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Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Cyanamides under high pressure	**Experiment number**: CH 1087
Beamline: ID30	**Date of experiment**: from: 26 April 2001 to: 28 April 2001	**Date of report**: 30 August 2001
Shifts: 6	**Local contact(s)**: Dr. Mohamed MEZOUAR	*Received at ESRF:*

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Report:

The structures of 11th and 12th group metal cyanamides were systematically studied at ambient conditions by using X-ray and neutron diffraction, recently, and the cyanamides display a rich degree of various crystal structures, depending on the cations present[1-3]. However, the high pressure behavior of cyanamides is unknown up to now. In addition to some general interest in the high pressure behavior of metal cyanamides, the C-N bond inside these compounds is of special interest in a number of fields with implication for low compressibility materials. In particular, polymerizing the CN_2^{2-} units could open a versatile access to three dimensional C/N networks. The research on phase transition and decomposition behavior of cyanamide using *in situ* high pressure techniques offers us an opportunity to study the intrinsic characteristics of C-N bonding and the decomposition dynamics of cyanamide under high pressure conditions.

The high pressure experiments were carried out at room temperature in a diamond anvil cell (DAC) apparatus, while the ruby fluorescence method was used for pressure calibration. The angle-dispersive X-ray powder diffraction experiments (wavelength 0.3738 Angstrom) in a DAC were performed for $HgCN_2$, Ag_2CN_2, and Na_2CN_2 at the beamline ID30. Diffraction patterns were recorded on an image plate and then converted to the intensity versus 2θ diffraction angle by using the program FIT2D.

From the XRD patterns of the $HgCN_2$ we can observe that additional diffraction peaks appear while the diffraction peaks of $HgCN_2$ keep stable at increasing pressure to 1.9 GPa. The new peaks can be indexed as α-Hg, this indicates the pressure induced decomposition of $HgCN_2$ to happen at about 1.9 GPa. However, the decomposition proceeds slowly, and does not finish even

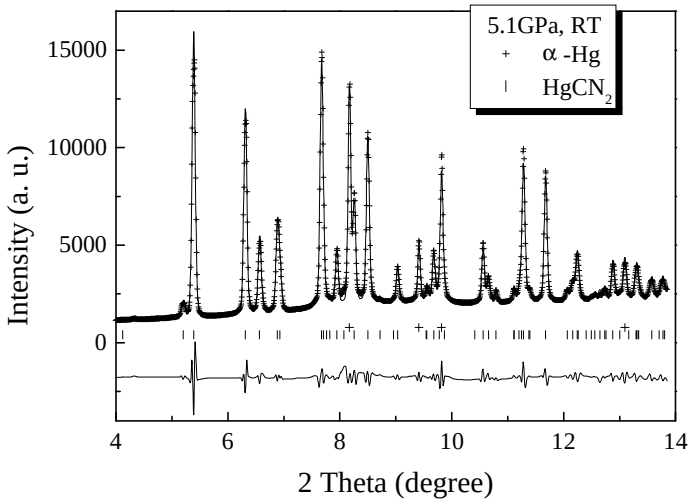

Fig. 1

as the pressure reaches 10 GPa. The product of decomposition should consist of mercury and C-N remnants. The possibility of some of C-N double bonds converting to single bonds and then forming a C-N single bond network under high pressure is the interesting point to check. However, only mercury could be observed in the diffraction patterns. The C-N remnants may have formed an amorphous network which has neither XRD peaks nor obviously new Raman active modes, the latter were measured in MPI für Festkörperforschung in Stuttgart[4].

Fig. 1 shows a typical Rietveld refinement result (using the program GSAS) of the powder pattern at 5.1 GPa at compression. At this condition two phases ($HgCN_2$ and α-Hg) coexist. In the pressure range of 7.0 GPa to 10 GPa, α-Hg (rhombohedral, *R -3m*) partly transforms to β-Hg (tetragonal, *I4/mmm*). This phase transition should happen at 3.7 GPa for pure mercury. The delay of this phase transition may be attributed to small amounts of impurities of carbon and nitrogen resulting from the decomposition. Neglecting the decomposition, the equation of state for mercury cyanamide could be fitted according to second order ($K_0' = 4$) Birch equation. The zero pressure bulk modulus (K_0), estimated as 38.5 GPa, indicates mercury cyanamide to be a very soft compound.

H_2CN_2 is a weak acid and for the metal cyanamides low stability is expected. However, Ag_2CN_2 shows, surprisingly, very stable under pressure within 10 GPa, and its zero pressure bulk modulus was estimated as 102 GPa if setting K_0' as 4 (Birch equation of state). On the other hand, Na_2CN_2 was observed a phase transition happen at very low pressure, and the phase analysis is still in progress. In this case no pressure medium was used due to Na_2CN_2 is very sensitive to moisture. Every compound of the cyanamide family shows special kind of behavior under high pressure maybe due to its intrinsic instability. Further investigations will give us new insight into the different grade and reason of stability, and may lead into new access to amorphous C/N networks.

References:

1. M. Becker, and M. Jansen, Synthesis and characterisation of mercury cyanamide, Z. ANORG. ALLG. CHEM. 626: (7) 1639-1641, 2000
2. M. Becker, J. Nuss, and M. Jansen, Crystal structure and spectroscopic data of silver cyanamide, Z. NATURFORSCH. B 55: (5) 383-385, 2000
3. M. Becker, J. Nuss, and M. Jansen, Synthesis and characterization of sodium cyanamide, Z. ANORG. ALLG. CHEM. 626: (8) 2505-2508, 2000
4. H. Liu, W. Klein, H. Bender, and M. Jansen, High pressure behavior of mercury cyanamide $HgCN_2$, Z. ANORG. ALLG. CHEM., 628: (1) 4-6, 2002.