



	<b>Experiment title:</b> Negative thermal expansion and compression mechanisms in the $M(\text{CN})_2$ family ( $M=\text{Zn}, \text{Cd}, \text{Hg}$ ): polyhedral distortions or rigid unit motion?	<b>Experiment number:</b> HS-4434
<b>Beamline:</b> BM01A	<b>Date of experiment:</b> from: 16/11/11 to: 19/11/11	<b>Date of report:</b> 18/11/13
<b>Shifts:</b> 9	<b>Local contact(s):</b> Vladimir Dmitriev	<i>Received at ESRF:</i>
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## Report:

The tetrahedral metal cyanides  $M(\text{CN})_2$  ( $M=\text{Zn}, \text{Cd}$ ) have emerged as one of the key families of flexible framework materials.<sup>1-4</sup> In their structures, the cyanide ions act as linear  $M-\text{CN}-M$  bridges, producing three-dimensional frameworks with the cubic diamond-type topology.<sup>1</sup> Because the  $M-\text{C}-\text{N}$  angles can bend so easily, the framework lattices are incredibly flexible and this leads to a host of unusual structural and mechanical properties. For example, they exhibit the strongest-known isotropic negative thermal expansion (NTE) behaviour—more than double that of  $\text{ZrW}_2\text{O}_8$ ;<sup>1</sup>  $\text{Zn}(\text{CN})_2$  becomes mechanically softer on compression ( $B' < 0$ ) in its ambient- $p$  phase,<sup>2</sup> then exhibits a rich series of high-pressure phase transitions that culminate in eventual pressure-induced amorphisation (PIA);<sup>4</sup> correlated Cd displacements in  $\text{Cd}(\text{CN})_2$  produce highly-structured diffuse X-ray scattering patterns, and the material undergoes an associated displacive phase transition on cooling below 150 K.<sup>1</sup> NTE offers a valuable mechanism of countering the usual positive thermal expansion of engineering materials; likewise crystal–amorphous transitions such as PIA are seeing widespread use in data-storage. There is a strong drive to understand the microscopic origin of both effects in this family in order to design the best possible NTE/PIA materials for practical application. This aim of this study was to investigate the high- $p/T$  behaviour of the three key  $M(\text{CN})_2$  NTE/PIA materials ( $M=\text{Zn}, \text{Cd}, \text{Hg}$ ) on BM01A. For all three materials, the underlying goal is to determine the relative roles of distortion and rigid unit motion in their unusual mechanical properties, by characterising the structural deformations associated with their high- $p$  phase transitions.

We measured high quality diffraction data on BM01A at pressures of up to 12 GPa (fluorinert pressure transmitting medium; diamond-anvil cell) on  $\text{Zn}(\text{CN})_2$  and  $\text{Hg}(\text{CN})_2$ . Data analysis is still underway for the latter compound. In the case of  $\text{Zn}(\text{CN})_2$ , a first-order displacive phase transition to an orthorhombic phase occurs at 1.5 GPa, with the corresponding atomic displacements characterized by correlated collective tilts of pairs of Zn-centered tetrahedra. This displacement pattern sheds light on the mechanism of negative thermal expansion in ambient-pressure. Full details of this study have been published in the following reference:

HOMOLOGOUS CRITICAL BEHAVIOR IN THE MOLECULAR FRAMEWORKS  $\text{Zn}(\text{CN})_2$  AND  $\text{Cd}(\text{imidazolate})_2$

I. E. COLLINGS, A. B. CAIRNS, A. L. THOMPSON, J. E. PARKER, C. C. TANG, M. G. TUCKER, J. CATAFESTA, C. LEVELUT, J. HAINES, V. DMITRIEV, P. PATTISON, A. L. GOODWIN

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- [3] A. E. Phillips et al., *Angew. Chem. Int. Ed.* **47**, 1396 (2008)
- [4] H. K. Poswal et al., *J. Solid State Chem.* **182**, 136 (2009)