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Pressure-induced structural transformation in solid xenon studied by Raman spectroscopy

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High-pressure transformation from face-centered cubic (fcc) to hexagonal close-packed (hcp) structures of solid xenon has been observed between 5 and 41 GPa in a diamond-anvil cell by Raman spectroscopy. The transverse optic E_{2g} mode, which is Raman active in the hcp phase, starts to appear around 40 cm^{-1} at a pressure of 5 GPa. The Raman frequency increases to 95 cm^{-1} at 41 GPa. Moreover, the intensity of the Raman band grows with pressure and shows a remarkable increase around 20 GPa. These vibrational properties were reproduced almost quantitatively by first-principles calculations. The behavior of high-pressure fcc-to-hcp transformation is compared with previous x-ray experiments and theoretical calculations on solid Xe.

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Rare-gas solids are usually believed to be the simplest substances in nature because of their closed-shell electronic configurations. These solids are an important class of materials[1–3] that provide an ideal system, allowing fruitful comparisons between theory and experiments.[1] A number of studies have been carried out to investigate the pressure-induced transformation in the heavy rare-gas solid xenon (Xe) from face-centered cubic (fcc) to hexagonal close-packed (hcp) structures by x-ray diffraction experiments[4–7] and theoretical calculations.[5,8–10]

High-pressure x-ray diffraction study at room temperature has shown that Xe transforms at 14 GPa from the fcc structure to an intermediate close-packed phase, and then transforms completely to hcp structure at 75 GPa.[4] Laser heated diamond-anvil cell (DAC) experiments showed, however, that the direct fcc to hcp transformation occurs at 21 GPa and is kinetically sluggish.[5] On the other hand, recent angle-resolved x-ray diffraction data revealed that a martensitic fcc-to-hcp transformation takes place between 3 and 70 GPa without any intermediate phase. The transformation is very sluggish, and two phases coexist over a wide pressure range.[6] Furthermore, for the fcc-to-hcp transformation in solid Xe, the fraction of hcp phase as a function of pressure was estimated from the relative intensity ratio of hcp (100) and fcc (200) reflections by using an angle dispersive x-ray diffraction.[7] Recently, first-principles calculations have revealed the origin of the sluggishness during the fcc-to-hcp transformation and the underlying mechanism for the persistence in completing this transformation.[9] Most recently, first-principles study has also been performed to investigate the electron-phonon coupling in the high-pressure hcp phase of Xe for the prediction of pressure-induced superconductivity at ultrahigh pressures.[10]

Until now, there is no optical spectroscopic study for the pressure-induced fcc-to-hcp transformation in solid Xe. High-pressure Raman scattering is a suitable method to probe the hcp phase in which a Raman-active vibrational mode appears as a different single Raman band. This is in contrast to the fcc phase where no Raman-active mode is allowed.

In this Brief Report, high-pressure Raman spectroscopy is applied up to 41 GPa to reveal the phase transformation from fcc to hcp structure in solid xenon, and this experimental result is examined by making the first-principles calculations. This structural transformation of solid Xe around 5−41 GPa is investigated by comparing with the previous x-ray experiments and theoretical calculations.

High-pressure Raman experiments were carried out using a DAC with a metal gasket. The hole of the gasket, serving as the sample chamber, was set to about 100 μm in diameter and 100 μm in thickness. For loading the Xe sample in the DAC, we condensed commercial gaseous Xe by spraying the vapor into the gasket hole of the DAC cooled in a liquid nitrogen bath (freezing temperature of Xe is about 116 K). To avoid contaminations, loading of Xe was carried out in a dry nitrogen atmosphere. Single phase fcc crystals of Xe were grown by adjusting the pressure on seed crystals, which coexist with the fluid Xe at about $P=0.4$ GPa and room temperature. No pressure transmitting medium was used because solid Xe is a soft material. The pressure was measured by the ruby-scale method.[11] To minimize the effect of pressure gradient in the sample across the anvil, we used a tightly focused laser spot less than 10 μm, which is much smaller than the sample size (about 50 μm). Raman spectra were measured in a backscattering geometry with a micro-Raman spectrometer (JASCO NR 1800) equipped with a triple polychromator and a charge-coupled device detector. The 532.0 nm line of a solid laser (Coherent Verdi2W) was used for the excitation at a power level of about 100 mW. The spectral resolution was about 1 cm^{-1}.

First-principles calculations of Raman frequencies and intensities were performed using linear response pseudopotential plane wave method in the framework of density-functional perturbation theory.[12] The local density approximation was used. A Troullier-Martins norm-conserving pseudopotential was constructed with radius cutoff of 2.1, 2.1, and 2.5 a.u. for the *s*, *p*, and *d* orbitals, respectively. The first Brillouin zone integration employed a $12\times12\times8$ Monkhorst-Park mesh.[13] All calculations were performed with the QUANTUM-ESPRESSO code.[14] The Raman cross sections were calculated with the *ab initio* density-functional scheme using the PWSCF package. The basic con-

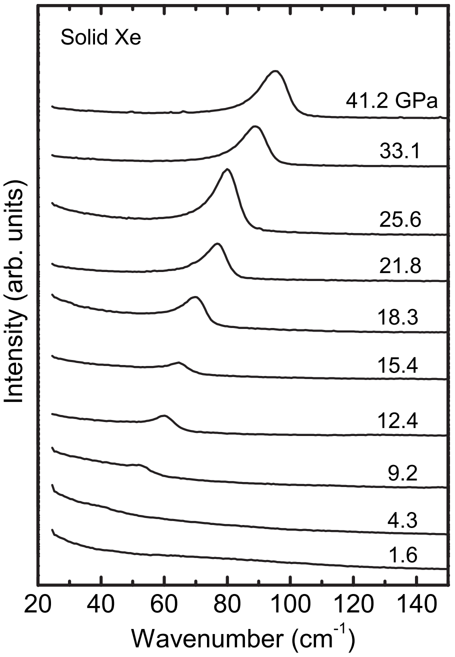

FIG. 1. Pressure-induced Raman spectra of solid xenon at various pressures up to 41 GPa. The E_{2g} (TO) vibrational mode, which is Raman active in the hcp phase, appears at about 40 cm^{-1} and around $P=5$ GPa, and its Raman-band intensity increases with increasing pressure.

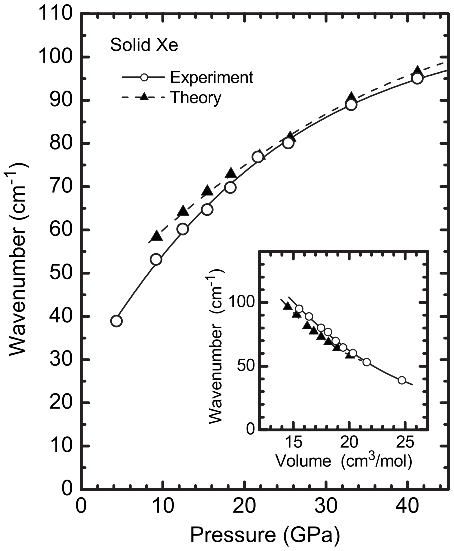

FIG. 2. The frequency of transverse optic E_{2g} mode as a function of pressure up to 41 GPa in the hcp phase. Open circles and solid triangles show the present experimental and first-principles calculations, respectively. The inset shows the volume dependence of experimental and theoretical Raman frequencies.

cept is solving the change of charge polarizations due to the perturbations introduced by the vibration (zone-center phonon). The background theory and computational techniques have been described in Refs. 12 and 13.

Figure 1 shows Raman spectra of solid Xe at various pressures up to 41 GPa. A Raman band starts to appear around 5 GPa at a wave number of 40 cm^{-1}. The Raman frequency increases with pressure, reaching 95 cm^{-1} at 41 GPa (open circles in Fig. 2). The Raman profiles are asymmetric at high pressure due to the pressure gradient in the probed area. As mentioned above, no Raman-active mode is allowed for the fcc solid Xe. However, in the hcp phase, the transverse optic (TO) E_{2g} mode appears as a Raman-active band. The appearance of this new Raman band indicates directly the presence of a hcp structure in the fcc phase. Since small hcp phase crystals appear at random in the fcc phase crystals, the hcp phase crystals are expected to be polycrystalline. Therefore, the Raman signals show the average properties of the E_{2g} mode. To characterize this E_{2g} phonon mode, we performed first-principles calculations at high pressures. The calculated Raman frequencies as a function of pressure are shown as solid triangles in Fig. 2. The inset shows the volume dependence of experimental and theoretical Raman frequencies. It can be seen that the calculated E_{2g} vibrational frequencies are in good agreement with the experiment except for pressures lower than 20 GPa. This little difference is to be expected, since the weak van der Waals interactions which dominate at low pressures are not described correctly by the density-functional theory. The appearance of the hcp phase at 5 GPa is in good agreement with previous x-ray experiments[4,6] and theoretical calculations.[5,8] For lattice dynamics, we can estimate the mode Grüneisen parameter γ (E_{2g}) of the hcp phase from $\gamma = -d \ln \nu / d \ln V$, where ν is Raman frequency and V is volume.[15] Using the equation of state of solid Xe (Ref. 16) and the present Raman data at high pressures, $\gamma(E_{2g})=2.1$ was determined at pressures of 5–20 GPa. This value falls within the normal values, which range approximately from 1.3 to 2.3 at room temperature.[17]

To investigate the pressure-induced fcc-to-hcp transformation, we estimated the pressure dependence of the integrated intensities of observed Raman bands (Fig. 1) shown as open circles and open triangles in Fig. 3. The Raman measurements at various pressures were performed carefully to maintain the same experimental conditions such as laser power, sample position under incident laser, and the detection system of scattered light. As indicated by the thick solid curve in Fig. 3, the Raman intensity increases gradually at 5–10 GPa, but shows a remarkable increase around 20 GPa and becomes almost constant around 41 GPa. The deviation of the Raman intensity from the thick solid line at about 25 GPa may be related to a recent study by Kim *et al.*,[9] which revealed a change in the mechanism of pressure-induced fcc-to-hcp transformation at 25 GPa, i.e., the fcc and hcp phases coexist between 5 and 41 GPa, and above this, changes in the Raman vibrational frequencies and intensities imply that the hcp phase continuously evolves from the fcc phase and both phases coexist between 5 and 41 GPa. Above this pressure, the conversion to the hcp phase is almost completed.

The Raman-scattering cross section of the transverse E_{2g} mode was estimated from first-principles calculations. The results are respresented by open squares and a thin solid line in Fig. 3. The calculated intensity vs pressure curve shows a small kink around 25 GPa, and then the intensity increases continuously up to 41 GPa. The predicted behavior is

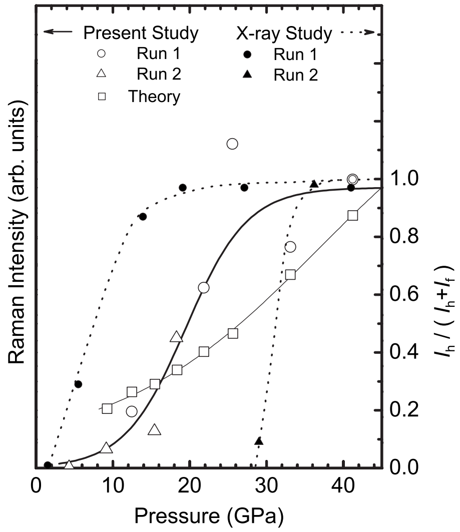

FIG. 3. Pressure dependences of the integrated Raman-band intensities are shown by open circles and open triangles, and a thick solid curve shows the experimental tendency in spite of a jumped point of Raman intensity at about 25 GPa. First-principles calculations are presented by open squares and shown by a thin solid line. For comparison, x-ray data of the relative proportions of fcc and hcp phases (Ref. 7) are shown by solid circles and solid triangles as a function of pressure, where broken lines also serve as a guide for the eye. The x-ray saturated level at high pressure is set to $I_h/(I_h+I_f)=R=1$, where I_f and I_h are the integrated intensities of the fcc (200) and hcp (100) reflection peaks, respectively. Here, experimental and theoretical Raman intensities are scaled by arbitrary units, but their saturated points at highest pressure are set nearby the x-ray saturated $R=1$ for convenience.

sligthly different from the experimental Raman results, and the theoretical results provide supporting evidence on the growth of the hcp phase with pressure.

Errandonea *et al.*[7] have determined the relative amounts of hcp to fcc phase at high pressures. In Fig. 3, their results of $I_h/(I_h+I_f)=R$ are plotted by solid circles and solid triangles as a function of pressure. I_f and I_h are the integrated area of the fcc (200) and hcp (100) reflection peaks, respectively. The pressure dependence of R, i.e., the observed trend of hcp growth, is consistent with the present Raman experiments. Cynn *et al.*[6] also observed two types of pressure dependence of R, depending on the thermodynamic path (P-T history) of samples: (1) a linear increase of R against pressure, and (2) the sudden jump of R from 0.55 to 0.85 around $P=25$ GPa. Most recently, this sudden jump around 25 GPa has been interpreted to be due to the appearance of an orthorhombic distortion.[9]

It has been known that Xe transforms from the fcc to hcp phase over a wide range of pressure.[4–10] This seems to be originated from (1) the mechanism of the fcc-to-hcp transformation[4,6,9] and (2) different experimental conditions.[6,7] For example, the transition pressure is dependent on the thermodynamic path (P-T history) and the hydrostatic condition of the observed area (the difference in the pressure gradient probed by large-size x-ray beam and small-size laser beam). At present, it is not easy to provide a clear reason to rationalize the different pressure ranges observed for the coexistence of the two phases. The present results show that the fcc and hcp phases coexist from 5 to 41 GPa, which is in agreement with the observation of Errandonea *et al.*,[7] but is much narrower than about 70 GPa reported earlier.[4,6] It is noteworthy that Raman measurements offered two notable advantages than previous experimental methods. (1) There is ambiguity in identifying the hcp phase as this can be characterized by a different and unique Raman band, and the intensity can be used to monitor the growth of the hcp phase. (2) A tightly focused laser beam less than 10 μm helps to minimize the effect of the nonhydrostatic condition. Therefore, we believe that the present application of Raman spectroscopy to the fcc-to-hcp transformation of solid Xe is significant, and will present additional evidence for further studies of Xe under extreme conditions.

Finally, we investigate the relation between the hexagonal structure and the E_{2g} phonon mode. E_{2g} is a zone-center transverse optic shear mode, in which successive hexagonal planes perpendicular to the c axis vibrate against each other. Therefore, the E_{2g} mode probes the interlayer interactions. An increase in Raman frequency with compression indicates the strengthening of interplanar interactions. An increase in Raman intensity implies the growth of hcp structure and corresponds to the evolution of hcp domains, i.e., the successive introduction of more and more hexagonal stacking faults in the fcc phase.[6]

The elastic shear modulus C_{44} can be extracted from the frequency of the E_{2g} mode using the relationship $\gamma(E_{2g})=(1/2\pi)[4\sqrt{3}a^2C_{44}/(mc)]^{1/2}$, where a and c are the lattice constants and m the atomic mass.[18] This relation was derived from simple concepts like three-body forces. Therefore, one should be cautious on the validity of this model.[17] Nevertheless, using $c/a=1.63$, because of almost ideal ratios at high pressures,[4,7] we have estimated approximate values of C_{44} to be about 14.9 GPa at $P=10$ GPa and 39.2 GPa at $P=30$ GPa. In the near future, high-pressure Brillouin scattering study[3,19] will directly reveal all of elastic constants in solid Xe.

In summary, pressure-induced fcc-to-hcp structural transformation in solid xenon has been unambiguously observed by Raman spectroscopy in a diamond-anvil cell. The increase in the intensity of Raman-active transverse optic E_{2g} band indicated that the hcp phase continuously evolves in the original fcc phase of solid Xe at a wide pressure range between 5 and 41 GPa. The experimental results were reproduced by first-principles calculations. The trends in the Raman frequencies and intensity were compared with previous x-ray experiments and theoretical calculations. The mode Grüneisen parameter (γ) and elastic shear modulus (C_{44}) in the hcp phase were estimated to be $\gamma(E_{2g})=2.1$ at $P=5-20$ GPa, and $C_{44}=14.9$ GPa at $P=10$ GPa and 39.2 GPa at $P=30$ GPa.

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