X-ray diffraction and electroresistance measurements under high pressure and temperature using a large-volume cell

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Abstract. In this communication we report about original experimental techniques for in-house x-ray diffraction and electrical resistance measurements under high-temperature and high pressure conditions, using large volume cells in the opposite anvil recessed geometry. The high-pressure devices we are currently using are a compact Paris-Edinburgh (PE) V5 150 Tons press and a 50 Tons standard hydraulic press, coupled usually with WC anvils and 10 mm or 7 mm boron-epoxy or pyrophyllite biconical gaskets for x-ray diffraction and resistance measurements respectively. Limiting pressures, using such a non-toroidal sample assembly and WC anvils, are about 10 GPa on samples of large sizes (10-20 mm$^3$). Samples can be heated using an hollow graphite cylinder as a crucible reaching temperatures as high as 2300 K, while the temperature can be measured up to 1300 K by using a K-type thermocouple. The highly automated setup developed for resistance measurements is described in details. In particular, we present electroresistance measurements of Bi melting under pressure and measurements of the Ge and LiF EOS (equation of state) at high temperature and pressure obtained using x-ray diffraction showing the sensitivity of the techniques. The relevance of these experiments to the exploitation of the potential of equipments available at synchrotron radiation facilities is emphasized.

1. Introduction

Recently, an advanced experimental facility has been developed at our home laboratories with the aim of collecting useful data about matter under extreme condition of temperature and pressure, complementing those obtained at large scale facilities. [1] Particular attention has been devoted to high pressure research. Two large volume presses have been installed: a compact “Paris-Edinburgh” (PE) V5 press (150 Tons) and a standard hydraulic press (50 Tons). Both the presses currently operate in the recessed non-toroidal geometry, using two opposite steel anvils with a WC insert. The former press has been coupled to an advanced energy dispersive x-ray diffraction (EDXD) setup, the latter has been connected to a sophisticated data acquisition apparatus for electrical resistance measurements. Also an original setup including a diamond anvil cell (DAC) and an x-ray tube dedicated to angular dispersive x-ray diffraction is currently under development. Details about these equipments and the general context of this research are given in ref. [1]. In this paper we focus the attention on our large volume equipments, reporting more technical details and first experimental results, finally indicating possible future developments.
2. Electroresistance measurements

The experimental setup for electrical resistance measurements consists of a power supply, an automated control unit and a 50 Tons hydraulic press, adapted to match the size of typical PE V5 steel anvils. A PE press can be also used as a pressure device, with the same setup.

Usually electroresistance scans are carried out at fixed pressure, changing the sample temperature (isobaric measurements). The sample can be heated directly when it is connected to the power supply, or indirectly through a crucible. In order to put to a test and calibrate our setup we have carried out a set of electroresistance measurements on several metallic samples using the direct heating approach.

In the direct heating geometry the sample is typically positioned inside an insulating hollow cylinder (sleeve) which fits a hole drilled in a biconical gasket as depicted in fig. 1 (middle panel). The gasket is then placed between two steel recessed anvils with a WC insert as shown in figure 1 (left panel). Two conductive metal foils (Cu in this work) are positioned between the gasket and the anvils to measure the voltage drop upon the sample environment and to improve the electrical contacts with the steel anvils (fig. 1, middle panel).

The power supply (“DELTAM 15-200 D”) operating as a current generator has been used for voltage drop measurements and heating. This device, connected to the anvils by means of copper cables of suitable size, can supply a high stabilized continuous current up to 200 A (maximum voltage is 15 V).

The electroresistance measurements are controlled by a 16 bit acquisition board PCI-DAS1602/16 by Measurements and Computing installed on a PC running a Linux operating system (Red Hat 9.0, kernel 2.4.20-18.9). A set of dedicated C language programs controls the board. This control system can collect valuable experimental data in real time such as sample voltage, electrical current, oil pressure, and calculate other parameters such as electroresistance and heating power. These operations are performed while the sample pressure or temperature are changing, thus allowing for recording both isothermal and isobaric electroresistance measurements. The data acquisition is performed under thermodynamical equilibrium conditions, guaranteed by a proportional-derivative (PD) algorithm which stabilizes the heating power prior each data collection.

In figure 2 a set of electroresistance measurements on Bi is shown, recorded upon increasing the heating power for different fixed sample pressures within the range 0.4-2.1 GPa. For these measurements we have used a Bi wire (Ø0.5 mm), positioned in a BN sleeve inside a pyrophyllite gasket (Ø7 mm). Two graphite disks have been placed at the ends of the Bi wire to improve the electrical contacts and to partially limit the temperature gradient along the sample. The onset of the Bi I melting transition occurs upon the well defined maxima. In the figure inset the melting transition at 0.4 GPa is evidenced by a steep change of the first derivative of the electroresistance.
Figure 2. *Left panel:* Electroresistance of a Bi wire (Ø0.5 mm) positioned in a BN sleeve (see fig. 1, middle panel) as a function of pressure and heating power (temperature). The sample pressure increases from ≈ 0.4 GPa (lower curve) up to ≈ 2.1 GPa (upper curve) as indicated by the arrow. In the inset the derivative of the electroresistance as a function of the heating power is calculated for the curve collected at 0.4 GPa. *Right panel:* EDXD scan at ambient pressure and room temperature at a given collecting angle (θ=19.66°) for a Ge sample mixed with LiF (Ge:LiF 1:10) at room pressure. The typical spectral shape obtained with the Mo X-ray anode is noticeable. A large contribute to the background is due to the diffuse scattering mainly from the B-epoxy gasket. Other sharp peaks are associated with Ge fluorescence and with the strong Mo X-ray emission lines (Kα and Kβ).

Increasing the pressure the heating power requested to melt the sample decreases, as expected due to the negative slope of Bi melting line (ice-like behavior). The accuracy and the quality of the data are very good and in excellent agreement with previous measurements carried out with toroidal cells [2].

3. X-ray diffraction measurements
The experimental setup for energy dispersive x-ray diffraction (EDXD), consists of a powerful rotating anode Rigaku RU300, a Paris-Edinburgh (PE) V5 150 Tons press, a power supply “DELTA SM 30-100 D” and an energy sensitive Ge solid state detector (SSD).

The PE press is usually coupled with a 10 mm or 7 mm boron-epoxy biconical gasket [3, 4], which allows to reach safely pressures of about 8 GPa. The boron-epoxy gaskets are produced by us using an original preparation procedure while small inner parts of the sample assembly (crucibles, sample containers, thermocouple) are either commercial products or machined by external companies.

The sample, positioned in a hollow graphite cylinder and confined in the gasket, is indirectly heated using the graphite as a crucible, thus obtaining a very homogeneous temperature along the whole sample. High temperatures well up to 2300 K can be easily reached and maintained. The temperature is monitored up to 1300 K by using a K-type insulated thermocouple (Inconel sheath) positioned in the sample environment. Usually the sample is a micrometric powder dispersed in a inert low-Z insulating matrix which can be used as a pressure marker. The press
is installed on a high-precision YZ translation stage, which allows an accurate positioning of the sample along the beam. A precise collimation systems (sellers and slits) is aligned between the sample and the detector for confining the scattering region within the sample volume. The detection system is a LEGe detector by Canberra Ltd with energy resolution of 195 eV at 5.9 keV. A lead shield is used to minimize counting of background scattering radiation from the environment. The scattering angle can be tuned continuously using a high-precision translation motor and a rotating stage orienting the collimators and detector system in order to select scattering area and resolution.

Here we present results of a first experiment aimed to check the sensitivity of our equipment measuring the EOS of simple systems. The sample was a compacted mixture of fine Ge and LiF powders filling a graphite heater, placed inside the B-epoxy gasket. The Paris-Edinburgh press was used for measurements in the (0.0±5.3)GPa-(25±580)°C pressure and temperature ranges.

The solid-state Ge detector has been positioned at a fixed angle of 19.66 degrees. The q range accessible at this collecting angle using an x-ray white beam with components up to 50.0 keV is 1.4 Å ≤ q ≤ 8.6 Å and can be easily extended by changing the scattering angle with the motorized translator. In figures 2 (right panel) the EDXD spectrum recorded at ambient pressure and room temperature using the above described setup is presented. Although typical emission lines from Mo anode target (Mo-Kα, Mo-Kβ) and fluorescence lines of germanium (Ge-Kα, Ge-Kβ) are also visible, there is large energy region available for structural studies. Particular attention has been paid to the calibration of the energy scale. We found that this is a crucial aspect of these measurements and we checked carefully calibration of each EDXD pattern. In particular, it is well-known that a small degree of non-linearity is always present in the conversion between channel numbers and photon energy. In our data treatment, we adopted a quadratic function for channel-to-energy conversion because seems to provide the best results [5]. The calibration was performed using radioactive radiation sources (241 Am, 55Fe) and X-ray fluorescence lines (Ag-Kα, Ag-Kβ) having well known energy emission lines. Data analysis of EDXD spectra has been performed using the PEAKFIT and EDXRD programs, that are part of the GNXAS package for XAS/XRD analysis (see [6, 7] for previous applications of this software). Many Bragg peaks were included in the fitting procedure that provided an accurate determination of LiF and Ge parameter cells as function of temperature and pressure. The sensitivity to the variation of the parameter cell value of LiF can be appreciated looking at the magnified trends of the selected Bragg peaks LiF (111). In fact the figure 3 shows the effects of the temperature at fixed pressure (left panel) and of the pressure along an isothermal line at Room Temperature (right panel). The results obtained in the P-T range (0±5.3)GPa-(25±580)°C allow us to estimate for Ge and LiF the bulk modulus B0, its derivative B′0 and volume thermal expansion αV using suitable expressions for the temperature-dependent equation of state (EOS) starting from two equivalent analytic approximations for the EOS proposed by Vinet et al. [8, 9] and H11 as given in ref [10]. The coefficients of the Vinet or H11 EOS have been determined using the results of EDXD data analysis, showing compressibility values in substantial agreement with literature data within current uncertainty (B0_{LiF} = 66.5 GPa, B′0_{LiF} = 4.3, B0_{Ge} = 77.0 GPa, B′0_{Ge} = 4.3). Here those EOS are put to a test also at high temperatures, taking account the very different thermal expansion values (αV_{LiF} = 10.5 × 10^{-5} K^{-1}, αV_{Ge} = 1.8 × 10^{-5} K^{-1}).

4. Conclusions and future developments
Large volume non-toroidal cells are invaluable experimental tools for investigating condensed matter under extreme conditions in the range of moderate pressures (P<10 GPa ) and temperatures (T<2000°C).

In this paper we have given an overview of possible in-house applications of these devices showing that accurate investigations about the structure and phase transitions in materials
under extreme high pressure and temperature conditions are accessible in our laboratory.

We have shown that both electroresistance and x-ray diffraction high quality measurements can be carried out. The electroresistance setup has been found to be useful to highlight the occurrence of phase transitions. The EDXD setup allows us to check the EOS and characterize accurately the structure of the samples under examination.

The promising preliminary results stimulate a further development of both the techniques aimed to perform both x-ray diffraction and electroresistance measurement under extreme conditions. Such a setup is a useful and unique tool for studying condensed matter structure under the action of pressure and temperature and may be installed both in in-house laboratories and in large scale facilities.

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