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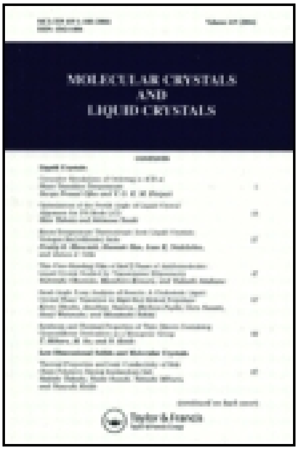

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Electronic Structures of Sodium-Hydride-Graphite Intercalation Compounds

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ELECTRONIC STRUCTURES OF SODIUM-HYDRIDE-GRAPHITE INTERCALATION COMPOUNDS

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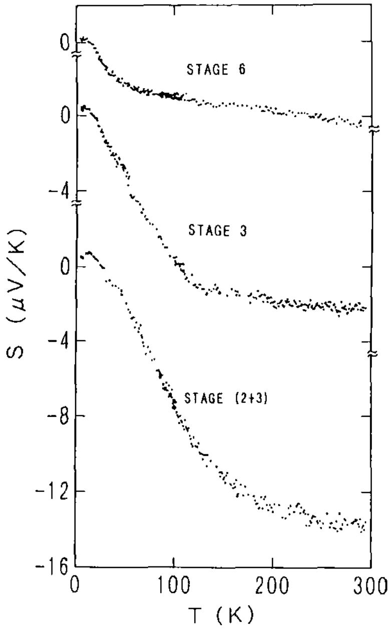
Abstract Sodium-hydride-graphite intercalation compounds have an ionic Na^+-H^--Na^+ triple atomic layer intercalate structure with stoichiometric composition Na/H=1. The analysis of the thermoelectric power shows that the charge transfer from the NaH-intercalate to graphitic sheets is considerably smaller than that in isostructural KH-GICs. This suggest that the ionic NaH intercalate with Na/H=1 makes a complete charge transfer within the intercalate layers, resulting in the presence of small concentration of graphitic π-electron carriers.

INTRODUCTION

Alkali-metal-hydride-graphite ternary intercalation compounds have ionic donor intercalates consisting of alkali-metal-hydrogen-alkali-metal sandwiched triple atomic layers in graphitic galleries. In potassium-hydride-graphite ternaries (KH-GIC) $C_{4n}KH_{0.8}$, the presence of excess potassium in the K^+H^- intercalate works to give carriers to the graphitic π-system, and, consequently, a novel two-dimensional metallic hydrogen layers is formed between metallic graphitic sheets.[1,2] In the alkali-metal-hydride-graphite ternaries, the electronic structure of the intercalate is expected to become more ionic when we go from heavier alkali metal to lighter one. The change in the electronic structure reflects their intercalate structure. In sodium-hydrogen-graphite ternaries (NaH-GIC) $C_{an}NaH$ (a=2.5-4.5, n=stage index), the composition of the intercalate becomes stoichiometric with Na/H=1.[3] This situation in the structure will make the electronic structure of NaH-GICs different from that of KH-GICs. Namely, the charge transfer is completed in the intercalate with the stoichiometric composition, resulting in the well ionic Na^+H^- structure, so that considerably small amount of carriers are expected to be generated in the charge transfer between intercalate and graphite.[4,5] In this work, we investigate thermoelectric power of NaH-GICs in order to clarify the electronic structure.

RESULTS AND DISCUSSION

Figure 1 shows temperature dependence of in-plane thermoelectric power for stage-3 and -6 NaH-GICs (The data for a mixed stage compound with stage-2 and -3 phases are also presented). In the whole temperature range, thermoelectric powers have negative sign except at low temperatures below about 30K, suggesting that the majority carriers are electrons generated in the graphitic π-band through the charge transfer from the NaH intercalate to graphitic planes. The



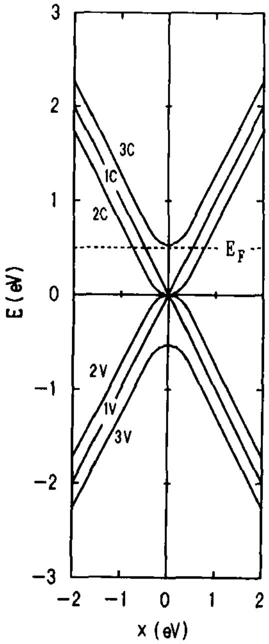


FIGURE 1 (left) Temperature dependence of the in-plane thermoelectric power S for stage--(2+3), -3, and -6 NaH-GICs.

FIGURE 2 (right) Band structure of stage-3 NaH-GIC on the basis of Blinowski-Rigaux model. The units of the abscissa are $x=(3/2)\gamma_0 bk$. 1c, 2c and 3c denote conduction bands while 1v, 2v and 3v are valence bands.

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positive contribution below 30K is associated with the presence of impurity phases with high stage structures. The thermoelectric power increases and tends to saturate as the temperature is elevated for all the compounds. An increase in stage number depresses the magnitudes of thermoelectric power, as shown in Fig.1. This is an opposite trend from that in ordinary GICs. We analyze the results of the thermoelectric powers on the basis of the Blinowski-Rigaux tight binding electronic structure model.[6] Thermoelectric powers are expressed in terms of the electron diffusion term and the phonon-drag term.[7] The electron diffusion term is given in the following equation;

$$S_d = \frac{\pi^2 k_B^2}{3e} \frac{1 + P}{E_F} T, \qquad (1)$$

where E_F and P are the Fermi energy and the exponent in the energy dependence of the relaxation time $\tau(E)=\tau_0 E^P$ associated with the acoustic phonons. A band with a linear energy dispersion has P=-1, while one with a parabolic energy dispersion has P=0. The contribution of the phonon-drag term is expressed as follows;

$$S_p = \frac{\langle C_P R \rangle}{2eN}, \qquad (2)$$

where N is the π-carrier density and C_p denotes the specific heat of the phonon system, which can interact with the π-electrons. R is the momentum transfer ratio through the electron-phonon interaction from the phonon system to carriers and the q-dependence of R is given by

$$R = \frac{aq}{b + aq + fq^3 + BqT^3}, \qquad (3)$$

which includes processes of (1) the electron-phonon scattering (aq), (2) the domain boundary scattering (b), (3) the Rayleigh scattering associated with point defects and also due to the strain-field scattering (fq^3), and (4) the phonon-phonon scattering (BqT^3). The domain boundary scattering is related to the domain size L as $b=v_s/L$, where v_s is the sound velocity of the acoustic phonons. In GICs, the introduction of guest species into graphitic galleries in an intercalation

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reaction generates domain structures (Daumas-Hérold domains[8]), depending on stage indices. The Rayleigh scattering, the electron-phonon scattering and the phonon-phonon scattering all depend on the phonon momentum q, so that the shape and the size of the Fermi surface affect the behavior of R and of the phonon-drag contribution through these scattering processes since the momentum of phonons available to these processes is cut off at $q=2k_F$.

Here, we analyse the in-plane thermoelectric powers for stage-3 compound. According to the Blinowski-Rigaux model,[6] the stage-3 compound has three conduction π-bands (1c, 2c and 3c), to which electrons from the NaH-intercalates are transferred, as shown in Eqs.(4)-(6) and Fig.2;

$$E_1 = |(3/2)\gamma_0 bk|, \tag{4}$$

$$E_2 = \sqrt{\gamma_1^2 + (9/4)\gamma_0^2 b^2 k^2 - \sqrt{\gamma_1^4 + (9/2)\gamma_0^2 \gamma_1^2 b^2 k^2}}, \tag{5}$$

$$E_3 = \sqrt{\gamma_1^2 + (9/4)\gamma_0^2 b^2 k^2 + \sqrt{\gamma_1^4 + (9/2)\gamma_0^2 \gamma_1^2 b^2 k^2}}, \tag{6}$$

where b is the in-plane C-C distance (1.42Å), and the intra- and inter-layer resonance integrals are denoted by γ_0=3.16eV and γ_1=0.39eV, respectively. Band 1c has a linear energy dispersion, while the energy dispersions of bands 2c and 3c are approximately expressed as parabolic function in the low energy region below $|E|$<0.5eV. Figure 2 shows that the bottom of the conduction band 3c is shifted up by $\sqrt{3}\gamma_1$=0.54eV from the bottoms of band 1c and 2c. As shown in later discussion, the Fermi energy E_F is below about 0.5eV, so that only bands 1c and 2c are occupied by the electrons transferred from the NaH-intercalates. Therefore, we take into account band 1c and 2c for the calculation of thermoelectric powers. In this analysis, for boundary scattering, Rayleigh scattering and phonon-phonon scattering, we employ the parameters for pristine graphite; $v_s=2.1\times10^6$cm/s, $f=2.5\times10^{-12}$cm^3/s and $B=2.7\times10^{-5}$cm/s.K.[7]

Using Eqs.(1)-(6), a least square fitting of the measured data is carried out in terms of the following fitting parameters; Fermi wave numbers k_F, effective masses m^* and domain size L. The calculated result is shown in Fig.3 in comparison with the experimental results,

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where a good agreement is achieved with $k_{F,1}=0.7\times10^{7}\mathrm{cm}^{-1}$, $m_1^*=0.08m_e$, $k_{F,2}=1\times10^{7}\mathrm{cm}^{-1}$, $m_2^*=0.12m_e$ for bands 1c and 2c, respectively, P=-0.90 and L=10000Å. The fact that the experimental value of P is between 0 and -1 suggests that both bands 1c and 2c contribute to the electron diffusion term and also band 2c deviates from a purely parabolic curve to some extent. From the estimated k_F, the Fermi energy is derived to be E_F=0.45eV, which is located just below the bottom of the band 3c as shown in Fig.2. The charge transfer rate f_c from the NaH intercalate to graphitic layer (per carbon atom) can also be estimated to be $f_c=3.7\times10^{-3}$ from the Fermi energy and the following equation;

$$E_F = \gamma_0\sqrt{\sqrt{3}\pi f_c}. \tag{7}$$

The very small Fermi energy and charge transfer rate obtained in the thermoelectric powers demonstrate that the NaH-intercalates do not transfer charge to graphitic π-system to the same extent as occurs for the intercalates in ordinary GICs. Moreover, in the system with the small Fermi energy (small Fermi wave number), the term b becomes predominant in the denominator of Eq.(3). An increase in stage indices decreases the size of domains, resulting in an increase in b, according to the Daumas-Hérold model. Therefore, the opposite trend

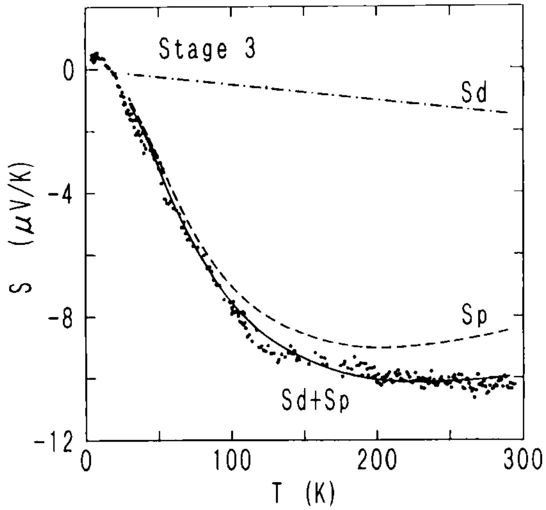

FIGURE 3 Comparison of the experimental results with the calculated thermoelectric power in stage-3 NaH-GIC. S_d, S_p and S_d + S_p are the calculated electronic diffusion term, the phonon-drag term and the total thermoelectric power, respectively.

in the stage dependence of thermoelectric power from that for ordinary GICs also supports the small charge transfer rate in NaH-GICs.

SUMMARY

The electronic structures of NaH-GICs, which have ionic triple atomic layers Na^+-H^--Na^+ in their graphitic galleries, are investigated using thermoelectric power measurements. The thermoelectric power, which is explained in terms of electron diffusion and phonon-drag effects, anomalously decreases as the stage index increases. This behavior is explained by the important role played by the domain scattering mechanism of phonons in the phonon-drag effects, and proves that the Fermi surface of the graphitic π-electrons is small. The results of thermoelectric power measurements give the Fermi energy at E_F=0.45eV for a stage-3 NaH-GIC, which is considerably smaller than that for isostructural compounds KH-GICs. From these experimental results, it is suggested that the ionic NaH intercalate with a stoichiometric composition of Na/H=1 makes a complete charge transfer within the intercalate layer, resulting in the presence of a small concentration of graphitic π-electron carriers and the absence of conduction carriers in the intercalate layers.

ACKNOWLEDGEMENT

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REFERENCES

1. T. Enoki, S. Miyajima, M. Sano, and H. Inokuchi, J. Mater. Res., 5, 435 (1990).
2. T. Enoki, K. Nakazawa, K. Suzuki, S. Miyajima, T. Chiba, Y. Iye, H. Yamamoto, and H. Inokuchi, J. Less-Common Metals, 172-174, 20 (1991).
3. D. Guérard, N. E. Elalem, S. El Hadigui, L. Ansari, P. Lagrange, F. Rousseaux, H. Estrade-Szwarckopf, J. Conard, P. Laginie, J. Less-Common Metals, 131, 173 (1987).
4. T. Enoki, K. Shindo, N. Sakamoto, and K. Suzuki, Mol. Cryst. Liq. Cryst., 216, 253 (1992).
5. T. Enoki, N. Sakamoto, K. Nakazawa, K. Suzuki, K. Sugihara, and K. Kobayashi, Phys. Rev., B47 (1993), in press.
6. J. Blinowski and C. Rigaux, J. Physique, 41, 667 (1980).
7. K. Sugihara, Phys. Rev., B28, 2157 (1983).
8. N. Daumas and A. Hérold, C. R. Acad. Sci. Ser., C268, 373 (1969).

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