

Observation of a New Polyhalide Phase in Ag-Cl₂ System at High Pressure

Adam Grzelak^{1*}, Jakub Gawraczyński¹, Mariana Derzsi², Viktor Struzhkin³, Maddury Somayazulu³, Wojciech Grochala¹

¹ Center of New Technologies, University of Warsaw, 02089 Warsaw, Poland; j.gawraczynski@cent.uw.edu.pl (J.G.); w.grochala@cent.uw.edu.pl (W.G.)

² Advanced Technologies Research Institute, Faculty of Materials Science and Technology in Trnava, Slovak University of Technology in Bratislava, 917 24 Trnava, Slovakia; mariana.derzsi@gmail.com

³ Center for High Pressure Science and Technology Advanced Research, Shanghai 201203, China; viktorstruzhkin@yahoo.com

⁴ HPCAT, X-ray Science Division, Argonne National Laboratory, Lemont, IL 60439, USA; zulu@anl.gov

* Correspondence: a.grzelak@cent.uw.edu.pl

SUPPLEMENTARY MATERIAL

S1. Raman spectra of solid Cl₂ and pressure dependence of band frequencies

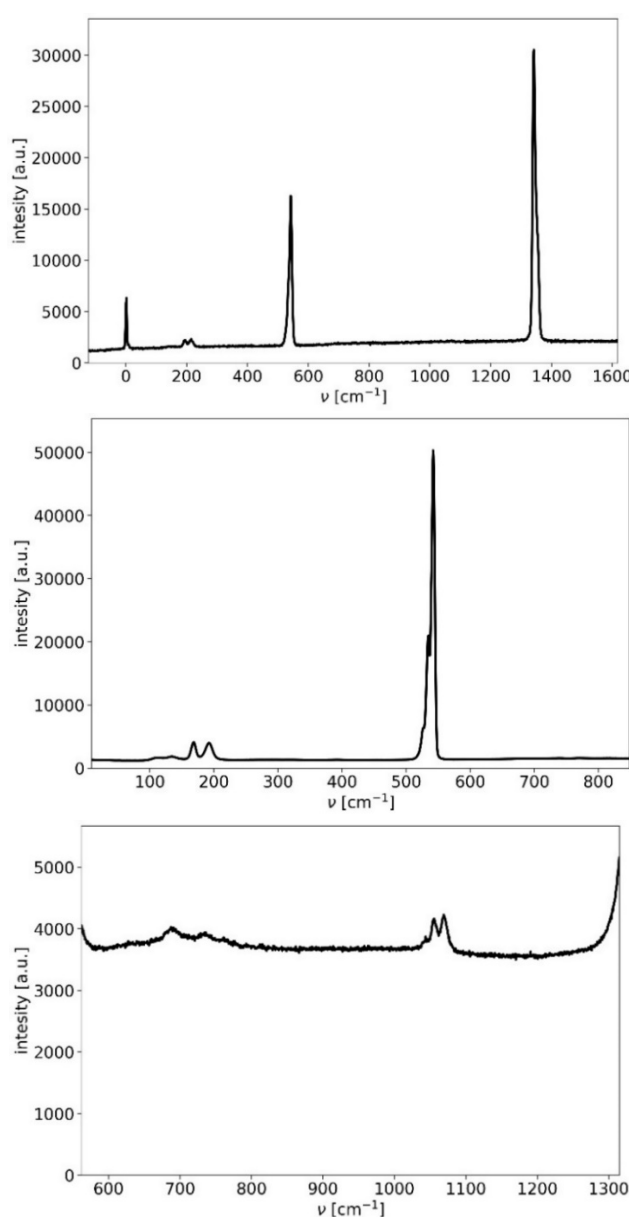


Figure S1. Spectra of solid chlorine obtained at 8 GPa. The high-intensity band at ca. 1350 cm⁻¹ originated from diamond anvil.

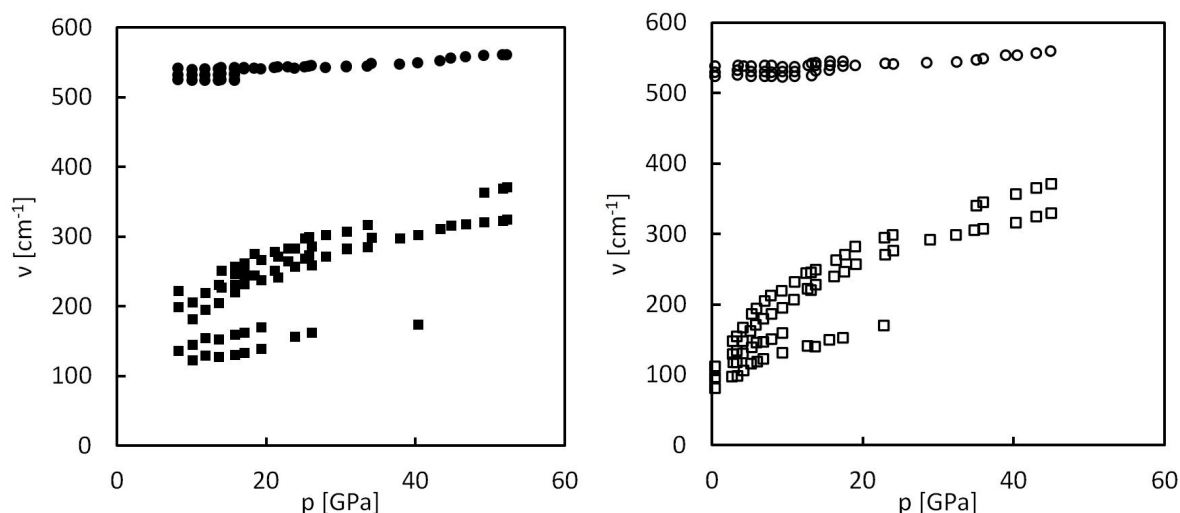


Figure S2. Comparison of pressure dependence of chlorine bands in this work (left panel) and in Johannsen *et al.* [1]. Circles are Cl-Cl₂ intramolecular vibrations and squares are lattice phonons.

Raman spectra for solid Cl₂ obtained in this work, and subsequent pressure dependence of bands identified in those spectra, are in good agreement with ref. [1] (Figure S2). Accordingly, the bands appearing in the region ca. 100-400 cm⁻¹ are designated as lattice modes – from lowest to highest frequency: B_{1g}, B_{2g}, A_g, B_{3g}. Disappearance of B_{1g} and B_{2g} modes above certain pressures is also in agreement with ref. [1]. The bands at ca. 520-550 cm⁻¹ originate from intramolecular Cl-Cl vibrations. The main band in this group is also the most intense in the spectrum of chlorine. Its splitting, i.e. shoulders appearing at lower pressures, is an isotopic effect [1]. Pressure dependence of this band is relatively flat, testifying to rigidity of the Cl-Cl bond, as compared to weak intermolecular interactions in the Cl₂ molecular crystal.

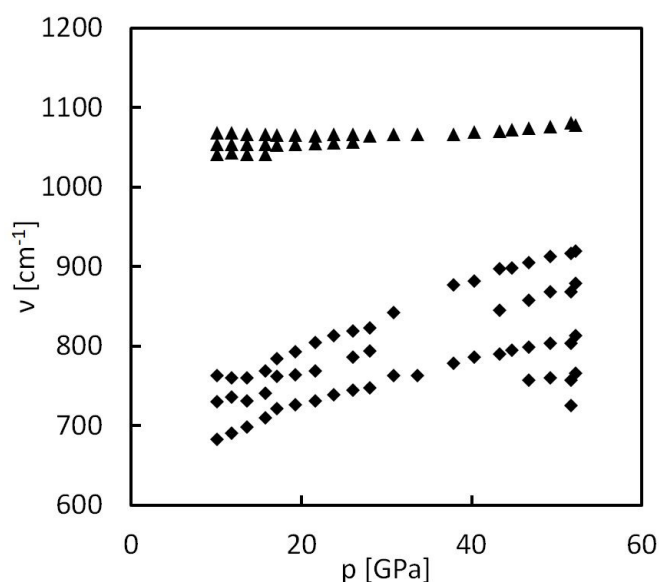


Figure S3. Pressure dependence of bands designated as originating from Cl₂ in the 600-1200 cm⁻¹ range – this work.

In Figure S3 we plot the pressure dependence of bands in the region above 600 cm^{-1} , which were not discussed or shown in ref. [1]. The bands appearing at ca. 1020-1080 cm^{-1} are interpreted to be overtones of intramolecular Cl-Cl vibration bands mentioned above, due to their frequency, slope of pressure dependence, and splitting. The bands appearing in the ca. 650-900 cm^{-1} range are most likely combination bands – Cl-Cl vibron (A_g) + one of the lattice phonon modes (B_{1g} , B_{2g} , B_{3g}). These bands are very weak in intensity compared to the rest of those discussed. Multiplying the corresponding irreducible representations, we get the overtones: $B_{1g} \times A_g = B_{1g}$, $B_{2g} \times A_g = B_{2g}$, and $B_{3g} \times A_g = B_{3g}$. An example analysis of such combination mode is shown in fig. S4.

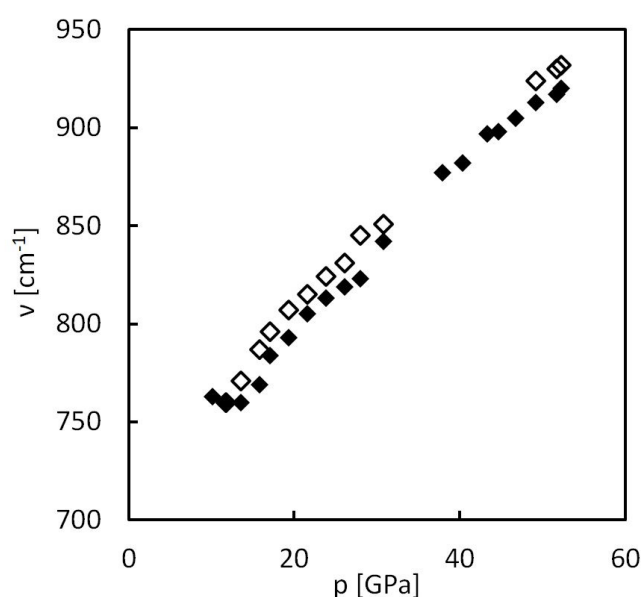


Figure S4. Pressure dependence of one of the combination modes ($B_{3g} \times A_g = B_{3g}$) observed in the spectrum of Cl_2 . Filled diamonds – observed frequencies, hollow diamonds – pressure dependence of the sum of frequencies of B_{3g} lattice phonon and A_g Cl_2 vibron. Note the anharmonicity of the observed combination mode, i.e. a lower observed frequency compared to the simple sum.

S2. Pressure dependence of simulated (DFT) frequencies of the overtone of IR-active T_{1u} mode of AgCl in CsCl structure.

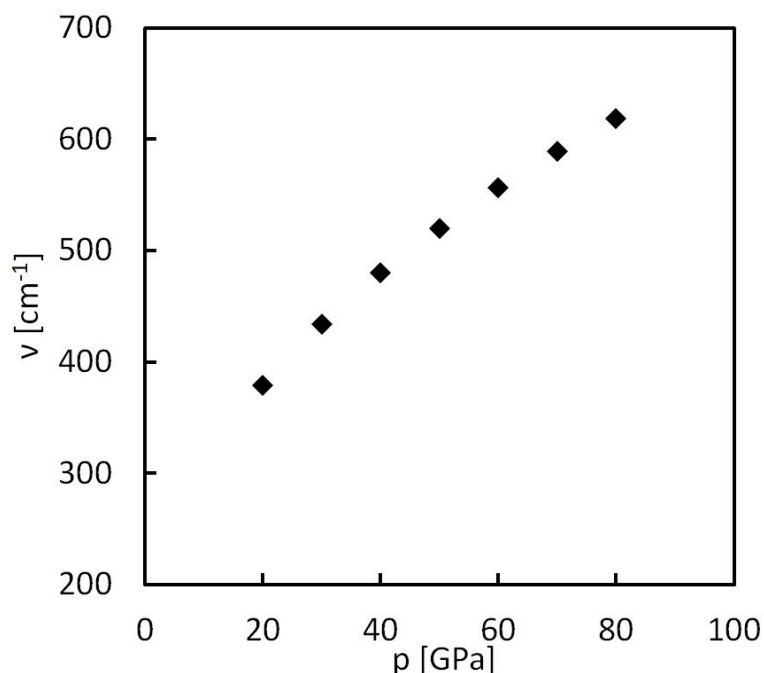


Figure S5. Pressure dependence of simulated (DFT) frequencies of the overtone of IR-active T_{1u} mode of AgCl in CsCl structure.

Figure S5 shows pressure dependence of simulated frequency of the overtone of T_{1u} mode in CsCl-type AgCl ($Pm\bar{3}m$), which is a stable polymorph of AgCl above ca. 13 GPa [2]. Calculations were carried out using VASP software [3–7], with GGA-type Perdew-Burke-Ernzerhof functional adapted for solids (PBEsol) [8] was used. Plane-wave cutoff energy was set to 800 eV, with self-consistent field convergence criterion set to 10^{-7} eV. Integration grid of 11x11x11 k-points was used.

S3. Picture of the one of the samples



Figure S6. Picture of sample from experiment A after initial compression and laser heating. Note the brown color of the irradiated spot.

References

1. Johannsen, P.G.; Holzapfel, W.B. Effect of Pressure on Raman Spectra of Solid Chlorine. *Journal of Physics C: Solid State Physics* **2000**, *16*, L1177–L1179, doi:10.1088/0022-3719/16/33/001.
2. Hull, S.; Keen, D. Pressure-Induced Phase Transitions in AgCl, AgBr, and AgI. *Physical Review B* **1999**, *59*, 750–761, doi:10.1103/PhysRevB.59.750.
3. Kresse, G.; Hafner, J. Ab Initio Molecular Dynamics for Liquid Metals. *Physical Review B* **1993**, *47*, 558–561, doi:10.1103/PhysRevB.47.558.
4. Kresse, G.; Hafner, J. Ab Initio Molecular-Dynamics Simulation of the Liquid-Metamorphous-Semiconductor Transition in Germanium. *Physical Review B* **1994**, *49*, 14251–14269, doi:10.1103/PhysRevB.49.14251.
5. Kresse, G.; Furthmüller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. *Computational Materials Science* **1996**, *6*, 15–50, doi:10.1016/0927-0256(96)00008-0.
6. Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Physical Review B - Condensed Matter and Materials Physics* **1996**, *54*, 11169–11186, doi:10.1103/PhysRevB.54.11169.
7. Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Physical Review B* **1999**, *59*, 1758–1775, doi:10.1103/PhysRevB.59.1758.
8. Perdew, J.; Ruzsinszky, A.; Csonka, G.; Vydrov, O.; Scuseria, G.; Constantin, L.; Zhou, X.; Burke, K. Restoring the Density-Gradient Expansion for Exchange in Solids and Surfaces. *Physical Review Letters* **2008**, *100*, 136406, doi:10.1103/PhysRevLett.100.136406.