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Vibrational and elastic properties of As_4O_6 and $As_4O_6 \cdot 2He$ at high pressures: study of dynamical and mechanical stability

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A. Lattice dynamics

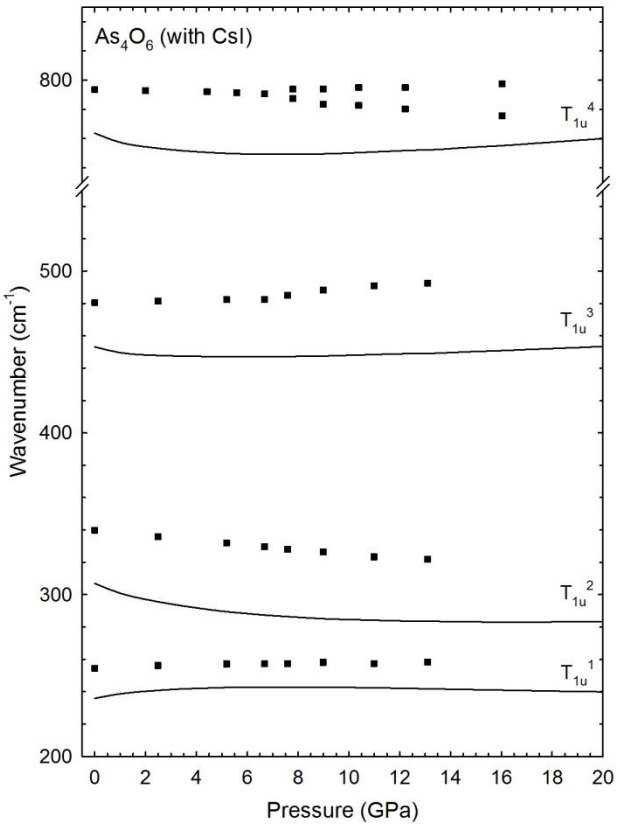

Figure S1. Experimental and theoretical pressure dependence of the IR-active modes in As_4O_6. Experimental data measured using CsI as a PTM are taken from Ref. S1.

Table SI. Theoretical and experimental zero-pressure frequencies and pressure coefficients of IR-active modes in As_4O_6 at 0 GPa. Experimental data are taken from Ref. S1.

	Ab initio calculations		Experimental	
Mode (Sym)	ω_0 (cm^{-1})	$\frac{\partial\omega}{\partial P}$ $\left(\frac{cm^{-1}}{GPa}\right)$	ω_0 (cm^{-1})	$\frac{\partial\omega}{\partial P}$ $\left(\frac{cm^{-1}}{GPa}\right)$
T_{1u}^{1} (IR)	236.0	2.7	254.5	0.8
T_{1u}^{2} (IR)	306.7	-5.7	339.8	-1.5
T_{1u}^{3} (IR)	453.1	-3.8	480.4	0.1
T_{1u}^{4} (IR)	763.5	-6.6	793.4	-0.2

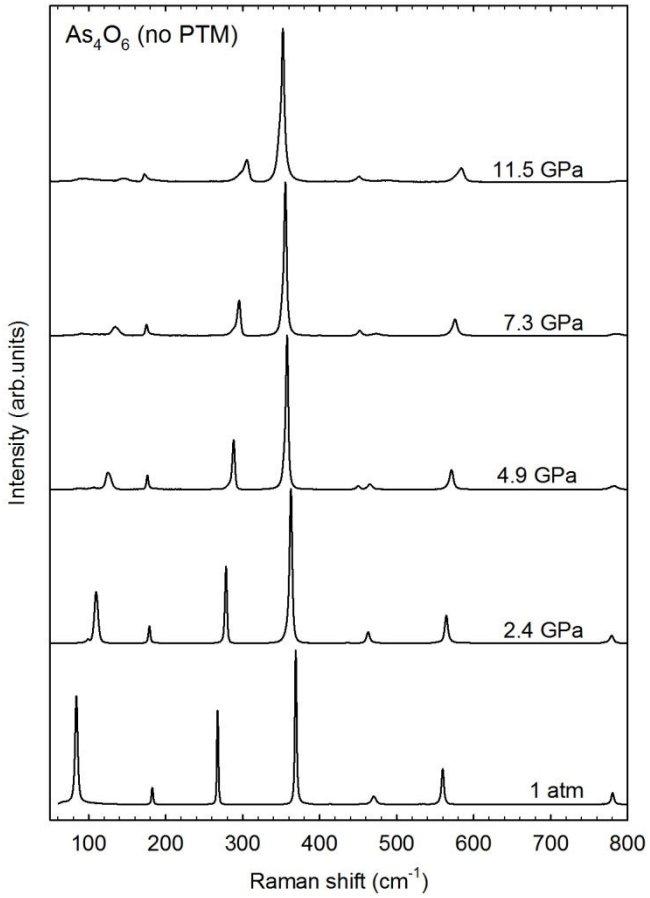

Figure S2. Raman scattering spectra of arsenolite at selected pressures without any PTM. Raman spectra are vertically shifted for the sake of clarity.

A progressive shift of the Raman-active mode frequencies of all peaks of the cubic structure with increasing pressure is observed in As_4O_6 compressed without any PTM. Absence of new peaks at high pressure clearly indicates that no phase transition occurs along the pressure range studied. Many Raman modes undergo a progressive asymmetric broadening with increasing pressure. This broadening is likely caused by the increase of intermolecular interactions; i.e., the increase of interactions among As_4O_6 cages, which finally results in the onset of PIA above 15 GPa.

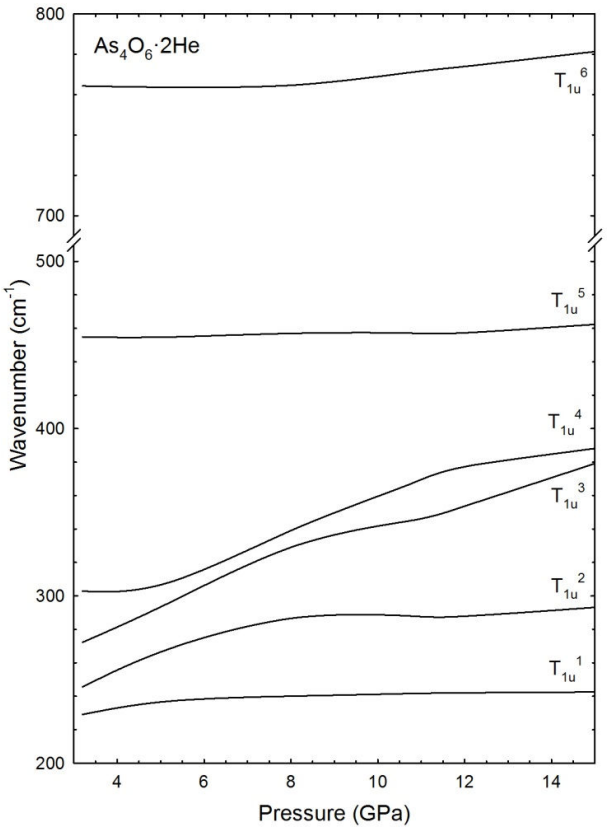

Figure S3. Theoretical pressure dependence of the IR-active modes in $As_4O_6 \cdot 2He$.

There are two additional IR-active modes in $As_4O_6 \cdot 2He$ than in As_4O_6. The two extra modes are located between the two lowermost IR-active modes of As_4O_6 and have a much larger pressure coefficient than IR-active modes of As_4O_6 thus leading to anticrossings with the mode above 300 cm^{-1}.

Table SII. Theoretical frequencies and pressure coefficients of IR-active modes in $As_4O_6 \cdot 2He$ at 3 GPa.

	Ab initio calculations	
Mode (Sym)	ω_0 (cm^{-1})	$\frac{\partial \omega}{\partial P}$ $\left(\frac{cm^{-1}}{GPa}\right)$
T_{1u}^{1}	230.0	3.3
T_{1u}^{2}	247.5	11.2
T_{1u}^{3}	271.6	12.5
T_{1u}^{4}	300.3	0.3
T_{1u}^{5}	455.1	-0.7
T_{1u}^{6}	763.8	-1.1

B. Thermodynamic properties

The Debye temperature is a fundamental parameter that correlates with many physical properties of solids, such as specific heat, elastic constants, and melting temperature. One of the standard methods to calculate the Debye temperature, θ_D, is from elastic constant data using the semi-empirical formula **[S2]**:

$$\theta_D = \frac{h}{k_B}\left[\frac{3n}{4\pi}\left(\frac{N_A\rho}{M}\right)\right]^{1/3} v_m$$

where h is the Planck's constant, k_B is the Boltzmann's constant, n is the number of atoms in the molecule, N_A is the Avogadro's number, ρ is the density, M is the molecular weight, and v_m is the averaged sound velocity. As reported in **Table SIII**, the values of θ_D at 0 GPa using the Hill approximation are 196.2 K (222.7 K) in As_4O_6 ($As_4O_6{\cdot}2He$). We note that the Debye temperature in $As_4O_6{\cdot}2He$ is slightly greater than that of As_4O_6. **Figure S4(a)** reports the evolution with pressure of the Debye temperature, θ_D, for both oxides. It is observed that θ_D follows a similar dependence than v_m with increasing pressure; i.e., increases at low pressures in both oxides and decreases above 8 GPa in As_4O_6 while it increases in $As_4O_6{\cdot}2He$ at least up to 35 GPa.

The thermal conductivity is the property of a material that indicates its ability to conduct heat. In order to estimate the theoretical minimum of the thermal conductivity, we have used the following expression **[S3]**:

$$\kappa_{\min} = k_B v_m \left(\frac{M}{n\rho N_A}\right)^{-2/3}$$

The values of κ_{min} in As_4O_6 ($As_4O_6{\cdot}2He$) at 0 GPa using the Hill approximation are 0.36 (0.42) W m^{-1} K^{-1} (see **Table SIII**). Therefore, both oxides are low κ materials **[S4]. Figure S4(b)** reports the evolution with pressure of the minimum thermal conductivity, κ_{min}, for both oxides. As in the case of θ_D, κ_{min} first increases with pressure and latter it decreases with pressure because of the decreasing of v_m with pressure for As_4O_6, while κ_{min} increases with pressure up to 35 GPa in $As_4O_6{\cdot}2He$. On the other hand, if we use the simplified formula for κ_{min} that considers $v_m = 0.87\sqrt{E/\rho}$ **[S3]**, the decreasing of κ_{min} with pressure in As_4O_6 can be explained by the decreasing of the tensile stiffness of As_4O_6 as pressure increases above 9 GPa.

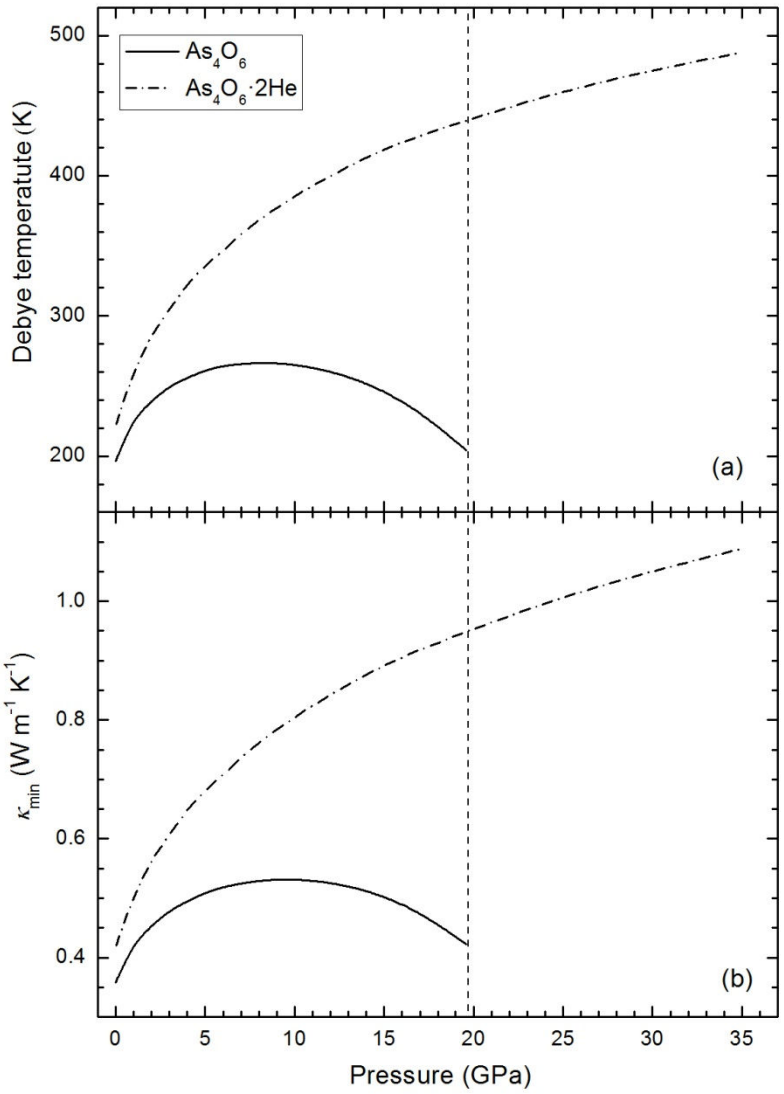

Figure S4. Evolution with pressure of the theoretical Debye temperature (a) and theoretical minimum thermal conductivity, κ_{min}, (b) in As_4O_6 and $As_4O_6 \cdot 2He$.

Table SIII. Debye temperature (θ_D in K), and minimum thermal conductivity (κ_{min} in W m^{-1} K^{-1}) in As_4O_6 and $As_4O_6 \cdot 2He$ at 0 GPa. Data are given in the Hill approximation.

	As_4O_6	$As_4O_6 \cdot 2He$
θ_D	196.2	222.7
κ_{min}	0.36	0.42

References

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