Structural and Vibrational Properties of Condensed Phases in Xenon Molecular Binary Systems: He-Xe, H₂-Xe

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Abstract. We present both structural and vibrational (Raman) results of compressed xenon binary systems of He and H₂ to a maximum pressure of 142 GPa. In the He-Xe mixture 15% vol. Xe and balance He, we observe no evidence for van der Waals compound formation. Pure fcc Xe can be crystallised from the 2-phase Xe-He fluid at 0.6 GPa. The expected fcc-hcp transition is accompanied by extensive diffuse scattering and the emergence of hcp reflections at higher pressures. There is no apparent volume expansion of the measured Xe equation of state in helium indicating a near-zero (iso-structural) solubility of He in Xe. In the H₂-Xe system, X-ray diffraction revealed the presence of two solid-phase structures in a 15% by volume mixture, one of which was best indexed on an orthorhombic cell. Raman spectroscopic studies of both 15% and 7.5% Xe binary mixtures by volume in H₂, showed shifted vibron frequencies relative to the normal, pure (bulk) H-H stretch mode (vibron) that soften with pressure and appear to cross the pressure-frequency trajectory of the H₂ vibron. The 7.5 vol % Xe-H₂ mixture freezes at 5.3 GPa to a solid occupying the bulk of the available sample volume in the DAC, indicating a close-to-stoichiometric composition for one Xe-H₂ solid phase.

1. Introduction
Interest in the behaviour of the elemental molecular solids hydrogen and xenon under compression has a long history related to both unusual (or unknown) structural phase transitions, and insulator-to-metal transitions, already observed in xenon, and still the subject of substantial debate in solid hydrogen. In addition to the elemental solids, recent interest in condensed binary mixtures has grown rapidly since the first reported stoichiometric van-der-Waals (vdW) solid He(N₂)₁₁ [1]. A rare gas binary system not only offers the possibility of the discovery of unusual stoichiometric compounds, but also a means to “matrix isolate” molecular hydrogen in order to study its detailed intra-molecular response to compression. Studies on Ar(H₂)₂ showed strong vibrational similarities with pure H₂ [2,3].

Here we present both structural and vibrational (Raman) results of compressed xenon binary systems with He and H₂. Our motivation derives from investigating whether the martensitic character of the fcc-hcp transition in solid Xe is preserved under true hydrostatic conditions, but more importantly, we also explore the forced condensation of molecular solids with extreme molecular weight and size contrast. Unlike the H₂-Ar system, H₂-Xe may show hybridization of electronic states

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at pressures above the insulator-metal transition expected in solid Xe or other unusual vibronic properties not revealed in low-atomic-weight vdW compounds.

2. Experiment
Mixtures of xenon (15% vol.)-helium and xenon (15%, 7.5% vol.)-hydrogen from commercial, high purity pre-mixed gas bottles were separately loaded at 0.2 GPa into diamond-anvil cells (DAC’s) of various designs. To preserve xenon resource, all purging of the gas vessel was performed with high-purity hydrogen many times to reduce atmospheric gas contamination to trace levels before a single purge of the xenon mixture. Cylinders were delivered months in advance of the experiments and ideal mixing was assumed. X-ray powder and single-crystal diffraction under pressure was performed at beamline I15, Diamond Light Source, UK. Gas loading and Raman spectroscopic measurements were made at the University of Oxford.

3. The He-Xe system
Figure 1 shows the formation of multiple xenon crystallites on rapid pressure increase to 9 GPa on gas loading, with predominant clustering of xenon at the gasket edge as revealed by the thicker, dark rim adjacent to the reflective gasket. The gradation in cluster density toward the gasket hole centre leads to an expected decrease in quality of the powder pattern (right hand panel, Fig. 1). This unusual separation and distribution of crystallites may be due to surface tension and viscosity effects on approaching the helium freezing point pressure at room temperature.

We made several attempts to prepare a xenon single crystal by temperature and pressure cycling (Figure 2). Although eventual success was achieved with separation of Xe from He near 1 GPa (right-hand panel 4, Figure 2) it was clear that the high melting temperatures of pure Xe made any crystal growth in the several-GPa pressure range increasingly difficult from fragmented crystallites. In addition, internal phase boundaries and fluid-solid separation exhibited a complex morphology at low pressure (left-hand panels 1-3, Figure 2) that maybe explained by surface melting (possible Xe-He fluid mixing) along grain boundaries and/or possible stratification of xenon below a lighter helium fluid layer, all superposed in vertical illumination and micrography. The brightness contrast varies with microscope illumination suggesting strong refractive index contrast between helium and xenon.
Powder x-ray diffraction measurements of the dense clusters of xenon in helium exhibited an apparently identical structural transition sequence to 60 GPa to that observed in pure Xe. A mixed phase of fcc and hcp begins near 12 GPa and is preserved to the maximum pressure. The volume-pressure relation of Xe in He (Figure 3) is identical within error to previous studies (Jephcoat et al. 1987; Cynn et al. 2001). Barrat & Vos, (1992) predicted the possible stoichiometric binaries of Xe(He)$_{13}$ and Xe(He)$_2$ based on hard-sphere packing rules, but we observed no compound formation or deviation from fcc-hcp indexing over this pressure range. Because of the agreement of the measured xenon volumes at pressure, we also conclude that there is no iso-structural solubility of He atoms in the Xe lattice due to interstitial trapping or other mechanism.

As discussed by Cynn et al., [5] the fcc-hcp transition is characterised by strong diffuse scattering and proceeds by a martensitic mechanism. The presence of a helium pressure medium, unexpectedly, had little effect on this process: It was to be expected that hydrostatic conditions may relieve the stress-induced effects on the transition mechanism. In fact, the mechanism may be little dominated by internal stress and more intrinsic to the small fcc-hcp energy difference. The interpretation is also supported by lack of observed effect of laser heating on the stacking disorder [5]. The diffuse scattering between fcc peaks (111) and (200) exhibits varying degrees of fine structure. It disappeared in one loading near 16 GPa giving rise to the hcp peak (101). Other loadings preserved coarser diffuse scattering to higher pressures suggesting a possible correlation with xenon grain size. Figure 4 shows
an expanded region of an image plate pattern showing the confinement of the diffuse scattering between powder rings from Xe in He and the variety of stacking disorder effects.

Figure 4. Enlarged region of a Xe-in-helium diffraction pattern after pressure decrease to 3 GPa, recorded directly onto an image plate. The streaks and spots associated with diffuse scattering are bounded by the H(100) (inner) and F(200) (outer, complete) diffraction rings.

4. The H₂-Xe system
Both pure H₂ and solid xenon have long been investigated in the pure phase with regard to important electronic properties. Xenon metallises above 137 GPa, whereas pure, solid H₂ undergoes a series of complex transitions. The expected destabilisation of the molecular bond, as evinced by softening and disappearance of the intramolecular vibron, associated with onset of band-gap closure, has yet to be clearly demonstrated. Further, matrix isolation experiments in pure argon [2,3] show that the vdW compound formed shows no turnover in the H₂ vibron frequency. The prediction of a new pathway to metallic hydrogen isolated in the light rare gases has yet to be realised. One of the motivations for the present study was that the high polarisability and associated s-d electronic transition in solid Xe may provide additional electronic degrees of freedom that could perturb the H-H bond and consequently the H₂ vibron behaviour with pressure.

4.1. Solid-phase morphology
Crystal growth was characterized by multiple crystallite formation (Figure 5) at various pressures with a 15% by volume Xe mixture in pure H₂. In the H₂-Xe system we observed two apparently separate solid phases crystallize in addition to pure solid Xe. On compression, a complex series of crystallization phenomena were observed indicating both liquid-liquid interaction and solid phase formation that varied with pressure and the apparent Xe concentration.
Figure 5. Morphological aspects of crystal formation in the Xe(15% vol)-H$_2$ system. Top left panel: A xenon single crystal grows from fluid at 3.0 GPa and 298 K. On slow pressure increase additional phase separation occurs (top right to bottom left panel) accompanying apparent break up and loss of identity of the pure xenon phase by 4.4 GPa (bottom right).

4.2. X-ray diffraction

X-ray diffraction patterns as function of pressure were collected from the 15% vol. Xe mixture as observed in Figure 5. In order to obtain powder diffraction data of sufficient quality, the coarsely crystallized sample at 4.4 GPa was reduced in pressure to near 2 GPa where crystal melting was observed, and then raised rapidly again increasing the numbers of crystallites. Figure 6 shows selected patterns taken at different positions in the sample chamber. Two Xe-H$_2$ solid phases are identified, consistent with morphological observations.
Both phases co-exist over the pressure range studied. On pressure decrease below 5.6 GPa, it was possible to collect a pattern from one single phase (plus FCC Xenon). This phase appeared orthorhombic and is assigned Space Group C222₁ with $a=11.4200(2)$ Å, $b=4.3416(1)$ Å, $c=4.1445(1)$ Å and Volume: 205.49 Å$^3$ at 5.6 GPa [7].

4.3. Raman spectra of solid Xe-H$_2$ in the region of the intra-molecular stretching frequency.

In a separate experiment with 7.5% vol. Xe in H$_2$, the mixture crystallized to a clearly delineated single-crystal phase at 4.7 GPa that filled ~86% of the gasket chamber volume with a minor residual phase attributed to excess H$_2$ (Figure 7a). Assuming that the crystallite filled the whole chamber thickness, a consistent stoichiometry based on ideal mixing alone would be Xe(H$_2$)$_4$, but cannot be verified in the absence of diffraction data for this composition. Raman scattering data only were obtained for the experiment and the crystallite remained intact on compression to over 142 GPa. In contrast to Ar(H$_2$)$_2$ [2,3], we observe a turnover of the H$_2$ vibron mode ($Q_1(1)$ branch) in $S_1$, but with the vibron frequency down-shifted by ~12 cm$^{-1}$ from the pure H$_2$ mode at low pressure near 8 GPa, crossing at 50 GPa and ~26 cm$^{-1}$ higher (but weaker and broader) by 136 GPa (Figure 7b) [8].
Figure 7a. Photomicrograph of a crystallite readily condensed from a 7.5% vol Xe in hydrogen mixture at 8 GPa. A clear straight edge is visible separating Xe(H\(_2\))\(_n\) above and residual hydrogen below.

Figure 7b. Raman spectra of the Q\(_1\)(1) mode in the Xe-H\(_2\) solid formed from a 7.5% vol. Xe-H\(_2\) mixture, showing the Xe-H\(_2\) vibron (high-lighted in green) crossing the pure H\(_2\) mode. The spectra were obtained by spatially-resolved scattering either side of the crystallite boundary visible in (a).

References
[1] Vos, W.L. et al., Nature, 358, 46 (1992).
[2] Loubeyre, P. et al., Phys. Rev. Lett., 72, 1360 (1994).
[3] Ulivi, L., et al., Phys Rev. B, 60, 6502 (1999).
[4] Jephcoat, A.P., et al., Phys Rev. Lett., 59, 2670 (1987).
[5] Cynn, H. et al., Phys. Rev. Lett., 86, 4552 (2001).
[6] Barrat, J-L., & W.L. Vos, J. Chem. Phys., 97, 5707 (1992).
[7] Amboage, M., et al., to be published.
[8] Jephcoat, A.P. et al., to be published.