



High pressure evolution of the electronic and local structure of Bromine

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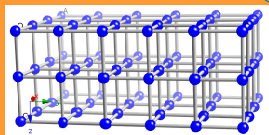
INTRODUCTION

The halogens form diatomic molecules and **molecular crystals**: the intra-molecular distance is much smaller than any other interatomic distances within the crystal. Among the molecular crystals, bromine is one of the simplest. In spite of this simplicity it still reserves many hidden surprises^[1].

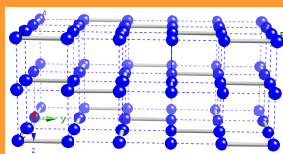
The formation of diatomic molecules is the result of a **Peierls distortion** of a simple cubic structure.

One distance is shortened and the remaining five distances are elongated as shown schematically. This is an example of the **Octet rule**.

a) The **pressure** is known to **destroy** the Peierls distortion like e. g. in arsenic. At a transition pressure the inter-molecular distance becomes identical to the dimer inter-atomic distance and the molecule is said to **dissociate**. In general this takes place abruptly through a first order phase transition and for bromine this happens at a rather high pressure of 80 GPa.



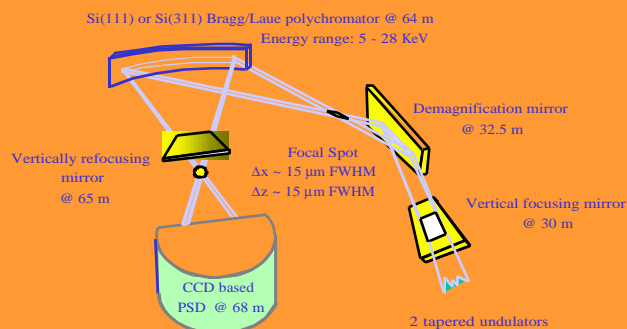
Top : simple cubic structure (P > 80 GPa)
Bottom : structure of Br₂ (schematic)



b) However, we have recently shown^[2] that the semiconducting Br₂ crystal, **metallizes** at a much lower pressure of about 25 GPa. Is the bromine molecule ignoring these drastic changes that deeply modify the electronic structure of the crystal?

High pressure studies by EXAFS on ID24 (ESRF)

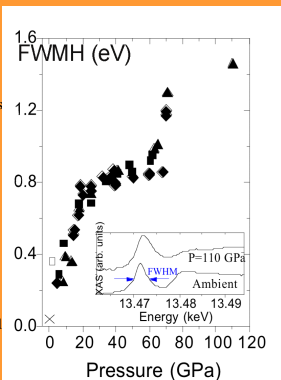
The XAS is the ideal technique to study the structural and electronic properties of systems under high pressures as it the most sensitive tool to measure the short interatomic distances (EXAFS) and a valuable probe to measure the width of the unoccupied conduction band (XANES). We have studied the high pressure evolution of the bromine molecular crystal using the high pressure dedicated ID24 beamline at ESRF, sketched below.



XANES Spectra : width of the unoccupied band as a function of pressure

At **25 ± 5 GPa** we observe a slope change in the evolution of this width. Comparison with published calculations of the electronic density of states indicates that the physical origin of the slope change is compatible with the **metallisation** process. This is also confirmed by a simple tight binding calculation. In addition, the metallisation pressure value is in agreement with calculated ones.

At **68 ± 5 GPa** a discontinuity in the evolution of the width of the sigma antibonding band points out the **onset of a phase transformation**. This result could be compatible with the observed phase transformation near 80 ± 5 GPa by X-ray diffraction that is associated with the **molecular dissociation**[3]. Other possibilities are the presence of a "modulated" phase as observed in iodine or an in-plane metallisation.

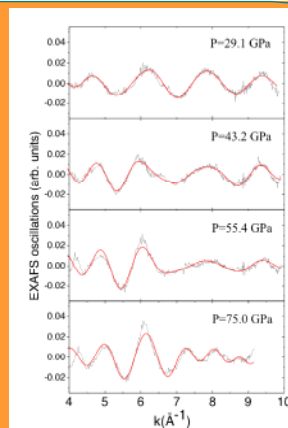


EXAFS Spectra

The figure shows the pressure evolution of the EXAFS oscillations that contain the information of the local structure around a bromine atom.

The fit of the oscillations was done using a constrained structural model including the crystallographic parameters obtained by high pressure X-ray diffraction experiments and, as shown, the fit is entirely satisfactory.

This study constitutes the **highest pressure EXAFS experiment** ever done.

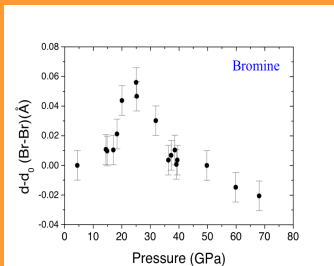


Interatomic distances : a surprising insulator-metal transition

The evolution of the bromine interatomic distance in the molecule is shown here.

a) The first surprise is that the evolution of the bromine intra-molecular distance is **not monotonic**, but it first increases decreasing at a higher pressure. (no structural transformation has been observed below 80 GPa.)

b) The second surprise is that this change of behaviour takes place precisely at the **metallization pressure**.



CONCLUSIONS

Our results demonstrate that from the electronic point of view we have two totally different types of molecular crystals sharing the same crystal structure,

- a) Below 25 GPa : **insulating molecular crystal**
- b) Above 25 GPa : **metallic molecular crystal**

Finally above 80 GPa, an **atomic metallic crystal** appears.

This is very reminiscent of the behaviour of H₂ (as well as Se, Te, H₂O...) showing the universal behaviour of systems with **broken symmetry under pressure**.

References

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