

Comment on “Synthesis and properties of selenium trihydride at high pressures”

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A recent article by Zhang *et al.* [*Phys. Rev. B* **97**, 064107 (2018)] claimed the high-pressure synthesis and metallization of H_3Se , or selenium trihydride, at 23 GPa and 203 K. Here, we demonstrate that the synthesised compound is not H_3Se but the previously reported, and already well characterized, $(\text{H}_2\text{Se})_2\text{H}_2$. The claim of metallization is unsubstantiated by the experimental evidence and can be explained by the decomposition of $(\text{H}_2\text{Se})_2\text{H}_2$ into metallic Se and molecular H_2 .

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Zhang *et al.* [1] synthesise H_2Se directly from heating elemental Se in H_2 media at pressures of 0.3 GPa. The synthesis process of forming the H_2Se from the constituent elements at high temperature was already reported recently by Pace *et al.* [2]. In both reports, a molecular compound is formed on compression at ~ 4.2 GPa and characterized through both synchrotron x-ray diffraction and Raman spectroscopy. Zhang *et al.* claim to form a new compound, “selenium trihydride”; however, here we show that the experimental evidence for this new compound is entirely consistent with the previously reported $(\text{H}_2\text{Se})_2\text{H}_2$.

Reference [1] presents the room-temperature powder x-ray diffraction pattern of the synthesized compound at 7 GPa (Fig. 4 in Ref. [1]). The authors compare the observed reflection positions with those of a face-centered orthorhombic phase space group *Cccm*, predicted by theory [3]; however, no refinement was performed against the observed data, as evidenced by the lack of unit-cell dimensions reported in the text. Furthermore, the authors have not displayed tick marks for all the expected reflections of the predicted *Cccm* structure. While many of these predicted reflections are weak, they are *not* systematically absent. In total, the authors of Ref. [1] omit 27 reflections in the 2θ range for the data set at 7 GPa. In Fig. 1(a), we show for comparison the tick marks presented in Ref. [1] (shown in red) and include the additional tick marks (shown in gray) that should be present for the predicted *Cccm* structure.

The predicted “ H_3Se ” structure presented by [3] contains 16 Se atoms bonded to 32 H atoms with the remaining 16 H atoms forming H_2 molecules, giving a formula of $(\text{H}_2\text{Se})_2\text{H}_2$. This structure differs from that reported by Ref. [2] only in the “freezing out” of hydrogen atom positions as a result of the calculation being performed at 0 K. This reduction in symmetry doubles the volume of the unit cell. The stoichiometry of

this structure is identical to that reported in Ref. [2] and does not contain any “ H_3Se ” molecules as implied by “selenium trihydride.”

Distinguishing between these structures requires locating hydrogen atom positions, but hydrogen is an extremely weak scatterer of x rays and cannot typically be located accurately by high-pressure x-ray diffraction. The observed scattering is therefore due entirely to Se atoms. The Se atom positions in the *Cccm* phase and the previously reported *I4/mcm* structure are indistinguishable. To illustrate the direct relationship between the structures, we present the refinements of both unit cells against the x-ray diffraction data from Ref. [1], (a) at 7 GPa and 300 K and (b) at 39.5 GPa and 170 K. We find that the *I4/mcm* structure reported in Ref. [2] explains the observed scattering without redundant reflections or enlarged unit cell. The refined unit-cell dimensions are $a = 7.262(1)$ Å, $c = 6.094(4)$ Å at 7 GPa and $a = 6.304(1)$ Å, $c = 5.430(5)$ Å at 39.5 GPa. This analysis, and the fact that the volumes reported in Ref. [1] (see Fig. 6) match that of $(\text{H}_2\text{Se})_2\text{H}_2$ in Ref. [2], demonstrates the equivalence of “ H_3Se ” and the previously reported $(\text{H}_2\text{Se})_2\text{H}_2$.

In Fig. 2 we present a comparison of the Raman data between that of Ref. [1] at 203 K and Ref. [2] at 300 K as a function of pressure. Below 20 GPa, both data sets are in excellent agreement, with slight modifications in frequency due to the temperature difference between the two studies. The appearance of a second hydrogen vibrational mode is not attributed to the formation of H_3Se as described in Ref. [1] but is indicative of the formation of $(\text{H}_2\text{Se})_2\text{H}_2$, and the behavior is analogous with the formation of $(\text{H}_2\text{S})_2\text{H}_2$. At ~ 20 GPa, we see slight deviation in the appearance of the spectra, but this can be attributed to the ability to resolve the spectra at low temperature, while at 300 K, $(\text{H}_2\text{Se})_2\text{H}_2$ is close to decomposition pressure.

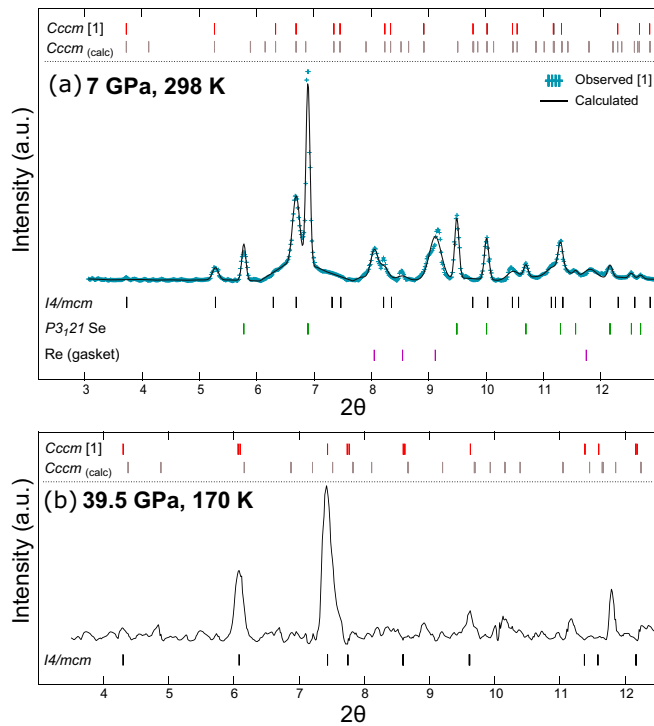


FIG. 1. (a) Le Bail refinement of $I4/mcm$ fitted to the x-ray diffraction data from Ref. [1] (Fig. 4) at 7 GPa and 298 K. Reflections in fit: $(H_2Se)_2H_2$ $I4/mcm$ (black), $P3_121$ Se (green), Re (purple). (b) X-ray diffraction data from Ref. [1] (Fig. 5) at 39.5 GPa and 170 K, showing reflections for $(H_2Se)_2H_2$ $I4/mcm$ (black). Top panels in Figs. 1(a) and 1(b) show the difference between the reflections predicted for $Cccm-H_3Se$ and the reflections that were actually presented in Ref. [1].

At room temperature, both Refs. [1,2] are in agreement that H_2Se [and $(H_2Se)_2H_2$] decomposes due to laser light, synchrotron radiation, and also when compressed to pressures above ~ 21 GPa. However, at pressures above 23 GPa and 203 K, Zhang *et al.* claim that “ H_3Se ” transforms into a metallic state. The evidence for such a transition relies on the sample becoming “visually nontransparent and shiny” together with the significantly weakened Raman spectra. Visual observation evidence is insufficient to claim a transition to a metallic state, with similar results being recently used in support of the widely criticized metallization of hydrogen [4,5]. The limited evidence presented for metallization of “ H_3Se ” is entirely equivalent to that presented for the decomposition, either light or pressure induced, at 300 K. As the x-ray diffraction data still show the persistence of $I4/mcm-(H_2Se)_2H_2$, we conclude that the compound is stabilized at low temperature at this pressure but on x-ray/laser irradiation is partially

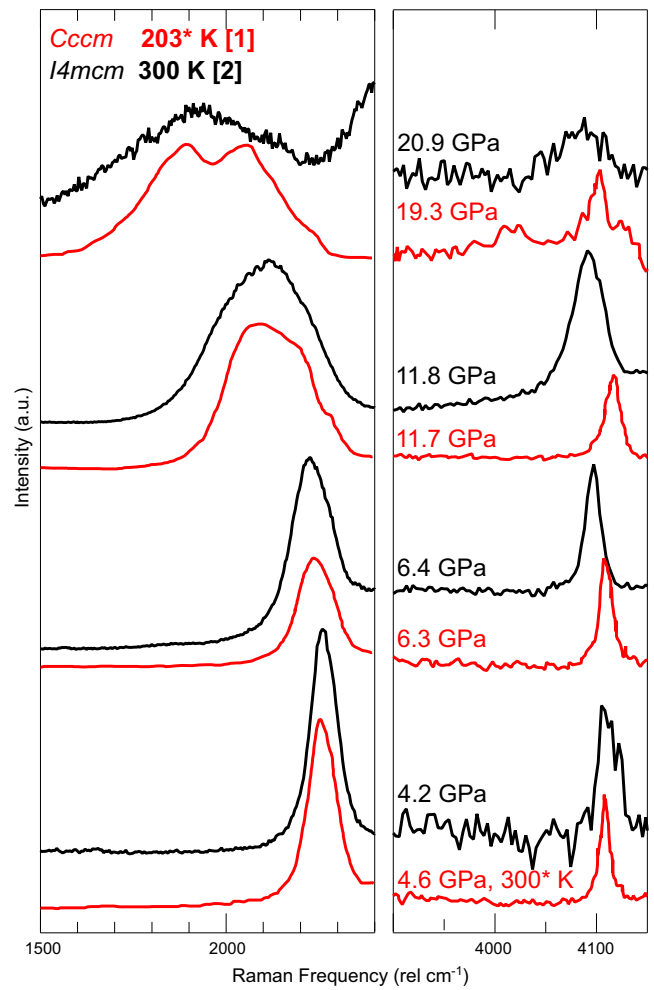


FIG. 2. Comparison of Raman spectra as a function of increasing pressure: Ref. [1] (red) “ $Cccm-H_3Se$ ” at 203 K (300 K at 4.6 GPa), Ref. [2] (black) $I4/mcm-(H_2Se)_2H_2$ at 300 K.

decomposed, giving *nontransparent and shiny* elemental selenium. Figure 1(c) of Ref. [1] shows that the appearance of the decomposed sample is exactly the same as that of the excess Se precursor in Fig. 1(a).

In conclusion, by applying structural analysis to the data presented by Zhang *et al.*, we find that the claimed compound is not $Cccm-H_3Se$ but instead $I4/mcm-(H_2Se)_2H_2$, which has already been reported and characterized at room temperature [2]. The nomenclature of either H_3Se or “selenium trihydride” is incorrect, misleading, and should not be applied to a molecular compound containing molecular hydrogen selenide and molecular hydrogen. The claims for metallization are unsupported by the evidence, and to the contrary, indicates the much simpler explanation of sample decomposition.

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