Comment on "Melting Line of Hydrogen at High Pressures"

A recent Letter by Deemyad and Silvera [1] presented measurements of the H_2 melting curve up to ~81 GPa and claimed a sharp maximum at ~65 GPa and 1050 K. In this Comment we wish to point out several experimental issues that make that conclusion highly questionable. The data presented are inconsistent with the extrapolation of previous *in situ* high *P-T* measurements [2,3], and no plausible explanation is presented as to why new results are so unexpectedly different from previous findings.

The presence of H_2 in the sample chamber is crucial. Since this was shown in previous work [2] (Fig. 1), it is important to examine possible artifacts and reasons for the proposed unusual melting line [1]. Unfortunately, Ref. [1] failed to provide any measurable physical parameter of hydrogen to prove its presence in the sample chamber. Hot compressed hydrogen has high mobility and reactivity, requiring multiple experiments to cross-check and confirm results [2,3]. Reference [1] presented only one experimental run with 4 pressure points for which the temperature of the Pt absorber was measured. The authors even stated that they were not able to detect H_2 vibron because the Pt "absorber almost completely filled the gasket hole at the highest pressures," which is consistent with partial or complete loss of hydrogen in the sample cavity as a result of diffusion or chemical reaction; this could explain the observed maximum (see below).

In Ref. [1] the melting of H_2 was observed by speckle motion or as a plateau of the peak *T* versus average laser power. The former technique does not provide a clear diagnostic of melting, since recrystallization, phase transformations, or chemical reactions can give rise to similar observations. The Pt absorber temperature versus power curves reported using the latter technique do not rise above the plateau (cf. work from the same group [4]), which makes them insufficient to prove melting. Instead, this observation may simply correspond to the maximum temperature that can be reached for a particular sample arrangement. This temperature depends critically on the thickness of the thermal insulation. If H_2 diffuses out the sample cavity as pressure increases, the insulation thickness decreases, causing the observed decrease in the inferred melting temperature.

The temperature measurements by optical pyrometry need to be carefully examined. The temperature of the Pt absorber is not necessarily equal to that of the transparent sample [5]; known chemical reactions involving Pt at extreme conditions [6] would drastically change the properties of the Pt emissivity, rendering the radiative *T* measurements erroneous, and the formation of new phases can cause speckle motion unrelated to the melting of hydrogen.

Finally, the claimed sharp maximum in the melting line requires a dramatic change in the Clapeyron slope that would in turn imply the presence of 2 distinct liquids (fluids) [7] of different densities. However, Ref. [1] erroneously suggests 2 solids (cf. the Na melting maximum [8]), contradicting the 180° rule [9] which states that no phase has a stability field occupying more than a 180° angle at a triple point. Figure 1(a) shows with arrows the *P-T* paths taken in previous *in situ* Raman studies [2] in the regions [Fig. 1(b)] of the possible different fluids. Some of the *P-T* paths cross the melting line proposed by Ref. [1] which should have been clearly observed together with detectable differences in Raman spectra associated with the implied changes in the fluid state.

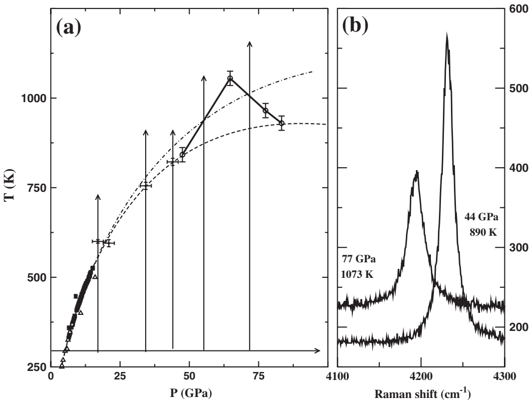

FIG. 1. (a) Melting curve of H_2. Open circles and thick solid line are from Ref. [1]. All other symbols are data and Ketchin fits from Refs. [2,3]. The arrows show *P-T* paths taken in Ref. [2]. (b) H_2 vibrons on both sides of the melting maximum proposed in Ref. [1].

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