggesting the contribution from the three-body forces is small (Fig. 2, dashed curves). This conclusion is however incorrect: while pure pair potentials give a good description of volume dependencies, to obtain the pressure dependencies of the Raman frequencies we need the EOS, in which three-body forces contribute appreciably. Thus, calculated Raman frequencies are rather sensitive to the many-body component of the potential.

The volume dependencies of the Raman frequencies $\nu(V)$ of all hcp RGS (including also He and Kr) are shown in Fig. 3. For Ar, Kr, and Xe the calculated $\nu(V)$ curves cross: at small compression the calculated phonon frequencies increase (at the same volume) following the sequence Ar-Kr-Xe but at high compressions the sequence is reversed. The reason for this behavior is that for a given volume the mode-Grüneisen parameter $\gamma = -\partial \ln \nu / \partial \ln V$ (Fig. 3, inset) is the largest for Ar and the smallest for Xe. We found that $\gamma(E_{2g})$ strongly decreases with volume for all hcp RGS. For example, for Xe it decreases from 1.8 at 5 GPa down to 1.5 at 20 GPa (in contrast with the constant value of 2.1 obtained in Ref. 12 in this pressure range) and further falls to 1.25 at 75 GPa. The calculated Raman frequencies for solid He (both DFT and many-body semiempirical) agree with existing Raman¹¹ and neutron¹⁰ data. At higher pressures, theoretical frequencies agree with the data estimated from the experimental elastic constant C_{44} ²⁸ using the relation between $\nu(E_{2g})$ and C_{44} (Refs. 31 and 32): $\nu(E_{2g}) = (2\pi)^{-1} [4\sqrt{3}a^2 C_{44} / (mc)]^{1/2}$, where a, c are the lattice parameters and m is the atomic mass.³³ The calculated volume dependence of the Grüneisen parameter γ at high pressures agrees with that obtained from the mean sound velocity,²⁸ while at lower pressures it increases somewhat faster than the experimental value (theoretical γ equal to 2.07 and 2.24 in comparison with the Raman values¹¹ of 1.81 and 1.94 at

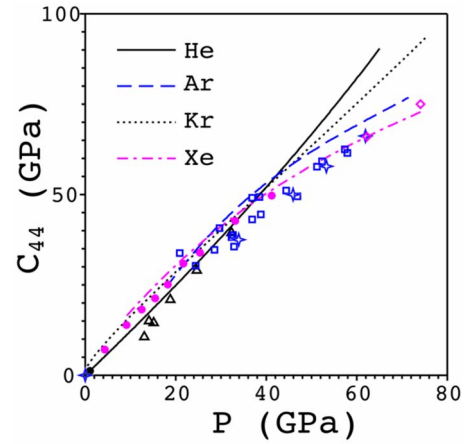


FIG. 4. (Color online) Calculated C_{44} as a function of pressure for all hcp RGS. Lines correspond to theoretical Raman frequencies. Symbols: He—empty triangles are experimental C_{44} data from Ref. 28; Ar—four-pointed stars are data of *ab initio* calculations, other symbols are C_{44} values corresponding to experimental Raman frequencies: He—black full circles,¹¹ Ar—empty squares (this work), Xe—full circles¹², and empty diamonds (this work).

7.74 and 9.06 cm^3/mol , respectively); this is presumably due to an increase in anharmonic effects at large volume.

The good agreement between the semiempirical and first-principles results holds up to much higher compressions for He than for Ar and Xe (Fig. 3). As discussed above, the discrepancy between these theoretical approaches indicates that many-body forces higher than three-body become essential. At the same time, the absence of such discrepancy to fivefold compression and higher does not mean that these higher-order forces remain insignificant. Our explanation of the difference between the situation in He and other RGS is the following. It is known that the He lattice is swelled due to large zero-point vibrations. To estimate this dilatation, we first note that the zero-pressure molar volume of heavy RGS (Ne, Ar, Kr, and Xe) with good accuracy follows a scaling law $V_0/\sqrt{m} \approx 3 \text{ cm}^3/\text{mol}$, where V_0 is the zero-pressure molar volume (in cm^3/mol) and m the atomic mass number. If zero-point vibrations were not present, solid He would obey this scaling and its effective zero molar would be $V_0^{\text{eff}} \approx 6 \text{ cm}^3/\text{mol}$, i.e., the swelling effect is huge. Until the volume reaches about V_0^{eff} the main effect of the external pressure is the suppression of the zero-point vibrations and not the compression of the electron shells. The effective compression should be evaluated relative to V_0^{eff} and the compressions reached in experiment are thus smaller.

Figure 4 displays the shear elastic modulus C_{44} estimated for all the hcp RGS using the harmonic lattice dynamics relation between the Raman frequency $\nu(E_{2g})$ and C_{44} (see Ref. 33). In the absence of direct experimental data such estimates could be very useful especially under extreme conditions. For He and Kr as well as for Ar and Kr at low compressions we used our semiempirical frequencies. At higher compressions the DFT frequencies were used. Also shown are C_{44} values calculated using experimental Raman frequencies. In the case of He due to the availability of experimental data on C_{44} up to 32.3 GPa,²⁸ it was possible to

check that the relation between $\nu(E_{2g})$ and C_{44} works fairly well, as might be expected, since this is the range of pressures where the pair plus three-body potential is valid, that is, the conditions (1)–(3) (see Ref. 33) are fulfilled. *Ab initio* calculated C_{44} for Ar using the stress-strain method shown in Fig. 4 are consistent with the analysis. That is why it is believed that for other hcp RGS the estimates for C_{44} obtained in this work from Raman frequencies are quite reliable. It is interesting to note that the $C_{44}(P)$ curves (Fig. 4) display distinct behavior at high and low compressions: C_{44} for Kr increases with pressure near linearly; for Ar and Xe C_{44} increases at a sharply decreasing rate, in contrast, for He the rate of increase in C_{44} increases with pressure.

IV. CONCLUDING REMARKS

In conclusion, we present experimental Raman frequencies as a function of pressure for hcp Ar and Xe to megabar pressures as well as theoretical results using complementary approaches. As the metallization transition is approached, in Xe the E_{2g} peak broadens markedly suggesting an increase in the electron-phonon interaction. The first-principles DFT Raman frequencies are in good agreement with experimental data throughout the experimentally studied pressure ranges; this includes up to the metallization pressure of Xe (volume

compression of ~ 3.4). However, at low compressions the DFT results are somewhat worse than semiempirical calculations. The semiempirical results for Ar and Xe based on the two- plus three-body potential agree with experiment up to volume compressions of 2.6–2.7. At higher compressions the semiempirical calculations tend to overestimate the phonon frequency because they neglect higher-order many-body contributions. The general systematics in the pressure and volume dependencies of the Raman frequencies in the hcp RGS family (He, Ar, Kr, and Xe) are analyzed and explained in terms of the volume behavior of the mode-Grüneisen parameter and more fundamentally in terms of interatomic interactions. Due to the large zero-point vibrations, the behavior of solid He under pressure is a special case in the hcp RGS family.

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- ³⁰It should be noted that this effective potential has a drawback as applied to lattice dynamics calculations: since the potential function has only two continuous derivatives at the joint point it gives rise to a nonphysical kink at the resulting curves; this is

readily seen (Fig. 2) for Ar in the point where the dotted curve goes over to the dashed curve.

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³³This relation follows from lattice dynamics studies of the hcp crystal lattice (Ref. 31) and is exact if the following conditions are met: (1) anharmonic effects are negligible, (2) interactions beyond the next-nearest neighbors are negligible, and (3) four-body and higher many-body interactions are negligible. If some of the conditions (1)–(3) are invalid one might expect that the simple relation between C_{44} and $\nu(E_{2g})$ breaks down. The applicability of this relation for various hcp metals was examined

(see, for example, Refs. 34 and 35) and it was shown to hold fairly well even though the fulfillment of the conditions (2) and (3) is questionable. For the hcp van der Waals solids (He, H₂, D₂, and β -N₂) the same question has been analyzed in Ref. 32. For these substances, especially for solid helium and hydrogens near normal pressure, the most critical is the condition (1). Nonetheless, the departure from the relation was shown to be small.

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