ESRF	**Experiment title: Equation of state and structural properties of Nitromethane (CH3NO2, CD3NO2) at room temperature and up to 40 GPa**	**Experiment number**: HS 2157
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Report:

Introduction

The present report concerns our first investigation on the structural parameters and of the equation of state (EOS) of nitromethane (and deuterated nitromethane) (CH_3NO_2, CD_3NO_2) at room temperature in the pressure range up to ~ 40 GPa.

Nitromethane is the simplest nitroalkane and a basic energetic material used as a propellant and for its detonation properties. Under pressure nitromethane was mainly investigated at high temperature, where it was found to decompose;[1] recently we found at room temperature a very interesting feature: nitromethane was observed to transform chemically from 27 GPa to a product which can be recovered.[2] Consequently data on its structural parameters under pressure are needed for the understanding of the chemical transformation and the determination of its EOS and for the identification of the formed product.

General considerations on chemical transformation of compressed crystals, composed of multiple bonds molecules, to amorphous products were given in the application sent in August 2003. We found by infrared spectroscopy that, contrary to compounds with adjacent multiple bonds, the chemical transformation of nitromethane is a slow process occurring over a pressure range. This transformation starts at ~ 27 GPa. The reaction rate was found to increase on further compression. It was proposed for the decomposition mechanism, which occurs at 440 K and at 1.6 GPa, a process whose first step involves the formation of an hydroxyl group arising from the interaction of the methyl and the nitro group.[1] It is likely that the interaction between the methyl and the nitro groups is at the origin of the chemical transformation under pressure at room temperature. This assumption is supported by the observation we did on the deuterated compound whose transformation was observed to start at ~ 40 GPa, that is far above 27 GPa observed for CH_3NO_2, actually the deuterium is obviously less "mobile" than the hydrogen.

Till now structural investigations were performed by x-rays and neutrons up to 6 and 5.5 GPa respectively.[3,4] We report here the first conclusions of our investigation up to more than 40 GPa.

Experimental

The hole gasket was either filled at 295 K with liquid CH_3NO_2 (or CD_3NO_2) from a syringe or from a spray aimed at the nitrogen cooled anvil where the gasket was placed. Accordingly the sample was directly compressed in the diamond cell (DAC). At 295 K crystallization occurs at 0.4 GPa. We used angle-dispersive powder-diffraction method with a MAR 345 image-plate detector on beam line ID09A. Pressure was determined by the ruby luminescence technique. We performed seven runs, the upper pressure reached for both hydrogenated and deuterated compounds were close to 43 GPa.

Results

At room pressure nitromethane crystallizes in the orthorhombic system $P2_12_12_1$ with Z=4. Accordingly the number of reflections is very large: for a 2θ diffraction angle ranging from 4.5 to 25 ° more than 255 reflections are expected. Actually and for the time being we used the data collected only up to 2θ = 15°. The 2D-powder rings collected on the image plate were integrated to conventional profiles through FIT2D. Due to the fact that the transformation is not completed, reflections were observed well above 27 GPa for the hydrogenated compound. We found that the profiles obtained were consistent with the $P2_12_12_1$ structure, in other words no evidence of structural transition was found up to 43 GPa, this conclusion holds particularly for the deuterated compound where the reflections were better observed. The lattice parameters a, b, c were computed in the full pressure range through DATLAB. Results for the volume cell *vs* pressure are plotted in Fig. 1. Above 10 GPa hydrogenated nitromethane was found slightly more compressible and the deuterated product.

From the fit of our data the bulk modulus B_0, and its pressure derivative B'_0, were found close to 8.5 GPa and 5.8 and 9.75 GPa and 5.5 for CH_3NO_2 and CD_3NO_2 respectively. Our B_0 values depart from those of ref. 3 and 4 by + 1.5 GPa. Comments will be given elsewhere.

References

* This work is part of a European Thesis in collaboration with the LENS (Firenze).

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3. D.T. Cromer, R.R. Ryan, and D. Schiferl, **J. Phys. Chem.** 89, 2315 (1985).
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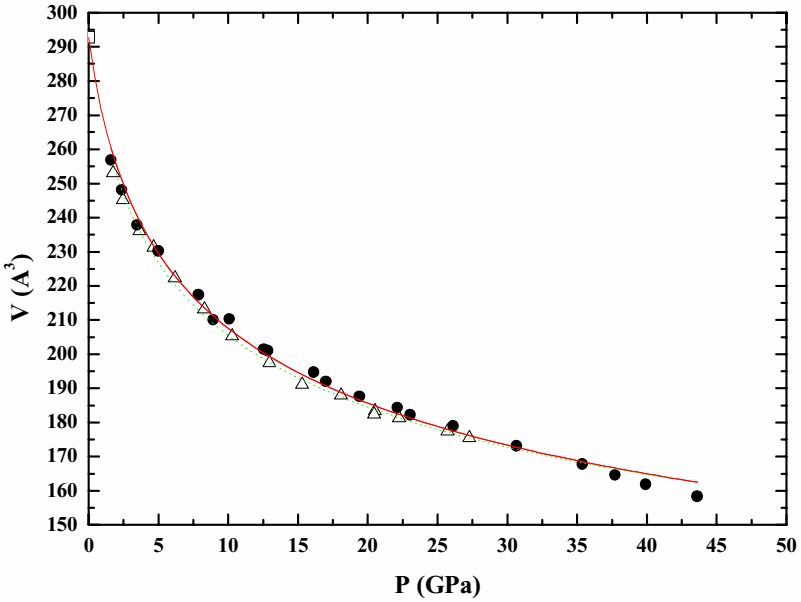

Figure 1 Cell volume of nitromethane as a function of pressure.

Open symbols :CH_3NO_2. Close symbols: CD_3NO_2.

Dotted and solid lines fit with the Murnaghan EOS, CH_3NO_2 and CD_3NO_2 respectively .