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Conductivity and Structure of Crystalline Carbon Diselenide

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CONDUCTIVITY AND STRUCTURE OF CRYSTALLINE CARBON DISELENIDE

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Abstract Crystalline poly(carbon diselenide) is a new synthetic metal. The room-temperature resistivity of the compaction sample is 0.02-0.05 Ωcm . The thermoelectric power is as small as 13 $\mu\text{V/K}$ at room temperature. Metallic sample gave sharp X-ray powder pattern. Poly(carbon diselenide) becomes less conductive when crystalline imperfection increases. EXAFS spectra showed the existence of Se-Se bonds. The coordination number of Se in metallic poly(carbon diselenide) is almost 2.0, indicating the infinite chain of Se atoms.

INTRODUCTION

Recent development in the field of the synthetic metals has revealed that the intermolecular interaction between charcogen atoms in the π -conjugated systems plays a central role to realize the high conductivity. Carbon diselenide is the simplest π -conjugated molecule with Se atom. We have prepared high conducting poly(carbon diselenide) (abbreviated hereafter as $(\text{CSe}_2)_x$).¹ The conductivity of the crystalline $(\text{CSe}_2)_x$ is 10^4 - 10^5 times larger than that of amorphous $(\text{CSe}_2)_x$ obtained by Okamoto and Wojciechowski.² We consider that the crystalline $(\text{CSe}_2)_x$ is a new synthetic metal.

RESULTS

Liquid CSe_2 was pressurized in the teflon cell at about 5 Kbar and heated at 80-100 $^\circ\text{C}$. Then the pressure was released and heated at 100-130 $^\circ\text{C}$. A black solid was obtained. By changing the applied pressure and the heat temperature, we obtained various types of solid poly(CSe_2)_x. In high conducting solid, the resis-

tivity of the compaction sample is 0.02–0.05 Ωcm (Fig.1). The resistivity at 1.7 K is only 2–3 times larger than the room-temperature value. Extremely small temperature dependence will be arised from the resistance between compacted particles. The thermoelectric power is as small as 13 $\mu\text{V/K}$ at room temperature (Fig. 2). Its linear temperature dependence ($T > 50$ K) suggests the existence of the free electrons. The magnetic susceptibility is temperature independent between 1.5–300 K, also suggesting the metallic nature of $(\text{CSe}_2)_x$.³ Besides the metallic samples, there are insulating ($>10^8$ Ωcm), low-conducting ($\sim 10^3$ Ωcm) and semiconducting (~ 0.2 Ωcm) samples. Figure 3 shows the X-ray powder diffraction patterns. Metallic sample gave sharp patterns (A). Insulating solid was amorphous to X-ray diffraction (B). Semiconducting sample gave broad Debye rings and low-conducting material showed faint and diffuse patterns. These patterns suggest that $(\text{CSe}_2)_x$ is metallic

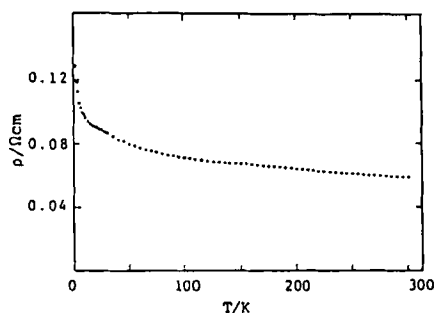


Fig. 1. Electrical resistivity of crystalline $(\text{CSe}_2)_x$.

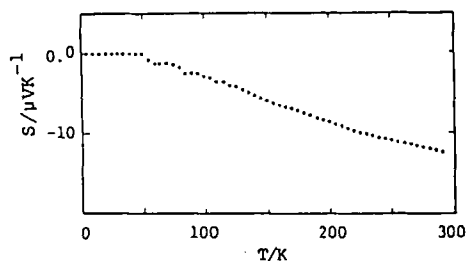


Fig. 2. Thermoelectric power ($\text{S}/\mu\text{VK}^{-1}$) of crystalline $(\text{CSe}_2)_x$.

in an ordered crystalline state and it becomes less conductive, when crystalline imperfection increases.

The measurements of the EXAFS spectra were made at KEK Synchrotron Radiation of National Laboratory for High Energy Physics. The Fourier transform of the EXAFS oscillation, $k^3\chi(k)$ for metallic $(\text{CSe}_2)_x$ is quite similar to that of Se powder (so-called "metallic Se") but different from that of insulating $(\text{CSe}_2)_x$ (Fig. 4). The prominent peak in the Fourier transform corresponds to Se-Se bond. The Se-Se bond appears at about 2.0 Å, which is 0.3–0.4 Å shorter than true value due to the phase shift of Se atom. The coordination number of Se obtained by curve fitting

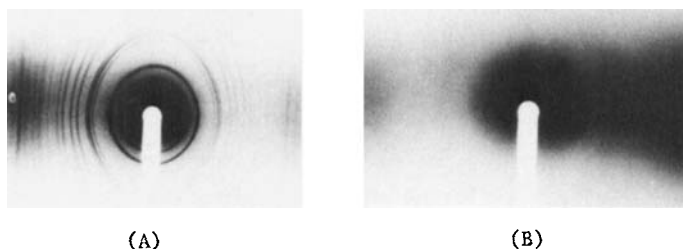


Fig. 3. X-Ray diffraction patterns of $(\text{CSe}_2)_x$.

(A) Metallic $(\text{CSe}_2)_x$ (B) Insulating $(\text{CSe}_2)_x$

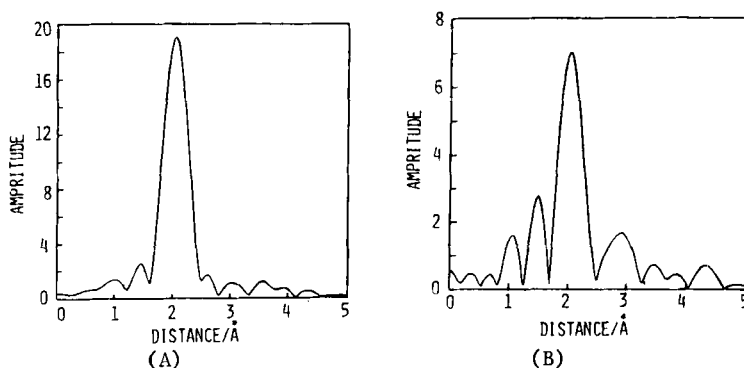


Fig. 4. Fourier transform of $k^3\chi(k)$

(A) Metallic $(\text{CSe}_2)_x$ (B) Insulating $(\text{CSe}_2)_x$

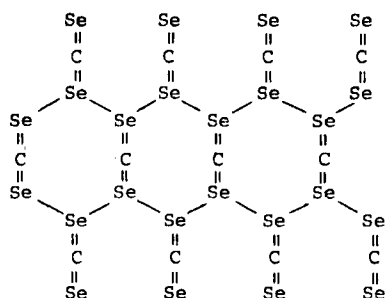


Fig. 5. Structural model of metallic $(CSe_2)_x$.

analyses is almost equal to 2.0, indicating that each Se atom has two neighbouring Se atoms. While in insulating sample, the peak of Se-Se bond decreases and the coordination number is very small (0.68). Since the analyses of EXAFS spectra strongly suggest that every Se atom in the metallic $(CSe_2)_x$ is bonded to two neighbouring Se atoms with Se-Se distance of 2.35 Å, its structural model can be easily derived (Fig. 5). This model explains the correlation between the conductivity and the orderness of the crystal. Small coordination number of insulating solid indicates the imperfect network of Se atoms. Then the conduction pathway will be broken and the crystalline state becomes imperfect.

According to the extended Huckel calculations of CSe_2 molecule and the crystalline $(CSe_2)_x$, the chain formation of Se atoms results in the overlapping of the energy bands and leads to the existence of the Fermi surface, which is consistent with the metallic nature of the crystalline $(CSe_2)_x$.³

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