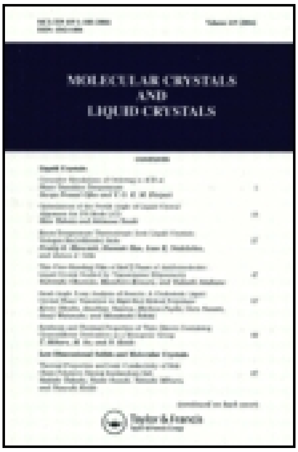

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Electrical Conduction of Halogen-Bridged Metal Complexes Ni 1- x Pd x (chxn) 2 Br 3

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Electrical Conduction of Halogen-Bridged Metal Complexes $Ni_{1-x}Pd_x(chxn)_2Br_3$

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The resistance and thermopower of the quasi-one-dimensional halogen-bridged metal complexes $Ni_{1-x}Pd_x(chxn)_2Br_3$ are studied. Pressure dependence of the resistance indicates the crossover from SDW state to CDW state at x=0.84-0.95. For almost all x region, thermopower is negative. For x<0.5, thermopower is independent of temperature, while it is semiconducting for x>0.6.

Keywords: halogen-bridged metal complex; resistance; pressure; anisotropy; thermopower

INTRODUCTION

Quasi-one-dimensional halogen-bridged metal complexes have attracted attentions because of the interplay among various electronic states and possible switching between them by external perturbations, such as light, pressure, etc. Among these compounds, $Ni(chxn)_2Br_3$ (chxn=1R,2R-cyclohexandiamine) takes the average-valenced Ni^{3+} state due to the strong electron correlation (SDW state) and $Pd(chxn)_2Br_3$ takes the Pd^{2+}-Pd^{4+} mixed-valence state due to the electron-phonon interaction effect (CDW state). Much interest has been paid on the crossover of the two states since mixed crystals of $Ni_{1-x}Pd_x(chxn)_2Br_3$ was successfully synthesized[1]. The infrared and Raman spectra indicate the crossover occurs near x=0.5[1]. On the other hand, ESR measurements show that the spin susceptibility enhances indicating the appearance of the Pd^{3+} states in the intermediate x region and that the crossover occurs above x=0.7[2]. This is supported by theoretical calculation based on the Peierls-Hubbard model[3]. The alternation of the halogen-metal bond in the CDW state has been found by X-ray diffuse scattering for x>0.7[4].

As for the electrical conduction, the activation energy is reported to be 0.08-0.16 eV[5]. This is remarkably smaller than the optical gap of 0.5-1.4 eV[6]. The pressure dependences of the end compounds were measured previously[7]. The pressure dependence of the resistance of $Ni(chxn)_2Br_3$ is weak. While $Pd(chxn)_2Br_3$ shows one order of magnitude decrease of the resistance at 1 GPa. Large pressure dependence of $Pd(chxn)_2Br_3$ implies that the CDW mixed valence state becomes unstable in the pressure. This is consistent with the observation of the IR spectra under pressure in which two N-H vibration lines of $Pd(chxn)_2Br_3$ merges each other at 1.7 GPa like $Ni(chxn)_2Br_3$. In this report, we show the hydrostatic pressure dependence of the resistance for the mixed crystal of $0<x<1$ at room temperature. In order to get insight of the charge carrier, we also measured the temperature dependences of resistivity and thermopower.

EXPERIMENTAL

Single crystals of $Ni_{1-x}Pd_x(chxn)_2Br_3$ were grown with an electrochemical oxidation method[1,5]. Resistance was measured mainly by a four-probe method. The electrodes were made with Pt wire attached with carbon paste. The single crystal has often its long axis within the crystallographic *ac* plane that is perpendicular to the one-dimensional chain. In order to evaluate the resistance along the direction of the one-dimensional chain, we used the Montgomery method[8]. The pressure was applied with a BeCu clamp cell. The thermopower was measured along the long axis within the *ac* plane with a temperature gradient of 2-3 K. MMR Seebeck measurement system with a high impedance card was used with a constantan wire as reference.

RESULTS

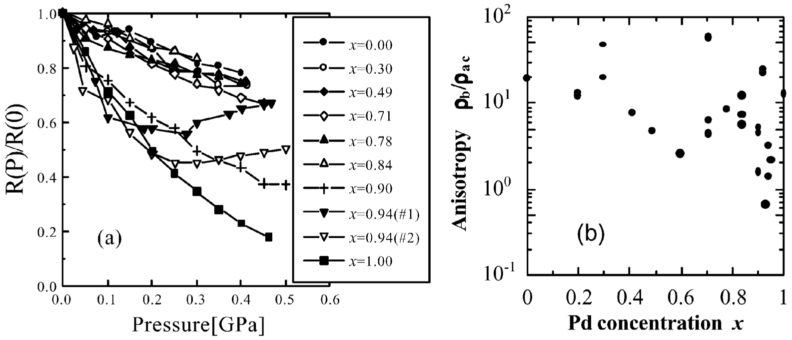

FIGURE 1 Pressure dependence of the *ac*-plane resistance at room temperature (a) and the resistivity anisotropy at ambient pressure (b).

In Figure 1(a), we show the hydrostatic pressure dependence of the resistance along the crystallographic *ac*-plane of the mixed single crystals at room temperature. The resistance value is scaled with that at zero pressure for each x. The resistance decrease under pressure is relatively small for x=0, and is large for x=1, in agreement with the former reports[7]. For x<0.84, the resistance decrease is as small as the $Ni(chxn)_2Br_3$, as shown in Figure 1(a). At x=0.84-0.95, intermediate behaviors are found, indicating that a crossover between SDW and CDW states locates around x=0.84-0.95, in consistent with ESR results.

Temperature dependence of the resistance is semiconducting with activation energy of 0.08-0.16 eV, which agrees with the former report[5]. This value does not change significantly in the pressure up to 0.5 GPa. With Montgomery method, we evaluate the anisotropy of the resistivity. In Figure 1(b), we depict the anisotropy of the resistivity at ambient pressure. In spite of the one-dimensional chain structure, the anisotropy of the resistivity is less than 50. At x=0.8-1, the anisotropy is almost the order of unity. The anisotropy is almost unchanged under pressure or at temperatures of T>120 K. This suggests that the conduction is not limited along the MX chain. Hoppings among the MX chains occur as frequent as those along the chain.

In Figure 2, we show the thermopower of the mixed single crystals at room temperature (a) and at T=200-300 K (b). For x=0 and x=1, the temperature dependence cannot be measured because voltage readout was unstable due to too high resistance. Other than the sample with x=0.94 and x=0.95, the thermopower is, indicating that the major carrier

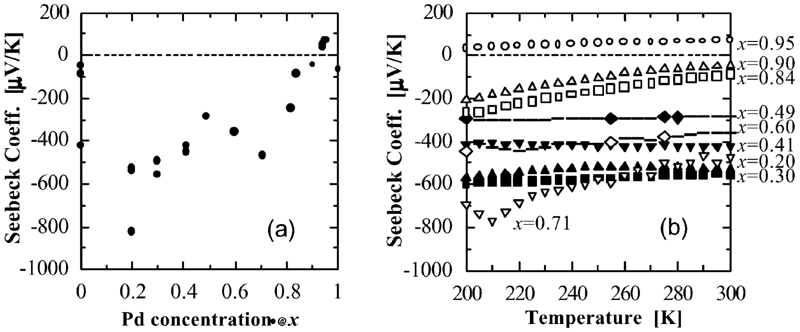

FIGURE 2 Thermopower of the mixed crystals at room temperature (a) and its temperature dependence at 200-300 K (b).

is negatively charged. For the sample with $x<0.5$ (closed symbols in Figure 2(b)), the thermopower is independent of temperature. The absolute value of the Seebeck coefficient $|S|$ differs sample to sample of the same x, however, an overall tendency of $|S|$ increasing with the increase of x is found. For the sample with $x>0.6$, the thermopower shows semiconducting behavior (open symbols in Figure 2(b)). For $x>0.71$, $|S|$ is reproducible among the samples of the same x and reduces with the increase of x.

In Figure 3, we show the activation energies deduced from the resistivity measurements and the themopower measurements for $x>0.6$. The activation energies for the thermopower are smaller than that for the resistivity measurement for $x=0.8$-0.9.

DISCUSSION

In this section we discuss on the possible charge carrier in the present system. For $x<0.5$, the thermopower is independent of temperature. This suggests that the carriers are not thermally activated, but exist inherently in the grown crystal. In the case of hopping conduction of small polarons, temperature-independent thermopower is written as,

$$S=(k_B/e)\ln[N/n], \tag{1}$$

at enough high temperature, where n is the carrier number and N is the

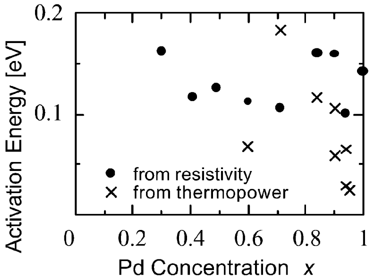

FIGURE 3 The activation energy from resistivity and thermopower measurements.

possible hopping sites in the crystal[9]. Typical value of $|S|=500\mu V/K$ corresponds to $n/N=0.003$. This value is the same order as the Curie spin concentration of the present material found by ESR measurements[2]. In $x<0.5$, the nature of the charge carrier is similar to that in the $Ni(chxn)_2Br_3$, resulting in the same pressure dependence of the resistance as that at $x=0$. In the present case, Ni^{2+} or Pd^{2+} accompanied by halogen displacements forming small polarons are most probable negative carriers. The semiconducting behavior of the resistivity is caused by the temperature-dependent hopping mobility.

For $x>0.6$, thermally activated carriers contribute to the conduction exhibiting semiconductive thermopower. It has been discussed that the thermal activation of neutral solitons along the one-dimensional MX chain contributes to the spin susceptibility[6], and NMR relaxation[10] in the $Pd(chxn)_2Br_3$ with activation energy of the order of 0.1 eV. In the Pd-rich compounds, charged soliton-like excitations related to the Pd^{2+}-Pd^{4+} segments may be activated thermally and contribute to the conduction with activation energy shown in Figure 3. Some of them are negatively charged, but some of them may be positively charged in terms of the background charge neutrality. This causes the sign change of the thermopower at $x=0.95$. Such carriers originate from the MX chains, however, they hop also among the chains resulting in the nearly isotropic transport. Under pressure where halogen-metal bond alternation is suppressed, such segments may dissolve into independent carriers as the case of the Ni-rich compounds.

The threshold concentration appearing the large or intermediate pressure dependence of resistance and thermally activated thermopower is different; the former is $x=0.84$ while the latter is $x=0.6$. It is possible that the collective excitations are pinned by the presence of the Ni^{3+} and do not contribute to the real electrical conduction up to x=0.8.

CONCLUSION

The electrical conduction of the halogen-bridged metal complexes $Ni_{1-x}Pd_x(chxn)_2Br_3$ is studied. From the pressure dependence of the resistance, the crossover between SDW and CDW states is found at x=0.84-0.95. Thermopower results imply that charge carriers are small polarons localized at divalent metal ions for $x<0.5$. For $x>0.6$, thermally activated carriers contribute to the conduction.

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