High-pressure fcc-to-hcp phase transition in solid krypton studied by Raman spectroscopy

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High-pressure Raman measurements of solid Kr have been performed to investigate the face-centered-cubic (fcc) to hexagonal-close-packed (hcp) phase transition up to 75 GPa at room temperature. The E_{2g} phonon mode, which is Raman active in the hcp phase, appears around $P=20$ GPa at wave number of 90 cm^{-1}. The Raman frequency increases to 145 cm^{-1} at 75 GPa, which is in good agreement with analytical calculations based on the semiempirical many-body potential. The intensity of the Raman band increases with pressure, indicating the growth of the hcp phase. This result is compared with the previous x-ray study for the coexistence of fcc and hcp phases in Kr. Elastic shear modulus C_{44} in the hcp phase was estimated from the vibrational frequency of the E_{2g} phonon, and compared with the recent theoretical results for solid Kr and Xe.

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The properties of rare-gas solids (RGSs) at high pressures are of fundamental interest because they provide an ideal system due to their closed-shell electronic configurations, allowing fruitful comparisons between experiments and theory.[1] Furthermore, they are excellent materials as a hydrostatic pressure medium in high-pressure experiments using a diamond-anvil cell (DAC).[2,3] They form the face-centered cubic (fcc) structure at low-pressure region except He. Pressure-induced fcc-to-hcp (hexagonal-close-packed) phase transition was found in RGSs Xe, Kr, and Ar, by using the x-ray diffraction method; the wide pressure range for the coexistence of fcc and hcp structures was observed in Xe from 1.5 to 41 GPa, for Kr from 3.2 to 50 GPa, and for Ar beyond 49.6 GPa.[4–6]

Very recently, Shimizu *et al.*[7] applied high-pressure Raman spectroscopy to investigate the phase transition from fcc to hcp structure in solid Xe, and observed that the increase in the intensity of Raman-active transverse optic E_{2g} band is evidence of the continuous evolution of the hcp structure in the original fcc phase at a wide pressure range between 5 and 41 GPa. Freiman *et al.*[8] measured the E_{2g} phonon in the hcp Xe up to metallization near 135 GPa and in hcp Ar up to 58 GPa, and compared the results with theoretical calculations.

In this Brief Report, high-pressure Raman measurements of solid krypton up to 75 GPa at room temperature are presented to fill the gap between our previous Xe and Ar studies for fcc-to-hcp transition properties.[7,8] The pressure dependence of Raman frequency for hcp Kr is compared with those of hcp Xe and Ar experiments, and is examined by making analytical calculations based on the semiempirical many-body potential. The behavior of high-pressure fcc-to-hcp phase transition of solid Kr is compared with the previous x-ray experiments. Pressure dependence of shear elastic moduli C_{44} of hcp Kr and Xe estimated from the frequencies of E_{2g} phonon is compared with recent theoretical study.[8]

High-pressure Raman measurements were made by using a DAC with a metal gasket. The hole of the gasket serving as the sample chamber was initially set to about 40 μm in diameter and 50 μm in thickness. For loading a Kr sample in the DAC, we compressed commercial gaseous Kr (99.995%, Takachiho Chemical Industrial Co., Ltd.) in a high-pressure vessel including the DAC, and sealed condensed fluid Kr in the sample chamber of the DAC. Single crystals of Kr were grown by adjusting the pressure on seed crystals, which coexist with fluid Kr at about $P=0.90$ GPa and room temperature. No pressure transmitting medium was used because solid Kr is a soft material. The pressure was measured by the ruby-scale method. To minimize the effect of the pressure gradients in the Kr sample across the anvil face, we used a tightly focused laser spot less than 10 μm, which is smaller than the sample size (about 40 μm). Raman spectra were measured in a back-scattering geometry with a micro-Raman spectrometer (JASCO NR 1800) equipped with a triple polychromator and a charge-coupled device (CCD) detector. The 532.0 nm line of a solid-state laser (Coherent Verdi2W) was used for the excitation at power level of about 100 mW. The spectral resolution was about 1 cm^{-1}.

To reproduce Raman vibrational properties of hcp Kr, we have performed lattice dynamics calculations based on a many-body potential U_{tot}, which included pair (U_p) and triple (U_{tr}) forces ($U_{tot}=U_p+U_{tr}$). As has been shown for hcp Ar and Xe,[8] for volume compressions up to $2.6\sim2.7$ the accuracy of this approach is somewhat better than that of first-principles density-functional theory (DFT) calculations. We used the Aziz Kr-Kr pair potential[9] which reproduces a variety of experimental data for a diluted Kr gas phase, as well as zero-temperature zero-pressure properties of the solid-state phase. As known, the pure pair potential does not describe properly the properties of solid-state phase and many-body corrections should be taken into account. At low pressures the main correction comes from the three-body dispersion (Axilrod-Teller) interaction. At high pressures the many-body exchange effects are the most essential. Here we restrict ourselves to the three-particle exchange terms which were used in a Slater-Kirkwood form.[10] An explicit expression and parameters of the potential U_{tot} are given in a previous study.[11]

Figure 1 shows typical Raman spectra of solid Kr at various pressures up to 75 GPa. A Raman band appears around 20 GPa at wave number of 90 cm^{-1}, and its Raman fre-

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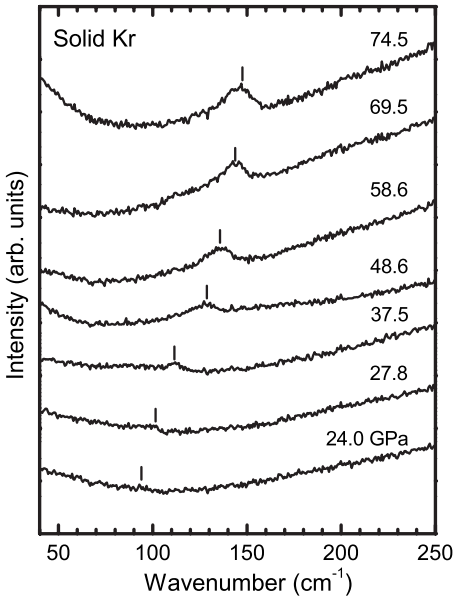

FIG. 1. Pressure-induced Raman spectra of solid Kr at various pressures up to 75 GPa. The E_{2g} (TO) phonon mode, which is Raman-active in the hcp phase, appears at about 90 cm^{-1} and around $P=20$ GPa, and its Raman-band intensity increases with increasing pressure.

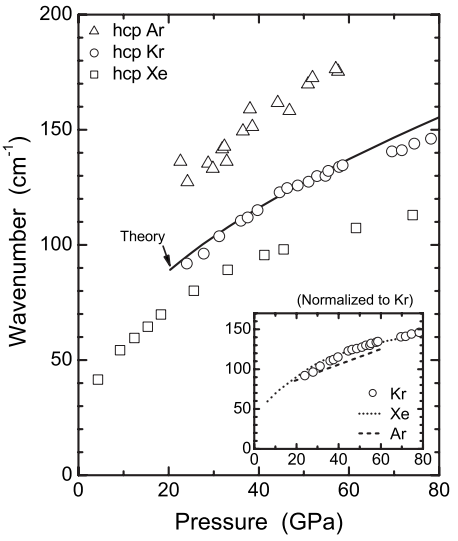

FIG. 2. The frequency of E_{2g} phonon mode as a function of pressure up to 80 GPa in the hcp phase. Open circles and solid line show the present experimental and analytical calculations, respectively. For comparison, previous hcp Xe and Ar Raman frequencies (Refs. 7 and 8) are shown by open squares and triangles, respectively. The inset shows Raman frequencies of Xe and Ar normalized to the Kr frequency, by considering the square root of their mass ratios, where Kr are the open circles, Xe is the dotted line, and Ar is the broken line.

quency increases with pressure to 145 cm^{-1} at about 75 GPa. No Raman-active mode is allowed for solid fcc Kr, but in hcp phase the transverse optic (TO) E_{2g} phonon mode appears as a Raman-active band. This mode is a zone-center TO and shear mode in which successive hexagonal planes are vibrating against each other perpendicular to the c axis as mentioned in a previous Raman study.[7,8] Therefore, the E_{2g} mode probes the interlayer bonds: The increase in Raman frequency means the strengthening of its bonds with compression and the increase in Raman intensity implies the growth of hcp structure, which corresponds to the evolution of hcp domains, i.e., the successive introduction of more and more hexagonal stacking faults in the original fcc phase. The present starting pressure around 20 GPa is higher than $P=3.2$ GPa of previous x-ray experiments,[5] which could detect only 2% growth of the hcp phase at 3.2 GPa. However, Raman intensity of E_{2g} phonon in hcp Kr is very weak; therefore the direct comparison of their transition pressures may be troublesome; the growth of hcp structure is significantly influenced by the microscopic distortion caused by the crystal (sample) condition, i.e., powder or single (poly) crystal, and by the hydrostatic condition[5] within the observed area (the difference in the pressure gradients 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 transition pressures, but we can say definitely that the appearing pressure of hcp phase observed by Raman study is fairly near to that studied by XRD.

The frequency of E_{2g} phonon for hcp Kr increases with pressure as shown by open circles in Fig. 2, and this behavior is examined by making comparative calculations based on the semiempirical many-body potential (see solid line). We can find the excellent agreement between experiments and theoretical calculations. The previous experimental results of the Raman frequency for hcp Xe (Refs. 7 and 8) and Ar (Ref. 8) are shown in Fig. 2 for comparison. The vibrational frequencies of these RGSs Xe, Kr, and Ar seem to be dominated by the mass effect of their atoms. By considering the square root of their mass ratios, $(M_{Xe}/M_{Kr})^{1/2}=1.25$ and $(M_{Ar}/M_{Kr})^{1/2}=0.690$, we normalized Raman frequencies (ν_i) of Xe and Ar to the Kr frequencies at all pressures, as shown on the inset in Fig. 2. Good agreement among Kr, scaled Xe, and Ar means that their force constants (K_i), roughly corresponding to the bond strength, are almost the same by using the relation of $\nu_i=(1/2\pi)(K_i/M_i)^{1/2}$, i=Xe, Kr, and Ar. This implies that the shapes of their potential wells are almost the same near the equilibrium position because the force constant is the curvature of the potential well.

To investigate the pressure-induced fcc-to-hcp phase transition, we estimated the pressure dependence of the Raman intensities as shown by solid circles in Fig. 3, where the integrated Raman intensities were estimated from the area above a smooth background of the spectrum (Fig. 1). We carefully made Raman measurements to keep the same experimental conditions at various pressures, such as laser power, sample position under incident laser, and the detection system of scattered light. 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. Raman intensities show almost linear increase, though the data points around 55 GPa are scattering due to the crystal condition for the different samples prepared many times. This nearly linear trend implies that the hcp phase continuously evolves from the fcc phase, and is consistent with the

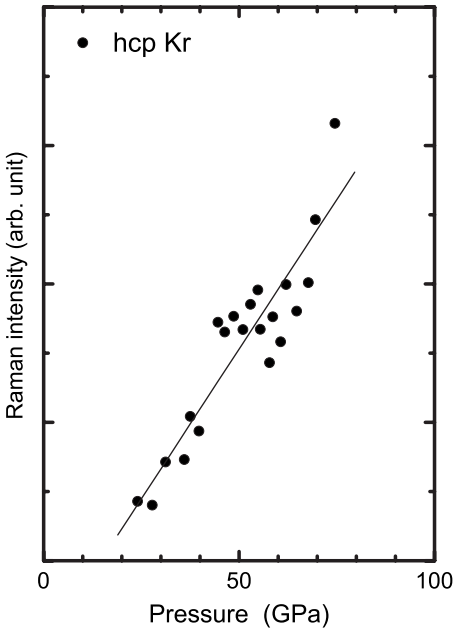

FIG. 3. Pressure dependence of the integrated Raman intensities shown by solid circles. Solid line is a guide for eyes.

following XRD studies by Errandonea *et al.*:[5,6] Their result of $I_h/(I_h+I_f)$ shows almost linear behavior with pressure up to 50 GPa, where I_f and I_h are the integrated area of the fcc (200) and hcp (100) reflection peaks, respectively.

Finally, we investigated the relation between the E_{2g} phonon and the shear elastic modulus C_{44}. The frequency of the E_{2g} mode is represented by the following: $\nu(E_{2g}) = (1/2\pi)[4\sqrt{3}a^2C_{44}/(mc)]^{1/2}$, where a and c are the lattice constants and m is the atomic mass.[12] This relation was derived from simple concepts such as three-body forces. Therefore, one should be cautious on the validity of this model.[7,8,13,14] Nevertheless, using $c/a=1.63$, because of almost ideal ratios at high pressures,[5,15] we have estimated the values of C_{44} as shown by open circles in Fig. 4. For comparison, our results of solid Xe are also plotted by open squares.[7,8] At pressures up to 35 GPa, solid Kr and Xe show almost the same values of C_{44}, and above this pressure solid Xe shows a lower value than Kr. These behaviors are in good agreement with the recent theoretical study by Freiman *et al.*[8] as shown by solid and dotted lines in Fig. 4. We can investigate the relation of elastic constants in the hcp and fcc phases of solid Kr. By considering the acoustic phonon propagating along the axis perpendicular to the stacking plane of fcc or hcp crystal, the TA modes are expressed as follows:[14] $\rho v^2=(C_{11}-C_{12}+C_{44})/3$ in the fcc phase and $\rho v^2 = C_{44}$ in the hcp phase, respectively, where ρ is density and v is acoustic velocity. Therefore, C_{44} in the hcp phase corresponds elastically to $(C_{11}-C_{12}+C_{44})/3$ in the fcc phase. The fcc experimental results of $(C_{11}-C_{12}+C_{44})/3$ estimated by high-pressure Brillouin scattering[16] are plotted by solid circles up to 8 GPa in Fig. 4. We can find the good connection between fcc and hcp elastic properties against pressure. The scaling relation of the Raman frequency and the C_{44} elastic constant, which follows from lattice dynamics studies of the hcp crystal lattice, should be of current interest.[17] This study is highly needed in a next stage.

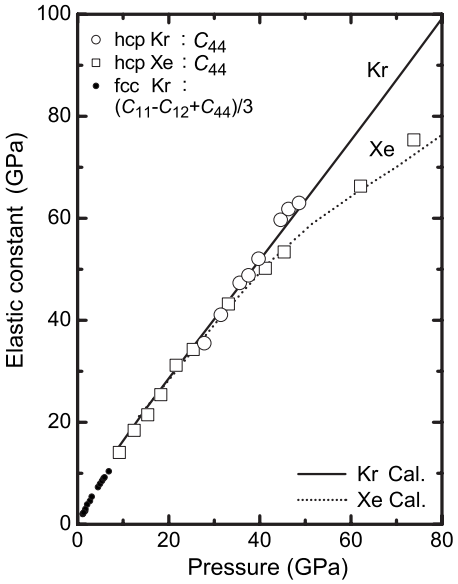

FIG. 4. Pressure dependence of elastic constant C_{44} of hcp Kr and Xe (Refs. 7 and 8) estimated from Raman frequencies of E_{2g} phonon is presented by open circles and squares, respectively. Solid and dotted lines show theoretical calculations of hcp Kr and Xe, respectively (Ref. 8). Solid circles show $(C_{11}-C_{12}+C_{44})/3$ in the fcc Kr phase obtained by high-pressure Brillouin spectroscopy up to 8 GPa (Ref. 16), which corresponds to C_{44} in the hcp Kr phase.

In summary, pressure-induced fcc-to-hcp structural transformation in solid Kr was clearly observed by using Raman spectroscopy with a diamond-anvil cell. The pressure dependence of Raman-active E_{2g}-phonon frequency for hcp Kr was successfully reproduced by making comparative calculations based on the semiempirical many-body potential, and their Raman frequency was compared with those of hcp Xe and Ar, by considering the mass effect of their atoms. The increase in the Raman intensity of E_{2g} band in the hcp phase indicated that the hcp phase continuously evolves in the original fcc phase of solid Kr at a wide pressure range. These behaviors concerned with fcc-to-hcp transformation support the previous studies by x-ray experiments and theoretical calculations. Pressure dependence of shear elastic moduli C_{44} of hcp Kr and Xe estimated from the frequencies of E_{2g} phonon is well compared with recent theoretical study.

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