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## X-RAY DIFFRACTION MEASUREMENTS FOR EXPANDED FLUID SE USING SYNCHROTRON RADIATION

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### Abstract

X-ray diffraction measurements at high temperatures up to 1500 °C and pressures up to 843 bar have been carried out using synchrotron radiation at SPring-8 for the first time to investigate structural change in the semiconductor-to-metal transition in expanded fluid Se. The signal-to-noise ratio in the intensity spectra was much better than the previous one using in-house x-ray source, while it is found important to estimate the background from a sapphire cell to deduce a structure factor of fluid Se with greater accuracy from the spectra. The preservation of the two-fold coordinated chain structure and the contraction of the covalent bond are reconfirmed in the transition. When metallic character was enhanced, the first peak in the pair distribution function became asymmetric towards larger distance and the first minimum became larger. These results may imply the modification on the chain structure in the transition.

## 1 Introduction

The dc conductivity of liquid (l-) Se shows anomalous behaviour that it increases from a semiconducting value to a metallic one with volume expansion at high temperature and high pressure [1]. Many researchers have investigated the structural, thermodynamic and electronic properties of fluid (f-) Se [2]–[11] to understand the semiconductor-to-metal (SC-M) transition in the supercritical region (The critical constants [10];  $T_c=1615$  °C,

$p_c=385$  bar,  $\rho_c=1.85$  g/cm<sup>3</sup>).

As is well known, l-Se has two-fold coordinated chain structure near the melting temperature. On the other hand, there had been few structural studies for metallic f-Se due to experimental difficulties under high temperature and pressure. One of the authors developed a high pressure vessel and a sapphire cell for energy-dispersive x-ray diffraction measurements at high temperature and pressure and the experimental technique was applied to study the structure of metallic f-Se for the first time [7]. The results show that the two-fold coordinated structure is largely preserved in the metallic f-Se and that the covalent bond becomes short in the SC-M transition. Recent experimental studies including x-ray absorption fine structure (XAFS) measurements [11] have suggested that the transition occurs around the conductivity of  $30 \Omega^{-1}\text{cm}^{-1}$  [8].

Recently theoretical studies have been carried out using a computer simulation [12]–[14], which gives atomic and electronic configurations in f-Se. Although the previous experimental results filled the role that they stimulate theoreticians, the obtained structure factor,  $S(k)$ , may not necessarily have enough quality at the present stage because of the weak x-ray source. To improve the signal-to-noise ratio in  $S(k)$  greatly, the use of a synchrotron radiation is needed. In this paper, we report new structural data obtained from x-ray diffraction measurements up to 1500 °C and 843 bar using a synchrotron radiation at SPring-8.

## 2 Experimental procedure

We have performed energy-dispersive x-ray diffraction measurements for expanded fluid Se using a synchrotron radiation on the BL-04B1 at SPring-8. The storage ring at SPring-8 is operated at 8 GeV with 20 mA during the present experiments. White x-rays ranging in energy to 150 keV are used as the primary beam collimated to  $0.2 \times 0.2$  mm<sup>2</sup> using the horizontal and vertical tungsten slits at the upper stream. The scattered photons are detected and energy-analyzed by a pure Ge solid state detector (SSD).

The experimental conditions of high temperatures up to 1500 °C and high pressures up to 843 bar are achieved with an internally heated high-pressure vessel made of a super-high-tension steel which permits the measurements up to 1650 °C and 2000 bar. The

construction of the vessel is described in the literature [15]. The Be windows for scattered x-ray beams are located at the scattering angles of  $2\theta$  of 5, 10, 20 and  $33^\circ$  to cover a sufficiently wide range of scattering wave number  $k$ . The vessel is pressurized by He gas (99.9999%) and pressures are measured with a Heise gauge, having an accuracy of  $\pm 3$  bar.

Se sample (99.999%) is contained in a single-crystal sapphire cell being transparent to x-rays and resistant to chemical corrosion by hot f-Se. The detailed construction around the fluid sample is described in the literature [7]. Two cells with sample thicknesses of 200  $\mu\text{m}$  and 400  $\mu\text{m}$  are used for the present experiments. The cell is heated by a heating element made of W wire set around a Mo tube with a slit for scattered x-rays. Temperature is measured by two Pt-30%Rh:Pt-6%Rh thermocouples which are put into the holes of the Mo tube and the ends are close contact with the wall of the cell.

### 3 Results

To obtain  $S(k)$  of expanded f-Se from the experimental scattering intensity, several data corrections have to be made. The details of the data analysis are described in the literature [7].

Using synchrotron radiation, the signal-to-noise ratio in the intensity spectra becomes much better. However we found that more accurate treatment for the background from the sapphire cell is necessary to deduce structure factor,  $S(k)$ . Figure 1 (a) shows the intensity spectra of the empty cell for  $2\theta = 20^\circ$  at 25  $^\circ\text{C}$  and 1000  $^\circ\text{C}$ . The observed Compton scattering from the cell contains some coherent scattering which may arise from mosaic structure of the single crystal though strong Laue spots are eliminated. The amplitudes of the coherent peaks around 5.5  $\text{\AA}^{-1}$  and 7  $\text{\AA}^{-1}$  increase with increasing temperature. Figure 1 (b) shows  $S(k)$  of f-Se at 300  $^\circ\text{C}$ , 1000  $^\circ\text{C}$  and 1500  $^\circ\text{C}$  without any correction for the background. With increasing temperature, noise appears around the  $k$ 's. The amplitude of the oscillation of  $S(k)$  decreases with increasing temperature and increasing  $k$ . As the results, the background from the cell becomes relatively larger in larger  $k$  region and  $S(k)$  in larger  $k$  region are not obtained for the metallic f-Se in the present analysis.

Figure 2 shows  $S(k)$  of f-Se from the semiconducting liquid near the melting temperature to the metallic fluid at 1500 °C and 843 bar after smoothing the noisy parts. The spectra obtained using the sample with the thickness of 200  $\mu\text{m}$  are weighted for  $S(k)$  in smaller  $k$  region and those of 400  $\mu\text{m}$  are weighted for  $S(k)$  in larger  $k$  region.  $S(k)$  below  $1\text{\AA}^{-1}$  is interpolated to  $S(0)$  estimated from the thermodynamic properties of fluid Se.  $S(k)$  at 300°C and 10bar agrees well with those of the previous measurements [7, 9]. The agreement becomes worse with increasing temperature, which may mean that  $S(k)$  in Ref [9] has errors due to the effect of the coherent peaks from the cell. It is noticed that the phase around  $8\text{\AA}^{-1}$  starts changing in  $S(k)$  at 1000°C, which is a little less than the temperature in the previous experiments [9, 11].

Figure 3 shows the pair distribution function,  $g(r)$ , obtained from Fourier transformation of  $S(k)$  shown in Fig. 2. For comparison,  $g(r)$ 's around the first and second peaks at 800 °C and 1500 °C are shown in the inset of Fig. 3.  $g(r)$ 's at 300 °C and 600 °C have oscillations due to the effects of termination because the oscillation in  $S(k)$  is still large around  $20\text{\AA}^{-1}$ . At higher temperatures  $g(r)$ 's have a smoother oscillation because of dumping of the amplitude of the oscillation with increasing  $k$  in  $S(k)$ .

## 4 Discussion

The first peak in  $g(r)$  at 300 °C and 10 bar is located around  $2.35\text{\AA}$ . The second peak around  $3.7\text{\AA}$  is considered to be due mainly to the intrachain second nearest neighbour distance. The broad distribution around the second peak may be due to neighbouring atoms in adjacent chains. The first and second peaks are clearly separated in the semiconducting region, which may indicate relatively small interchain interaction. With increasing temperature the first and second peaks become broad and the probability that atoms are distributed around the first minimum increases. The second peak remains at high temperatures up to 1200 °C. When f-Se is metallic above 1300 °C, the first peak starts becoming asymmetric towards larger distance and the second peak becomes broad.

To see the structural change in the SC-M transition, it is necessary to investigate the variation in the nearest neighbour distance and the coordination number of f-Se. We consider two definitions of the nearest neighbour distance,  $r_1$  and  $r_m$ .  $r_1$  is the position

of the first peak in  $g(r)$  and  $r_m$  means the center of the half maximum of the first peak. From  $g(r)$  and density data,  $n_0$ , we calculate the radial distribution function,  $4\pi n_0 r^2 g(r)$ , and obtain the coordination number. We calculate the coordination number using two methods. The number,  $N_A$ , is twice that obtained from integrating  $4\pi n_0 r^2 g(r)$  in the range from the minimum distance to the peak position in  $g(r)$ . On the other hand,  $N_B$  is obtained from the integration in the range to the first minimum in  $4\pi n_0 r^2 g(r)$ . The calculated  $N_A$ ,  $N_B$ ,  $r_1$  and  $r_m$  together with the previous results [9] are shown in Fig. 4 as a function of temperature.

As shown in the figure,  $N_A$  decreases with increasing temperature while  $N_B$  remains about 2 in the semiconducting region and becomes slightly more than 2 in the metallic region. The temperature dependence of  $N_B$  shows the increase of the atomic distribution in the first minimum of  $g(r)$  in the SC-M transition region.  $r_1$  starts decreasing at 1000 °C. On the other hand  $r_m$  is almost constant to 1500 °C. The difference between  $r_1$  and  $r_m$  is correlated with the enhancement of the asymmetric distribution in the first coordination. The temperature dependence of  $N_A$  is in good agreement and that of  $r_1$  is in fairly good agreement with the previous one [9].

To explain the anomalous bending of the isochores near the SC-M transition region, it has been proposed that threefold coordinated centers in branched chain are largely created in the high temperature and pressure region and they cause the volume contraction as in the case of l-Te proposed by Cabane and Friedel [16]. Recent experimental evidence suggests that there remains chain structure in l-Te and the intrachain covalent bonds alternate a short one with a long one [17]. A computer simulation by Bichara et al. [18] supports the observed local structure of l-Te. They conclude that the structure is an asymmetric variant of the one proposed by Caban and Friedel with three different neighbour distances; short and long intrachain distances and a distance bridging two chains. As seen in the inset of Fig.3, the enhancement of the asymmetric distribution in the first neighbours of f-Se in the SC-M transition may imply the appearance of short and long covalent bonds as in the case of l-Te. However the present results give no evidence that metallic f-Se consists mainly of threefold coordinated centers as in l-Te though the increase of the atomic distribution in the first minimum seen in the inset of Fig. 3 may

mean an increase of the centers bridging two chains. It is necessary to deduce  $S(k)$  of metallic f-Se in larger  $k$  region, which cannot be obtained in the present analysis, to investigate detailed structure in the nearest neighbours.

The present results reconfirm that the twofold coordinated structure is largely preserved in the metallic region and that the nearest neighbor distance decreases with increasing metallic properties as long as  $r_1$  is defined as the average bond length. The results of our XAFS measurements for supercritical f-Se show similar contraction of the covalent bond in the metallic region [11]. As a possible mechanism of the SC-M transition for supercritical f-Se, we have proposed that chains with a planar zigzag conformation may be formed in the transition [7, 9].

Theoretical studies on f-Se at high temperature and high pressure have been developed [12]–[14]. Recently Ohtani et al. [12] introduced structural models for expanded Se and calculated the electronic states and wave functions of these models by simulated annealing method. They have clearly shown that when some of Se-Se bonds in the "helical chain" are weakened in the process of expanding, the splitting between the bonding and anti-bonding levels is reduced and consequently the anti-bonding band is relatively lowered, which leads to the disappearance of the band gap between the anti-bonding and lone pair band. They pointed out, furthermore, that the mechanism of the SC-M transition in f-Se accompanying the volume expansion is completely new and different from those of the case of the nonmetal-metal transition occurring with the volume reduction, such as the Wilson transition induced by the band overlap or the Mott transition concerning the change of the electron correlation.

Shimojo et al. [13] have carried out *ab initio* molecular-dynamics simulation using the generalized-gradient-corrected density functional theory and succeeded in reproducing the metallic density of states in the supercritical f-Se at high temperature and pressure. They show that bond breaking makes electronic states with bonding or non-bonding character unstable while it makes those with anti-bonding character stable and they claim that this is one of the elemental processes of the SC-M transition in f-Se. Their simulation reproduces the experimental results such as the preservation of the two-fold coordinated chain structure and a little contraction of the average bond length in the metallic f-Se.

The planar zigzag conformation is not necessary in their mechanism and they do not find a stable zigzag chain in the supercell containing 81 atoms in the metallic state. Kirchoff et al. [14] performed also an *ab initio* simulation for fluid Se and obtained the results almost consistent with those of Shimojo et al. [13].

Further investigation on the local structure in the metallic f-Se is necessary after obtaining  $S(k)$  in larger  $k$  region. The asymmetric distribution in the first coordination may give structural information besides the local structure shown by the simulation. The measurements using synchrotron radiation really have enough potential to observe  $S(k)$  ranging up to larger  $k$  and in the near future  $g(r)$  with higher resolution will be obtained.

## 5 Conclusion

Using synchrotron radiation, it is found important to estimate the background from a sapphire cell to deduce a precise structure factor of f-Se from the spectra. The preservation of the chain structure and the contraction of the covalent bonds are reconfirmed in the SC-M transition. After more precise  $S(k)$  is deduced, detailed structural changes will be made clear.

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## Figure Captions

- Figure 1 (a)      The scattering intensity from sapphire empty cell at 25 °C and 1000 °C.
- Figure 1 (b)      The temperature variation in the structure factor,  $S(k)$ , of f-Se without any correction.
- Figure 2             $S(k)$  of f-Se at various temperatures and pressures.
- Figure 3            The pair distribution function,  $g(r)$ , of f-Se obtained from Fourier transform of  $S(k)$  shown in Fig. 2. The inset shows  $g(r)$ 's around the first and second peaks at 800 °C and 1500 °C.
- Figure 4            The temperature dependence of the coordination number,  $N_A$  (solid triangles) and  $N_B$  (solid squares), the first nearest neighbor distance,  $r_1$  (solid circles), the middle position  $r_m$  (solid diamonds), for f-Se together with the previous  $r_1$  (open circles) and  $N_A$  (open triangles) [9]. The definition of above parameters are described in this text. The broken line is to guide the reader's eye.

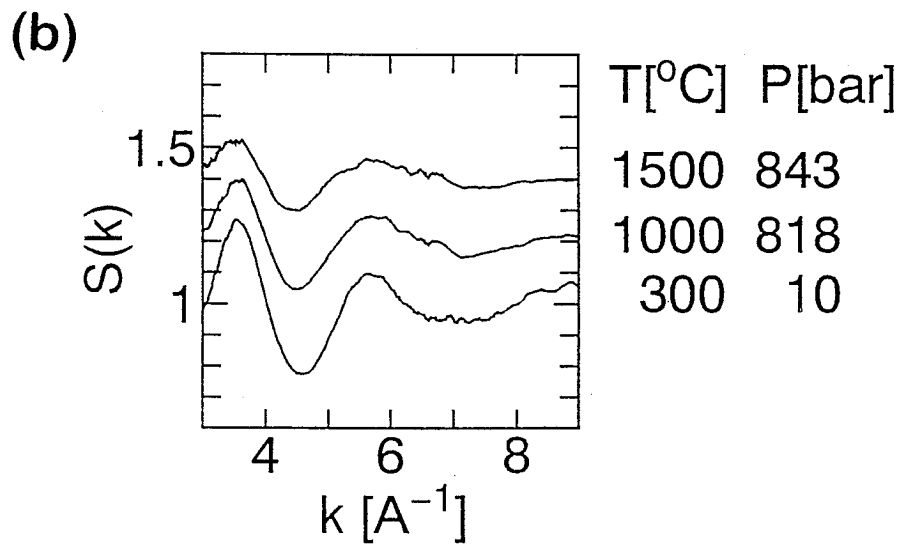
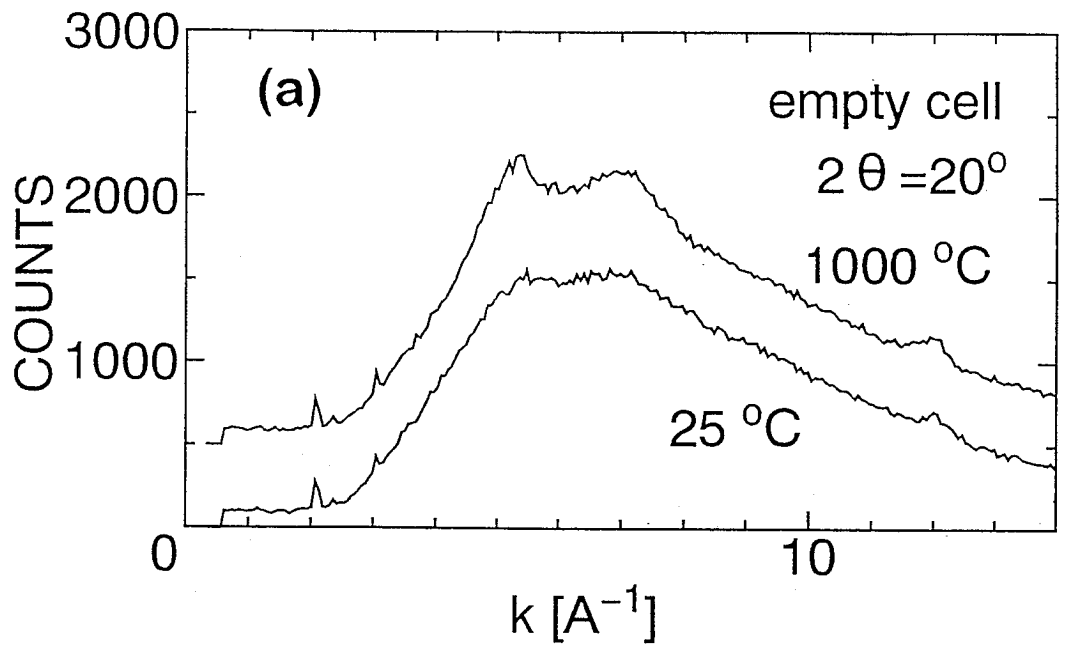


Fig.1

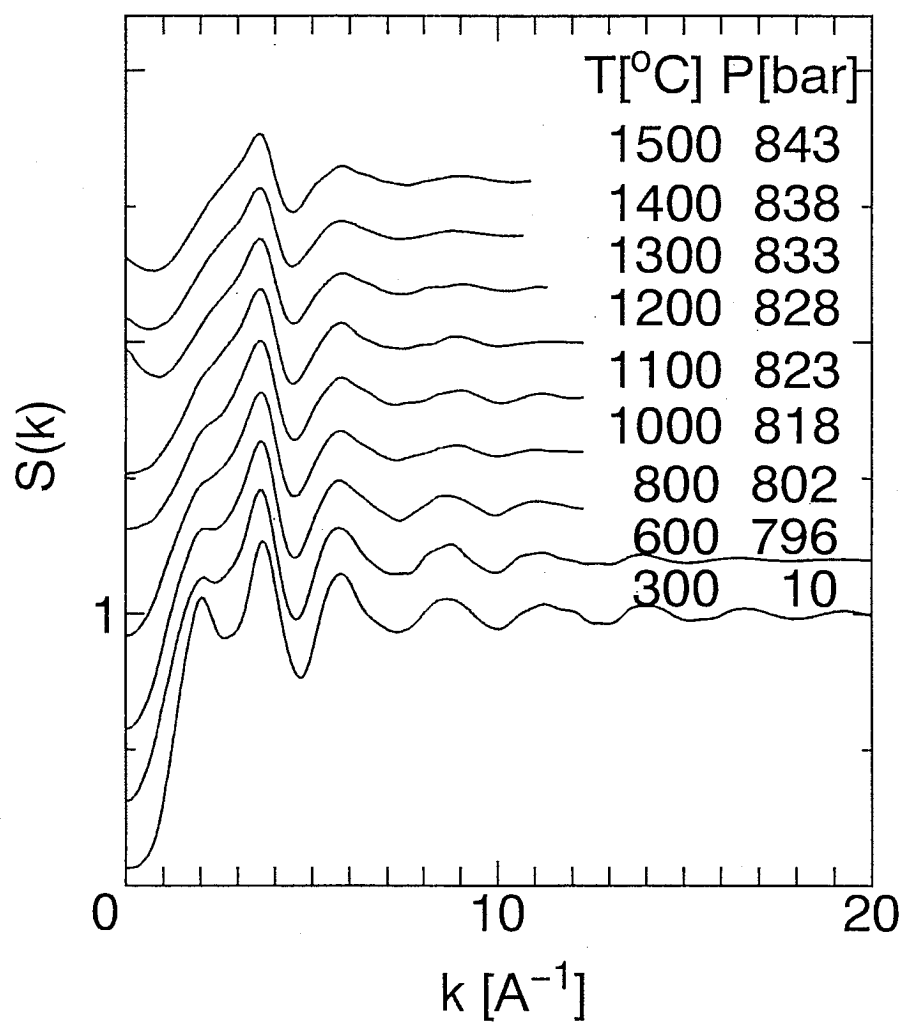


Fig.2

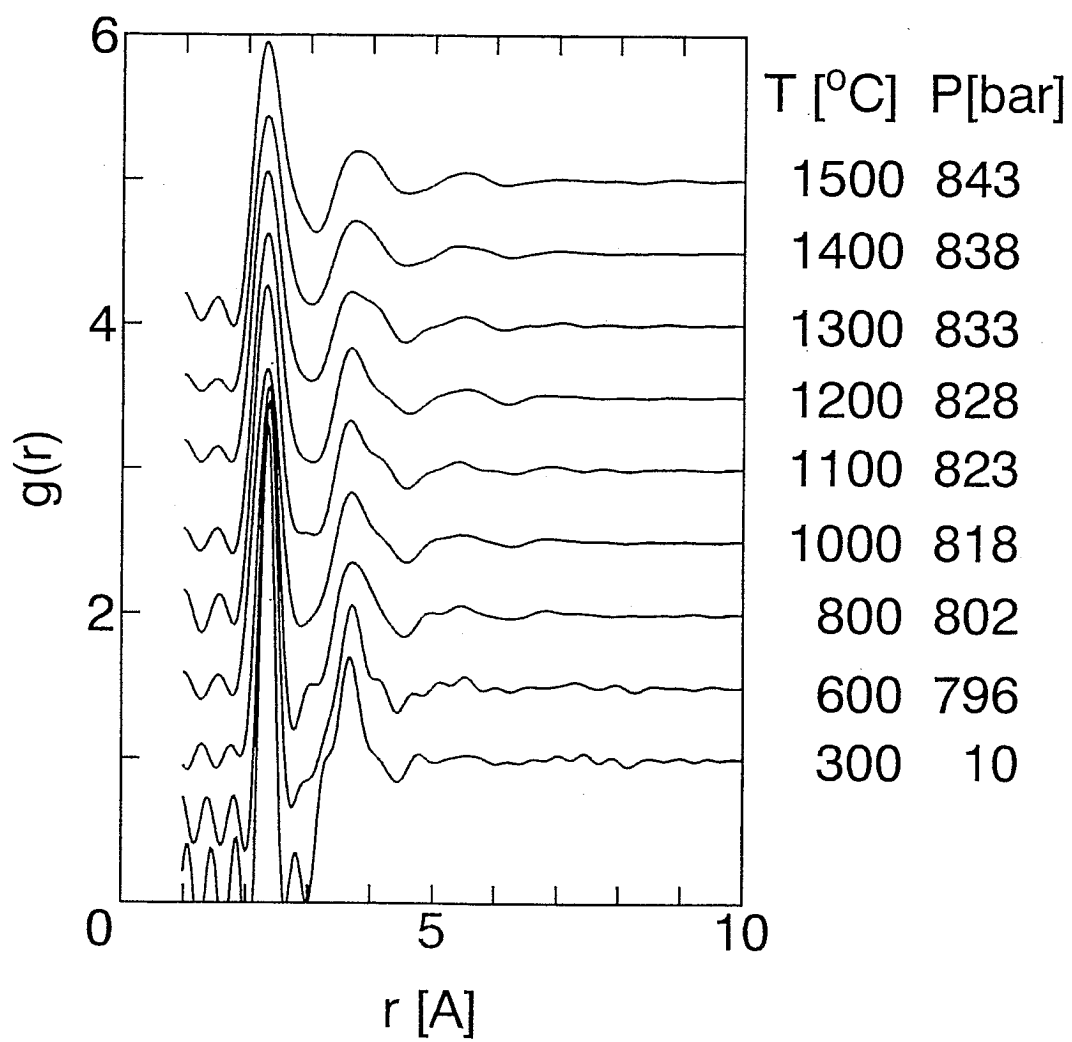


Fig.3

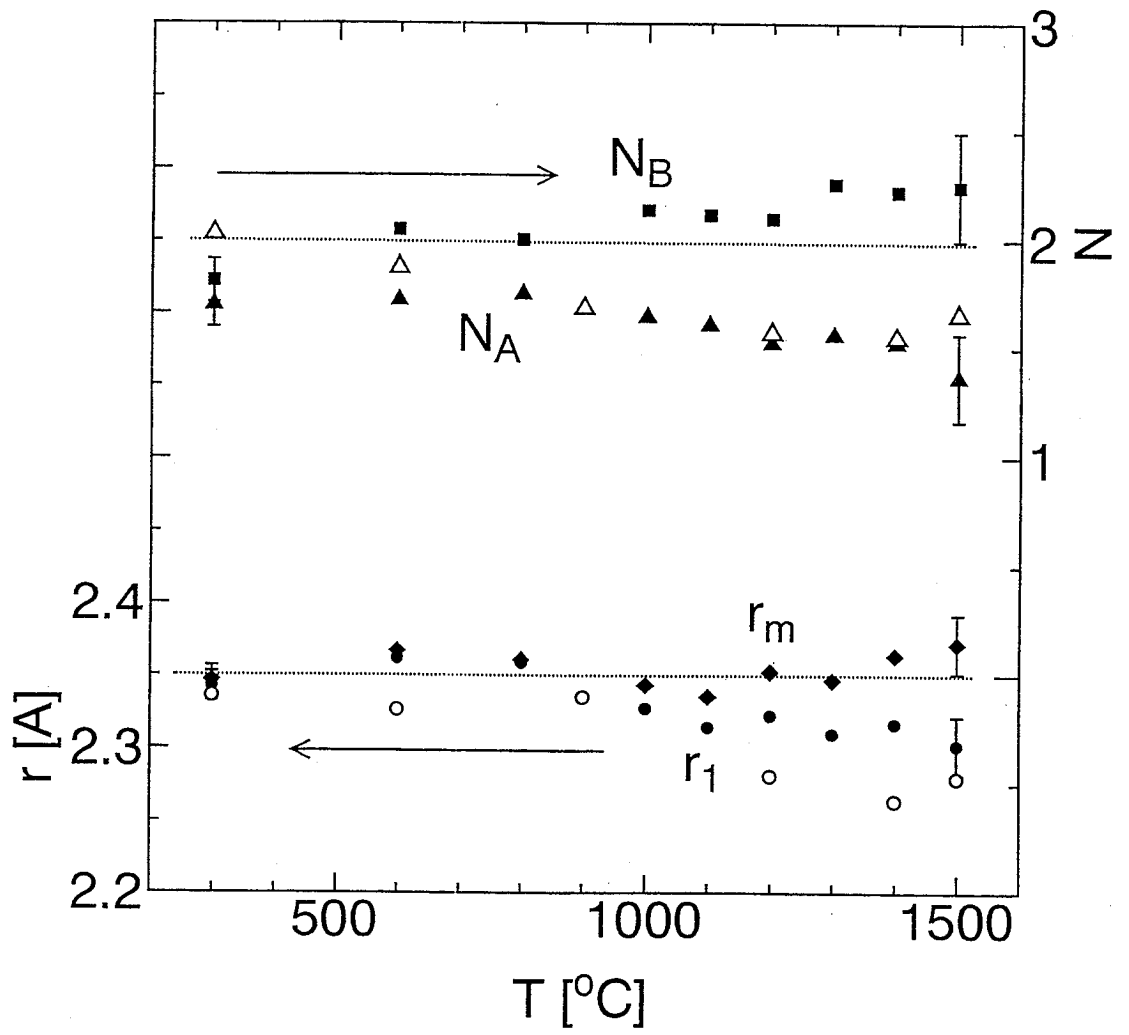


Fig.4