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Phase Diagram of Dense H$_2$-He Mixture: Evidence for Strong Chemical Association, Miscibility and Structure Change

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Abstract

The phase diagram of hydrogen-helium mixture is presented to 75 GPa, underscoring the formation of metastable H$_2$-rich crystallite in He-rich fluid mixtures and the structural phase transition in He lattice at ~52 GPa. The Raman data also indicates a significant level of mixing between H$_2$ and He even in solids, giving rise to new vibrational bands in He-rich solid at ~2400 cm$^{-1}$ for H-He stretching and 140 cm$^{-1}$ for the lattice phonon of H$_2$ incorporated hcp-He. Therefore, the present result signifies unexpected, strong chemical association of the interstitial-filled guest molecules (H$_2$ or He) with the host lattice (hcp-He or H$_2$) in this quantum solid mixture.
Hydrogen (H$_2$) and helium (He) are two most fundamental solids abundant in the Universe. Compression behaviors of H$_2$ and He are critical to understand many body effects of these quantum solids [1,2]; develop new condensed matter theories [3-5]; and get insights into the internal structure of the Giant planets [6,7]. The equations of state (EOS) of H$_2$ and He, for example, provide the critical constraints for modeling the internal structure, dynamics and conductivity of the planets. Recent theories have predicted the phase separation of H$_2$ and He at high pressures and temperatures [8,9]. As such, it is thought that heavier He precipitating down from the upper H$_2$-He layer generates gravitational energy that drives planetary dynamics and contributes to the luminosity observed in Saturn [9]. The exact pressure-temperature (P-T) conditions, chemical states (i.e., liquid, solid, metallic, insulating, etc.), and properties (EOS, diffusivity, miscibility, etc.) of H$_2$ and He, on the other hand, provide critical constraints for the thickness and chemical composition of layer boundaries and the origin of giant magnetic fields observed in these Giant planets [10].

Recently, there has been a rapid progress in understanding the phase diagram of hydrogen at high pressures [11-15]. Several new phases including phase IV [11], V [12], and VI [13] have been suggested in the pressure regime where hydrogen is reported to become a narrow bandgap semiconductor (above 250 GPa [14]) and even a metallic solid (above 400 GPa [15]). Helium is known to stay in hcp phase to ~58 GPa at room temperature [16] in contrast to the theoretical prediction of fcc phase [17]. This makes He unique from other inert gas solids, underscoring its large anharmonicity and quantum effect [3]. On the other hand, a little is known about the binary phase diagram of H$_2$ and He, since the first phase diagram presented to 10 GPa four decades ago in 1973 [18] and 1987 [19]. This is despite the interesting features observed in the isothermal pressure-composition phase diagram of H$_2$+He, such as the presence of immiscible two-fluids.
phase region and collective compression of H$_2$ in fluid He. Yet, no information is known about the structure and phase stability of solid H$_2$ and He mixtures above 12 GPa.

The considerable mobility of H$_2$ (or He) can contribute to its miscibility with He (or H$_2$) and the planetary “ices” (H$_2$O, NH$_3$ and CH$_4$), which can significantly affect the EOS and other properties such as the conductivity and diffusivity. The mixing of hydrogen with the planetary ices, for example, can be readily observed, when hydrogen isotope deuterium (D$_2$) is introduced in H$_2$O in the form of the proton exchange between H$_2$O and D$_2$ as evident from the Raman spectra even at 50 GPa [20]. A similar level of high mobility and miscibility is expected in He mixtures with other elemental solids [21-24]; yet, proving this conjecture in H$_2$ + He mixtures remains extremely challenging because of the difficulty probing the presence of He in those mixtures. In this Letter, using a sensitive confocal micro-Raman system, we present the spectral evidence that there is a sufficient level of mixing in H$_2$ + He solid mixtures, resulting in strong chemical association of H$_2$ in hcp-He lattice in He-rich solid even at pressures well below 100 GPa where H$_2$ and He have been considered as chemically inert [3, 25].

The present results are summarized in the binary phase diagram of H$_2$-He mixture (Fig. 1), consisting of homogenous H$_2$-He mixture F (below 5 GPa), H$_2$-rich fluid F$_1$, He-rich fluid F$_2$, H$_2$-rich solid S$_1$ and S$_1’$ (appeared in fluid He + solid H$_2$ mixtures in the He-rich fluid), He-rich solid S$_2$ and S$_3$ (appeared above 52 GPa). This phase diagram is constructed based on the reproducible Raman data taken from a large number (twenty three) of high-pressure samples with seven different compositions (including pure H$_2$ and pure He). The detailed experimental method and the spectral data are presented in the Supplementary Information (Figs. S1-S17).

Figure 2 shows Raman spectra of 1:1 H$_2$:He mixture to 75 GPa, plotted for the high
frequency region of H$_2$ vibron. At 2.2 GPa H$_2$ and He form a homogeneous fluid mixture (F), of which H$_2$ vibron appears blue-shifted (4204.8 cm$^{-1}$) and broadened (FWHM = 26.0 cm$^{-1}$) compared to those of pure H$_2$ vibron (4183.6 cm$^{-1}$, FWHM = 12.0 cm$^{-1}$) at the same pressure (shown in the grey spectrum). Upon the solidification of H$_2$ between 5.1 and 6.4 GPa, the homogeneous fluid mixture separates into three distinctive regions (see the inset photo): solid H$_2$ (S$_1$), H$_2$-rich fluid (F$_1$) and He-rich fluid (F$_2$), which can be identified by the corresponding H$_2$ vibrons. The sharp H$_2$ vibron (4214.3 cm$^{-1}$, FWHM = 7.5 cm$^{-1}$) of S$_1$ (here-to-after call it as the S$_1$ vibron) at 6.4 GPa agrees well with that of pure solid H$_2$ (4211.9 cm$^{-1}$, FWHM = 7.1 cm$^{-1}$) [26]. The asymmetric tail of the S$_1$ vibron at 6.4 GPa is due to an incomplete phase transition of S$_1$ out of F$_1$. Interestingly, the F$_1$ vibron appears blue shifted (4229 cm$^{-1}$) and broadened (FWHM = 25.3 cm$^{-1}$) from the S$_1$, while the F$_2$ vibron has even stronger blue shift (4343.3 cm$^{-1}$) and broadness (FWHM = 66.8 cm$^{-1}$). The strong blue shift of the F$_2$ vibron is due to the larger compressibility of fluid He than solid H$_2$ [18,27]. Note that pure H$_2$ solidifies at around 5.5 GPa. Therefore, the fact that the F$_1$ is even present at 6.4 GPa is an indication of He inclusions disturbing the ordering of H$_2$ molecules. Above 6.5 GPa, the F$_1$ completely transforms to the S$_1$, of which vibron well tracks that of pure H$_2$. However, the F$_2$ vibron remains strongly blue shifted and extremely broad, until the F$_2$ transforms into He-rich solid S$_2$ at 11.9 GPa.

Upon the completion of the F$_2$ to S$_2$ transformation at 12.6 GPa, the S$_2$ vibron splits into two sharp peaks, arising from the interstitial filled H$_2$ molecules in He lattice (S$_2$). A small vibron overlapping with the S$_1$ vibron is apparently from the S$_1$ and S$_2$ boundary. The 2:1 intensity ratio of the S$_2$ doublet is consistent with the degeneracy ratio of tetrahedral and octahedral sites in hcp-He. Importantly, the S$_2$ doublet disappears abruptly above 52 GPa, whereas the S$_1$ vibron still remains strong. This result clearly indicates a structural change in H$_2$.
incorporated \textit{hcp}-He at 52 GPa. All spectral changes observed in the S2, including the doublets at \(\sim 4300 \text{ cm}^{-1}\) and \(\sim 2400 \text{ cm}^{-1}\), and the low frequency phonon at \(\sim 140 \text{ cm}^{-1}\), occur irreversibly upon the pressure downloading from above 52 GPa. The irreversible spectral change, in turn, indicates a small energy difference between two He phases and thereby a close packed structure for the new high-pressure phase [28].

The present spectral data also reveals unexpected Raman features in a relatively low frequency region of H\textsubscript{2} vibron (Fig. 3), suggesting strong chemical association between H\textsubscript{2} and He in the S\textsubscript{2} phase. The S\textsubscript{2} peaks at \(\sim 140 \text{ cm}^{-1}\) and \(\sim 2350 \text{ cm}^{-1}\) (doublet) begin to appear upon the solidification at 11.9 GPa and disappear above 52 GPa, analogous to the pressure dependence of the blue-shifted S\textsubscript{2} vibron in Fig. 2. These new features are weak but reproducible over all concentrations and in different sample configurations (see Figs. S8-S17). Moreover, the intensity of the 2350 cm\(^{-1}\) peak increases considerably (by a factor of ten) as increasing the He concentration above 50 \% (Fig. 3 inset). We attribute these peaks to a lattice phonon (E\textsubscript{2g} shear mode of H\textsubscript{2} incorporated \textit{hcp}-He) at \(\sim 140 \text{ cm}^{-1}\) and a H-He vibron at 2350 cm\(^{-1}\) of the S\textsubscript{2}. The E\textsubscript{2g} phonon was observed in pure He at 20 K and 1 GPa– not at ambient temperature and higher pressures [29]. In fact, the calculated frequency of H-He stretching in linear HHeF is about 2304 cm\(^{-1}\) [30] in a good agreement with the observed frequency 2350 cm\(^{-1}\) considering the pressure difference.

The pressure-dependent Raman shifts of H\textsubscript{2} and He mixtures for five different concentrations are plotted in Fig. 4, together with that of pure H\textsubscript{2}: (a) high-frequency H\textsubscript{2} vibron below 11.9 GPa and (b) above 11.9 GPa, and (c) low-frequency H-H/H-He vibron to 75 GPa. In homogeneous fluid mixture F, the degree of the blue shift in H\textsubscript{2} vibron is proportional to He concentration as observed previously [19,27]. In the 7:3, 5:5, and 3:7 mixtures, phase F separates
into two immiscible F1 and F2 fluids between 5 and 6.5 GPa. As mentioned, H2 vibron in F2 is more blue-shifted than in F1, but the magnitude of pressure shift becomes independent of the composition. The peak position of S1 vibron faithfully tracks that of pure H2 to 75 GPa - the highest pressure studied 75 GPa (Fig. 4b). Above ~6.5 GPa the pressure shift of the S1 vibron well tracks that in pure H2. On the other hand, the F2 vibron remains as a singlet to 12 GPa, then upon the solidification to the S2 it splits into several peaks all strongly blue shifted from pure H2 vibron. Again, these S2 vibrons disappear abruptly at ~52 GPa. The 3:7 and 1:9 He-rich mixtures show even three blue-shifted H2 vibrons in S2, apparently coming from micro-crystallites (see Figs. S10 and S12) formed in He-rich area, presumably from the strong chemical associations. Especially, in 1:9 He-rich mixture a new crystallite formed in He-rich area (see the insets in Fig. 4). Note that these vibrons of the new crystal remain well beyond 52 GPa, the pressure-dependence similar to H2-rich solid (S1). Thus, we call it as S1’.

The low-frequency modes (Fig. 4c) exhibit a similar pressure dependence to the high-frequency H2 vibrons (Fig. 4b). That is, the disappearance of S2 modes above 52 GPa. It also shows the formation of S1’ in the 1:9 mixture, which exhibits a set of new peaks at ~3000-3200 cm\(^{-1}\) – the spectral region where H-H vibrons in hydrides appear such as CsH\(_7\) [31] and NaH\(_9\) [32]. The inset in Fig. 4a clearly shows the coexistence of three solid phases, S1, S2, and S1’ in the 1:9 mixture. Note that contrary to the S1 and S2, the S1’ forms a crystal-like solid only in highly He-rich mixture of which solidification pressure rapidly increases with He concentration (see Fig. 1). Therefore, it is likely that the S1’ is a H2-rich solid grown from fluid He.

The present results suggest the formation of strongly associate phases in both H2-rich and He-rich solid mixtures, indicating considerable miscibility between H2 and He at all
compositions studied (see Figs. S8-S17). This is unexpected because the previous study has reported a diminishing miscibility between solid H\(_2\) and solid He with increasing pressure above 12 GPa [33]. Nevertheless, the formation of strongly associated phase can be understood in terms of the polarization of small amount of H\(_2\) impurities captured in between hcp-He layers in He-rich solid S\(_2\), forming a paired charge transferred He hydrides, H\(_2\delta^+\) - He - H\(_2\delta^-\) - He. A similar dipolar pairing of H\(_2\) molecules (H\(_2\delta^+\)… H\(_2\delta^-\)) was observed in dense pure H\(_2\) (i.e., HA phase) [34]. Based on the previous single crystal X-ray data of He (a= 2.069 Å and c=3.379 Å at 17.4 GPa [35]), this model gives the interlayer H-He distance along the [100] to be ~0.85 Å, well compared with d(He-He) = 1.03 Å and d(H-H) = 0.75 Å. Then, the extended (i.e. charge paired H\(_2\)) nature of this model gives rise to two nearly degenerate in-phase and out-of-phase vibrational modes, as observed in Fig. 3. The intensity enhancement of the 2400 cm\(^{-1}\) bands at the higher He concentrations (Fig. 3c) reflects the greater polarizability of hydrogen, supporting the model.

In the S\(_1\)’ solid, on the other hand, the polarization may occur on the interstitial filled He to form hydrogen-rich He hydrides (H\(_2\))\(_n\)H\(_\delta^+\)He\(_\delta^-\) (n>1). The excess H\(_2\) molecules then help screen the hydride-hydride repulsion, as previously suggested for alkali metal hydrides [31,32]. The nature of local chemical bonding of HHeH can then be described in terms of a four-electron three-centered system (as if H\(_3\)’), consisting of \(\sigma_g^2\) bonding and \(\sigma_u^2\) non-bonding in the linear configuration. As pressure increases, the linear HHeH structure starts to distort (or bend), destabilizing the nonbonding orbital more toward the \(\sigma_g^*\) anti-bonding and eventually leading to a structural change.
The present data provides new constraints for the binary phase diagram of H\textsubscript{2} and He mixtures to 75 GPa as presented in Fig. 1. The present phase diagram emphasizes the formation of H\textsubscript{2}-rich crystallite (S\textsubscript{1}') in He-rich fluid mixtures and the structural phase transition in He lattice (from the S\textsubscript{2} to the S\textsubscript{3}) at ~52 GPa. It also indicates the phase separation of homogeneous H\textsubscript{2}+He mixture (F) into two immiscible fluids (F\textsubscript{1} and F\textsubscript{2}) in the narrow pressure region between ~5.0-6.5 GPa. Clearly, the S\textsubscript{1}' phase is metastable, formed by faster diffusion of solid H\textsubscript{2} crystallites in fluid He and, once it formed, exists at least to 75 GPa.

The presence of structural phase transition in He-rich lattice at 52 GPa is in contrast to the behavior of pure He, which remains in hcp at least to 58 GPa at ambient temperature [16]. Nevertheless, the present spectral data clearly indicates the disruption of hcp layers and thereby the interlayer H-He bonding. A potential structure for the new phase is obviously fcc – the phase exists only along the melt between 15 K and 285 K below 12 GPa in pure He. However, it is not known if the disorder introduced by adding H\textsubscript{2} impurities would expand the stability of fcc above 52 GPa at ambient temperatures [3,17]. Clearly, further structural studies are required to signify this conjecture and elucidate the role of H\textsubscript{2} impurities in this quantum solid H\textsubscript{2}-He mixture at high pressures.

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REFERENCES

36. See Supplementary Materials [url] for the detailed experimental data as obtained in this work, which includes seventeen figures (Figs. S1 to S17), corresponding captions, and Refs. [37-43].

**Figure Captions**

**Figure 1**  Binary phase diagram of H$_2$+He mixtures to 75 GPa, signifying the phase transition of He-rich solid S$_2$ to S$_3$ at 52 GPa and a formation of metastable H$_2$-rich solid S$_1'$ in He-rich mixtures. Closed (open) symbols with different colors denote compression (decompression) data for different He compositions as used for the rest of the figures. F, F$_1$, and F$_2$ refer respectively to homogenous H$_2$-He fluid mixture, H$_2$-rich fluid, and He-rich fluid, whereas S$_1$ and S$_1'$ are H$_2$-rich solids and S$_2$ and S$_3$ refer to He-rich solids.

**Figure 2**  Raman spectral changes of H$_2$ vibrons in 1:1 H$_2$:He mixture along the 300 K isothermal compression to 75 GPa. F, F$_1$, F$_2$, S$_1$, and S$_2$ signify a homogenous fluid mixture, H$_2$-rich fluid, He-rich fluid, H$_2$-rich solid, and He-rich solid, respectively, and their Raman spectra are plotted in different colors.

**Figure 3**  Raman spectral change of 1:1 H$_2$:He solid mixture at high pressures, plotted in the low frequency regions of (a) lattice phonon at 100-300 cm$^{-1}$ and (b) H-He vibron at 2340-2440 cm$^{-1}$. (c) The H-He vibron at 20 GPa is also plotted as a function of He concentration, for comparison. The inset shows the peak intensity at 2370 cm$^{-1}$, normalized to that of the 2$^{nd}$-order diamond Raman at 2570 cm$^{-1}$, as a function of He concentration. The S$_2$ and S$_3$ signify He-rich solids at pressures below and above 52 GPa, respectively.

**Figure 4**  Pressure-dependent Raman shift of H$_2$ vibron in H$_2$+He mixtures at various concentrations below 12 GPa: (a, b) in the high-frequency region (a) below and (b) above 12 GPa, and (c) in the low-frequency region to 75 GPa. The inset in (a) represents a microphotograph of 1:9 H$_2$:He mixture at 12.6 GPa, showing coexistence of three different solid
phases, $S_1$, $S_2$ and $S_1'$, and those of (b) and (c) refer to the H$_2$ vibrons of $S_1'$ at 28 GPa of the same mixture.
Figure 1
Figure 3

The graph shows the normalized intensity as a function of Raman shift (cm$^{-1}$) for different pressures and mole fractions of He in a mixture of H$_2$-He. The peaks labeled $S_2$ and $S_3$ are observed at 12.6 GPa and 56, respectively. The inset graph on the right plots the normalized intensity against the mole fraction of He, with data points marked at various pressures.
Figure 4

(a) Raman Shift (cm$^{-1}$) vs. Pressure (GPa)

(b) Raman Shift (cm$^{-1}$) vs. Pressure (GPa)

(c) Raman Shift (cm$^{-1}$) vs. Pressure (GPa)