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Reply to “Comment on ‘Synthesis and properties of selenium trihydride at high pressures’ [Phys. Rev. B 97, 064107 (2018)] by Pace *et al.*”

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Abstract

The Comment of Pace *et al.* [[Phys. Rev. B in press](#)] claims that structural analysis and nomenclature of Zhang *et al.* [[Phys. Rev. B 97, 064107 \(2018\)](#)] is incorrect, that this compound is not metallic at high pressures and 200 K, and that the compound instead decomposes. In this Reply we argue that there are no experimental data that can discriminate between theoretically predicted *Cccm* H₃Se and advocated by Pace *et al.* *I4/mcm* (H₂Se)₂H₂. The difference in nomenclature is due to different naming conventions. We find the name “H₃Se” more convenient to apply in the limit of high-pressure. We also substantiate the initial claims of the stability up to 40 GPa at 170 K of the H₃Se compound after synthesis at 4.6 GPa and argue that the pressure induced metallization above 23 GPa is a plausible explanation of the reported visual observations and Raman spectroscopy results.

Main text

According to Pace *et al.*¹, Zhang *et al.*² claim that they synthesized a new compound H₃Se which is different from the theoretically predicted one³ that was also synthesized under similar conditions by Pace *et al.*⁴. The material synthesized by Zhang *et al.*² is clearly the same as theoretically predicted³ and subsequently synthesized by Pace *et al.*⁴; this can be seen based on the presented x-ray diffraction (XRD) and Raman data. While we admit that Zhang *et al.*² use the nomenclature H₃Se for the molecular (H₂Se)₂H₂ at low pressure⁴, we stress that this was made on purpose to emphasize the connection to the expected high-pressure behavior that is analogous with the behavior of H₃S⁵⁻⁸.

Furthermore, Pace *et al.*¹ suggests that the structural description of the compound is incorrect proposing that *I4/mcm* space group is a better choice. However, they admit themselves that XRD of these structures are very similar as the predicted peak positions and intensities are mainly determined by the positions of heavy Se, and these positions are almost indistinguishable in these two structures. The XRD data presented by Zhang *et al.*² have been collected using very small samples (a few single crystals, each of which was a few micrometers in linear dimensions) that were synthesized by laser heating in a diamond anvil cell (DAC) at nearly 5 GPa. Unfortunately, a complete structural analysis was not possible in our DAC with a limited angular opening. In this case, it is plausible to use theoretical predictions as a guide, and the results of Zhang *et al.*² showed a quite good correspondence with the predicted *Cccm* structure³. XRD of this low symmetry structure has many peaks of very low intensities and many peaks coincide; to facilitate

the comparison, only the predicted peaks with the intensities larger than 1% were included (Fig. 4 in Ref. ²). For the low-temperature high-pressure experiments, the DAC could only be rotated by about 2 degree, so we were limited in observation of few classes of diffraction lines.

Nevertheless, Zhang *et al.* clearly show the structural stability of *Cccm* H₃Se up to 40 GPa as no substantial changes in XRD patterns, which could be related to amorphization, decomposition, and major polymorphism, were detected. We note that the structural analysis of Pace *et al.* ⁴ made on much larger samples is not decisive as no structural refinement is reported. In Fig. 1 we compare the reported by Pace *et al.* ⁴ data at 7.5 GPa and 300 K with two generated XRD patterns based on *Cccm* and *I4/mcm* structures. Both agree reasonably well with the experiment. On the other hand, Guigue *et al.* ⁷ offer a good quality Rietveld refinement for *Cccm* H₃S (at 75 GPa). We believe that in the absence of good structural data that are sufficient to yield the positions of the hydrogen atoms, it is not possible to conclude whether H₃Se is *Cccm* or *I4/mcm*.

Finally, Pace *et al.* suggests that metallization proposed by Zhang *et al.* in H₃Se above 23 GPa below 200 K can be explained by a decomposition to elementary compounds as they showed at 300 K ⁴. We argue that according to our observations no decomposition occurs. Indeed, visual observation show the stable images of the single-crystal like samples up to 40 GPa, while Raman and XRD show a clear correspondence between the signal collected and the area of observations. In both these experiments, the position of the x-ray and Raman laser probe was visually carefully controlled. To illustrate this, Fig. 2 shows XRD patterns at 40 GPa collected at different sample positions with a step of 3 μm with respect to the x-ray spot of approximately 4 μm in diameter. Please note that our XRD does not detect any trace of Se metal at the position of H₃Se crystal and the vicinity. On the other hand, our Raman spectra clearly show a pressure induced deterioration of the Raman spectra of *Cccm* H₃Se with a subsequent softening, broadening, and appearance of asymmetry in the vibron band corresponding to H₂ molecules of *Cccm* H₃Se. Concomitantly, visual observations show the loss of transparency and appearance of metallic lustre. This behavior is in line with that reported previously in H₃S, where very similar changes in optical and vibrational properties have been observed without change in structure ⁸. However, we realize (as clearly stated in the Ref. ²) that our observations are not sufficient to claim metallization and more direct probes such as of electrical conductivity and/or optical including infrared spectroscopy are needed to make the definitive assessment. We seek for contributions of that kind.

In conclusion, we show that criticism of Pace *et al.*, ¹ concerns only the style of presentation and it does not affect the main conclusions of the paper of Zhang *et al.* ². The low-temperature chemical behavior of H₃Se is different from that at 300 K and the observations suggest the similarity to the behavior of H₃S. The metallicity of H₃Se at high pressures requires more solid experimental probes in line with the discussions in our paper ². We thank the authors of Ref. ¹ for bringing up their comments which allowed us to make our position with respect to the raised issues clearer.

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Figure Captions

Fig. 1. XRD of $(\text{H}_2\text{Se})_2\text{H}_2$ at 7.5 GPa and 300 K reported by Pace *et al.* ⁴ in comparison with the generated diffraction lines for *I4/mcm* and *Cccm* space groups. The lattice parameters were refined. The x-ray wavelength is 0.4066 Å.

Fig. 2. XRD patterns of H_3Se at 39.5 GPa and 170 K collected at different sample positions with 3 µm step in the course of work of Zhang *et al.* ². The x-ray wavelength is 0.3344 Å.

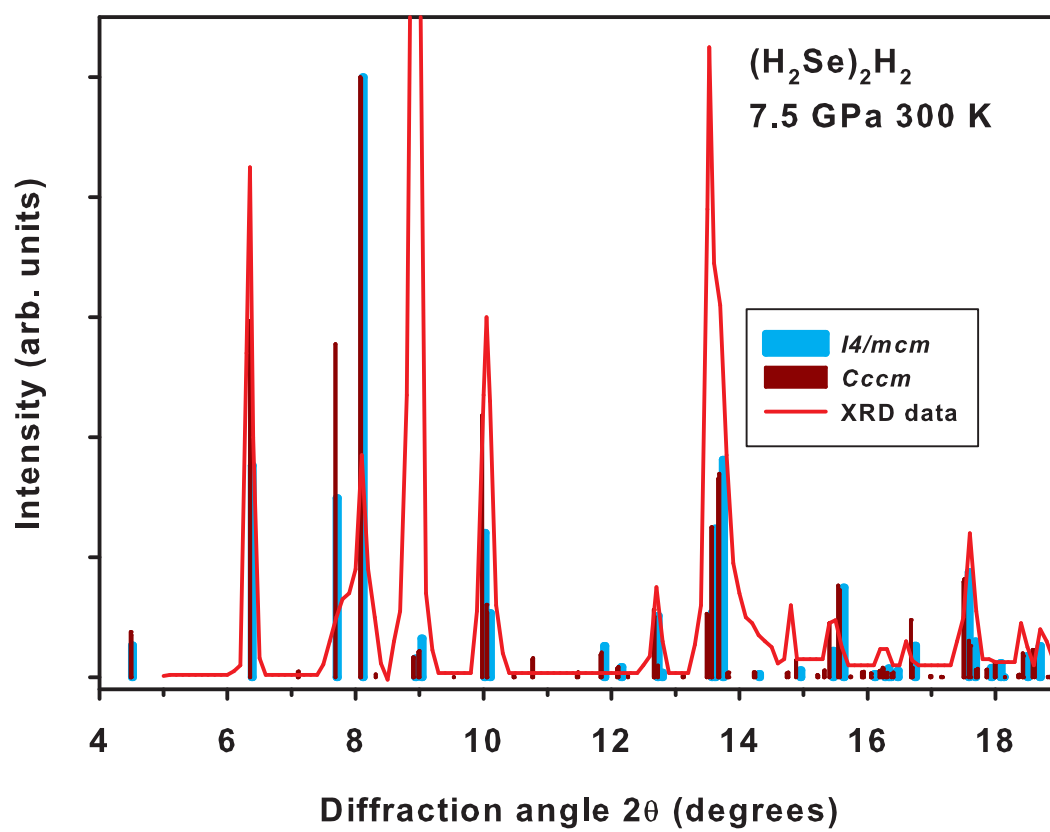


Figure 1

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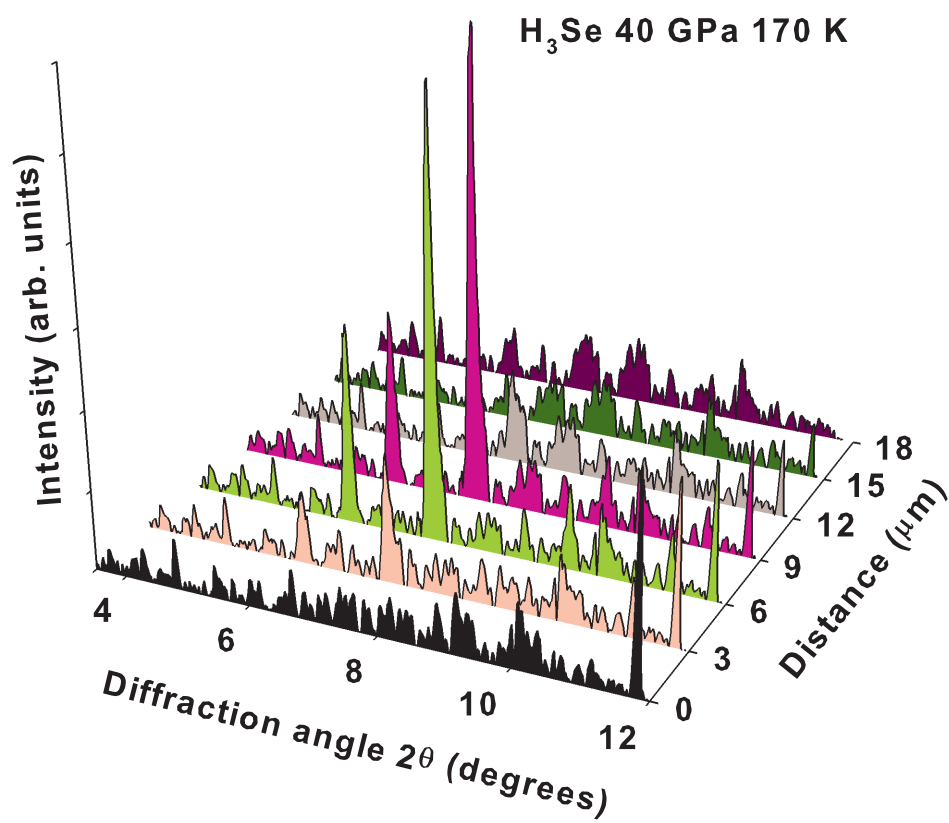


Figure 2

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