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Koji Kobayashi [a], Shinichiro Suzuki [a], Hisashi Oshima [a] & Ko Sugihara [a]

[a] College of Pharmacy, Nihon University, Funabashi, 274-8555, Japan

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Thermoelectric Power of Stage-2 IRr-GIC

KOJI KOBAYASHI, SHINICHIRO SUZUKI, HISASHI OSHIMA
and KO SUGIHARA

College of Pharmacy, Nihon University, Funabashi 274–8555, Japan

c-axis thermoelectric power (TEP) S_c of stage-2 graphite intercalation compound with iodine monobromide (IBr-GIC) was measured below the room temperature, and the calculation was carried out by our theory. The major part of S_c comes from the diffusion TEP $S_{c\text{-}d}$. However, a slight deviation exists between $S_{c\text{-}d}$ and the experimental result S_c and it can be removed in consideration of phonon drag TEP $S_{c\text{-}p}$. This situation was different from the case of graphite intercalation compound with iodine monochrolide (ICl-GICs). Above the room temperature, we attempted to measure the TEP of stage-2 IBr-GIC. It shows the phase transition similar to the case in ICl-GICs.

Keywords: thermoelectric power; calculation; c-axis; diffusion; phonon drag; phase transition

INTRODUCTION

Generally, the thermoelectric power (S) in good conductors are composed of two contributions

$$S = S_d + S_p , \tag{1}$$

where S_d denotes the diffusion term and S_p the phonon drag term.

Figure 1 (A) and (B) illustrate the observed c-axis TEP vs. temperature curves for the stage-2 ICl- and IBr-GIC. c-axis TEP (S_c) of ICl- and IBr-GICs, which are typical acceptor GICs, show a gradual slope change around 80-100K, though below the range S_c is nearly proportional to T. This behavior indicates that the majority of S_c comes from the diffusion term S_d and the slope change is ascribed to the change of energy dependence of $\Gamma^{(ph)}(E) \propto E^{r(ph)}$ with temperature, where $\Gamma^{(ph)}(E)$ is proportional to the scattering rate of carriers due to the in-plane vibrations. However, in the case of the IBr-GIC, a slight deviation exists between the calculation of the diffusion term and the experiment and it can be removed in consideration of phonon drag term. This situation is different from the case of ICl-GIC.[1], [2]

In Fig. 1(B), around 37°C (310 K) for ICl- and around 70°C(343 K) for IBr-GIC,

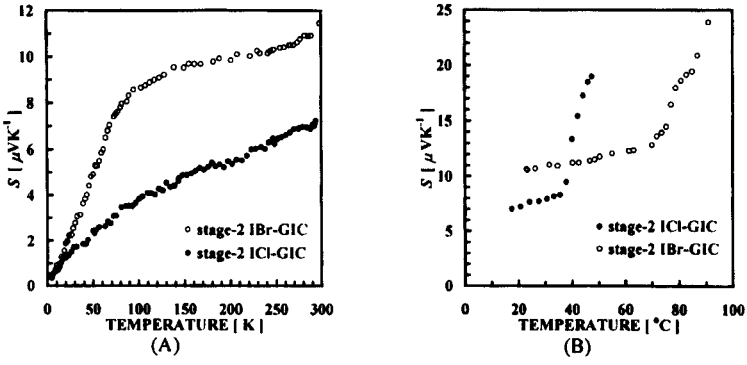

FIGURE 1 Temperature dependence of TEP for stage-2 IBr- and ICl-GIC, where (A) shows the observed results for 4.2-300 K and (B) for 10-90 °C.

TEP rapidly increase, which are attributed to a structural phase transition. These anomalies are related to the thermal expansion observed by Daio et al..[3]

CALCULATION OF DIFFUSION TERM

The Blinowski-Rigaux model[4] provides the following dispersion relation for stage-2 GICs:

$$E_i = \pm\frac{1}{2}\left(\sqrt{\gamma_1^2 + 4p_0^2k_i^2} - \gamma_1\right), (i = 1, 2), \quad p_0 = \sqrt{3}/2\,\gamma_0\, a, (a = 0.246\,\mathrm{nm}), \tag{2}$$

where ± corresponds to holes or electrons, γ_0 and γ_1 denotes the transfer integrals in the basal plane and along the c-direction, respectively. The thermoelectric power S_c is given by

$$S_c = \frac{\chi_c}{T\sigma_c}, \tag{3}$$

where σ_c is the c-axis conductivity and χ_c is related to Peltier coefficient Π_c by $\chi_c = \sigma_c \Pi_c$. χ_c is obtained from the expression for σ_c in ref.5 by replacing $e^2 \rightarrow e\,(E_k - \zeta)$. Thus, we obtain the diffusion term of c-axis TEP $S_{c\text{-}d}$:

$$S_{c\text{-}d} = \pm\frac{\pi}{3e}k_B^2T\frac{\sum_{i=1}^{2}\sum_m \Gamma_i^{(m)}\left(1 + p_i^{(m)}\right)/\Gamma_i^2}{\sum_{i=1}^{2}\left(E_F + \Delta_i\right)/\Gamma_i}, \quad \Delta_i = \begin{cases} \gamma_1/2 : i = 1 \\ -\gamma_1/2 : i = 2 \end{cases}, \tag{4}$$

$$\Gamma_i = \sum_m \Gamma_i^{(m)}, \quad \Gamma_i^{(m)} = \frac{\hbar}{2\tau_i^{(m)}} \propto E^{p_i^{(m)}},$$

where $1/\tau_i^{(m)}$ denotes the m-th scattering rate for i-th band in the basal plane, and $p_i^{(m)}$ takes the following values scattering to various scattering mechanisms.[5] (i) $\Gamma_i^{(ph)}$ and $p_i^{(DH)}$ denote the Daumas-Hérold boundary scattering, $p_i^{(DH)} = 0$, (ii) $\Gamma_i^{(Sh)}$ and $p_i^{(Sh)}$ the short range potential scattering, $p_i^{(Sh)} = -1$, (iii) $\Gamma_i^{(Io)}$ and $p_i^{(Io)}$ the ionized impurity scattering, $p_i^{(Io)} = 1 + 2\,\Delta_i/E_F$, (iv) $\Gamma_i^{(ph)}$ and $p_i^{(ph)}$ the in-plane phonon scattering, $p_i^{(ph)} = -1$ at high temperature and $p_i^{(ph)} = 0$ at low temperature. $\Gamma_i^{(m)}$ except $\Gamma_i^{(ph)}$ are temperature-independent, while $\Gamma_i^{(ph)}$ and $p_i^{(ph)}$ is given by[1]

$$\Gamma_i^{(ph)} = \frac{\hbar D^2}{4\pi v_s}\frac{E_i + \Delta_i}{p_0^2 k_{Fi}}\int_0^{2k_{Fi}} dq \frac{q}{\sqrt{1-(q/2k_{Fi})^2}}\frac{1}{e^{\beta\hbar\omega_q}-1},$$
$$p_i^{(ph)} = -\left[E_i \frac{d\Gamma_i^{(ph)}/dE_i}{\Gamma_i^{(ph)}}\right]_{E_i=E_F}, \quad \beta = \frac{1}{k_B T}, \tag{5}$$

where D is the electron-in-plane phonon coupling constant, v_s the sound velocity, and I_c the repeat distance along the c-direction. Figures 2 show the calculated results for $\Gamma_i^{(ph)}$ and $p_i^{(ph)}$, where following parameters are employed :

$$\gamma_0 = 3.16\ \text{eV}, \quad \gamma_1 = 0.38\ \text{eV}, \quad D = 16\ \text{eV},^{[6]} \quad v_s = 2.1\times10^6\ \text{cm sec}^{-1},^{[7]} \tag{6}$$

and from the galvanomagnetic experiment, we got the carrier density $8.0\times10^{20}\ \text{cm}^{-3}$, and the following values, the Fermi energy $E_F = 0.55$ eV, the Fermi wave vectors $k_{F1} = 1.403\times10^7\ \text{cm}^{-1}$ and $k_{F2} = 0.819\times10^7\ \text{cm}^{-1}$. With increasing temperature the factor $1+p_i^{(ph)}$ in eq.(4) becomes small. This is the reason why the S_c vs T curves exhibits the slope change as is shown in Fig.1(A).

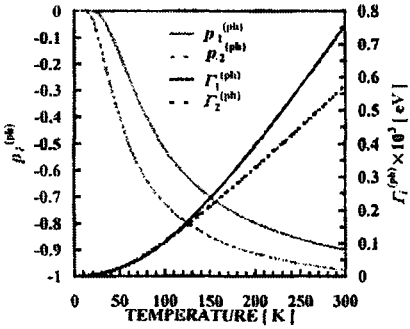

FIGURE 2 Temperature dependence of $\Gamma_i^{(ph)}$ and $p_i^{(ph)}$.

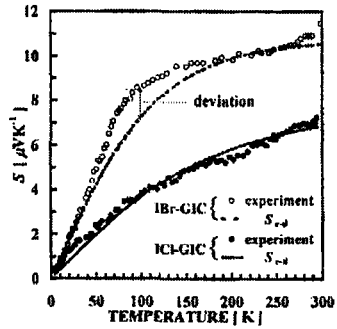

FIGURE 3 Temperature dependence of the calculated diffusion TEP.

Figure 3 shows the comparison between the observed S_c and the calculation, where fitting parameters $\Gamma_i^{(DH)}$, $\Gamma_i^{(Sh)}$ and $\Gamma_i^{(Io)}$ are chosen as follows (in eV unit) :

$$\Gamma_1^{(DH)} = \Gamma_2^{(DH)} \cong 0,\ \Gamma_1^{(Sh)} = \Gamma_2^{(Sh)} \cong 0,\ \Gamma_1^{(Io)} = 5.5\times10^{-4} \text{ and } \Gamma_2^{(Io)} = 2.7\times10^{-4}. \quad (7)$$

The curves $S_{c\text{-}d}$ in Fig.4 can not reproduce the observed TEP about 50-180 K. We assume this deviation stems from phonon drag effect. Therefore, we attempt to calculate the phonon drag TEP in the next section.

CALCULATION OF PHONON DRAG TERM

Before proceeding to the discussion on TEP we consider about the phonon relaxation processes in c-direction, which play an important in the phonon drag effect. The total phonon relaxation rate $1/t$ is represented by[7]

$$\frac{1}{t(q)} = \sum_i \frac{1}{t_i(q)}, \quad (8)$$

where i denotes the several scattering processes. Though the phonon drift velocity along the c-direction is zero in the absence of a temperature gradient, however, it becomes finite through the interaction with the carriers drifting along c-axis, therefore it is given by

$$v_{c\text{-}ph} = R(q)v_{c\text{-}d}, \quad v_{c\text{-}d} = \mu_c F, \quad (9)$$

where $v_{c\text{-}d}$ is the drift velocity of carrier and μ_c denotes the c-axis mobility and F the corresponding electric field. It should be noted that in calculating TEP we take the Peltier scheme. $R(q)$ is given by

$$R(q) = \frac{1/t_c(q)}{1/t(q)} = \frac{t(q)}{t_c(q)} < 1, \quad (10)$$

where $1/t_c(q)$ denotes the relaxation rate of phonon due to carrier-phonon interaction and $1/t(q)$ the total phonon relaxation rate. In most of the GICs the phonon drag term plays an important role in the in-plane thermoelectric power S_a and the R-factor can be described as follows[5], [8], [10] :

$$R(q) = \frac{t(q)}{t_c(q)} = \frac{aq}{b + aq + fq^3 + BqT^3}, \quad (q^2 = q_x^2 + q_y^2), \quad (11)$$

where (i) b is the phonon scattering rate due to crystallite boundary scattering and/or Daumas-Hérold boundary scattering ; (ii) aq denotes the phonon-carrier scattering and its concrete form was explicitly given[5], [8] ; (iii) fq^3 is due to the strain field scattering for 2D-

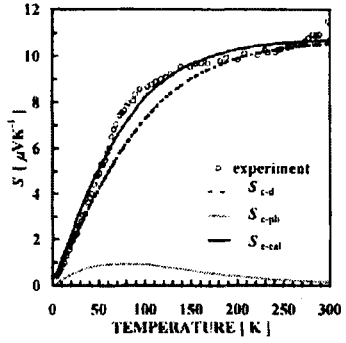

FIGURE 4 Temperature dependence of the calculated diffusion and phonon drag TEP.

in-plane ; (iv) BqT^3 is due to the normal phonon-phonon scattering process for 2D-phonons. In contrast with $R(q)$ for the in-plane phonons mentioned above we have no theory on $R(q)$, where the out-of-plane phonons play a dominant role in the present case. Then, we introduce the following assumption. Since the interaction between carriers and the out-of-plane phonons is weak, the numerator aq is taken as a constant. The remaining two terms corresponding to (iii) and (iv) processes are averaged over T and replaced by a term proportional to T^P ($P > 1$). Therefore, in the case of the c-axis conduction we assume $R(q) \rightarrow \overline{R}(T)$, in the following form:

$$\overline{R}(T) = \left(A + BT^P\right)^{-1}, \quad P > 1. \tag{12}$$

where A, B and P are fitting parameters. After long calculations, c-axis phonon drag TEP of GIC is given by[7], [8], [11]

$$S_{c\text{-ph}} = \frac{\overline{R}\left(k_B T\right)^3}{4\pi^2 n e \hbar \nu_c k_B T^2} \frac{\sum_{i=1}^{2} \frac{E_F + \Delta_i}{\Gamma_i} \left\langle q_{mi}^2 \right\rangle}{\sum_{i=1}^{2} \frac{E_F + \Delta_i}{\Gamma_i}} \int_0^{X_m} dX_m \frac{X^2 e^X}{\left(e^X - 1\right)^2}, \tag{13}$$

$$X_m = \frac{\hbar \nu_c q_m}{k_B T}, \quad q_m = \frac{2\pi}{l_c},$$

where $q_{o1} \cong k_{F1}$, $q_{o2} \cong k_{F2}$. Inserting $\nu_c = 3.5 \times 10^5$ cm sec^{-1} and several values into eq.(13), and adjusting the values of A, B and P, we obtained a best set of these prameters:

$$A = 22, B = 5.7 \times 10^{-6}, P = 3.0, \tag{14}$$

where inserting these values into eq.(12), it satisfies eq.(10).

Figure 4 shows the comparison between the calculation and the observed TEP, where the white circles (O) correspond to the observed values, $S_{c\text{-}d}$ and $S_{c\text{-}ph}$ represent the calculated values for the diffusion and phonon drag contribution, respectively and $S_{c\text{-}cal} = S_{c\text{-}d} + S_{c\text{-}ph}$.

SUMMARY

The c-asis thermoelectric power S_c of stage-2 IBr-GIC exhibites a deviation from the T-linear dependence above 80 K and its slope dS_c/dT decreases gradually with increasing T. By making use of our theory this behavior is explained by introducing the temperature dependence of in-plane phonon scattering parameter $\Gamma_i^{(ph)}$ and $p_i^{(ph)}$, and the Daumass-Hérold boundary scattering parameter $\Gamma_i^{(DH)}$ and the short range scattering $\Gamma_i^{(sh)}$ were negligible small. The deviation between the observed total TEP S_c and calculated one $S_{c\text{-}d}$ is caused by the existence of the phonon drag TEP. We succeeded in calculating the phonon drag TEP $S_{c\text{-}ph}$, and the total calculated TEP $S_{c\text{-}cal} = S_{c\text{-}d} + S_{c\text{-}ph}$ well reproduce the observed one.

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