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Ordered Helium Trapping and Bonding in Compressed Arsenolite: Synthesis of $As_4O_6{\cdot}2He$

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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 As_4O_6 cages. Our calculations indicate that, at relatively small pressures, helium establishes rather localized structural bonds with arsenic forming a new compound with stoichiometry $As_4O_6{\cdot}2He$. All properties of $As_4O_6{\cdot}2He$ are different to those of parent As_4O_6. In particular, pressure-induced amorphization, which occurs in arsenolite above 15 GPa, is impeded in $As_4O_6{\cdot}2He$; thus resulting in a mechanical stability of $As_4O_6{\cdot}2He$ beyond 30 GPa. Our work paves the way to explore the formation of new 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.

Keywords: Helium Trapping • Helium bonding • Molecular Solids • High Pressure
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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 or hydrogen bonds. 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 their potential industrial applications that covers hydrogen storage,[1] 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, pressure-induced helium trapping has not been studied in ordered crystallographic compounds, such as molecular solids, to our knowledge. On the other hand, previous studies have not revealed the pressure-induced reactivity of helium with the glass structure. Helium reaction is a challenge since is one of the most inert elements in Nature.[6] 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 new solid van der Waals compounds with exotic stoichiometries[7,8] ($He(N_2)_{11}$, $Ne(He)_2$) 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, like Na_2He.[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 new compounds by pressure-induced trapping and bonding of gases, small atomic and molecular species with molecular solids containing active lone electron pairs.

Arsenic oxide (As_2O_3) belongs to the sesquioxide family of group-15 elements, which also includes P_2O_3, Sb_2O_3 and

Bi_2O_3. In particular, As_2O_3 crystallizes either in a cubic structure [space group (SG) 227, Fd-3m, Z=16] (named arsenolite)[10] or in monoclinic structures [SG 14, P21/c, Z=4] (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 (As_4O_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 pseudo–tetrahedral units consisting of an arsenic atom surrounded by three oxygen ligands and a very active lone electron pair (LEP). Pseudo-tetrahedral units in arsenolite are configured in closed-compact adamantane-type As_4O_6 molecular cages (Fig. 1 left) bonded together due to weak van der Waals forces 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]

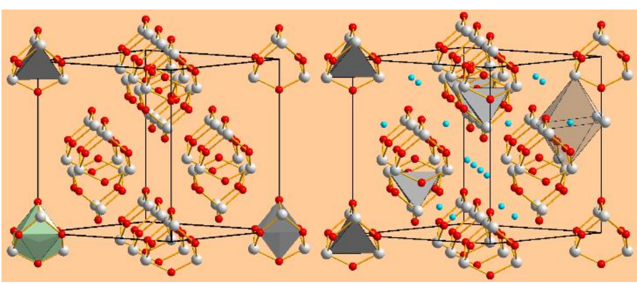

FIG. 1. (Color online) Detail of the cubic unit cell of arsenolite (As_4O_6) (left) and $As_4O_6{\cdot}2He$ (right). $As_4O_6{\cdot}2He$ is a new compound formed above 3 GPa by arsenolite with He atoms inserted into 16d Wyckoff sites. Big gray balls, medium-size red balls and small blue balls represent As, O, and He atoms, respectively.

HP-RS and HP-Fourier Transform Infrared measurements of arsenolite,[20] HP-RS measurements of arsenolite, claudetite, and glass,[21,22] and HP-XRD studies of arsenolite, claudetite and glass As_2O_3[21-24] have been published. However, the pressure dependence of the atomic structure of arsenolite and its equation of state (EOS) have not been properly addressed, neither experimentally nor theoretically. Moreover, the effect of different PTM on the properties of these polymorphs under compression has 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 reveal that arsenolite is one of the most compressible minerals and provide evidence for helium trapping above 3 GPa between adamantane-type As_4O_6 cages. Furthermore, our calculations indicate that, at relatively small pressures, He establishes localized structural bonds with As to form a new compound with $As_4O_6{\cdot}2He$ stoichiometry (Fig. 1 right).

Experimental XRD patterns of arsenolite compressed with different PTM (Fig. S1) 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 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).[25] EOS of As_4O_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. 2a and Table S1)[26] and with the bulk modulus obtained from experimental data of As_4O_6 compressed with He below 4 GPa.[27]

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). Moreover, arsenolite's bulk modulus is in the range of the softest molecular crystals[24,28-31] and smaller than related molecular solids, like minerals realgar (α-As_4S_4, B_0=8.1 GPa and B_0'=9.0)[30] and pararealgar (β-As_4S_4, B_0=10.9 GPa and B_0'=8.9).[31] These similar compounds[32] have a cage-like 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. 2a). 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 As_4O_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 As_4O_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. 2b the compressibility of arsenolite's constituting polyhedral units (see Fig. S4): i) adamantane-type As_4O_6 cage, centered around the 8a (0,0,0) Wyckoff site, ii) the quasi-octahedral unit centered around the 16c site[33] and iii) the distorted octahedron centered around the 16d site. A clear change in the compressibility of the volume of the distorted octahedron around 16d Wyckoff site is observed depending on the PTM used. A jump in the volume of this polyhedral unit (also in that of 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); so it is a clear evidence of He entering in the largest voids of the structure (16d sites). He does not enter into the smallest polyhedral units, and in particular into 16c sites, which feature the smallest distances between neighboring As_4O_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,[34] so one could expect the occupation of 16c sites because He has been proved to be inserted in interstitials voids of similar or slightly larger diameter than He in amorphous silica.[3-5]

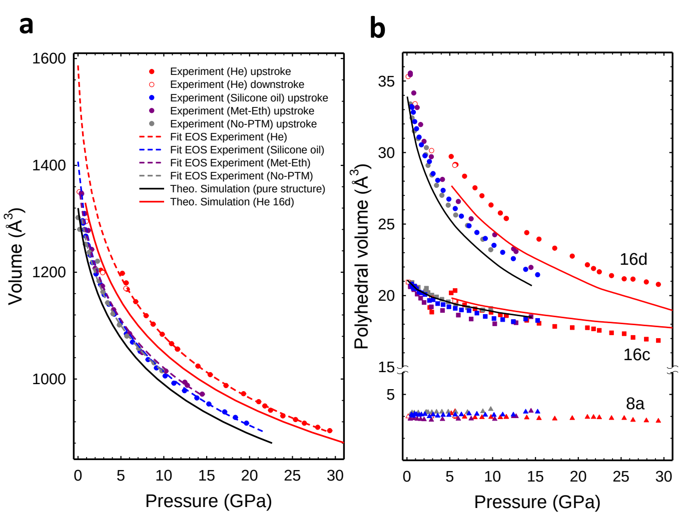

FIG. 2. (Color online) Evolution of the structural parameters of arsenolite under pressure for different PTM. Grey, blue, purple, and red symbols correspond to experimental data of arsenolite compressed without PTM, with silicone oil, with methanol-ethanol mixture and with He, respectively. Black (red) solid lines correspond to theoretical data of pure (He-inserted in 16d 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: 16d (circles), 16c (squares) and 8a (triangles).

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).

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). Theoretical EOS of He trapped in 16d Wyckoff sites shows a rather good agreement with experimental data in the range between 5 and 30 GPa (Fig. 2a). Therefore, our joint experimental and theoretical study of the bulk and polyhedral compressibilities with different PTM clearly point 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 supplementary material) performed with similar PTM as those used in HP-XRD measurements (Fig. S5). 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).

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). 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. Noteworthily, As_4O_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). To understand the different mechanical stability of As_4O_6 at HP depending on the PTM used we have analysed the experimental and theoretical evolution of the two characteristic As-As and As-O distances with increasing pressure (see Fig. S3a 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 considerably 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 cage-like structure.

Support for the different mechanical stability of arsenolite compressed with different PTM was provided by theoretical calculations of the pressure dependence of the elastic constants and stiffness coefficients in As_4O_6 and As_4O_6 with He at 16d sites (Fig. S7). 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); 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 As_4O_6 with He at 16d sites even at 30 GPa (Fig. S8b) which is in very good agreement with our experimental results.

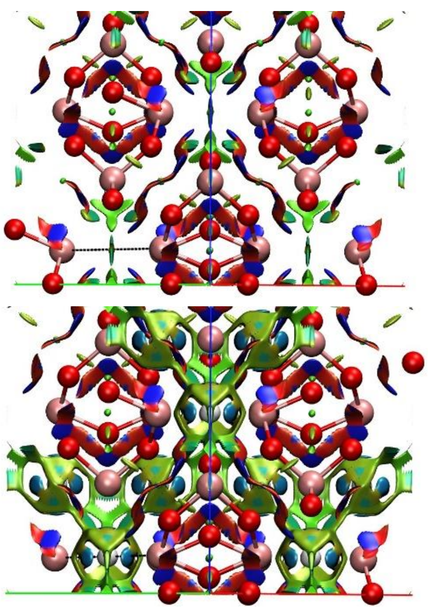

FIG. 3. (Color online) Isosurfaces of the reduced density gradient (*aka* NCI) evidencing non-covalent interactions in As_4O_6 (top) and $As_4O_6{\cdot}2He$ (bottom) near 16 GPa. As expected for a noble gas, van der Waals (green) interactions around the He atoms are revealed. However, unexpectedly localized interactions (in turquoise blue) also make their appearance along the He-As interaction lines.

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 $As_4O_6{\cdot}2He$ stoichiometry above 3 GPa.[35] Our calculations indicate a strong decrease of the indirect bandgap of As_4O_6 from 4 to 3 eV between 1 atm and 15 GPa, whereas they predict a very small increase of the indirect bandgap of $As_4O_6{\cdot}2He$ (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 of $As_4O_6{\cdot}2He$ at 14 and 31 GPa (Fig. S8) show bonding and antibonding contributions, with He 1s orbital character, to the valence band of the new compound. The bonding contribution mainly concentrates in the new 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 the new band group is a clear evidence of the new bonds formed by He reaction with arsenolite. Three features provide further evidence of the reaction of He with As_4O_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 using the NCI (Non Covalent Interaction) index[36] which is more adapted for identifying weak non-covalent 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 neighbours. 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), allow us to classify the character of the bonds established between He and As atoms as a 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 As_4O_6 resulting in the formation of $As_4O_6{\cdot}2He$. 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 Na_2He (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 absence of He (Fig. S13).

In summary, we have proved that arsenolite is one of the non-hydrated 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 As_4O_6 units separated and avoiding PIA at least up to 30 GPa. Furthermore, calculations indicate that He trapping in arsenolite modify 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 new compound with $As_4O_6{\cdot}2He$ stoichiometry (only stable above 3 GPa since He exits arsenolite structure below this pressure) whose properties are different from those of As_4O_6. The present results pave the way to explore the formation of new 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, like helium, must be performed with caution since they may result in unexpected results compared to other pressure-transmitting media due to entry (and reaction) of these elements with the structure of molecular compounds.

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[1] Y. Song. Phys.Chem. Chem. Phys. 15, 14524 (2013)
[2] S. Xiang et al. Nat. Comm. 3, 954 (2012)
[3] T. Sato, N. Funamori, and T. Yagi. Nature Comm. 2, 345 (2011).
[4] G. Shen et al. PNAS. 108, 6004 (2011).
[5] C. Weigel et al. Phys. Rev. Lett. 109, 245504 (2012).
[6] C. Herman. Nat. Chem. 4, 140 (2012)
[7] W. L. Vos et al. Nature 358, 46 (1992)
[8] P. Loubeyre, M. Jean-Louis, R. LeToullec, and L. Charon-Gerard. Phys. Rev. Lett. 70, 178 (1993)
[9] X. Dong et al. DOI: arXiv:1309.3827v3.984
[10] F. Pertlik. Czech. J. Phys. B. 28, 170 (1978).
[11] A.J. Frueh. Am. Mineralogist. 36, 833 (1951).
[12] W.B. White, F. Dachille, and R. Roy. Z. Kristall. 125, 450 (1967).
[13] F. Pertlik. Monatsh. Chem. 109, 277 (1978).
[14] A. Bertoluzza, M. A. Morelli, and C. Fogano. Lincei. Bend. Sci. Fis. Mat. Nat. (Italy). 52, 923 (1972).
[15] G. N. Papatheodorou, S. A. Solin. Phys. Rev. B. 13, 1741 (1976).
[16] P2O3 is not stable in solid form at ambient conditions.
[17] A. Matsumoto, Y. Koyama, and I. Tanaka, I. Phys. Rev. B. 81, 094117 (2010).
[18] A. Matsumoto, Y. Koyama, and I. Tanaka, I. Phys. Rev. B. 83, 214110 (2011).
[19] The reason for the molecular character of these materials is the strong activity of LEPs in group-15 elements and also in O and S.
[20] A. Grzechnik. J. Sol. State Chem. 144, 416 (1999).
[21] Q. Mei et al. J. Non-Cryst. Solids. 353, 1755 (2007).
[22] E. Soignard et al. Phys. Rev. B. 77, 144113 (2008).
[23] C. E. Weir. J. Res. Nat. Bureau Standards- A. Physics and Chemistry. 69A, 29 (1965).
[24] Q. Mei et al. J. Phys.: Condens. Matter. 19, 415103 (2007).
[25] Rietveld refinement was not possible above 15 and 20 GPa due to loss of hydrostaticity in the experiments without PTM and with silicone oil and methanol-ethanol, respectively.
[26] Slightly larger deviations between the experimental and theoretical pressure dependence are observed at pressures above 15 GPa likely due to the onset of PIA.
[27] EOS for arsenolite compressed with He below 3 GPa was not obtained because of the few data points mainly taken during downstroke due to He loading constraints.
[28] S. N. Vaidya, and G. C. Kennedy. J. Chem. Phys. 55, 987 (1971).
[29] T. Chattopadhyay, A. Werner, and H. G. von Schnering. J. Phys. Chem. Solids. 43, 919 (1982).
[30] M. A. Tuktabiev et al. J. Phys.: Condens. Matter. 21, 385401 (2009).
[31] G. O. Lepore et al. Mineralogical Magazine. 76, 963 (2012).
[32] A. Kyono. Phys. Chem. Minerals. 40, 717 (2013).
[33] To establish the compressibility around the 16c site we have taken the volume of the octahedron defined by the closest As atoms to a 16c site.
[34] A. Bondi. J. Phys. Chem. 68, 441 (1968).
[35] 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 $As_4O_6{\cdot}2He$.
[36] E. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A. Cohen and W. Yang, J. Am. Chem. Soc. 132, 6498 (2010).