

**Ordered helium trapping and bonding in compressed arsenolite: Synthesis of  $\text{As}_4\text{O}_6 \cdot 2\text{He}$** 

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Compression of arsenolite has been studied from a joint experimental and theoretical point of view. Experiments on this molecular solid at high pressures with different pressure-transmitting media have been interpreted thanks to *state-of-the-art ab initio* calculations. Our results confirm arsenolite as one of the most compressible minerals and provide evidence for ordered helium trapping above 3 GPa between adamantane-type  $\text{As}_4\text{O}_6$  cages. Our calculations indicate that, at relatively small pressures, helium establishes rather localized structural bonds with arsenic forming a compound with stoichiometry  $\text{As}_4\text{O}_6 \cdot 2\text{He}$ . All properties of  $\text{As}_4\text{O}_6 \cdot 2\text{He}$  are different from those of parent  $\text{As}_4\text{O}_6$ . In particular, pressure-induced amorphization, which occurs in arsenolite above 15 GPa, is impeded in  $\text{As}_4\text{O}_6 \cdot 2\text{He}$ , thus resulting in a mechanical stability of  $\text{As}_4\text{O}_6 \cdot 2\text{He}$  beyond 30 GPa. Our work paves the way to explore the formation of alternative compounds by pressure-induced trapping and reaction of gases, small atomic or molecular species, in the voids of molecular solids containing active lone electron pairs.

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Molecular solids are very soft materials with open-framework structures composed of molecular units, exhibiting strong covalent interatomic forces, which are linked by weak intermolecular forces, such as van der Waals interactions or hydrogen bonding forces. Pressure is a thermodynamic variable that allows tuning interatomic distances and consequently is a powerful tool to study atomic interactions and the connectivity of different molecular units – hence, the possibility of molecular solids to trap small atoms or molecules. In this sense, molecule trapping has received a lot of interest from the scientific community due to its potential industrial applications covering hydrogen storage [1] and  $\text{CO}_2$  segregation from other organic compounds [2], among others. Recently, the small size of helium has triggered the study of pressure-induced helium trapping and how this effect affects the compressibility of host compounds. Those first studies were focused on helium trapping in silica glass [3–5] that is an amorphous compound with disordered interstitial voids large enough to host and trap helium. However, more studies need to be made of pressure-induced helium trapping in ordered crystallographic compounds, such as molecular solids.

Helium reaction is a challenge since it is one of the most inert elements in nature [6]. Previous studies of helium trapping in glasses have not revealed the pressure-induced reactivity of helium with the glass structure. On the search of the formation of solid structures with helium, the study of

mixtures of helium with other noble gases at high pressures has exhibited successful results. The mix of those fluids under pressure allows the formation of solid van der Waals compounds with exotic stoichiometries [7,8] [ $\text{He}(\text{N}_2)_{11}$ ,  $\text{Ne}(\text{He})_2$ ] given by the solubility of helium and dominated by the crystallization process of the other noble gases. On the other hand, it is noteworthy to highlight the low reactivity of helium with solid compounds, which has required the use of extremely high pressures (more than 1 Mbar) to form solid alloys, such as  $\text{Na}_2\text{He}$  [9].

In this work, we provide experimental and theoretical proofs of the pressure-induced helium trapping and reactivity in a molecular solid (arsenolite) at relatively low pressures. Our results could trigger the formation of alternative compounds by pressure-induced trapping and bonding of gases, small atomic and molecular species, with molecular solids containing active lone electron pairs.

Arsenic oxide ( $\text{As}_2\text{O}_3$ ) belongs to the sesquioxide family of group 15 elements, which also includes  $\text{P}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_3$ , and  $\text{Bi}_2\text{O}_3$ . In particular,  $\text{As}_2\text{O}_3$  crystallizes either in a cubic structure [space group (SG) 227,  $Fd-3m$ ,  $Z = 16$ ] (which corresponds to mineral named arsenolite) [10] or in monoclinic structures [SG 14,  $P21/c$ ,  $Z = 4$ ] (which corresponds to mineral named claudetite I and claudetite II) [11–13]; however, it can also be obtained in an amorphous (glass) phase [14,15]. Most of the polymorphs of group 15 sesquioxides [16] show close structural connections since many structures could be derived from a defective fluorite structure through symmetry breaking and local distortions [17,18]. A few of those polymorphs constitute molecular solids, like arsenolite

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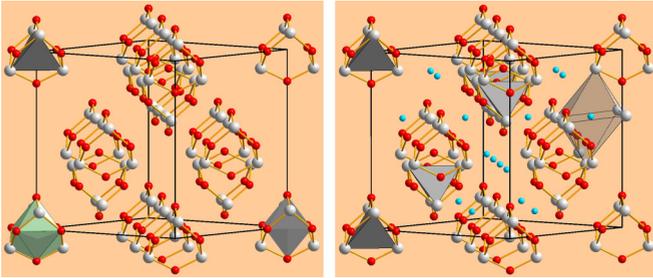


FIG. 1. Detail of the cubic unit cell of arsenolite ( $\text{As}_4\text{O}_6$ ) (left) and  $\text{As}_4\text{O}_6 \cdot 2\text{He}$  (right).  $\text{As}_4\text{O}_6 \cdot 2\text{He}$  is a compound formed above 3 GPa by arsenolite with He atoms inserted into 16*d* Wyckoff sites. Large gray balls, medium-size red balls, and small blue balls represent As, O, and He atoms, respectively.

( $\text{As}_4\text{O}_6$ ). This compound is a very soft and toxic mineral with an intermediate hardness between that of talc and gypsum, i.e., the softest minerals in the Mohs scale. In fact, arsenolite is composed of pseudotetrahedral units consisting of an arsenic atom surrounded by three oxygen ligands and a very active lone electron pair (LEP). Pseudotetrahedral units in arsenolite are configured in closed-compact adamantane-type  $\text{As}_4\text{O}_6$  molecular cages (Fig. 1, left), which are bonded together by weak van der Waals forces and with LEPs pointing towards the exterior of the molecular unit. Interestingly, the formation of molecular cages is also found in other sesquioxides and sesquichalcogenides of group 15 elements [19].

High-pressure (HP) Raman scattering (RS) and HP Fourier transform infrared measurements of arsenolite [20]; HP RS measurements of arsenolite, claudetite, and glass [21,22]; and HP x-ray diffraction (XRD) studies of arsenolite, claudetite, and glass  $\text{As}_2\text{O}_3$  [21–24] have been published. On the other hand, the atomic structure of arsenolite and its equation of state under different pressure transmitting media (PTM) were firstly reported in Ref. [25] and later by [26]. However, the possible reaction between those PTM and arsenolite studied from a joint experimental and theoretical approach have not been studied yet.

In this work, we provide a comprehensive understanding of the compression of arsenolite using different PTM (silicone oil, 4:1 methanol-ethanol mixture, and He) and without PTM. For this purpose, we combine two experimental techniques (XRD and RS) and *state-of-the-art ab initio* calculations providing structural, electronic, elastic, and lattice dynamical properties of arsenolite at different pressures. The comparison of the results of different experiments and its understanding on the light of *ab initio* calculations reveals that arsenolite is one of the most compressible minerals and provides evidence for helium trapping above 3 GPa between adamantane-type  $\text{As}_4\text{O}_6$  cages. Furthermore, our calculations indicate that, at relatively small pressures, He establishes localized structural bonds with As to form a compound with  $\text{As}_4\text{O}_6 \cdot 2\text{He}$  stoichiometry (Fig. 1, right).

Experimental XRD patterns of arsenolite compressed with different PTM (Fig. S1 in Supplemental Material [27]) reveal a progressive shift of the Bragg diffraction peaks of the cubic structure towards higher angles under compression, as expected for a decrease in the unit cell volume with

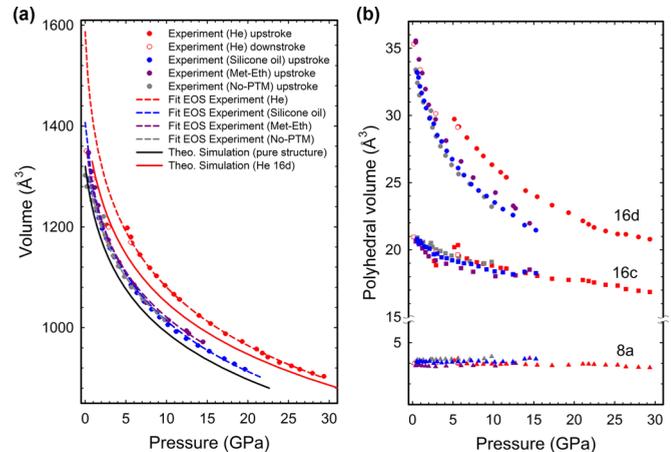


FIG. 2. Evolution of the structural parameters of arsenolite under pressure for different PTM. Gray, blue, purple, and red symbols correspond to experimental data of arsenolite compressed without PTM, with silicone oil, with methanol-ethanol mixture, and with He, respectively. Black (red) solid lines correspond to theoretical data of pure (He inserted in 16*d* sites) arsenolite. Dashed lines correspond to fit of experimental data. (a) EOS of arsenolite compressed with different PTM. (b) Compression of the polyhedral volume around different Wyckoff crystallographic sites: 16*d* (circles), 16*c* (squares), and 8*a* (triangles).

increasing pressure. Absence of new peaks at HP indicates that no phase transition occurs along the pressure range studied. The pressure dependence of the lattice parameter and atomic positions of arsenolite was obtained by Rietveld refinement along a large pressure range due to the relatively high quality of our experimental XRD patterns (Fig. S2 in Supplemental Material [27]) [28]. EOS of  $\text{As}_4\text{O}_6$  obtained from experiments using no PTM and silicone oil or methanol-ethanol as PTM yield an average bulk modulus of 7(2) GPa. This value is in good agreement with the theoretical EOS (see Fig. 2(a) and Table S1 in Supplemental Material [27]) [29] and with the bulk modulus obtained from experimental data of  $\text{As}_4\text{O}_6$  compressed with He below 4 GPa [30].

Notably, arsenolite's bulk modulus is smaller than those known for other sesquioxides of group 15 elements, which are well below 90 GPa, and much smaller than those of sesquioxides of group 13 elements, whose bulk moduli are well above 160 GPa (Table S2 in Supplemental Material [27]). Moreover, arsenolite's bulk modulus is in the range of the softest molecular crystals [24,31–34] and smaller than related molecular solids, like minerals realgar ( $\alpha\text{-As}_4\text{S}_4$ ,  $B_0 = 8.1$  GPa, and  $B'_0 = 9.0$ ) [33] and pararealgar ( $\beta\text{-As}_4\text{S}_4$ ,  $B_0 = 10.9$  GPa, and  $B'_0 = 8.9$ ) [34]. These similar compounds [35] have a cagelike structure based on As tetrahedra (Fig. 1, left) surrounded by anions in a closed-compact configuration. The reason for the small bulk moduli of sesquioxides and related molecular crystals of group 15 elements is the presence of the cation LEP which favors the formation of voids in the structural units resulting in open-framework low-compact structures with high compressibility.

Compression of arsenolite with He leads to a striking behavior above 3 GPa [Fig. 2(a)]. Unit cell volume decreases

with increasing pressure in a normal fashion below 3 GPa and above 5 GPa, but volumes at 3 and 5 GPa are rather similar, resulting in a jump of the  $P$ - $V$  curve of  $\text{As}_4\text{O}_6$  compressed with He with respect to  $P$ - $V$  curves of arsenolite compressed with other PTM. These results can be interpreted as a signature of He entering arsenolite's structure between 3 and 5 GPa and the consequent He trapping between  $\text{As}_4\text{O}_6$  cages above 5 GPa. The similar volume observed at 3 and 5 GPa can be explained as a compensation between the decrease of volume with pressure and the increase of volume due to He incorporation and trapping.

In order to understand where He gets trapped, we show in Fig. 2(b) the compressibility of arsenolite's constituting polyhedral units (see Fig. S4 in Supplemental Material [27]): (i) adamantane-type  $\text{As}_4\text{O}_6$  cage, centered around the  $8a$  (0,0,0) Wyckoff site; (ii) the quasioctahedral unit centered around the  $16c$  site [36]; and (iii) the distorted octahedron centered around the  $16d$  site. A clear change in the compressibility of the volume of the distorted octahedron around the  $16d$  Wyckoff site is observed depending on the PTM used. A jump in the volume of this polyhedral unit (also in that of the  $16c$  site but at a smaller rate) between 3 and 5 GPa is observed when He is used as PTM. This result is nicely explained by theoretical calculations including He in  $16d$  sites (a different experimental result would be found if He enters in  $16c$  sites according to calculations). Therefore, our measurements and calculations show a clear evidence of He entering in the largest voids of the structure ( $16d$  sites).

Helium does not enter into the smallest polyhedral units, and in particular into  $16c$  sites, which feature the smallest distances between neighboring  $\text{As}_4\text{O}_6$  cages and the smallest intermolecular As-As distance. This is a somewhat striking result since the smallest intermolecular As-As distance (around the  $16c$  site) is well above the van der Waals diameter of He [37], so one could expect the occupation of  $16c$  sites because He has been proved to be inserted in interstitial voids of similar or slightly larger diameter than He in amorphous silica [3–5].

In this respect, we want to stress that small He atoms can be diffused along the whole structure due to the existence of big connected spaces between  $16d$  sites without the need to enter in  $16c$  sites (see paths between He atoms at  $16d$  sites in Fig. S4 in Supplemental Material [27]).

The hypothesis of He incorporation and trapping in arsenolite above 3 GPa can also be checked by theoretically simulating the bulk compression of arsenolite with He located at  $8a$ ,  $16c$ , and  $16d$  Wyckoff positions (Fig. S2a in Supplemental Material [27]). Theoretical EOS of He trapped in  $16d$  Wyckoff sites shows rather good agreement with experimental data in the range between 5 and 30 GPa [Fig. 2(a)]. Therefore, our joint experimental and theoretical study of the bulk and polyhedral compressibilities with different PTM clearly points to the incorporation and trapping of He in  $16d$  sites of arsenolite above 3 GPa. Additional proofs confirming He trapping in arsenolite at HP are provided by HP RS measurements (see Supplemental Material [27]) performed with similar PTM as those used in HP XRD measurements (Fig. S5 in Supplemental Material [27]). Experimental HP RS spectra without PTM or with (4:1) methanol-ethanol mixture as PTM are similar to those already reported

and agree with theoretical calculations for pure arsenolite [20,22]. Remarkably, a different pressure dependence of the Raman-active mode frequencies in arsenolite is observed above 3 GPa when He is used as PTM (Fig. S6 in Supplemental Material [27]).

A remarkable broadening of Bragg peaks was observed in XRD experiments without PTM and with silicone oil or methanol-ethanol mixture above 15 and 20 GPa, respectively (Fig. S1 in Supplemental Material [27]). This feature can be ascribed to the onset of pressure-induced amorphization (PIA), as previously reported [21]. Comparison of XRD patterns of samples before and after compression reveal that recovered samples do not exhibit a good crystalline quality after the pressure cycle, which also suggests PIA of arsenolite. It is noteworthy that  $\text{As}_4\text{O}_6$  compressed with He shows no evidence of PIA up to the maximum pressure reached (29.4 GPa), as confirmed by the comparable crystalline quality of the sample before and after the pressure cycle (Fig. S1a in Supplemental Material [27]).

To understand the different mechanical stability of  $\text{As}_4\text{O}_6$  at HP depending on the PTM used we have analyzed the experimental and theoretical evolution of the two characteristic As-As and As-O distances with increasing pressure (see Fig. S3a in Supplemental Material [27] and related discussion). It can be concluded that the main modification upon entering He in the arsenolite structure is the enlargement of the closest As-As distance between adjacent molecular units (external As-As distance). Under compression of pure arsenolite, both internal and external As-As distances become nearly equal around 20 GPa, leading to strong steric repulsions between the different molecular units which result in PIA. Nevertheless, He trapping in arsenolite above 3 GPa leads to a considerable increase of the external As-As distance, thus avoiding the increase of the intermolecular interactions which turn the crystalline structure of arsenolite unstable. This feature explains the stability of arsenolite beyond 30 GPa when compressed with He and suggests that the stability of the molecular structure of arsenolite is related to the steric repulsion between the cationic As sublattice governing the formation of the cagelike structure.

Theoretical calculations of the pressure dependence of the elastic constants and stiffness coefficients in  $\text{As}_4\text{O}_6$  and  $\text{As}_4\text{O}_6$  with He at  $16d$  sites (Fig. S7 in Supplemental Material [27]) allow us to understand the different mechanical stability of arsenolite compressed with different PTM. Generalized Born stability criteria reveal a Born instability in arsenolite due to the violation of the  $M_2$  criterion at 19.7 GPa (Fig. S8a in Supplemental Material [27]), a pressure close to that experimentally observed for the onset of PIA in our HP XRD measurements using no PTM or using a PTM different from He. On the other hand, no mechanical instability is observed in  $\text{As}_4\text{O}_6$  with He at  $16d$  sites even at 30 GPa (Fig. S8b in Supplemental Material [27]) which is in very good agreement with our experimental results.

Finally, we have theoretically studied whether He trapping in arsenolite could lead to modification of other properties of arsenolite and even if He at  $16d$  sites could react with arsenolite to form a compound with  $\text{As}_4\text{O}_6 \cdot 2\text{He}$  stoichiometry above 3 GPa [38]. Our calculations indicate a strong decrease of the indirect band gap of  $\text{As}_4\text{O}_6$  from 4 to 3 eV between 1 atm and 15 GPa, whereas they predict a very small increase

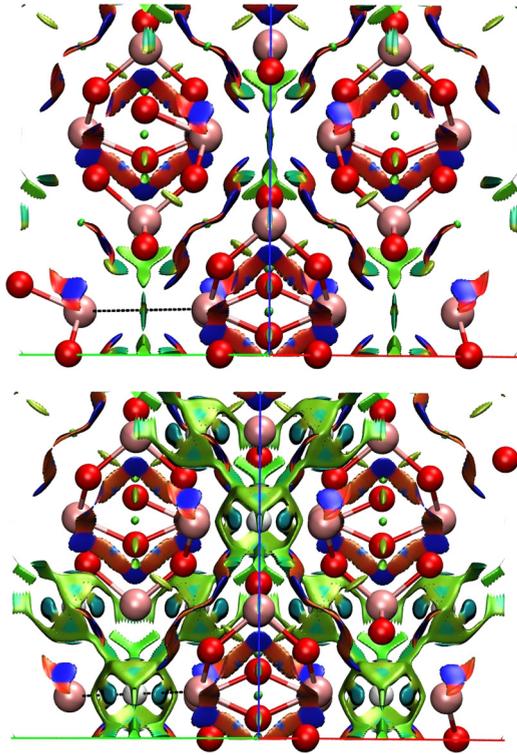


FIG. 3. Isosurfaces of the reduced density gradient (revealed by NCI index) evidencing noncovalent interactions in  $\text{As}_4\text{O}_6$  (top) and  $\text{As}_4\text{O}_6 \cdot 2\text{He}$  (bottom) near 16 GPa. As expected for a noble gas, van der Waals (green) interactions around the He atoms are revealed. However, unexpectedly localized interactions (in turquoise blue) also make their appearance along the He-As interaction lines.

of the indirect band gap of  $\text{As}_4\text{O}_6 \cdot 2\text{He}$  (also around 4 eV) as a function of pressure between 5 and 30 GPa. In fact, our theoretical calculations of the projected density of states in  $\text{As}_4\text{O}_6 \cdot 2\text{He}$  at 14 and 31 GPa (Fig. S8 in Supplemental Material [27]) show bonding and antibonding contributions to the valence band, with He 1s orbital character. The bonding contribution mainly concentrates in the extra band group, appearing just below the As 4s band group as He is incorporated into the structure, while the antibonding He 1s contribution concentrates mainly inside the As 4s band group. The presence of As 4s and O 2p contributions in this band group is a clear evidence of the new bonds formed by the He reaction with arsenolite. Three features provide further evidence of the reaction of He with  $\text{As}_4\text{O}_6$ : (i) a downward (upward) shift in energy of the bonding (antibonding) bands with increasing pressure, (ii) an increase of the bandwidth of both band groups with increasing pressure, and (iii) an increase in the projected density of states of the band group with antibonding He 1s character with increasing pressure.

Furthermore, we have analyzed our calculated charge density for pure arsenolite and arsenolite with He at 16d sites at different pressures looking for small interactions of He with surrounding atoms. For that purpose, we have used the NCI (noncovalent interaction) index [39] which is more adapted for identifying weak noncovalent bonds than the electron localization function (ELF). Figure 3 shows that there

are both localized and delocalized van der Waals interactions of He with its neighbors. In particular, localized interactions (revealed as compact surfaces) appear between He and six As neighbors. These interactions are strong enough to claim that He plays a role in the structure rather than simply occupying the 16d site, just like crystalline hydrogen bonded waters do. The low electronic density and the positive but weak values of the electronic Laplacian in this pressure range (Fig. S12 in Supplemental Material [27]) allow us to classify the character of the bonds established between He and As atoms as weak in nature, but the compact circular shapes obtained in NCI classify it as a localized structural type of bond. All these features allow us to conclude that there is a pressure-induced He bonding with  $\text{As}_4\text{O}_6$  resulting in the formation of  $\text{As}_4\text{O}_6 \cdot 2\text{He}$ . This notation, taken from crystalline water, stands for the fact that He is structurally added to the arsenolite structure. This bonding of He at pressures as small as 3 GPa is striking since the formation of helium-containing compounds has been recently reported only at extremely high pressures:  $\text{Na}_2\text{He}$  (113 GPa) [9].

The hypothesis of amorphization due to steric repulsion between neighboring As atoms is confirmed by theoretical calculations which show a strong increase of the repulsive interaction between low pressures and 15 GPa when arsenolite is compressed in the absence of He (Fig. S13 in Supplemental Material [27]).

In summary, we have proved that arsenolite is one of the nonhydrated molecular solids with the smallest bulk modulus and that He incorporates above 3 GPa into the arsenolite lattice at ordered 16d positions. He trapping helps to stabilize the arsenolite molecular structure keeping  $\text{As}_4\text{O}_6$  units separated and avoiding PIA at least up to 30 GPa. Furthermore, calculations indicate that He trapping in arsenolite modifies all the properties of arsenolite because there is a pressure-induced He bonding with arsenolite at relatively low pressures. The interaction of He and As atoms results in the formation of a compound with  $\text{As}_4\text{O}_6 \cdot 2\text{He}$  stoichiometry (only stable above 3 GPa since He exits arsenolite structure below this pressure) whose properties are different from those of  $\text{As}_4\text{O}_6$ . The present results pave the way to explore the formation of compounds by pressure-induced trapping and bonding of gases, small atomic and molecular species, with molecular solids having open-framework structures like those featuring active lone electron pairs. Moreover, these results suggest that compression of molecular solids with noble gases, such as helium, must be performed with caution since they may result in unexpected results compared to other pressure-transmitting media due to entry (and possible reaction) of these elements with the structure of the molecular compounds.

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- [29] Slightly larger deviations between the experimental and theoretical pressure dependence are observed at pressures above 15 GPa likely due to the onset of PIA.
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- [38] Taking into account that He incorporates into 16d sites, while As and O are in 32e and 48f sites, the stoichiometry of the new compound must be  $AsO \cdot 2He$ .
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