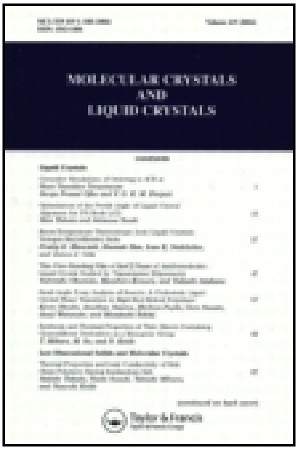

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Electronic Properties of Sodium-Hydride and Potassium-Mercury Ternary Graphite Intercalation Compounds

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ELECTRONIC PROPERTIES OF SODIUM-HYDRIDE AND POTASSIUM-MERCURY TERNARY GRAPHITE INTERCALATION COMPOUNDS

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Abstract

Sodium-hydride and potassium-mercury ternary graphite intercalation compounds are isostructural compounds where a hydrogen/mercury atomic layer is sandwiched between double alkali-metal layers in graphitic galleries. We invesitgated electronic structures of these two compounds by means of c-axis electrical conductivities.

INTRODUCTION

Graphite intercalation compounds (GICs) are metallic compounds formed by the intercalation of guest materials into graphitic galleries through the charge transfer process between host graphite and guest materials. The compound with an intercalated layer in every graphitic gallery is named a stage-1 compound, while one having an intercalated layer in every n graphitic galleries is a stage-n compound. Among the graphite intercalation compounds, alkali metal hydride ternary graphite intercalation compounds, where alkali metal-hydrogen-alkali metal sandwiched triple atomic layers are intercalated in the graphitic galleries, have been interesting from the point of metal-hydrogen systems.[1,2] While transition metal hydrides such as PdH_x are considered to be metal-hydrogen alloys with the delocalized electronic nature of hydrogen, the hydrogen in alkali metal hydride graphite ternaries has more localized electronic structures. Recently, the present authors demonstrated the presence of the novel two-dimensional metallic hydrogen lattice between graphitic layers in potassium hydride graphite intercalation compound (KH-GIC).[1-3] It is interesting to investigate the alkali metal dependence of electronic structures of hydrogen in the alkali metal hydride graphite ternaries, since the ionicity of the compounds increases in the order of Cs<Rb<K<Na.[1] Moreover, hydrogen can be substituted with mercury leading to isostructural ternary compounds consisting of alkali metal-mercury-alkali metal sandwiched intercalates.[4,5]

In this paper, we present c-axis electrical conductivities of sodium hydride and potassium mercury graphite ternary intercalation compounds, in order to clarify the difference in the electronic structures among these ternary intercalation compounds.

EXPERIMENTAL

Sodium hydride graphite ternaries (NaH-GICs) with the stoichiometry $C_{an}NaH$ (a=2.5-4.5) for a stage-n structure were prepared by the direct intercalation of NaH into highly oriented pyrolytic graphite (HOPG) samples.[6] Sodium hydride powder and HOPG sealed in a vacuum glass tube were heat-treated at 400-500 °C for one to several days to obtain stage-2 to -6 NaH-GICs. Preparation of stage-1 and -2 potassium mercury graphite ternaries (KHg-GICs) $C_{4n}KHg$ were carried out by the heat-treatment of HOPG with KHg and KHg_2 in vacuum at 270 °C and 250 °C for 1 to 3 weeks, respectively. C-axis resistivities were measured by means of the DC four probe technique between liquid helium and room temperatures.

RESULTS AND DISCUSSION

C-axis electrical resistivites are shown for stage-1 and -2 KHg-GICs in Fig.1, which behave metallic in the whole temperature range. The resistivity at room temperature is $2.5\times10^{-3}\Omega$ cm in stage-1 compound, which is about one order of magnitude smaller than that in stage-2 compound ($1.9\times10^{-2}\Omega$ cm). In stage-1 compounds, they have a linear temperature dependence down to liquid helium temperature with a superconducting transition (T_c) at 1.5K. The resistivities in stage-2 compound show an weak decrease with a discontinuous change at 230K down to about 70K, and then they decrease steeply below the temperature. In the low temperature range, they show a superconducting transition at 1.9K with an increase just above T_c. The increase in the resistivities is consiered to indicate the presence of the localization effects associated with the structural disorder in the KHg intercalates between graphitic layers.[7] From the results of the c-axis resistivities and the Fermi energies obtained by Timp et al.,[8] we estimate c-axis mean free paths of the conduction carriers ranging about 20Å and several Å for stage-1 and -2 KHg-GICs, respectively, which are about in the similar range to the c-axis repeat distance (I_c=10.24Å) for the former and are smaller than I_c=13.51Å. This finding means that the c-axis conduction processes are in between the band conduction and hopping mechanisms. Figure 2 presents the c-axis resistivities for NaH-GICs with different stages from 3 to 6. The resisitivities behave metallic for all compounds with different stages, even though the magnitudes of the resistivities are relatively high ranging from 0.5 to 1.5Ω cm with a specific stage dependence, where

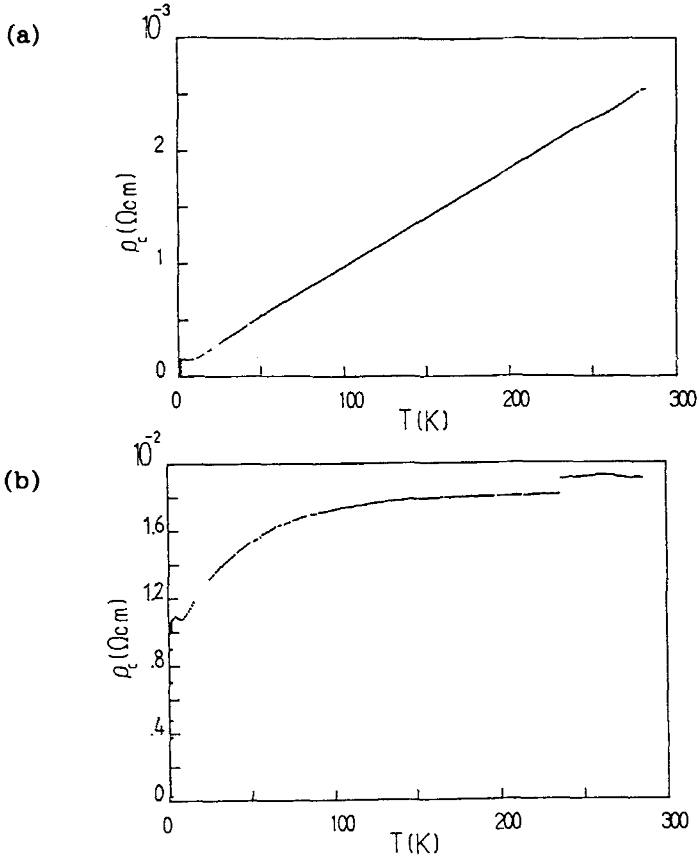

Fig.1. C-axis resistivities ρ_c for (a) stage-1 and (b) stage-2 KHg-GICs.

resistivities are minimum at stage-4 compound. The large resistivity values suggest that the c-axis conductions are ascribed to the hopping process in NaH-GICs. For the compounds with higher stage number than 4, resistivities have increases at low temperatures below about 70K. The anomalous changes in the resistivities shown just below room temperature in stage-(2+3) and -4 compounds might be associated with a degradation process taking place at high temperatures above about 250K.

In the c-axis stacking of graphite intercalation compounds, the sequence of atomic layers consists of the pristine graphitic layer stackings and the composite layer stackings forming double graphitic layers inserting an intercalate layer. Therefore, the c-axis resistivities are phenomenologically expressed in terms of the resistivity contributions from these two stacking components as

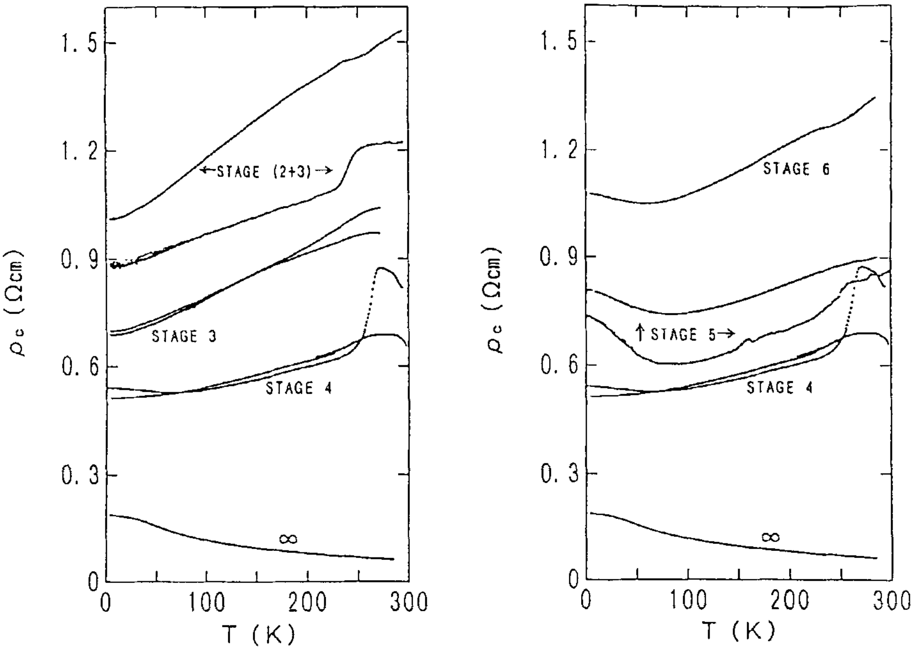

Fig.2. C-axis resistivities ρ_c for stage-(2+3), -3, -4, -5, and -6 NaH-GICs, where ∞ represents those of pristine HOPG.

Table.I. ρ_c(GIG) and ρ_c(GG) at room temperatures for the three ternary GICs.

	ρ_c(GIC) Ωcm	ρ_c(GG) Ωcm	$\frac{\rho_c(\mathrm{GG})}{\rho_c(\mathrm{GIC})}$
KHg-GIC	2.5×10^{-3}	3.6×10^{-2}	14
KH-GIC	0.1 [a]	0.7 [a]	7 [a]
NaH-GIC	~3	< 1	< 0.3

a:ref.9.

shown in the following equation;

$$\rho_c=(1/n)[\rho_c(\mathrm{GIG})+(n-1)\rho_c(\mathrm{GG})],$$

where ρ_c(GG) and ρ_c(GIG) denote the resistivity contributions from the former and the latter stacking constituents, respevtively, and n is a stage number. Using the experimental results of the c-axis resistivities with different stages and the above equation, ρ_c(GG) and ρ_c(GIG) are estimated at room temperature for NaH- and KHg-GICs as summarized in Table I, in comparison with KH-GICs $C_{4n}KH_{0.8}$.[9] The ratio of the two resistivity contributions, ρ_c(GG)/ρ_c(GIG), decreases in the order of KHg-GIC>KH-GIC>NaH-GIC. The ratios are larger than unity for KHg-GIC and KH-GIC ranging 14 to 7, while NaH-GIC has a smaller ratio than unity. Since the stacking constituent of the contribution ρ_c(GIG) includes the intercalate which makes a bridge between adjacent graphitic layers, the larger value of the ratio than unity means the electronic states of the intercalates contribute to the c-axis transport process for KHg-GICs and KH-GICs. The intercalates KHg in KHg-GICs are alloy systems which can afford to act as a donor to graphite, and the experimental results of the Shbunikov-de Haas oscillations gave the charge transfer rate per carbon atom from the intercalate to graphite at f_c=-0.094 and -0.064 for stage-1 and -2 KHg-GICs, respectively.[8] The large value of the ratio and the large charge transfer rate for KHg-GICs suggest that the intercalate carriers strongly contribute to the c-axis transport which ranges between the band and hopping conduction processes, consistent with the recent thermoelectric power experiments.[10] The experimental fact that the value of ρ_c(GG)/ρ_c(GIG) which is smaller than that of KHg-GICs and larger than unity means that the conduction carriers in the KH intercalates weakly contribute to the c-axis transport, and is considered to be correlated to the presence of the two-dimensional weakly metallic hydrogen lattice in the intercalate of KH-GICs.[3] Such a situation in the electronic structure is supposed to be achieved by the charge imbalance between the K^+ and H^- layers with an anomalous stoichiometry $C_{4n}KH_{0.8}$. The finding that the ratio in NaH-GICs is smaller than unity suggests the absence of charge carriers in the NaH intercalates. The stoichiometric ratio between Na and H is 1:1, so that the charge transfer is almost completed in the NaH intercalates which cannot afford to give a large concentration of electrons to the graphitic layers as donors.

SUMMARY

The electronic structures are compared among the isotructural ternary graphite intercalation compounds, NaH-GICs, KH-GICs and KHg-GICs on the basis of the experimental results of c-axis resistivities. The contributions of the intercalates to the c-axis transport decrease in the order of KHg-GICs>KH-GICs>NaH-GICs. The large ratio of ρ_c(GG)/ρ_c(GIG) in KHg-GICs suggests the presence of a large concentration of conduction carriers in the KHg intercalates which electronic state is involved in the conduction band as well as the graphitic π band. The intermediate value of

the ratio in KH-GICs is consistent with the presence of the two-dimensional weakly metallic hydrogen lattice in the KH intercalates. The ratio smaller than unity in NaH-GICs revealed the absence of conduction carriers in the almost purely ionic intercalate consisting of Na^+H^-.

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