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ABSTRACT. The layer compound $ZrSe_2$ can be grown as a degenerate semiconductor, which is ascribed to the charge transfer effect of the self-intercalated Zr atoms. The self-intercalation is much concerned with the magnitude of the energy gap in the mother crystal. We have ascertained this by the transport measurement of $ZrSe_{2-x}S_x$ and $Ti_xZr_{1-x}Se_2$. Intercalation of lithium in $ZrSe_2$ converts the mother crystal into a metallic one. $Li_xZrSe_2(x>0.4)$ is found to be superconductive below ca. 1.5K.

1. INTRODUCTION

The layer compound transition metal(IV_b , V_b and VI_b) dichalcogenides, MX_2 , exhibit a variety of physical properties. One of the most striking features is the discovery of the charge density wave in the quasi-two dimensional metal of $V_b-MX_2(1)$. On the other hand, IV_b - and VI_b-MX_2 are semiconductors except for $TiSe_2$ which is a semimetal. TiS_2 and $ZrSe_2$ of IV_b-MX_2 with a layered CdI_2 structure, however, show a metallic nature in their electrical resistivity, although they are known from optical spectra to possess energy gaps of 0.3-0.5eV and 1.0-1.2eV, respectively (2). A first systematic study by Takeuchi and Katsuta found a metallic behavior in TiS_2 through the measurements of electrical resistivity, Hall coefficient and magnetic susceptibility(3). Furthermore, the defect structure in non-stoichiometric TiS_2 was discussed from the lattice constant and the X-ray intensity. The excess Ti atoms of $Ti_{1+x}S_2$ were found to be self-intercalated in the van der Waals gap sites. The high conductivity and the large carrier concentration in this material are now interpreted as a charge transfer effect. Namely, the valence electrons of self-intercalated Ti atoms become conduction electrons, occupying the vacant t_{2g} -band of the mother crystal. A simple calculation shows that the excess Ti of $Ti_{1.0043}S_2$ gives a carrier concentration of $3 \times 10^{20} \text{ cm}^{-3}$, which is a measured value of a crystal grown by the usual procedure. Therefore, TiS_2 becomes a degenerate semiconductor.

The most fascinating property of TiS_2 is the temperature dependence of its electrical resistivity; $\rho = \rho_0 + AT^n$ ($n \approx 2$) above 30K. This was

first pointed out by Thompson and was discussed in terms of electron-electron scattering(4). This was later analyzed on the basis of the electron-hole scattering under a semimetallic picture or the homopolar optical scattering(5,6). Recently, this behavior was again interpreted by Klipstein et al. and Kaveh et al. from a viewpoint of a carrier scattering by acoustic phonons(7,8). A similar behavior was found by the present authors in $ZrSe_2$ (9). Therefore, this behavior may be a general phenomenon which occurs under a certain condition. What is it? It is a purpose of the present paper to clarify it.

Another property of transition metal dichalcogenides is an intercalation effect. Most of the atoms in the periodic table and organic molecules which are Lewis bases can be intercalated in the van der Waals gap sites, forming intercalation compounds(intercalates). One of the most striking features is a transport phenomenon. Alkali metal intercalates of IV_B- and VI_B-MX_2 , for example, Na_xMoS_2 or Li_xZrSe_2 become metallic and show a superconductivity at low temperatures(10,11). A charge transfer occurs between the alkali atom and the mother crystal. The alkali atom behaves as a donor intercalant and transfers a 2s-electron into the vacant band of the mother crystal. The Li_xZrSe_2 system was precisely investigated by Berthier et al.(12). They claimed the occurrence of a non-metal to a metal transition at $x=0.4$ in Li_xZrSe_2 through X-ray, electrochemical, conductivity, NMR and EPR measurements. On the other hand, superconductivity was found in Li_xZrSe_2 (11). The critical value of x in Li_xZrSe_2 showing superconductivity is however not known yet. The present paper also aims to clarify the Li_xZrSe_2 system from a view point of superconductivity.

2. EXPERIMENTAL

The single crystals of $ZrSe_2$, $ZrSe_{2-x}S_x$ and $Ti_xZr_{1-x}Se_2$ were grown by the usual iodine vapor transport method. The prereacted powder was put in one end of a quartz tube and the tube was sealed in vacuum. The ampule was heat-treated in such a way that the powder was at $900^\circ C$ and the temperature of the other end was ca. $780^\circ C$. Single crystals were grown not only in the lower temperature end(denoted as the L-sample) but also in the hotter one(the H-sample), as shown in the inset of Fig.1. Here, purities of materials were 99.6%-granule(denoted as 2N-G), 99.9%-granule(3N-G) and 99.9%-powder(3N-P) for Zr, 99.9%-powder for Ti, 99.9999% for S and 99.999% for Se.

The powder sample(2N-G) of $ZrSe_2$ was reacted with n-butyllithium in hexane solution to make lithium intercalates, Li_xZrSe_2 in a glove box filled with argon gas for ten days under a constant temperature of $30^\circ C$. The lithium content in Li_xZrSe_2 was determined by a flame analysis.

The electrical resistivity, ρ and Hall coefficient, R_H parallel to the layer plane were automatically measured by the ordinary DC method with the use of a microcomputer. The superconducting critical temperature, T_c was measured by the AC magnetic susceptibility method.

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

3.1 Transport property of $ZrSe_2$, $ZrSe_{2-x}S_x$ and $Ti_xZr_{1-x}Se_2$

We show in Fig.1 the typical temperature dependence of electrical resistivity for $ZrSe_2$ (3N-GL & GH). The electrical resistivity almost depends on the relation of $\rho = \rho_0 + AT^n$. The n-value is 2.0 for the L & H-samples. We remark here that the magnitude of the resistivity for the H-sample is smaller than the one for the L-sample. A similar result was obtained also for the 2N-G-sample. This is ascribed to the difference of the carrier concentration, as shown in a later figure. This behavior of the resistivity was interpreted by Klipstein et al. on the basis of

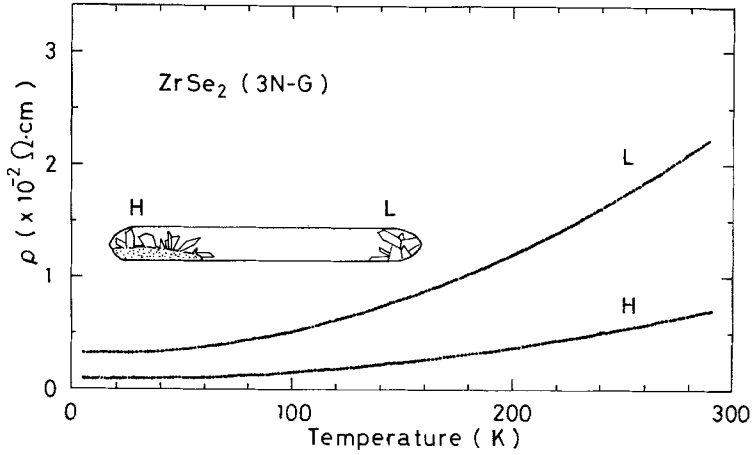


Figure 1. Temperature dependence of electrical resistivity of $ZrSe_2$ (3N-G).

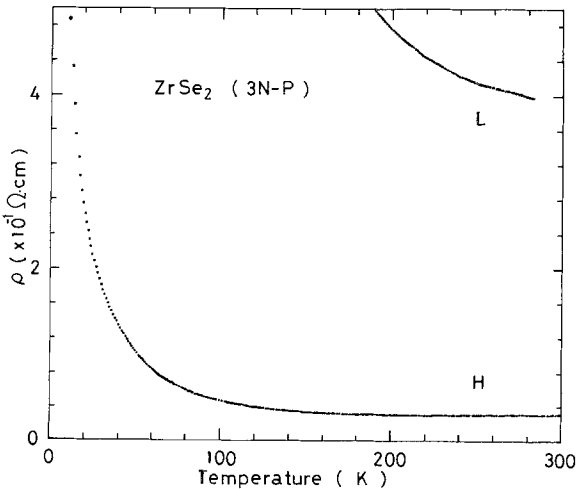


Figure 2. Temperature dependence of electrical resistivity of $ZrSe_2$ (3N-P).

the acoustic phonon scattering, although other ideas were not dismissed.

Contrary to the nearly metallic nature of the G-sample, semiconductive behavior is found for the 3N-P-sample, as shown in Fig.2. In this temperature region, the conduction due to the impurity level is dominant. The activation energy, Δ , is thus estimated as 0.009 eV from the relation of $\rho \propto \exp(\Delta/k_B T)$. Here, we must mention that the magnitude of resistivity for the H-sample is also smaller than the one for the L-sample. In the figure, the resistivity increase is found above 230K for the L-sample. A simple theoretical fitting for the typical two samples (3N-GL & 3N-PH) are as follows;

$$\rho = 3.02 \times 10^{-3} + 2.99 \times 10^{-7} T^{2.0} \quad (\Omega \cdot \text{cm}) \quad \text{for 3N-GL}$$

and

$$\rho = 1.65 \times 10^{-2} \exp(8.7 \times 10^{-3}/k_B T) + 8.00 \times 10^{-8} T^{2.0} \quad (\Omega \cdot \text{cm}) \quad \text{for 3N-PH.}$$

As shown in Fig.3, the fitting is fairly good.

The result of the Hall coefficient gives a key to solve the present problem. We show in Fig.4 the temperature dependence of the Hall coefficient for 3N-G & P-samples. The small resistivity for the H-sample corresponds to the small Hall coefficient, namely the large carrier concentration, as compared to the one for the L-sample. The Hall coefficients for the G-samples are temperature independent, showing a degenerate semiconductor. We can estimate the Fermi temperature, T_F , from the measured Hall coefficient under the assumption that the effective mass is equal to the free electron mass and the carrier is one kind, namely an electron. The T_F -value is ca. 600K for the G-samples. Therefore, the relatively large carrier concentration satisfies the degenerate condition.

The H-sample is usually less stoichiometric as compared to the L-sample. The excess Zr atoms can be intercalated in the van der Waals gap sites. As a result of a charge transfer effect, the H-sample

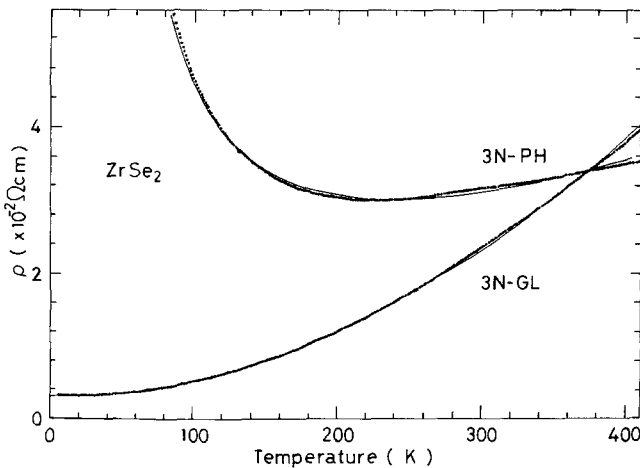


Figure 3. Temperature dependence of electrical resistivity of ZrSe_2 (3N-PH & GL). The solid lines are theoretical ones shown in the text.

possesses a large carrier concentration as compared to the L-sample. Furthermore, the carrier concentration of TiS_2 (10^{20} cm^{-3}), whose energy gap is about a half of the one for ZrSe_2 , is ten times larger than the one for ZrSe_2 (10^{19} cm^{-3}). The carrier concentration, which almost corresponds to the concentration of intercalated Zr or Ti atoms, increases with the decrease of the energy gap. We have thus measured the electrical resistivity and Hall coefficient of $\text{ZrSe}_{2-x}\text{S}_x$ and $\text{Ti}_x\text{Zr}_{1-x}\text{Se}_2$. According to the rigid band model shown in Fig.5, the energy gap becomes larger for $\text{ZrSe}_{2-x}\text{S}_x$ and smaller for $\text{Ti}_x\text{Zr}_{1-x}\text{Se}_2$ with the increase of the x-value. We show in Figs 6 and 7 the temperature dependence of electrical resistivity for $\text{ZrSe}_{2-x}\text{S}_x$ (3N-PH) and $\text{Ti}_x\text{Zr}_{1-x}\text{Se}_2$ (3N-PH), respectively. The activation type- electrical resistivity for $\text{ZrSe}_{2-x}\text{S}_x$ increases with the increase of the x-value. This is because the activation type-carrier concentrations for $x=0, 0.01,$

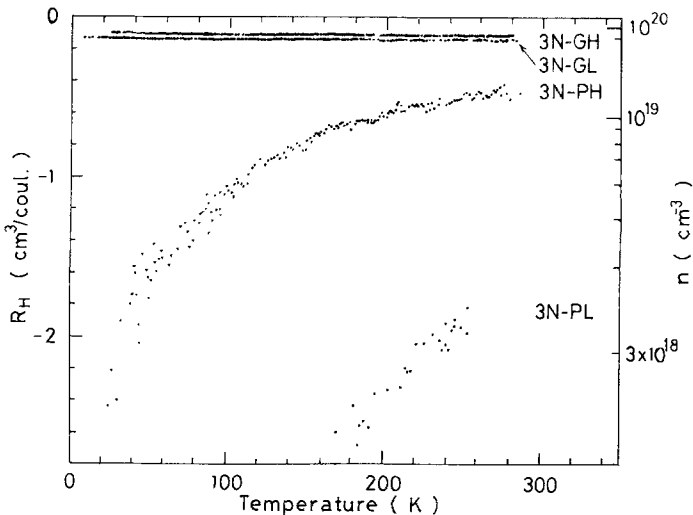


Figure 4. Temperature dependence of Hall coefficient for ZrSe_2 (3N-G & P). The vertical scale in the right hand means a carrier concentration.

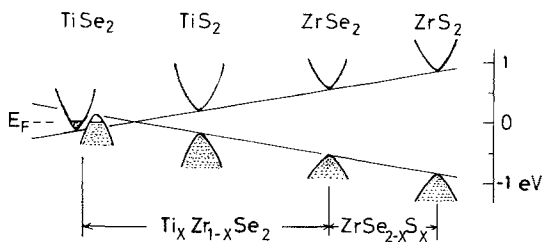


Figure 5. Energy gaps in $\text{ZrSe}_{2-x}\text{S}_x$ and $\text{Ti}_x\text{Zr}_{1-x}\text{Se}_2$.

0.05, 0.1, 0.2 and 0.4 are 1.45×10^{19} , 1.60×10^{19} , 1.30×10^{19} , 1.64×10^{19} , 1.00×10^{19} and 3.90×10^{18} cm^{-3} , respectively, at room temperature. On the other hand, the resistivity for $\text{Ti}_x\text{Zr}_{1-x}\text{Se}_2$ decreases with the increase of the x-value. The carrier concentration for $x=0, 0.2, 0.3$,

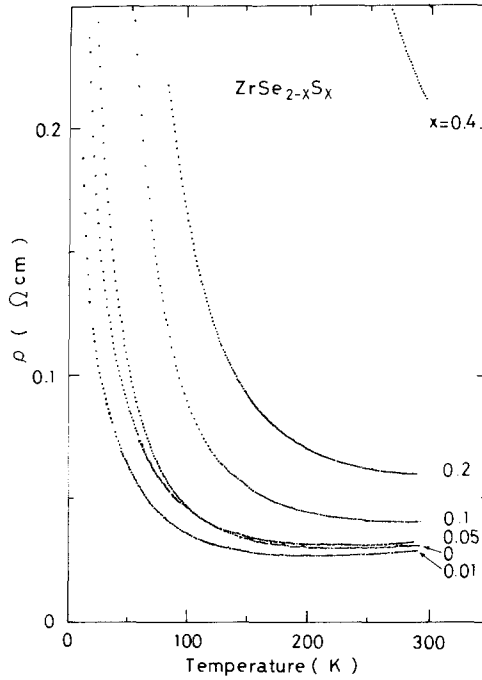


Figure 6. Temperature dependence of electrical resistivity of $\text{ZrSe}_{2-x}\text{S}_x$.

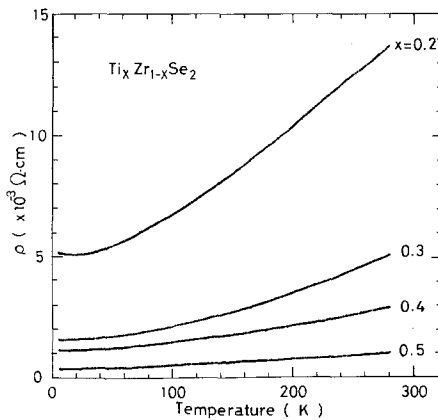


Figure 7. Temperature dependence of electrical resistivity of $\text{Ti}_x\text{Zr}_{1-x}\text{Se}_2$.

0.4 and 0.5 are 1.45×10^{19} , 1.64×10^{20} , 2.08×10^{20} , 6.94×10^{20} and 2.54×10^{21} cm^{-3} , respectively, at room temperature. Furthermore, we remark that the n -value of $\rho = \rho_0 + AT^n$ becomes smaller with the increase of the x -value. Namely, the n -values are 2.0, 1.5, 1.8, 1.6 and 1.5 for $x=0$, 0.2, 0.3, 0.4 and 0.5, respectively. The material of $\text{Ti}_x\text{Zr}_{1-x}\text{Se}_2$ gradually approaches the typical metal showing a $T^{1.0}$ -dependence. It may be given as a conclusion that the carrier concentration is much concerned with the magnitude of the energy gap. The energy gap of ca. 1 eV for ZrSe_2 is a critical value to become a degenerate semiconductor showing the T^n -dependence.

3.2 Lithium intercalation in ZrSe_2

We show in Fig.8 the temperature dependence of the AC-magnetic susceptibility for $\text{Li}_{0.95}\text{ZrSe}_2$. A step like change is the phase transition from the normal state to the superconducting one. We define the superconducting critical temperature, T_c , as 50% of the total susceptibility change, as shown in Fig.8. We have measured the AC-susceptibility of the Li_xZrSe_2 system and have found superconductivity in Li_xZrSe_2 in the composition range of $x=0.45$ to 0.95. The susceptibility change due to the superconducting phase transition is almost the same in the x -value of 0.45 to 0.95, and no change is observed in the x -value of 0.09 to 0.34. We show in Fig.9 the composition x -dependence of superconducting critical temperature. In the figure, the x -dependence of the cell voltage and the lattice parameter are also shown. Here, ZrSe_2 was reported by the present authors to show a high reversibility in the non-aqueous lithium cell, namely, the $\text{Li}/\text{LiClO}_4, \text{THF} + \text{DME}/\text{ZrSe}_2$ couple (13).

Now, no change is detected in the a - and c -values in the composition range of 0 to 0.34 in Li_xZrSe_2 , and above 0.4, a step like change occurs in the c -values. A similar change was observed in the cell voltage.

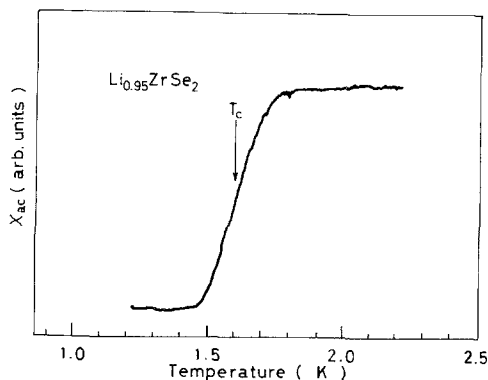


Figure 8. Superconductivity in $\text{Li}_{0.95}\text{ZrSe}_2$.

These results, except for the superconductivity, are the same as the previous report by Berthier et al.(12). They claimed the occurrence of a non-metal to a metal transition at $x=0.4$ by considering the NMR and EPR results. The present result shows that the material Li_xZrSe_2 becomes metallic. In other words, Li_xZrSe_2 in the x -range of 0.45 to 1 is a metal because superconductivity is detected.

A question arises why Li_xZrSe_2 in the x -range of 0.1 to 0.4 is not a metal. A simple calculation shows that the carrier concentrations of 1.3×10^{21} and $6.3 \times 10^{21} \text{ cm}^{-3}$ are estimated for Li_xZrSe_2 ($x=0.1$ and 0.5), respectively, under the assumption that lithium is fully ionized; Li^{1+} . In this respect, a partial electron of the valence electron was reported by Kanzaki et al. from the ESR spectra to be localized at the Li-site(14). Berthier et al. also suggested the influence of the lattice defect due to a random distribution of Li-ions within the van der Waals gap layer,

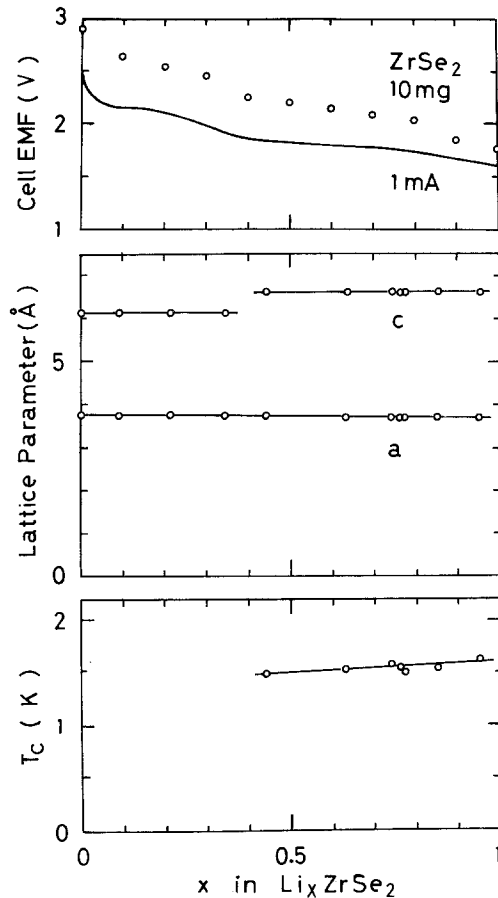


Figure 9. Composition x -dependence of cell voltage, lattice parameter and superconducting critical temperature in Li_xZrSe_2 .

producing Anderson localization. We should like to emphasise the present experimental result that $Ti_{0.5}Zr_{0.5}Se_2$ with a carrier concentration of $2.5 \times 10^{21} \text{ cm}^{-3}$ is not a typical metal, showing a $T^{1.5}$ -dependence in the resistivity. On the other hand, our previous result showed a $T^{1.0}$ -dependence above 100 K for $Li_{0.49}ZrSe_2$ (11). The resistivity of Li_xZrSe_2 ($x < 0.4$) seems not to be a metal due to the incomplete ionization and random distribution of lithium ions, although it might be degenerate. A step like change in the lattice parameter at $x=0.4$ and the non-stoichiometry in $Ti_{1+x}S_2$ reported by Takeuchi and Katsuta(3) suggest another mechanism not discussed here; the lithium ions in Li_xZrSe_2 ($x < 0.4$) may be inserted in the vacancy-sites in the intra-layer instead of the inter-layer of the van der Waals gap sites. This problem is open to future study.

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