X-ray photoemission study of a new allotrope of solid selenium
(rhombohedral Se consisting of Se$_6$ ring molecules)

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An x-ray photoemission spectrum of a newly found allotrope of solid selenium, rhombohedral Se containing only Se$_6$ ring molecules, has been presented, and compared with those of monoclinic, trigonal, and amorphous forms. The most remarkable points in the density of states of rhombohedral Se are (1) the intensity ratio of the $4p$ upper bonding band to the lower bonding band is reversed with respect to that of monoclinic Se, and (2) a relatively deep dip is observed at the center of the $4s$ band. The x-ray photoemission spectra have been analyzed with CNDO/S molecular-orbital calculations. The possibility of the existence of Se$_6$ ring molecules in amorphous Se has been also examined.

It is well known that solid selenium exists in three allotropes[1]: trigonal Se, the most stable form consisting of closely packed, infinite, and parallel hericoidal chains; monoclinic Se consisting of closely packed, slightly distorted, and puckered eight-membered rings; and amorphous Se, whose structure has not been well elucidated. Recently, however, we have found the fourth allotrope of solid selenium among small crystals grown from the saturated carbon disulfide solution.[2,3] X-ray diffraction studies have revealed that the new allotrope consists of hexameric molecules, Se$_6$, with symmetry D_{3d} and the crystal has a rhombohedral unit cell with lattice parameters in hexagonal axes $a = 11.36$ Å and $c = 4.43$ Å. The schematic view of the molecule and

(a)

(b)

FIG. 1. (a) Schematic view of the Se$_6$ ring molecule, and (b) the crystal structure of rhombohedral Se viewed along the [001] axis.

the crystal is shown in Fig. 1. Structural factors (bond length, bond angle, and dihedral angle) of rhombohedral Se are listed in Table I together with those of monoclinic and trigonal forms for comparison.

We have already reported the Raman and ir spectra of rhombohedral Se.[4,5] In this Rapid Communication we present the first x-ray photoemission spectrum (XPS) of rhombohedral Se, together with those of monoclinic, trigonal, and amorphous forms. The photoemission spectra have been analyzed with CNDO/S molecular-orbital calculations on six- and eight-membered ring molecules. The possibility of the existence of six-membered ring molecules in amorphous Se proposed by Richter and Herre[6] and Joannopoulos, Sclüter, and Cohen[7] has also been examined.

Rhombohedral Se was prepared by the same method as described before[2,3]: Rhombohedral crystallites were picked up one by one under the microscope among a mixture of small crystals grown from the saturated carbon disulfide solution. The typical size of the crystallite is about 20 μm $\phi \times 200$ μm length. Samples thus obtained were checked by x-ray diffraction and were confirmed to be almost rhombohedral (above 90%). An XPS sample of rhombohedral Se was prepared by crushing these crystallites onto a stainless-steel holder with a clean slide cover glass in an argon atmosphere,[8] then inserting them into the photoelectron spec-
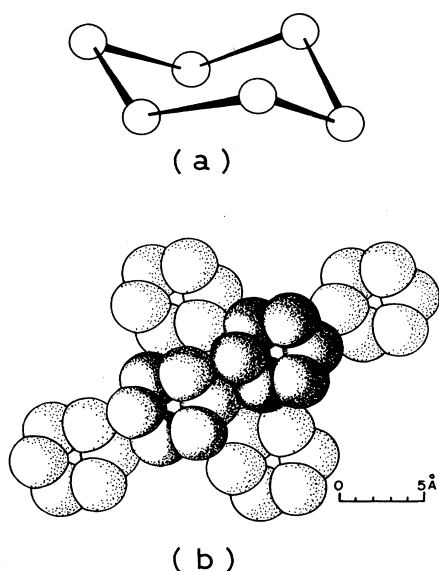
TABLE I. Bond length and bond and dihedral angles in rhombohedral, monoclinic, and trigonal Se.

	Se		
	Rhombohedral	Monoclinic	Trigonol
Bond length (Å)	2.36	2.34	2.36
Bond angle (deg)	100.9	105.3	103.7
Dihedral angle (deg)	76	102	101

trometer without exposing them to air. Although the surface of the sample was initially contaminated with oxygen and carbon, the selenium sample was observed to be self-cleaning under the ultrahigh vacuum in the spectrometer, and a reasonably clean sample could be obtained after a period of about one day.

XPS spectra were measured with a VG ESCALAB 5 photoelectron spectrometer (base pressure less than 1×10^{-10} Torr) with $MgK\alpha$ line (1253.6 eV) as an exciting source. The total resolution of the spectrometer was about 1.0 eV in a full width at half maximum. A valence-band spectrum with a good signal-to-noise ratio was obtained by a continuous scanning for about 24 h. An electron flood gun was used during the measurements to prevent the sample charging effect. In order to check damage of the sample by the x-ray irradiation, Raman and ir spectra of the sample were measured before and after the measurement, and no changes in the spectra were detected.

Figure 2 shows the XPS spectrum of the valence band of rhombohedral Se together with those of monoclinic, trigonal, and amorphous forms[9] measured with the same spectrometer. All the spectra have three main bands at about 2, 5, and 13 eV. The first and second bands are due to the $4p$ lone pair and the $4p$ bonding states, respectively, and the third band is ascribed to the $4s$ states.[7,10-14] The lone pair band of rhombohedral Se is apparently narrower than those of trigonal and amorphous forms (see Fig. 2). This represents the molecular character of rhombohedral crystal. The second band of rhombohedral, monoclinic, and trigonal forms consists of two subbands, which have been referred to as upper and lower bonding bands, respectively, while the $4p$ bonding states of amorphous Se form only one broad band. As is shown in Fig. 2, a remarkable difference ap-

pears in the $4p$ bonding and the $4s$ region of the spectra. The intensity ratio of the upper bonding band to the lower bonding band is reversed in going from rhombohedral Se to the monoclinic form, while the band ratios are similar between rhombohedral and trigonal forms. As for the $4s$ band, rhombohedral Se shows the narrowest $4s$ band, followed by the monoclinic form. Trigonal and amorphous forms have a broad and trapezoidal $4s$ band. It should be noted that the $4s$ band of rhombohedral Se has a relatively deep dip at the center of the band.

Figure 3 shows the one-electron density of states calculated on the basis of the CNDO/S method. Each CNDO eigenvalue is represented by a Gaussian of width 0.6 eV in constructing the CNDO/S calculated density of states. The calculated orbital eigenvalues are given in Table II. In the present CNDO calculations, we used the same framework as that of Salaneck, Duke, Paton, and Griffiths[13] except for the parameter of the two-center Coulomb integral, γ_{AA}: We used 7.12 eV for γ_{AA} instead of the value of Salaneck et al., 9.12 eV, so that the energy position of the upper bonding bands of six- and eight-membered ring molecules agrees better with the experimental results of rhombohedral and monoclinic Se, respectively. This choice of the parameter causes the exchange of the order of the two molecular orbitals of the eight-membered ring, $2e_2$ and $1b_1$, compared with the result of Salaneck et al., although the overall feature of the density of states shows little changes. The observed energy poisiton of the $4p$ upper and lower bonding bands and the $4s$ band (indicated by bars in Fig. 2) of rhombohedral and monoclinic Se with respect to the peak position of the respective $4p$ lone pair band is denoted by arrows in the calculated density of states of Se_6 and Se_8 ring molecules in Fig. 3. As is found in Figs. 2 and 3, the
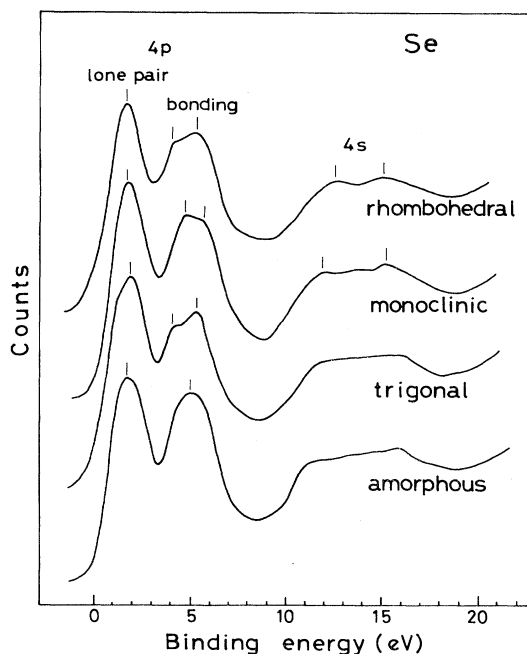

FIG. 2. XPS ($MgK\alpha$) spectra of rhombohedral, monoclinic, trigonal, and amorphous Se. Peak positions of some bands are indicated by bars.
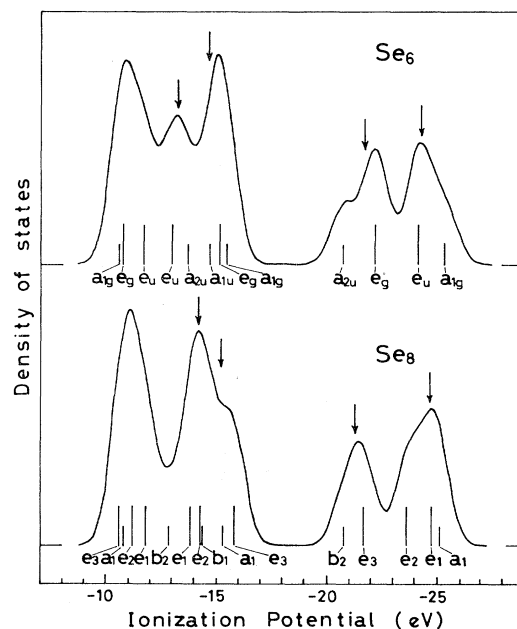

FIG. 3. Density of states of Se_6 and Se_8 ring molecules calculated by CNDO/S method. Each CNDO/S eigenvalue is broadened by Gaussian of width 0.6 eV in constructing the density of states. The observed peak positions of the $4p$ bonding and the $4s$ bands relative to the $4p$ lone pair peak are indicated by arrows.

TABLE II. CNDO/S eigenvalues for occupied states of Se_6 and Se_8.

Se_6 Symmetry (D_{3d})	Energy (eV)	Se_8 Symmetry (D_{4d})	Energy (eV)
$3a_{1g}$	-10.67	$3e_3$	-10.66
$3e_g$	-10.79	$3a_1$	-10.82
$3e_u$	-11.73	$3e_2$	-11.18
$2e_u$	-13.07	$3e_1$	-11.78
$2a_{2u}$	-13.81	$2b_2$	-12.85
$1a_{1u}$	-14.79	$2e_1$	-13.91
$2e_g$	-15.21	$2e_2$	-14.33
$2a_{1g}$	-15.51	$1b_1$	-14.38
$1a_{2u}$	-20.80	$2a_1$	-15.34
$1e_g$	-22.28	$2e_3$	-15.78
$1e_u$	-24.25	$1b_2$	-20.79
$1a_{1g}$	-25.42	$1e_3$	-21.64
		$1e_2$	-23.69
		$1e_1$	-24.79
		$1a_1$	-25.14

overall feature in the density of states is in excellent agreement between the experiments and calculations: The observed reversion of the intensity ratio of the upper bonding band to the lower bonding band is clearly reproduced in the calculations, and a relatively deep dip also appears in the calculated $4s$ band of the Se_6 ring molecule.

Here, we must comment on a previously reported calculation of the density of states of the six-membered selenium ring: Joannopoulos et al.[7] have already calculated the density of states of Se in a model structure containing only six-membered rings using the empirical psuedopotential method, and discussed the possibility of the existence of six-membered ring molecules in amorphous Se. In their calculated density of states, the intensity ratio of the upper bonding band to the lower bonding band is reversed with respect to the present calculations in Fig. 3, and is apparantly inconsistent with the experimental results of rhombohedral Se containing only six-membered rings. As for the $4s$ band, the agreement is fairly good between the previous calculations[7] and the present ones.

Finally, we discuss the possibility of the existence of six-membered ring molecules[6,7] in amorphous Se by comparing the photoemission spectra. At first, as pointed out before, the $4p$ lone pair band of amorphous (evaporated) Se is obviously wider than that of rhombohedral Se and is rather close to that of the trigonal form. It is very difficult to discuss the $4p$ bonding band because that of amorphous Se is featureless whereas the other three allotropes have two distinct subbands with different intensities. As for the $4s$ band, a remarkable difference is observed between rhombohedral and amorphous forms: The $4s$ band of amorphous Se shows a flat feature at the top similar to a trapezoid while that of rhombohedral Se closely resembles a triangle with a relatively deep dip at the top. The shape of the $4s$ band of amorphous Se is rather similar to that of trigonal Se. According to the above discussion, it is tentatively concluded that a six-membered ring molecule is not a main constituent of amorphous Se although the possibility of the inclusion in amorphous Se cannot be entirely excluded. The similarity in the $4p$ lone pair and the $4s$ band between amorphous and trigonal forms suggests that amorphous Se may consist of relatively long disordered chains.

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