

are used as solid electrolytes in chemical sensors, fluorine sources and batteries [4]. In particular, it has been shown that Ce-activated scintillators, show very good combinations of stopping power, speed, and luminosity and as a consequence there is a continued search for improved host crystals for the Ce activation [5]. Ternary fluorides $M(\text{II})\text{ThF}_6$ ($M=\text{Cd}, \text{Ba}, \text{Hg}, \text{Pb}$) have been identified to be good candidates for such applications [6].

We have investigated the structure of BaThF_6 as a function of temperature and pressure with single-crystal x-ray diffraction using synchrotron radiation [7]. The compound crystallizes in the tysonite structure, space group $P6_3/mmc$ ($a = 4.296(1) \text{ \AA}$ and $c = 7.571(1) \text{ \AA}$), at ambient conditions. It is stable at least down to 150 K and up to 4 GPa. In this range of pressures and temperatures, the fluoride is characterized by a high degree of disorder, both on the cationic and anionic positions. Despite the different valence states and sizes, both cations, Ba^{2+} and Th^{4+} occupy the same crystallographic site in the ideal tysonite structure.

The cationic disorder is described by two alternative approaches. The first model corresponds to a split-atom position model in which Ba^{2+} is maintained on a special position with site symmetry $-6m2$, while Th^{4+} is slightly displaced from the respective position. In the second model, both cations are maintained on the ideal position and anharmonic displacement parameters using a tensor of third order are introduced. Anharmonic displacement parameters could be refined not only from low temperature data, but also from high-pressure single-crystal x-ray data measured *in situ* in a diamond anvil cell. Our results have shown that the $\sin\theta/\lambda$ diffraction limit reached in high-pressure experiments is crucial for the successful application of the anharmonic approach. The feasibility and general problems of anharmonic refinements of high-pressure x-ray data will be further commented.

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High pressure structure of $\text{Mn}_2(\text{CO})_{10}$: an off-axis M-M bond

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The bond between transition metals has always attracted structural chemists, because of the intriguing features that characterize this interaction. In particular, Mn-Mn bond in $\text{Mn}_2(\text{CO})_{10}$ is one of the most characterized, because of the historical importance of this molecule [1]. Spectroscopic characterizations at high pressure have also been reported, suggesting the occurrence of a phase transition above 0.8 GPa producing a conformational change (from *staggered* to *eclipsed*) [2]. This transformation would be very similar to that we observed on species like $\text{Co}_2(\text{CO})_6\text{L}_2$ ($\text{L}=\text{AsPh}_3, \text{PPh}_3$) [3].

However, periodic DFT calculations and X-ray powder diffraction are not in agreement with the reported interpretation of the Raman

spectra. Indeed, no conformational change is observed on increasing the pressure, but a curious rotation of the two $\text{Mn}(\text{CO})_5$ moieties, leading to an unprecedented Mn-Mn off-axis bond (the Mn-Mn bond does not coincide with the Mn- $\text{CO}_{\text{apical}}$ axis, as in the gas phase molecular structure, see the Figure). Interestingly, this molecular geometry can be anticipated also from diffraction at ambient pressure, because the molecule shows an incipient distortion. Single crystal data at high pressure are not possible, because the samples easily break upon application of the pressure.

Theoretical calculations within the interacting quantum atom approach are also used to discuss the new geometry.



Figure 1. Left: the molecular conformation of $\text{Mn}_2(\text{CO})_{10}$ at ambient condition (*staggered*). Centre: the molecular conformation at 3GPa as hypothesized from Raman spectroscopy (*eclipsed*). Right: the conformation of $\text{Mn}_2(\text{CO})_{10}$ at 3GPa from P-DFT theoretical predictions and XRPD experiments.

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Atomic polarization and multipolar model

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When a molecule is placed in an external electric field, its electron distribution changes in response. A useful measure of this effect is the molecular dipole moment together with its first and second derivatives (polarizability, hyperpolarizability). Using the QTAIM theory [1] it is possible to decompose the dipole moments and the polarizabilities into the atomic components. It was previously discussed [2] that each atomic contribution can be expressed as the sum of “atomic polarization” and “charge transfer” contributions. The transfer contribution is given by the weighted translation vector from atom’s nucleus to the corresponding BCP, its sign and value strongly depend on the nature and number of bonded groups to the selected atom.

Here we present the relationship between the charge density distribution, obtained with the use of multipole model of Hansen and Coppens [3], and electric properties such as electric dipole moment, as well as the response of a molecule to the external electric field in simple organic molecules. It is well established that the multipolar reconstructed electron density (XD2006 [4]) can provide sufficiently accurate electric moments of a molecule in the crystal, however our preliminary results show that this does not hold for derivatives of the electric moments. In particular, while the bond polarity term is sufficiently well reconstructed (at least at zero field), the atomic polarization term is more problematic, even without the application of an external electric field. Empirical methods to estimate the polarizability based on the zero field electron density distribution will be tested, in order to allow estimation of linear optic properties from a multipolar model.