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Extended x-ray absorption fine structure studies of dense selenium vapor

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We have measured the extended x-ray absorption fine structure spectra for dense selenium vapor at high temperatures and pressures up to 1600 °C and 150 bar for the first time. For the experiment, we have developed a high-pressure vessel and a polycrystalline sapphire cell of our own design. We have found that dense selenium vapor under the present experimental condition consists mainly of Se_2 and the bond length is much shorter than that of liquid Se. With increasing pressure the bond length slightly increases. When the saturated vapor-pressure curve is approached, the bond is largely elongated.

I. INTRODUCTION

Selenium exhibits a complex structure in its vapor phase. A variety of molecules from Se_1 to Se_8 are present in its "low-density" vapor. The composition of such molecules in vapor Se ($\nu\text{-Se}$) was determined by the measurements of density,¹ mass spectroscopy,² and optical absorption spectra.³ These investigations revealed that Se_2 is the most stable species in the low-density vapor. Maxwell and Mosley⁴ performed the electron diffraction measurement for $\nu\text{-Se}$ and found that the bond length of Se_2 is $2.21 \pm 0.03 \text{ \AA}$, which is much shorter than that of liquid phase, about 2.38 \AA .⁵

Vapor of Se is of special interest when considered in the wide temperature and pressure region including the critical point. Figure 1 shows the pressure-temperature phase diagram of Se. Full curve shows the saturated vapor-pressure (SVP) curve and full circle denotes the liquid-gas critical point [$T_c = 1590 \text{ }^\circ\text{C}$, $p_c = 380 \text{ bar}$,⁶ $d_c = 1.85 \text{ g cm}^{-3}$ (Ref. 7)]. Rao⁸ carried out the density measurements for dense selenium vapor ($\nu\text{-Se}$) at various temperatures and pressures up to 1100 °C and about 40 bar, and obtained the molecular composition in the saturated vapors of Se. In the low-density vapor at lower temperatures below the boiling point at normal pressure (685 °C), the concentration of large molecules such as Se_5 , Se_6 , and Se_7 is very large, while that of Se_2 is a few ten percent. With increasing temperature, however, the concentration of the dimer increases rapidly, eventually becoming more than 70% at 1100 °C and about 40 bar. Recently, we have measured the optical absorption spectra of $\nu\text{-Se}$ at temperatures and pressures up to 1600 °C and 200 bar, and also found that the spectra are mainly formed by absorption peaks and shoulders originated from Se_2 molecules.⁹

It is evident that a further increase of pressure and temperature, indicated by the arrow in Fig. 1, causes the enhancement of the interaction between Se_2 molecules, which may force to change the structural parameter of molecules. When the critical point is approached, Se_2 molecules are pro-

gressively condensed into liquid consisting of short chain molecules.¹⁰

For the understanding of the molecular interaction and the mechanism of the molecular condensation, it is important to measure the structural parameters, such as nearest-neighbor distance, r_1 , and the coordination number, N_1 , for dense vapor in the wide temperature and pressure region including the critical point. However, information on the structure of $\nu\text{-Se}$ has been quite limited. As is well known, it is difficult to carry out the electron diffraction measurement under high pressure. X-ray or neutron diffraction measurements are also difficult under the extreme condition and, in addition, the number density of atoms in dense vapor is too small for the measurements. The extended x-ray absorption fine structure (EXAFS) measurement is the only method to obtain the structural parameters of dense vapor with the

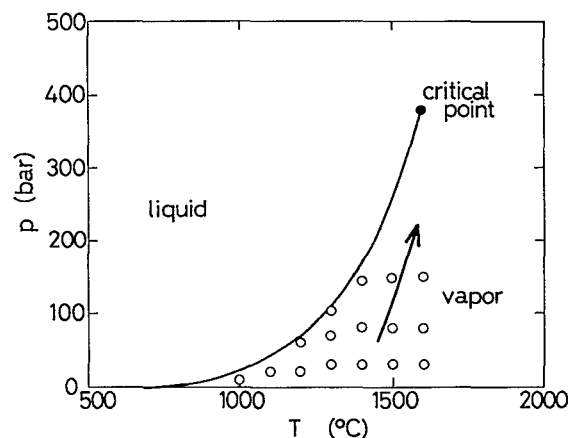


FIG. 1. Phase diagram of Se on the pressure-temperature plane. Full curve denotes the saturated vapor-pressure curve and the full circle indicates the liquid-gas critical point. Empty circles show the temperatures and pressures at which EXAFS spectra were measured in the present study.

same accuracy as those of liquid states. In fact, we have obtained a distinct EXAFS oscillation of ν -Se at 1200 °C under normal pressure.¹¹

In this paper we report for the first time the result of the EXAFS measurements for $\delta\nu$ -Se in the temperature and pressure range up to 1600 °C and 150 bar using a high-pressure vessel and a sample cell made of polycrystalline sapphire of our own design. Empty circles in Fig. 1 show the temperatures and pressures where EXAFS spectra were measured in the present study.

II. EXPERIMENTAL

A. Constitution of the apparatus for EXAFS measurements

EXAFS measurements for $\delta\nu$ -Se were performed, using the spectrometer installed at the beam line, BL-10B, of the Photon Factory at the National Laboratory for High Energy Physics (KEK), by the usual transmission method. Figure 2 shows the schematic diagram of the apparatus for the present measurements. With a Si (311) channel-cut monochromator, an energy resolution of 1.1 eV at 9 keV was achieved with a typical flux of 10^9 photons/mm² s when the storage ring was operated at 2.5 GeV and 300 mA.¹² The reproducibility of the energy axis was better than 0.0005 deg, which corresponds to 0.3 eV around Se K-absorption edge. The intensity of the incident beam, I_0 , and that of the transmitted beam, I , were measured using two ionization chambers with the path lengths of 17 cm filled with 85% N₂–15% Ar mixture and pure Ar, respectively. X-ray absorption spectra were measured over the range from 12.4 to 13.8 keV. The integration time for photon counting was 2 s per point. In the typical run, it took 30 min to survey the region around the Se K-edge.

In order to obtain the EXAFS oscillation, $\chi(k)$, as a function of photoelectron wave vector, k , the background level for higher shells and the absorption for an isolated atom were subtracted from the observed absorption, $-\ln(I/I_0)$, using a Victoreen fit and cubic spline technique.¹³

B. High-pressure vessel

The experimental conditions of high temperatures, up to 1600 °C, and high pressures, up to 150 bar, were achieved with an internally heated high-pressure vessel made of super-high-tension steel. Figure 3 shows the side view of the vessel, which is constructed of a main cylinder with an inner diameter of 50 mm and two flanges. As seen in the figure, the sample was located on the center axis of the vessel. The incident and transmitted x-ray beams passed through Be windows of thickness 10 mm and diameter 8 mm. Each window had a tapered shape, and was supported by the tapered area of a backup screw, which is illustrated in Fig. 4. Electrodes for heaters and thermocouples were brought out of the vessel through the flange of the right-hand side, where Bridgeman-type high-pressure seals were used. The vessel was pressurized by high purity grade (99.9999%) He gas, which has a low absorption constant for x-rays in the energy range of the present study. Pressures were measured with a Bourdon gauge having an accuracy of ± 3 bar. A water cooling jacket was placed around the outside of the cylinder. We have already used the same vessel for the density measurement of expanded fluid Se (Ref. 7) and the EXAFS measurement of liquid As₂Se₃.¹⁴

C. Sample cell

The Se sample must be contained in a cell made of a special material which is transparent to x-rays and resistant

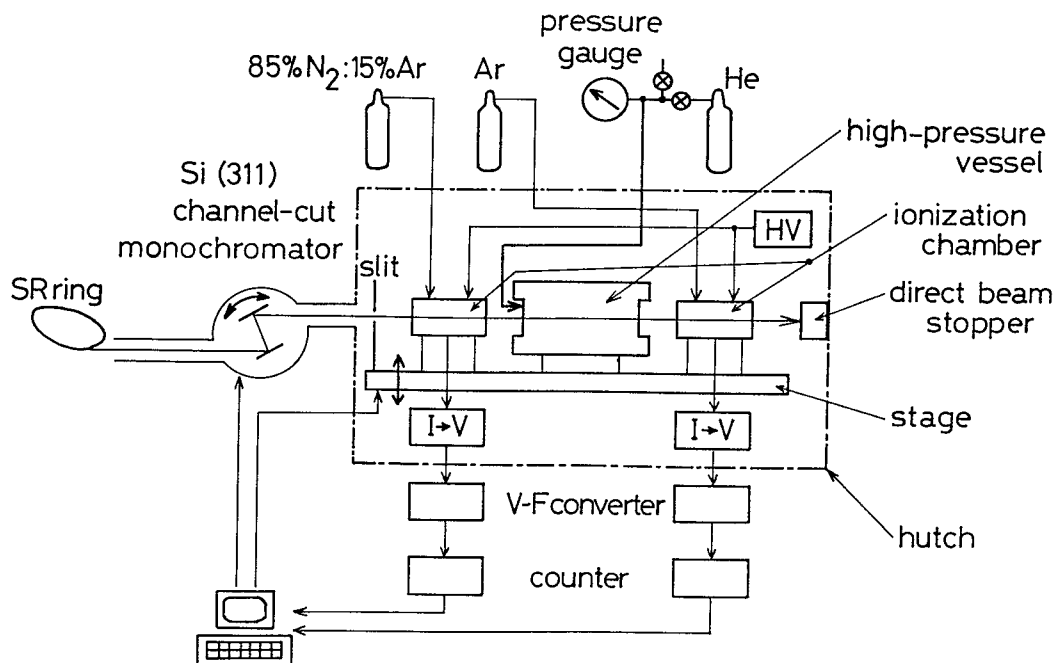


FIG. 2. Schematic diagram of the apparatus for the present EXAFS measurements.

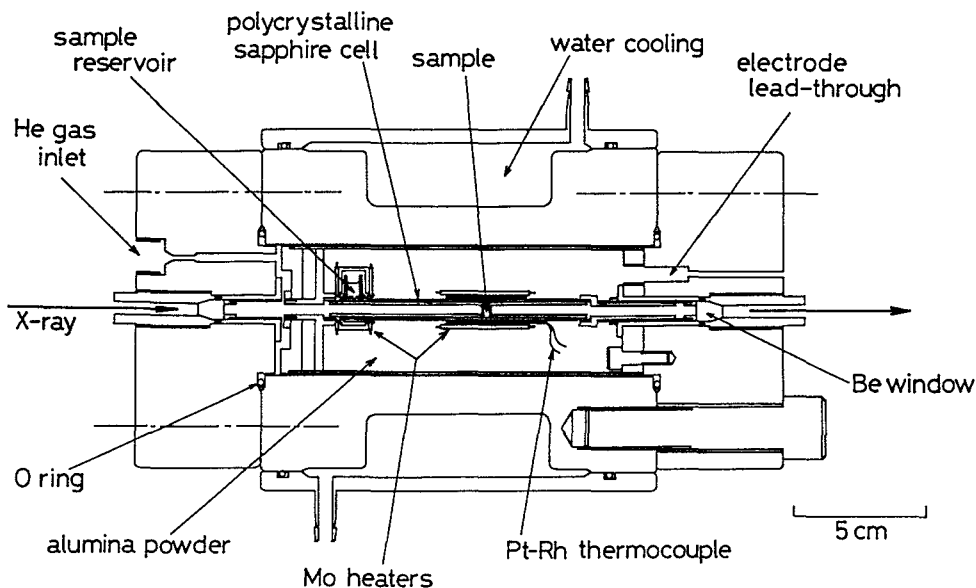


FIG. 3. Side view of the internally heated high-pressure vessel used for EXAFS studies of *dv*-Se.

to chemical corrosion by hot *dv*-Se. For this purpose, we have developed a sample cell made of polycrystalline sapphire (NGK Insulators, Co., Ltd. Type G-30,31). The cell assembly is illustrated in Fig. 5. Two sapphire tubes with outer diameters of 4.5 mm and inner diameters of 3 mm were prepared. The length of the longer tube was 55 mm and that of the shorter one 45 mm. Each of the tubes had one closed end. These tubes were inserted into another open tube having an inner diameter of 4.5 mm, and outer diameter of 6 mm and a length of 90 mm, in such a way that the closed ends of the inner tubes faced each other with a narrow and uniform gap between them. The closed ends were polished to a thickness of 250 μm in order to improve the efficiency of x-ray transmission. The thickness of the sample space was adjusted so that the jump in the x-ray absorption at the absorption edge, $\Delta\mu t$, was about unity. The thickness was from about 250 μm to 2.2 mm. It is useful to note that, when a single-crystalline sapphire cell was used, we observed spurious peaks in the EXAFS spectrum due to the Bragg reflections

from the cell. In the present study, therefore, we used polycrystalline sapphire with a grain size of about 15 μm . As shown in Fig. 5, the sapphire components were cemented with a high temperature glaze (Owen-Illinois, Inc. Type 01328-C). We have used a similar type of sample cell for the density measurement on expanded fluid Se (Ref. 7) and the EXAFS measurement for liquid Se-Te mixtures.^{11,15}

We used a commercial sample with a purity of 99.9999%. The sample was heated by a heating element made of Mo wire of diameter 0.5 mm. The Mo heater was set around a Mo tube which kept the temperature of the sample space uniform. The temperature was measured by three Pt-30%Rh/Pt-6%Rh thermocouples which were inserted into holes drilled in the Mo tube, and were in close contact with the sapphire wall in the vicinity of the sample space. The sample reservoir was maintained at 300 °C during the EXAFS measurements by another heating element made of Mo wire of diameter 0.5 mm. The reservoir was encased with Cu holder which trapped Se vapor escaping from the reservoir.

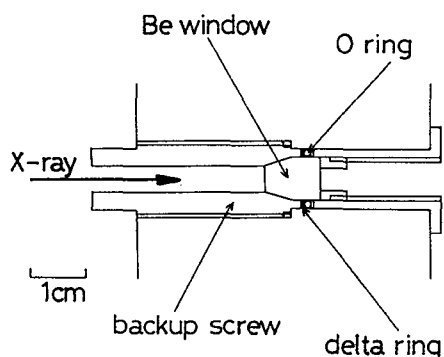


FIG. 4. The construction around the Be window.

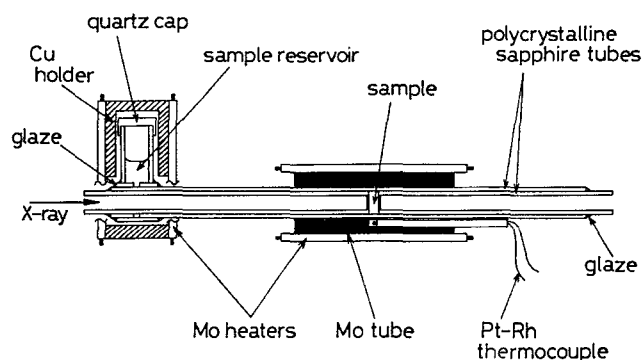


FIG. 5. The construction of a sample cell made of polycrystalline sapphire used for EXAFS studies of *dv*-Se.

The sample space was filled with *dv*-Se in the following way. First, the high-pressure vessel was evacuated and the sample space was heated to 400 °C. Then, the Se sample loaded in the reservoir was melted by heating it to 300 °C, and He gas at pressure of a few bars was introduced into the vessel to force the liquid sample to the sample space through a narrow channel between the outer and inner sapphire tubes. It was confirmed by means of x-ray photography that the liquid sample filled up the sample space completely. Finally, the sample of gaseous state was prepared by heating the sample space above the boiling point while maintaining the temperature of the reservoir at 300 °C.

For the measurement of *c*-Se at room temperature, solid sample was powdered and sandwiched between two layers of Scotch tape.

III. RESULTS AND DISCUSSION

Figure 6 shows EXAFS oscillation $\chi(k)$ of *dv*-Se at various temperatures and pressures up to 1600 °C and 150 bar.

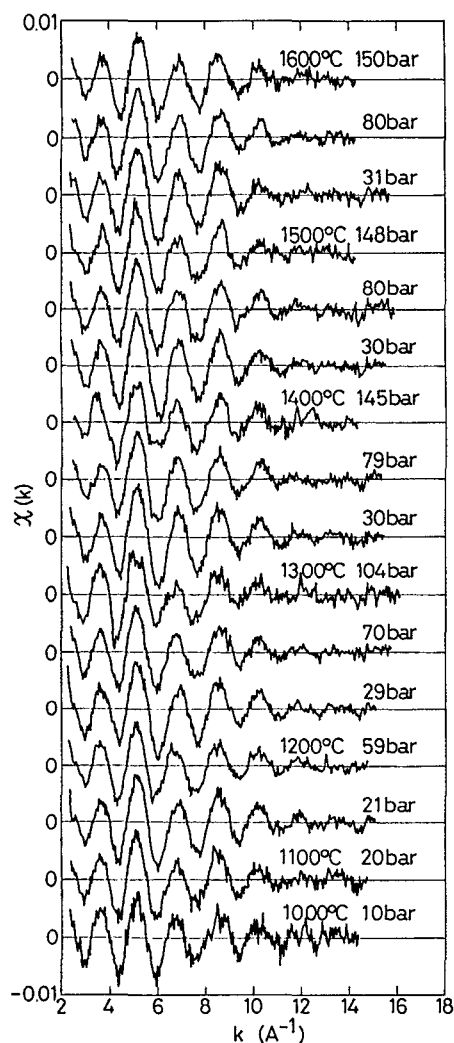


FIG. 6. EXAFS oscillation $\chi(k)$ of *dv*-Se. Temperatures and pressures are indicated at the upper right-hand sides of each data.

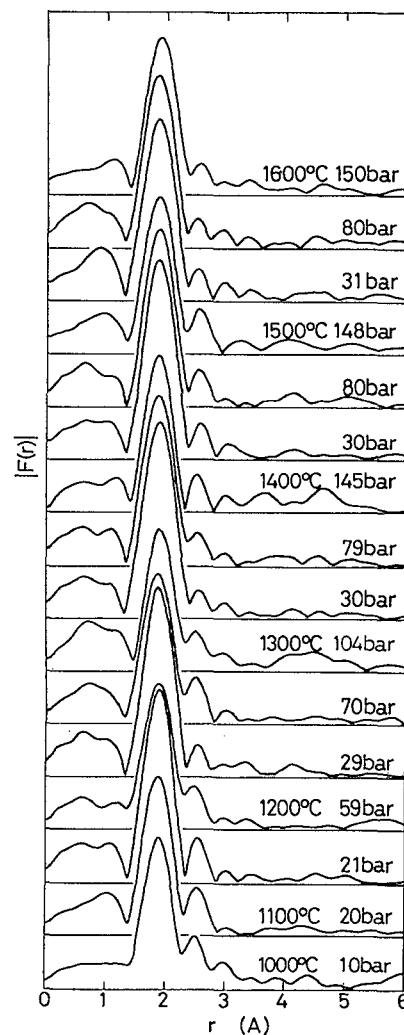


FIG. 7. The magnitude of Fourier transforms, $|F(r)|$, of $k\chi(k)$ for *dv*-Se. Temperatures and pressures are indicated at the upper right-hand sides of each of the data curves.

The temperatures and pressures where the EXAFS spectra have been measured are shown in Fig. 1 by open circles. Note that distinct oscillations appear in the EXAFS spectra even at 1600 °C; such a clear EXAFS oscillation has been observed in Br₂ vapor,¹⁶ which is often referred to as the most typical and simplest example of EXAFS phenomena, and also in other simple molecular vapors such as O₂, CO, and CO₂.¹⁷ The amplitude of $\chi(k)$ has a maximum around 5 Å⁻¹. Each curve shows a simple oscillation and is similar to all others. It should be noticed that $\chi(k)$ at temperatures and pressures near the SVP curve, i.e., 1200 °C/59 bar, 1300 °C/104 bar, and 1400 °C/145 bar, have rather small amplitude compared with others.

Figure 7 shows the magnitude of Fourier transforms, $|F(r)|$, of $k\chi(k)$ for *dv*-Se. The Fourier transform spectra clearly indicate a dominant interatomic distance. The first sharp peaks around 1.9 Å correspond to the nearest-neighbor distribution of molecules in *dv*-Se. With varying temperature or pressure, the position of the first peak seems to remain unchanged. At constant temperatures the height of the first peak becomes small with increasing pressure.

In order to determine the structural parameters such as bond length, r_1 , coordination number, N_1 , and root-mean-square displacement, σ_1 , we used a standard technique of Fourier filtering.¹³ In this analysis the first peak in $|F(r)|$ was backtransformed into k space. The resulting Fourier filtered spectrum, $\bar{\chi}(k)$, was fitted with the following formula:

$$k\bar{\chi}(k) = SB_{\text{Se}}(k')N_1 \exp(-2k'^2\sigma_1^2) \sin[2k'r_1 + \phi_{\text{Se}}(k')]/r_1^2$$

$$k' = (k^2 - \Delta E_0/3.81)^{1/2}.$$

Here $B_{\text{Se}}(k)$ and $\phi_{\text{Se}}(k)$ are the backward scattering amplitude and phase shift functions of Se, respectively. We used $B_{\text{Se}}(k)$ and $\phi_{\text{Se}}(k)$ calculated by McKale *et al.*¹⁸ In the curve fitting procedure, the scaling factor, S , which indicates the ratio of the experimental amplitude to the calculated one, was selected to be 0.65; this gives 2 as N_1 of *c*-Se. In order to alleviate a parameter correlation and false minima, ΔE_0 was fixed to be 6.55 eV, which gives the most reasonable value to r_1 of *c*-Se. The details of data analysis were given in the previous paper by Inui *et al.*¹⁹ The resulting r_1 at various temperatures and pressures are tabulated in Table I, together with the values of r_1 for the dimer determined from the electron diffraction measurement⁴ and the spectroscopic analysis,²⁰ and also for liquid Se near the melting point.⁵

TABLE I. The bond length r_1 , the coordination number N_1 , and the root-mean-square displacement σ_1 of *dv*-Se at various temperatures and pressures obtained from the curve fitting on the EXAFS spectra. The values of r_1 for Se_2 molecule determined from the electron diffraction measurement (Ref. 4) and the spectroscopic analysis (Ref. 20) and for liquid Se (Ref. 5) near the melting point are also presented.

	$T(^{\circ}\text{C})$	$p(\text{bar})$	$r_1(\text{\AA})$	N_1	$\sigma_1(\text{\AA})$
EXAFS	1000	10	2.189	0.712	0.0872
	1100	20	2.183	0.709	0.0834
	1200	21	2.171	0.735	0.0737
		59	2.195	0.675	0.0850
	1300	29	2.167	0.738	0.0751
		70	2.174	0.711	0.0860
		104	2.189	0.766	0.0976
	1400	30	2.164	0.842	0.0786
		79	2.173	0.722	0.0776
		145	2.186	0.611	0.0759
	1500	30	2.162	0.894	0.0819
		80	2.168	0.752	0.0793
		148	2.175	0.722	0.0844
	1600	31	2.162	0.794	0.0796
		80	2.163	0.774	0.0815
		150	2.171	0.732	0.0852
Electron diffraction	900		2.21 ± 0.03		
Spectroscopic	1000		2.1733		
	1300		2.1750		
	1600		2.1764		
Neutron diffraction (liquid Se)	265		2.38		

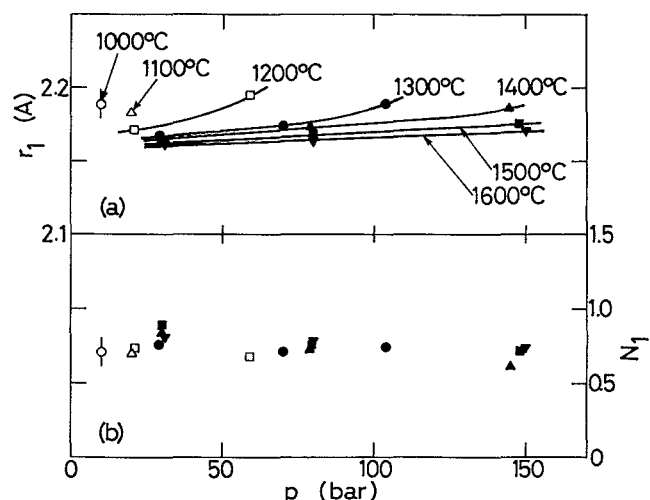


FIG. 8. Pressure variations of (a) the bond length r_1 and (b) the coordination number N_1 of *dv*-Se at various temperatures obtained from the curve fitting. Each symbol indicates the data at different temperatures; ○: 1000 °C, △: 1100 °C, □: 1200 °C, ●: 1300 °C, ▲: 1400 °C, ■: 1500 °C, and ▼: 1600 °C. For clarity error bars are shown only for the data at 1000 °C.

As seen in the table the values of r_1 obtained by the EXAFS measurements are nearly the same, within the error, as that determined from the electron diffraction measurements by Maxwell and Mosley.⁴ The value obtained by the electron diffraction measurement, however, is not as accurate as current spectroscopic data. By assuming a Boltzmann distribution of vibrational states of Se_2 and using the values of the spectroscopic constants given in Ref. 20, the average values of internuclear distance are calculated as shown in the table. These spectroscopic values are in good agreement with the r_1 column obtained by the EXAFS measurements. This suggests that the vapor consists mainly of Se_2 throughout the temperature and pressure region measured.

There is a discrepancy in the temperature variation of r_1 between the EXAFS and the spectroscopic data; in the former r_1 at constant pressures decreases with increasing temperature, but in the latter r_1 increases very slightly or remains almost unchanged. As is well known,²¹ a conventional analysis for the temperature variation of EXAFS data predicts an apparent contraction of the nearest-neighbor distance, contrary to the known expansion. The decrease of r_1 with increasing temperature in our EXAFS data, therefore, might be apparent. The data should be carefully examined by the more sophisticated analytical method. Variations of r_1 as a function of pressure, on the other hand, can be determined with more reliability as long as the data are compared to each other at constant temperatures.

Figure 8(a) shows r_1 of *dv*-Se as a function of pressure at different temperatures. As seen in the figure, r_1 increases almost linearly with increasing pressure; see, for e.g., the data at 1500 °C. A possible explanation for this is that the elongation of r_1 with increasing pressure is attributed to the enhancement of the correlation between Se_2 molecules. Suppose that the vapor at normal pressure is completely composed of Se_2 and behaves as an ideal gas, the average inter-

molecular distance, R , is estimated about 60 Å at 1500 °C, so Se_2 may be considered to be isolated from each other. By applying pressure of 150 bar, R becomes about 11 Å or less, which is only five times longer than the bond length of the dimer. Therefore, the correlation between Se_2 species should not be ignored. It is not so unreasonable to consider that the bond is weakened and elongated by the increase of the interaction between the Se_2 molecules with increasing pressure. A more plausible explanation for the elongation of r_1 is that the enhancement of the correlation between Se_2 molecules causes to produce higher molecular weight species which would start to contribute at higher pressures. Since Se_2 has a nominal double bond, whereas all higher molecular weight species are less bound, the higher species will have longer r_1 , which, on average, will appear to lengthen r_1 . This explanation may be also helpful to explain another interesting result in Fig. 8(a) that r_1 becomes large at temperatures and pressures near the SVP curve, i.e., 1200 °C/59 bar, 1300 °C/104 bar and 1400 °C/145 bar. When the gas-liquid phase boundary is approached higher molecular weight species may be produced, which is considered to be a precursor phenomenon in $dv\text{-Se}$ on the phase transition from the Se_2 vapor to the Se_n polymeric liquid. This results in the apparent increase of r_1 .

Figure 8(b) shows N_1 of $dv\text{-Se}$ as a function of pressure. The symbols represent the same ones as in Fig. 8(a). As seen in the figure, with increasing temperature and pressure N_1 remains almost unchanged within the experimental accuracy. All the values of N_1 at different temperatures and pressures are about 0.8, slightly smaller than unity. This is consistent with the fact that $dv\text{-Se}$ under the present experimental conditions consists of mainly Se_2 molecules, although the accuracy of N_1 obtained from EXAFS spectra is inferior to that determined by x-ray or neutron diffraction.

IV. SUMMARY

We have measured EXAFS spectra for $dv\text{-Se}$ at high temperatures and pressures up to 1600 °C and 150 bar for the first time. For the measurements, we have developed a high-pressure vessel and a polycrystalline sapphire cell. We have found that $dv\text{-Se}$ under the present experimental condition consists mainly of Se_2 and the bond length obtained is in good agreement with the data obtained by the electron diffraction measurement and the spectroscopic data, and much shorter than that of liquid Se. Despite that the experiments have been made in the temperature and pressure region far from the liquid-gas critical point, we have clearly observed

the effect of pressure on the structural parameter. The bond length in $dv\text{-Se}$ slightly increases with increasing pressure. Furthermore, the bond is largely elongated when the SVP curve is approached. This may be attributed to the formation of higher molecular weight species in $dv\text{-Se}$. Since the interaction between molecules is obviously much more enhanced near the critical point, larger molecules or clusters are expected to be formed. It would be very interesting to perform EXAFS measurements up to the critical point. Such an experiment is now in preparation.

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