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STRUCTURAL STUDY OF POLY(CARBON DISELENIDE)

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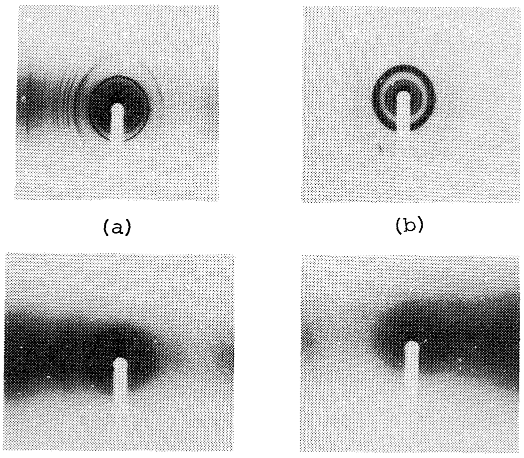
Poly(carbon diselenide) is metallic in an ordered crystalline state and it becomes less conductive when crystalline imperfection increases. EXAFS spectra show the existence of Se-Se bonds and the co-ordination number of Se in metallic poly(carbon diselenide) is almost 2.0, indicating the infinite chains of Se atoms. Extended Huckel calculation gave a reasonable interpretation of the metallic nature of crystalline poly(carbon diselenide).

Recent development in the field of the synthetic metals has revealed that the intermolecular interaction between chalcogen atoms in the π-conjugated systems plays central role to realize high conductivity. Carbon diselenide is the simplest π-conjugated molecule with Se atoms. We have prepared high conducting crystalline powder of poly(carbon diselenide)(abbreviated hereafter as $(CSe_2)_x$) under high pressure¹⁾ whose room-temperature conductivity is 10^4-10^5 times larger than that of amorphous $(CSe_2)_x$ reported by Okamoto and Wojciekovskii.²⁾ In the present report, a structural model of crystalline $(CSe_2)_x$ is proposed from the analysis of the Se K-edge EXAFS.

Liquid CSe_2 in the teflon cell was pressuarized at about 5 kbar and heated to 80-100 °C. Then the pressure was released and heated at 100-130 °C. By changing the applied pressure and the heat-treatment temperature, we obtained various types of solid. The conductivity of the compaction sample of the crystalline $(CSe_2)_x$ reaches 50 S cm^{-1}. The resistivity at 1.7 K is only 2-3 times larger than the room-temperature value. Extremely small temperature dependence will be induced from the resistance between compacted particles. The thermoelectric power is negative and as small as -12 μV/K at room temperature, suggesting the existence of free electrons.1) Skin effect of ESR and temperature independent magnetic susceptivility in the temperature range of 300-1.5 K also indicate metallic nature of the crystalline $(CSe_2)_x$.3)

Besides the high conducting samples, there are insulating, low-conducting and semiconducting samples. The conductivity of the insulating sample is less than 10^{-8} S cm^{-1} and that of the semiconducting sample is about 5 S cm^{-1} with



(a) (b) (c) (d)

Fig. 1. Diffraction patterns of $(CSe_2)_x$.

a) Metallic solid $(CSe_2)_x$,

b) conducting (5 S cm^{-1}) solid $(CSe_2)_x$,

c) low conducting solid $(CSe_2)_x$ (10^{-3} S cm^{-1}),

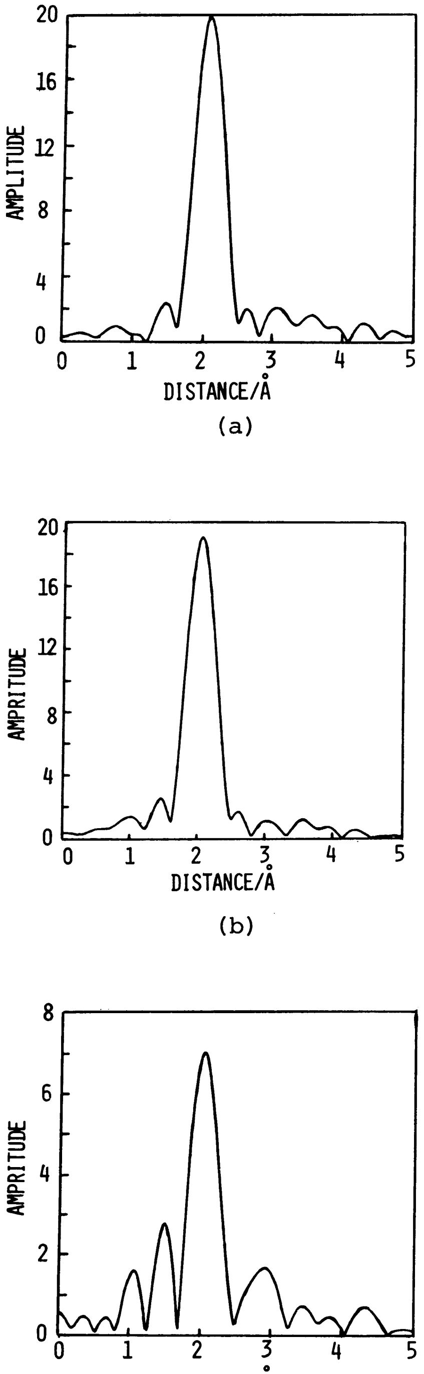
d) insulating solid $(CSe_2)_x$.

Table 1. Observed lattice spacings $(\mathrm{\AA}^{-1})$ and X-ray intensities of metallic solid $(CSe_2)_x$

d_{obsd}	I	d_{obsd}	I
3.837	36.3	1.321	5.1
3.375	0.8	1.227	3.4
3.039	100.0	1.243	5.8
2.198	15.3	1.180	5.7
2.087	36.3	1.126	4.6
2.014	20.9	1.083	17.2
1.906	1.6	1.037	7.1
1.777	19.6	0.967	2.7
1.652	20.1	0.960	3.1
1.514	17.7	0.883	4.5
1.434	11.1	0.879	2.7
1.378	3.3		

activation energy of 0.09 eV. The conductivity of low-conducting samples obtained by heating the insulating sample up to 250 °C is ca. 10^{-3} S cm^{-1}. High conducting metallic solid $(CSe_2)_x$ gave sharp powder X-ray diffraction patterns(Fig. 1a). Insulating solid was amorphous to X-ray diffraction (Fig. 1d). Semiconducting solid gave broad Debye rings (Fig. 1b). Low-conducting material showed faint and broad ring (Fig. 1c). These diffraction patterns show that the solid $(CSe_2)_x$ is metallic in an ordered crystalline state and it becomes less conductive when crystalline imperfection increases. Since the metallic solid $(CSe_2)_x$ gave sharp diffraction patterns, a detailed examination of the X-ray powder patterns was made using a Rigaku X-ray powder diffractometer. Intensities were obtained by scanning up to $2\theta=130°$(Cu Kα radiation, 35 kV, 15 mA) for a week running (0.72°/h). More than twenty peaks were obtained, whose lattice spacings and X-ray intensities are listed in Table 1. The IR spectrum was taken of a dispersion in KBr. The insulating sample showed the vibration of C=Se double bonds. The conducting sample was opaque down to at least 400 cm^{-1} probably due to the free carrier absorption.[2)]

The measurement of the EXAFS spectra was performed at the Photon Factory of National Laboratory for High Energy Physics (KEK-PF), using EXAFS facilities at the beam line 10-B with a Si(311) channel-cut monochromater. All the measurement were done on the powder samples. The Fourier transform of the EXAFS oscillation, $k^3\chi(k)$ for Se powder, metallic $(CSe_2)_x$ and insulating $(CSe_2)_x$ are shown in Fig. 2. The Fourier transform of metallic $(CSe_2)_x$ is different from that of insulating $(CSe_2)_x$ but is quite similar to that of Se powder (so-called"metallic Se"). The prominent peak in the Fourier transform of metallic $(CSe_2)_x$ corresponds to Se-Se bond. No indication of Se-C or Se=C bond is found except in the insulating sample. In the



(a)

(b)

(c)

Fig. 2. Fourier transform of the EXAFS oscillation, $k^3\chi(k)$ for (a) Se powder, (b) metallic $(CSe_2)_x$ and (c) insulating $(CSe_2)_x$; the second highest peak will correspond to C-Se or C=Se bond.

Table 2. The Se-Se bond distances(d/Å^{-1}) and co-ordination numbers(N) of Se atoms. The Se atom was used as a model compound

	N	d	Conductivity/S cm^{-1}
Se(metallic Se)	2.0	2.37	10^{-5}
Metallic $(CSe_2)_x$ (Fig. 1a)	2.0	2.36	50
Insulating $(CSe_2)_x$ (Fig. 1b)	0.7	2.35	$< 10^{-8}$
$(CSe_2)_x$ (Fig. 1c)	1.8	2.35	5
$(CSe_2)_x$ (Fig. 1d)	1.7	2.33	$\approx 10^{-3}$

insulating compound, the hight of Se-Se peak is significantly lower as compared with the metallic sample. The bond distances and co-ordination numbers obtained by the curve-fitting analyses with empirical parameters are given in Table 2. Since so-called "metallic Se" has a hexagonal unit cell with a helical structure of Se-Se distance of 2.37 Å,[4)] the co-ordination number of Se in "metallic Se" was fixed as 2.0. The co-ordination number of metallic $(CSe_2)_x$ is almost 2.0, which indicates that each Se atom has two neighbouring Se atom. On the other hand, insulating CSe_2 has the co-ordination number of 0.7. Se-Se distances are almost the same for all the samples.

Although the EXAFS analyses cannot give a precise three-dimensional structure, two-dimensional local structure could be derived (Fig. 3). In the case of the polymerization of CSe_2 molecules, if a C atom bonds to Se atoms with hybrid orbitals of sp^2 or sp^3, the neighbouring Se-Se distances become longer than 3.0 Å, which is not consistent with the results of EXAFS analyses. Therefore, CSe_2 molecules are considered to polymerize forming the Se-Se infinite chain shown in Fig. 3. This model explains the reason why less conducting samples have smaller co-ordination numbers. The small co-ordination number in insulating sample suggests the imperfect chain structure of Se atoms. Then the conduction pass way will be broken and crystalline state becomes

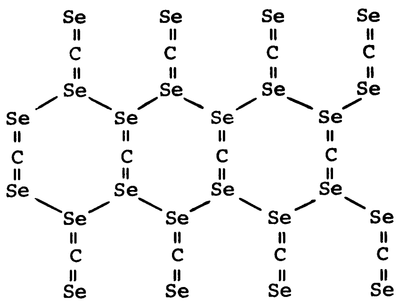


Fig. 3. Two-dimensional structure model of $(CSe_2)_x$.

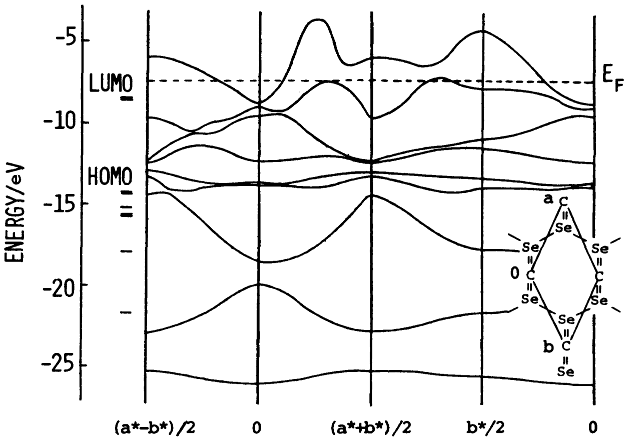


Fig. 4. The energy level of CSe_2 molecule and the energy band for the structure model of two-dimensional network of $(CSe_2)_x$.

imperfect. Recent ESR measurements have revealed that in the insulating samples there are two kinds of Se radicals which indicate the existence of the broken Se-Se bonds.$^{3)}$

As mentioned before, we considered the infinite chain formation is essential for the high conductivity. So we examined the electronic structure of $(CSe_2)_x$ in order to examine the origin of its metallic nature. The simple extended Huckel approximation was adopted. The Slater exponents and the ionization potentials are used those in the reference 5. Results of the examination of the energy level of CSe_2 molecule and the energy band obtained for the structure model of two-dimensional network of $(CSe_2)_x$ are shown in Fig. 4. Since the energy separation between HOMO and LUMO is not so large, the large transfer integral due to the bond formation through Se atoms results in the overlapping of the energy band and Fermi level crosses energy bands. Therefore, the existence of the Fermi surface is a natural consequence of the infinite Se-Se bond formation. Although it appears to leave a room for improvement on the details of the structure model, the chain formation of Se atoms revealed by the EXAFS analysis gives a reasonable interpretation for the metallic nature of $(CSe_2)_x$. Mulliken's atomic orbital bond populations of C=Se and Se-Se in metallic $(CSe_2)_x$ are 1.009 and 0.410, which indicates the delocalization of the electrons.

References

1) H.Kobayashi, T.Mori, R.Kato, A.Kobayashi, Y.Sasaki, G.Saito, and H.Inokuchi, Chem. Lett., 1984, 1407.
2) Y.Okamoto and P.S.Wojciechowski, J. Chem. Soc., Chem. Commun., 1982, 386.
3) A.Kobayashi et al. to be published.
4) P.Cherin and D.Unger, Acta Crystallogr., Supplement, 21, A46 (1966).
5) M.-H.Whangbo, Solid State Commun., 43, 277 (1982).

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