X-ray diffraction measurements for liquid Ge–Si alloys using synchrotron radiation

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Abstract

Energy dispersive X-ray diffraction measurements have been carried out for liquid $Ge_{1-x}Si_x$ alloys ($x = 0.0, 0.3, 0.5, 1.0$) using synchrotron radiation at SPring-8. We measured the X-ray diffraction spectra of liquid Ge and Si up to a high temperature range, (liquid Ge from 1270 to1870 K and liquid Si from 1680 to 2020 K), liquid $Ge_{0.7}Si_{0.3}$ at 1620 K, and liquid $Ge_{0.5}Si_{0.5}$ at 1540, 1590, 1670 and 1720 K. The total structure factors of the liquid Ge–Si alloys have a characteristic shoulder on the high-wave-vector side of the first peak. We deduced a pair distribution function from the Fourier transform of the observed structure factor, which was weakly dependent on the temperature. The nearest-neighbor coordination number of liquid Ge–Si alloys is close to that of pure liquid Ge and Si. The first peak of the pair distribution function moved to a shorter distance with increasing Si concentration. These results may indicate that the atomic radii of the Si and Ge atoms in the pure liquid are preserved in the liquid alloys.
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1. Introduction

Ge and Si are typical elements of a semiconductor and they have a diamond structure in crystalline form at ambient conditions. When Ge and Si are melted, their dc conductivity increases up to 10^4 $(\Omega\,cm)^{-1}$, and they undergo a semiconductor–metal transition on melting. Neutron diffraction measurements for liquid Ge [1] and X-ray diffraction measurements for liquid Si [2,3] confirm that the nearest-neighbor coordination number of about 6 is much smaller than that of typical liquid metals. X-ray absorption fine structure (XAFS) results from Ge fine droplets in carbon powder up to 1610 K were reported by Filipponi and

Di Cicco [4]. They analyzed the data using the pair distribution function deduced from the diffraction measurements and obtained information on the local structure of liquid Ge. *Ab initio* molecular dynamics simulations for liquid Si [5] and liquid Ge [6] were carried out to investigate the semiconductor–metal transition on melting. Their simulations suggest that covalent bonds remain in the liquid and it has an open structure compared to the closed packing of liquid metals.

Crystalline Ge–Si alloys are expected to be applied to the optics for a high brilliant X-ray source from synchrotron radiation as well in electronic devices because of their properties of good miscibility. The alloys form random solid solutions over the entire concentration range. The lattice constants of the alloys depend linearly on their concentration, which is known as Vegard's law [7], and their optical gap continuously changes with the concentration.

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The origin of such interesting properties may already appear in the liquid state. Inui et al. [8] carried out XAFS measurements for liquid Ge–Si alloys and reported a local structure around a central Ge atom. The results obtained from that analysis on the assumption of a Gaussian distribution show that the nearest neighbor distance around a Ge atom in the liquid alloys is much shorter than that expected from diffraction measurements. To obtain reliable nearest neighbor distance, we need diffraction data of the liquid alloys. However, the high melting point of Ge–Si alloys makes structural studies difficult. Tamura and Inui [9] installed a high-pressure gas apparatus and have carried out X-ray diffraction measurements for expanded fluid metals at high temperature and high pressure using synchrotron radiation at SPring-8. The technique may easily be applied to X-ray diffraction experiments for materials with high melting temperature. In this paper, we describe the results of X-ray diffraction measurements for liquid Ge–Si alloys.

2. Experimental

X-ray diffraction experiments were carried out using synchrotron radiation at SPring-8. The storage ring at SPring-8 was operated at 8 GeV with 100 mA during the present experiments. We made energy-dispersive X-ray diffraction measurements for liquid Ge–Si alloys of Ge, $Ge_{0.7}Si_{0.3}$, $Ge_{0.5}Si_{0.5}$ and Si using a high-pressure vessel installed at BL28B2.

The diffractometer was up-graded compared to the previous one [9] and the sample position was more exactly adjusted at the center of the diffractometer. The high-pressure vessel has seven Be windows for the scattered X-ray beams, which are located at the scattering angles of 2θ of 4°, 7°, 11.5°, 15°, 20°, 25° and 33° as shown in Fig. 1. The angles cover a sufficiently wide range of the modulus of the scattering vector k ($k = 4\pi E \sin\theta / hc$, where h is Planck's constant, c is the velocity of light and E is the energy of the X-ray). The vessel was pressurized by He gas (99.9999%) at 4 bar to suppress evaporation of the liquid sample. Details of the high-pressure vessel for X-ray diffraction experiments were described in the literature [9].

Ge–Si alloy samples (99.999%) were contained in a single-crystal sapphire cell. The sample of 0.4 mm in thickness was used for pure liquid Ge and the cell for liquid Ge had an original design by Tamura [10], which had a sample reservoir. However, it was difficult to heat up the sample reservoir above the melting points (T_m) of liquid Ge–Si alloys because they are higher than T_m of a powder glass to fix the sapphire parts. To measure X-ray diffraction spectra of Ge–Si alloys, we inserted a disk of the alloy of 0.5–1.0 mm in thickness between inner and outer sapphire tubes with a closed end together with a ring spacer to keep the proper thickness during the measurements, and heated it up to 2000 K. The background was measured using the empty cell of the same design.

3. Results

Energy depressive X-ray diffraction measurements were carried out for liquid $Ge_{1−x}Si_x$ alloys ($x = 0.0, 0.3, 0.5, 1$). The spectra of liquid Ge were measured above T_m ($= 1210.4$ K) at 1270, 1370, 1470, 1570, 1670, 1770, 1820 and 1870 K. Those of liquid Si were measured above T_m ($= 1682$ K) at 1700, 1770, 1820, 1870, 1970 and 2020 K. Those of liquid $Ge_{1−x}Si_x$ alloy were measured at 1520 K for $x = 0.3$ and at 1720, 1670, 1590 and 1540 K for $x = 0.5$. The observed spectra were transformed to the total structure factor, $S(k)$, after several corrections and the background subtraction as explained in the literature [9]. The subtraction of the incoherent scattering from the liquid binary alloys was needed to deduce $S(k)$ in the present analysis. We estimated the density of liquid Ge–Si alloys from the pure liquids by assuming linear volume dependence. We neglected the temperature variation of the alloy density due to narrow temperature range observed. The density of liquid $Ge_{1−x}Si_x$ alloys used in this analysis is listed in Table 1. Fig. 2 shows $S(k)$ of liquid Ge, Si and $Ge_{1−x}Si_x$ alloys. Many corrections are needed to deduced $S(k)$ in the energy dispersive method and the profiles at small k has less reliability than the angle dispersive method with monochromatized X-ray. However in the present results, the first peak of liquid Ge is located at 2.54 Å^{-1}, which agrees with the previous data [1] within our experimental error. $S(k)$ of liquid Si is also in fairly good agreement with the reported data [2] while the height of the present first peak is slightly lower. The first peak in $S(k)$ of liquid $Ge_{1−x}Si_x$ alloys has a characteristic shoulder at larger k. With increasing temperature, the first peak and the shoulder become slightly broad and obscure. Besides
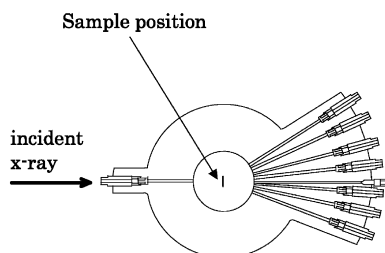

Fig. 1. Top view of a high-pressure vessel for X-ray diffraction measurements with energy-dispersive method.

Table 1
Density of liquid Ge–Si alloys used in the present analysis

	T (K)	Density (g cm^{-3})	Number density (Å^{-3})
Ge	1270	5.51	0.0457
Ge	1870	5.15	0.0453
$Ge_{0.7}Si_{0.3}$	1520	4.6	0.052
$Ge_{0.5}Si_{0.5}$	1550	4.0	0.046
Si	1700	2.50	0.0470
Si	2020	2.40	0.0451