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Density measurements of liquid under high pressure and high temperature

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A new method for density measurements by means of X-ray absorption under high pressure and high temperature using synchrotron radiation has been developed. The method has been modified for a large-volume Paris–Edinburgh press and combined with intense high-energy X-rays at the ESRF. In order to overcome effects of deformation of sample shape under pressure, a ruby cylinder was used as a sample container. The density was determined from the intensity profile of transmitted X-rays. The densities of crystalline and liquid Bi were successfully measured up to 750 K at 1 GPa.

Keywords: density; X-ray absorption; high pressures; high temperatures.

1. Introduction

Recent X-ray diffraction studies on liquid metals under high pressure have revealed that each metal has a characteristic pressure dependence on local structure (Tsuji, 1990, 1995). For example, the nearest-neighbour distances of Se and Te increase in spite of the volume contraction while those of liquid alkali metals decrease almost linearly as the cubic root of the volume. Those of liquid Ga and Bi are almost independent of the volume. Moreover, Brazhkin *et al.* (see, for example, Umnov *et al.*, 1992) have found liquid–liquid transitions in several elements, such as Bi, Se, Te, I, Sn *etc.*, under high pressure by means of thermobaroanalysis and electrical resistance measurements.

Although the densities of liquids over a wide temperature and pressure range provide valuable information about the structural changes, there have been few measurements owing to experimental difficulties. A simple X-ray absorption method cannot be applied to high-pressure high-temperature experiments because it is difficult to determine sample thickness, which is indispensable to the method. We solved the problem by introducing a sapphire ball as a thickness calibrant in the sample capsule (Katayama, 1996). If the X-ray absorption coefficient of the ball is much smaller than that of the sample, the image of the ball inside the sample would be clearly detected when the transmission of X-rays was measured as a function of sample position. The density was determined from the profile. Using this method we measured the density of Te up to 4 GPa and up to 970 K and detected density changes at the phase transitions in the solid and that upon melting. However, the precision of the measurements was not good enough to detect the proposed liquid–liquid transition (Katayama, Tsuji *et al.*, 1997). Possible origins of the experimental error were the following: (i) the X-ray beam was not intense enough; (ii) errors in the precision of the sample position because the movement of the press was not smooth; (iii) deviations from the ideal sample shape due to anisotropic deformation of the sample. To improve on this we used a lightweight Paris–Edinburgh press and intense high-energy X-rays at the ESRF. The sample geometry was also modified. The densities of solid and liquid Bi were measured up to 750 K at 1 GPa.

2. Experimental

Absorption experiments were carried out using a large-volume Paris–Edinburg press on ID11/BL2 Materials Science Beamline at the ESRF. This press was developed for neutron diffraction experiments (Besson & Nelmes, 1995) and then adapted for X-ray diffraction experiments (Grima *et al.*, 1995). EXAFS experiments using the press were also carried out (Katayama, Mezouar *et al.*, 1997). Fig. 1 shows the experimental arrangement. Synchrotron radiation from a wiggler source was monochromated by an Si(111) double-crystal monochromator. The energy of the X-rays was 65 keV. The size of the X-ray beam was reduced to 0.1 × 0.1 mm by two slits. The incident and transmitted X-ray

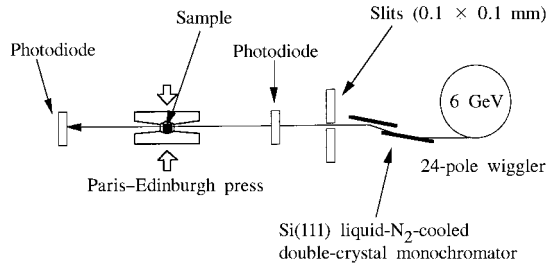

Figure 1
Schematic diagram of the experimental arrangements.

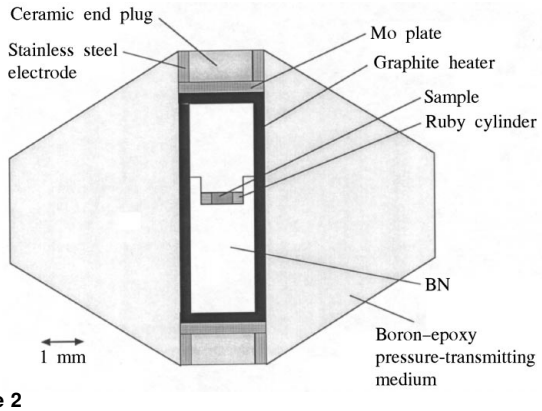

Figure 2
Sample assembly.

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intensities, I and I_0, respectively, were measured by photodiodes. The high-pressure chamber consisted of two tungsten carbide opposed anvils which had conical hollows. Fig. 2 shows the sample assembly. The Bi sample was confined in a ruby cylinder of inner diameter 0.5 mm, outer diameter 1.0 mm and height 0.3 mm. The sample and the ruby cylinder were surrounded by a capsule made of BN. A graphite cylinder was used as a heater. Mo sheets and a stainless-steel tube were used as electrodes. All elements were put into a hole of a gasket made of a mixture of boron and epoxy. The pressure was estimated from the load and from a number of previous experiments under the same conditions, which provided a reasonably accurate pressure load calibration. The temperature was estimated from the heater power, which has a linear relation with the temperature. The relation was calibrated based on the melting temperature of Bi (Young, 1991).

The position of the press was controlled by an xz stage, whose minimum step was 1 μm. We first found the vertical centre of the sample and then measured the variation of I/I_0 along the horizontal axis at the centre of the sample. The typical step width of the scanning of the sample was 0.01 mm and the typical integration time for one step was 3 s. The total measurement time for one scan was several minutes.

3. Results

Fig. 3 shows an example of the measurement. The logarithm of I/I_0 for liquid Bi at 1 GPa and at 750 K is plotted as a function of sample position x. The circles indicate the experimental data. We can clearly see the image of the sample shape. We fitted the data using the formula

$$I/I_0 = C \int_{\text{beam}} \exp[-\mu\rho l(x)]\,\mathrm{d}x,$$

with

$$l(x) = [r^2 - (x - x_0)^2]^{1/2},$$

where C is a constant, μ is the mass absorption coefficient of the sample, ρ is the density of the sample, $l(x)$ is the length of the path in the sample, r is the diameter of the sample and x_0 is the centre of the sample. The integration was performed over the beam size. The mass absorption coefficient was calculated from an empirical relation given by Victreen (Koch *et al.*, 1968). The fitting well reproduced the position dependence of the absorption.

Fig. 4 shows the density of Bi at 1 GPa as a function of temperature. The sudden change of density between 470 and 520 K corresponds to the melting. The positive jump at the melting is consistent with the negative slope of the melting curve ($\mathrm{d}T_m/\mathrm{d}P < 0$). In the solid and liquid phases, the density decreases with increasing temperature. From the slope we can evaluate the thermal expansion coefficients of Bi at 1 GPa to be $3 \times 10^{-5}\ \mathrm{K}^{-1}$ for the solid and $1.2 \times 10^{-4}\ \mathrm{K}^{-1}$ for the liquid. These values are reasonable because they are close to the values at ambient pressure ($4 \times 10^{-5}\ \mathrm{K}^{-1}$ for the solid and $1.1 \times 10^{-4}\ \mathrm{K}^{-1}$ for the liquid).

4. Conclusions

The quality of the data was better than that of the previous experiments at the Photon Factory (Katayama, 1996). The error estimated from the scattering of the data points was less than 1%. The possible causes of the improvement are summarized as follows: (i) the X-ray beam in this energy region is about 100 times more intense at the ESRF; (ii) the position of the press was controlled more precisely thanks to the compactness of the press (the weight of the Paris–Edinburg press is about 50 kg while that of MAX90 is more than 1000 kg); (iii) the sample was confined in a ruby cylinder which kept the sample shape cylindrical.

The present results demonstrate the feasibility of the method. Further improvements, such as *in-situ* pressure and temperature measurements, accurate determination of the absolute value of the density *etc.*, are currently underway. The possibility of measuring density in a wide pressure and temperature range is a significant result for condensed matter research and materials science.

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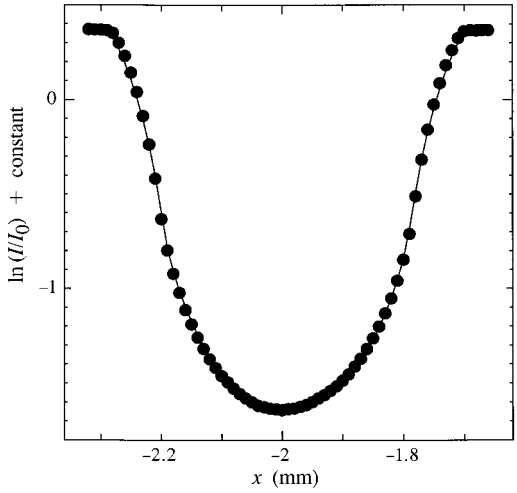

Figure 3
Logarithm of I/I_0 for liquid Bi at 1 GPa and at 750 K as a function of sample position. Circles are experimental data. The line is the result of parameter fitting.

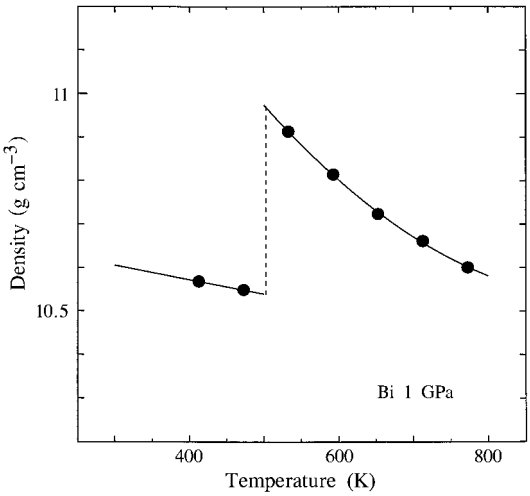

Figure 4
Density of crystalline and liquid Bi at 1 GPa as a function of temperature. The lines are guides for the eyes.

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