Thermoelectric power of graphite intercalation compounds with iodine monobromide

Koji Kobayashi^{a),*} and Ko Sugihara^{a),†}

Graphite intercalation compounds (GICs) with interhalogens, iodine monochloride (ICl-GICs) and iodine monobromide (IBr-GICs), are acceptor-type materials. They have a layer structure, and consequently, their thermoelectric power (TEP) along the basal plane (in-plane) is quite different from that in the vertical direction (*c*-axis). The in-plane TEP shows an approximately linear temperature dependence at low temperatures, which is ascribed to the diffusion term, and levels off above 200 K. This behavior stems from a phonon drag effect. However, the *c*-axis TEP shows approximately linear temperature dependence, which is a characteristic feature of the diffusion term. By choosing an appropriate set of parameters, the theory developed by Sugihara is found to give good agreement with the observed TEP results. We discuss the similarities and differences of both in-plane and *c*-axis TEP of IBr-GICs and ICl-GICs.

KEYWORDS : Graphite, Intercalation, Thermoelectric power, In-plane, *c*-axis

1. Introduction

Graphite intercalation compounds (GICs) have the staging structure and inserted intercalate layers periodically arrayed between graphite layers without destroying the stacking structure of graphite. Consequently, physical properties of GICs along the basal plane (in-plane) behave quite differently from those along the vertical direction (*c*-axis).

GICs with interhalogens, iodine monochloride (ICl), and iodine monobromide (IBr), are typical examples of the acceptor GICs. These physical properties have been extensively studied^{1)–8)}. These studies proved that GICs have metallic properties, in contrast with the semi-metallic one of host graphite.

In this work, in-plane TEP of the stage-2 IBr-GICs is measured between 5 to 300 K, and the main purpose of the present work is to examine the similarities and differences of in-plane TEP behavior of different intercalants by comparing this result with in-plane TEP of ICl-GICs²⁾. Observed TEP of this sample shows a linear increase with *T* at low temperature, which is characteristic of the diffusion term. This behavior is similar to the TEP of ICl-GICs, carried out by us²⁾. Above 100 K, the TEP exhibits a saturation behavior which is attributed to the phonon drag effect. This saturation temperature is different from those of ICl-GICs. Three kinds of parameters P_i , f and B are included in the theory developed by Sugihara,^{2),9)} where P_i denotes an

exponent of the relaxation time assumed in the form $\tau_i(E) \propto E_i^{P_i}$, f and B are the parameters related to the phonon relaxation caused by strain field and/or point defects and vacancies, and by phonon-phonon interaction, respectively. These parameters of the stage-2 IBr-GICs are determined in comparison with the observed results.

C-axis TEP of the interhalogen GICs^{1),3)–6)} shows approximately linear temperature dependence, which is a characteristic feature of the diffusion term. This is because in the acceptor GICs, the carrier conduction in *c*-axis direction is due to hopping conduction where carriers jump through conduction paths generated between the graphite layers^{9)–12)}. **Fig. 1** illustrates the mechanism for TEP of GICs.

2. Specimen and Experimental Results

Specimens used in the present study were prepared by synthesis of highly oriented pyrolytic graphite (HOPG) and IBr through the vapor transport method at 105 K. By means of X-ray diffraction measurement and the mass measurement, the repeat distance along the *c*-direction as $I_c = 1.055$ nm, the chemical composition and density were obtained as $C_{17.8}IBr$ and $d = 2.85 \times 10^3$ kg m⁻³, respectively.

Fig. 2 illustrates in-plane (●) and *c*-axis (○) TEP of the stage-2 IBr-GICs vs. temperature (*T*) curves. TEP (*S*) is composed of the two contributions.

$$S = S_d + S_p \quad \dots\dots\dots (1)$$

* Corresponding Author, E-mail: kobayashi.koji@nihon-u.ac.jp

(Received July 18, 2018, Accepted October 17, 2018)

a) School of Pharmacy, Nihon University: 7-7-1 Narashinodai, Funabashi, Chiba 274-8555, Japan

† Deceased August 16, 2016

<http://dx.doi.org/10.7209/tanso.2019.2>

Fig. 1 The mechanism for TEP of GICs.

Fig. 2 The temperature behavior of in-plane (●) and c-axis^(5),6) (○) thermoelectric power of the stage-2 IBr-GICs.

where S_d is the diffusion term, and S_p denotes the phonon drag term. In-plane TEP curves in Fig. 2 shows a gradual slope change around 80 ~ 110 K, though below and above this temperature range, it shows an almost linear temperature dependence. The result shows that at low temperatures (~ 30 K) the contribution to S mainly comes from S_d which shows approximate linear temperature dependence, while at intermediate temperatures (30 ~ 120 K) S_p indicating the phonon drag effect appears in addition to S_d , and at high temperatures (120 K ~) S becomes saturated and in this region S_p turns into a decrease. However, c -axis TEP is 1.1×10^{-5} V/K at 300 K, this is about half the value of in-plane TEP. Its curves shows an approximate linear temperature dependence, which is a characteristic feature of the diffusion term, though its slope changes gradually around 80 ~ 100 K^(5),6).

3. In-plane Thermoelectric Power of IBr-GICs

3.1 Diffusion term of in-plane TEP

In multi-carrier system S is given by

$$S = \frac{\sum_i \sigma_i S_i}{\sum_i \sigma_i}, \quad \sigma_i = \frac{N_i e^2 \tau_i v_{Fi}}{\hbar k_{Fi}}, \quad \dots (2)$$

where for the i -th carrier system, σ_i is the partial electrical conductivity, S_i the partial TEP, τ_i the partial relaxation time, k_{Fi} represents the partial Fermi wave vector, N_i is the carrier density,

$$N_i = \frac{2 \times 2}{(2\pi)^3} \frac{2\pi}{I_c} \pi k_{Fi}^2 = \frac{k_{Fi}^2}{\pi I_c}, \quad \dots (3)$$

and v_{Fi} the Fermi velocity,

$$v_{Fi} = \frac{1}{\hbar} \left(\frac{\partial E_i}{\partial k} \right)_{E_i}, \quad (k^2 = k_x^2 + k_y^2). \quad \dots (4)$$

for the i -th carrier system, the diffusion TEP S_{di} is given by

$$S_{di} = \frac{\pi^2 k_B^2}{3e} T \left[\frac{\partial \log \sigma_i}{\partial E_i} \right]_{E_i}, \quad \dots (5)$$

Using the Blinowski-Rigaux band model⁽¹³⁾ for the stage-2 compound, the dispersion relaxations E_1 and E_2 are obtained by changing the sign of the each hole band,^(13),14)

$$E_1 = \frac{1}{2} \left[(\gamma_1^2 + 9\gamma_0^2 b^2 k^2)^{1/2} - \gamma_1 \right],$$

$$E_2 = \frac{1}{2} \left[(\gamma_1^2 + 9\gamma_0^2 b^2 k^2)^{1/2} + \gamma_1 \right], \quad \dots (6)$$

where γ_0 is the in-plane energy overlap parameter for neighboring carbon atoms, γ_1 is the out-of-plane energy overlap parameter for neighboring carbon atoms and b is the C-C distance (0.142 nm). By assuming the relaxation time τ_i ^(2),14) as

$$\tau_1 = \tau_{01} E_1^{P_1}, \quad \tau_2 = \tau_{02} (E_2 - \gamma_1)^{P_2}, \quad \dots (7)$$

eqs. (2) ~ (4) and (6) lead to

$$S_{d1} = \frac{\pi^2 k_B^2}{3e} T \left[\frac{2E_F + \gamma_1}{E_F^2 + E_F \gamma_1} + \frac{P_1}{E_F} - \frac{2}{2E_F + \gamma_1} \right],$$

$$S_{d2} = \frac{\pi^2 k_B^2}{3e} T \left[\frac{2E_F - \gamma_1}{E_F^2 - E_F \gamma_1} + \frac{P_2}{E_F - \gamma_1} - \frac{2}{2E_F - \gamma_1} \right]. \quad \dots (8)$$

where E_F is the Fermi energy measured from $E_1=0$.

3.2 Phonon drag term of in-plane TEP

For the i -th carrier system, the phonon drag TEP (S_p) is in general represented by the following formula:⁽¹⁵⁾

$$S_{p_i} = \frac{\langle C_{p_i} R \rangle_i}{2eN_i}, \quad (9)$$

where C_{p_i} denotes the specific heat of the phonon system, which can interact with π -electron of GICs. R is the momentum transfer ratio through the electron-phonon interaction from the phonon system to carriers, which is defined by

$$R = \frac{t}{t_c}, \quad (10)$$

where t is the total phonon relaxation time included t_c which is the carrier-phonon relaxation time.

The phonon relaxation process plays an important role in the phonon drag effect. According to the theory developed by Sugihara, the total phonon relaxation rate $1/t$ is presented by⁹⁾

$$\frac{1}{t} = \frac{1}{t_b} + \frac{1}{t_c} + \frac{1}{t_l} + \frac{1}{t_p}, \quad (11)$$

where each component of relaxation rate is due to the following scattering processes.

(i) The relaxation rate ($1/t_b$) due to the scattering caused at crystallite boundary,

$$\frac{1}{t_b} \approx \frac{v_s}{L} \equiv b, \quad (12)$$

where L is the crystallite dimension.

(ii) The relaxation rate ($1/t_c$) due to the scattering caused by the interaction between carrier and in-plane phonon. Ignoring the intraband transition, $1/t_c$ is given by

$$\frac{1}{t_c} = \sum_i \frac{1}{t_{ii}} = \sum_i \frac{\alpha_{ii} \hbar q k_{Fi}}{\pi^2 I_c p_0^2} \equiv a q, \quad (13)$$

where $p_0 = (3/2)\gamma_0 b$, $\alpha_{ii} = \pi D^2/d$, D is the coupling constant between carrier and in-plane phonons and d is the density.

(iii) The relaxation rate ($1/t_l$) due to Rayleigh scattering¹⁶⁾ associated with point defects and vacancies and also due to the strain-field scattering, where both scattering processes give rise to the same q -dependence. For two-dimensional phonons, $1/t_l$ is given by

$$\frac{1}{t_l} = f q^3. \quad (14)$$

(iv) The relaxation rate ($1/t_p$) due to the phonon-phonon scattering process, which for two-dimensional phonons has the functional form^{15),17),18)}:

$$\frac{1}{t_p} = B q T^3. \quad (15)$$

From eqs. (12) ~ (16), eq (11) becomes

$$R = \frac{t}{t_c} = \frac{a q}{b + a q + f q^3 + B q T^3}. \quad (16)$$

In eq. (10), $\langle C_{p_i} R \rangle_i$ takes the form^{2),9)}:

$$\langle C_{p_i} R \rangle_i = \frac{1}{2\pi I_c} \int_0^{k_{Fi}} dq q \frac{(\hbar \omega_q)^2}{k_B T^2} N_q (N_q + 1) R(q), \quad (17)$$

where N_q is the equilibrium in-plane phonon distribution. Rewriting eq. (17) introducing $\hbar v_s q T = k_B T$ and $x = \hbar v_s q / k_B T$, we have

$$\langle C_{p_i} R \rangle_i = \frac{k_B q_T^2}{2\pi I_c} \int_0^{x_{\max,i}} dx x^3 \frac{e^x}{(e^x - 1)^2} R(x),$$

$$x_{\max,i} = \frac{2\hbar v_s k_{Fi}}{k_B T}. \quad (18)$$

From eqs. (3), (4) and (18) the phonon drag TEP for the stage-2 IBR-GICs becomes

$$S_{p_i} = \frac{k_B^3}{4e k_{Fi}^2 \hbar^2 v_s^2} T^2 \int_0^{x_{\max,i}} dx x^3 \frac{e^x}{(e^x - 1)^2} R(x),$$

$$x_{\max,i} = \frac{2\hbar v_s k_{Fi}}{k_B T} \quad (i=1, 2). \quad (19)$$

3.3 Comparison between calculated results and observed in-plane TEP

In stage-2 GICs eq. (2) becomes

$$S = \frac{\sigma_1 S_1 + \sigma_2 S_2}{\sigma_1 + \sigma_2}. \quad (20)$$

It is needed to estimate the ratio σ_1/σ_2 . Equations (2), (3) and (4) lead to

$$\frac{\sigma_1}{\sigma_2} = \frac{k_{F_1}^2 k_{F_1}^R k_{F_1} (2E_F - \gamma_1) k_{F_2}}{k_{F_2}^2 k_{F_2}^R k_{F_2} (2E_F - \gamma_1) k_{F_1}} = \frac{k_{F_1}^{R+2} (2E_F - \gamma_1)}{k_{F_2}^{R+2} (2E_F - \gamma_1)}. \quad (21)$$

At low temperatures we take the same assumption $P_1 = P_2 = 0$ employed by Issi *et al.*^{2),14)} At high temperature range, we have no information on the ratio σ_1/σ_2 , where $P_1 \neq 0$ and $P_2 \neq 0$ are expected since the phonon scattering participates in the scattering process. Thus, we have

$$\frac{\sigma_1}{\sigma_2} = \frac{k_{F_1}^{R+2} (2E_F - \gamma_1)}{k_{F_2}^{R+2} (2E_F - \gamma_1)} = 1.42. \quad (22)$$

For simplicity, we use the assumption that eq. (22) holds at high temperatures. Combining eq. (22) with (21) we have

$$\frac{k_{F_1}^R}{k_{F_2}^R} = 1 \quad \text{and} \quad \frac{P_1}{P_2} = 0.97. \quad (23)$$

In calculating TEP, the following parameters are taken from the graphite:

$$\gamma_0 = 3.16 \text{ eV}, \quad \gamma_1 = 0.38 \text{ eV}, \quad D = 16 \text{ eV},$$

$$v_s = 2.1 \times 10^4 \text{ ms}^{-1}, \quad L = 10^{-6} \text{ m}. \quad (24)$$

From the galvanomagnetic experiment by our unpublished work and Barati *et al.*⁸⁾, following parameters are obtained:

$$E_F = 0.55 \text{ eV}, \quad k_{F_1} = 1.4 \times 10^9 \text{ m}^{-1},$$

$$k_{F_2} = 0.82 \times 10^9 \text{ m}^{-1}. \quad (25)$$

Inserting these values into eqs. (12) and (13), we obtain following parameters for the relaxation rate ($1/t_b$) and ($1/t_c$):

$$b = 2.1 \times 10^{10} \text{ s}^{-1}, \quad a = 1.4 \times 10^{11} \text{ m}^3 \text{ s}^{-1}. \quad (26)$$

Using these values for eqs. (8), (16) and (19), and adjusting values P_i , f and B , we obtain a best set of these four parameters.

Fig. 3 Comparison of the theoretical calculation (solid line) and observed TEP (●) for the stage-2 IBr-GICs. The dashed line (S_p) and the broken line (S_d) represent the calculated values for the phonon drag and the diffusion TEP.

$$P_1 = -0.18, \quad P_2 = -0.19, \\ f = 2.4 \times 10^{-18} \text{ m}^3 \text{ s}^{-1}, \quad B = 6.0 \times 10^{-6} \text{ ms}^{-1} \text{ K}^{-3}. \quad (27)$$

Fig. 3 shows the comparison between the observed TEP and the calculated results for the stage-2 IBr-GICs, where the black circles (●) correspond to the observed values, S_d and S_p represent the calculated values for the diffusion and phonon drag contribution, respectively. And the total calculated TEP is $S = S_d + S_p$.

Assuming $P_1 = P_2 = 0$ and substituting eqs. (24), (25) into eq. (8) and applying eqs. (20), (22), the total diffusion TEP S_d is $2.1 \times 10^{-5} \text{ VK}^{-1}$ at 300 K, which exceeds experimental results at room temperature range (**Figs. 2, 3**). However, by employing the values of P_1 and P_2 in (27) calculated TEP agrees well with experiments (**Fig. 3**). The total phonon relaxation rate obtained from these values of parameters f and B is equivalent to those obtained by Issi *et al.*¹⁹⁾ from the thermal conductivity of a similar acceptor type compound, the stage-2 FeCl_3 -GICs. Therefore, the values of (27) are considered appropriate.

4. C-axis TEP of IBr-GICs

C-axis thermoelectric power (S_c) is given by

$$S_c = \frac{\chi_c}{T\sigma_c}, \quad (28)$$

where σ_c is the c -axis conductivity^{4)-6),20)}, which results from hopping conduction along the conduction path present in c -axis direction^{9)-12),20)}. 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 by replacing $e^2 \rightarrow e(E_k - \zeta)$ ²⁰⁾. Using Eq. (6), the diffusion term of c -axis TEP S_{c-d} is following expression,

Fig. 4 Temperature dependence of $\Gamma_i^{(\text{ph})}$ and $p_i^{(\text{ph})}$ for the stage-2 IBr-GICs⁶⁾. Reprinted with permission from ref. 6. Copyright 2000 Taylor & Francis and Copyright Clearance Center.

$$S_{c-d} = \pm \frac{\pi}{3e} k_B^2 T \frac{\sum_{i=1}^2 \sum_m \Gamma_i^{(m)} (1 + p_i^{(m)}) / \Gamma_i^2}{\sum_{i=1}^2 (E_F + \Delta_i) / \Gamma_i}, \quad (29)$$

$$\Delta_i = \begin{cases} \gamma_1/2 : i=1 \\ -\gamma_1/2 : i=2 \end{cases}, \quad \Gamma_i = \sum_m \Gamma_i^{(m)},$$

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

where $1/\tau_i^{(m)}$ denotes the m -th scattering rate i -th band in basal plane, and $p_i^{(m)}$ takes the following values scattering to various scattering mechanisms²⁰⁾. (i) $\Gamma_i^{(\text{DH})}$ and $p_i^{(\text{DH})}$ denote the Daumas-Hérolde boundary scattering, $p_i^{(\text{DH})} = 0$ and $\Gamma_1^{(\text{DH})} \approx \Gamma_2^{(\text{DH})}$, (ii) $\Gamma_i^{(\text{Sh})}$ and $p_i^{(\text{Sh})}$ the short range potential scattering, $p_i^{(\text{Sh})} = -1$, (iii) $\Gamma_i^{(\text{Io})}$ and $p_i^{(\text{Io})}$ the ionized impurity scattering, $p_i^{(\text{Io})} = 1 + 2\Delta/E_F$, (iv) $\Gamma_i^{(\text{ph})}$ and $p_i^{(\text{ph})}$ the in-plane phonon scattering, $p_i^{(\text{ph})} = -1$ at high temperature and $p_i^{(\text{ph})} = 0$ at low temperature. $\Gamma_i^{(m)}$ except $\Gamma_i^{(\text{ph})}$ are temperature-independence, while $\Gamma_i^{(\text{ph})}$ and $p_i^{(\text{ph})}$ is given by³⁾

$$\Gamma_i^{(\text{ph})} = \frac{\hbar D^2}{4\pi v_s} \frac{E_i + \Delta_i}{p_0^2 k_F} \int_0^{2k_F} dq \frac{q}{\sqrt{1 - (q/2k_F)^2}} \frac{1}{e^{\beta\hbar\omega_q} - 1}, \quad (30)$$

$$p_i^{(\text{ph})} = - \left[E_i \frac{d\Gamma_i^{(\text{ph})}/dE_i}{\Gamma_i^{(\text{ph})}} \right]_{E_i=E_F}, \quad \beta = \frac{1}{k_B T}.$$

Fig. 4 shows the calculated results for $\Gamma_i^{(\text{ph})}$ and $p_i^{(\text{ph})}$, where values of eqs. (24) and (25) are employed. With increasing temperature, the factor $1 + p_i^{(\text{ph})}$ in eq. (29) becomes small. This is reason why the S_c vs. T curves exhibits the slope change as is shown in **Fig. 2**.

Fig. 5 shows the comparison between the observed S_c and the calculated results S_{c-d} for the stage-2 IBr^{-5),6)} and ICl⁻⁴⁾GICs, where fitting parameters $\Gamma_i^{(\text{DH})}$, $\Gamma_i^{(\text{Sh})}$ and $\Gamma_i^{(\text{Io})}$ are chosen as follows, respectively (in eV unit):

Fig. 5 Comparison of the observed c -axis TEP and the theoretical calculated c -axis diffusion TEP for the stage-2 IBR-GICs and ICI-GICs⁶⁾. The deviation shows the difference between the observed c -axis TEP and the calculated diffusion one for stage-2 IBR-GICs. Reprinted with permission from ref. 6. Copyright 2000 Taylor & Francis and Copyright Clearance Center.

$$\left. \begin{aligned} \Gamma_1^{(\text{DH})} = \Gamma_2^{(\text{DH})} \cong 0, \quad \Gamma_1^{(\text{Sh})} = \Gamma_2^{(\text{Sh})} \cong 0, \\ \Gamma_1^{(\text{lo})} = 5.5 \times 10^{-4}, \quad \Gamma_2^{(\text{lo})} = 2.7 \times 10^{-4}, \end{aligned} \right\} \text{(for IBR-GICs), }^{5,6)} \\ \left. \begin{aligned} \Gamma_1^{(\text{DH})} = \Gamma_2^{(\text{DH})} = 4.67 \times 10^{-4}, \\ \Gamma_1^{(\text{Sh})} = 3.26 \times 10^{-4}, \\ \Gamma_2^{(\text{Sh})} = 1.97 \times 10^{-4}, \quad \Gamma_1^{(\text{lo})} = 9.20 \times 10^{-4}, \\ \Gamma_2^{(\text{lo})} = 5.56 \times 10^{-4} \end{aligned} \right\} \text{(for ICI-GICs). }^{4)} \quad (31)$$

In **Fig. 5**, though the curves S_{c-d} for the stage-2 ICI-GICs reproduce the observed TEP, however, the curves S_{c-d} for the stage-2 IBR-GICs can not reproduce the observed TEP about 50-180 K. We assume this deviation between S_{c-d} and S_c , stems from the phonon drag effect. Therefore, we attempt to calculate the phonon drag TEP as follows.

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 is represented by eq. (11) similarly to the in-plane TEP. 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 carriers drifting along the c -axis, therefore it is given by

$$v_{c-ph} = R(q)v_{c-d}, \quad v_{c-d} = \mu_c F, \quad \dots (32)$$

where v_{c-d} is the drift velocity of carrier and μ_c denotes the c -axis mobility and F the corresponding electric field. In contrast with $R(q)$ for the in-plane phonons mentioned the previous section, 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 ($1/t_c$) is taken as a constant. The remaining

Fig. 6 Comparison of the theoretical calculation (solid line) and the observed c -axis TEP ($\circ$) for the stage-2 IBR-GICs. The dashed line (S_{c-d}) and the shadow line (S_{c-ph}) represent the calculated values for the diffusion and the phonon drag TEP⁵⁾. Reprinted with permission from ref. 5. Copyright 1999 The Physical Society of Japan.

two terms corresponding to $1/t_l$ and $1/t_p$ processes are averaged over T and replaced by a term proportional to T^P ($P > 1$). Therefore, in the case of c -axis conduction, we assume $R(q) \rightarrow R_c(T)$, in the following form:

$$R_c(T) = (A + BT^P)^{-1}, \quad P > 1, \quad \dots (33)$$

where A , B and P are fitting parameters. After long calculations, c -axis phonon drag TEP of GICs is given by

$$S_{c-ph} = \frac{R_c(k_B T)^3}{4\pi^2 n e \hbar v_c k_B T^2} \frac{\sum_{i=1}^2 \frac{E_F + A_i}{\Gamma_i} \langle q_{ai}^2 \rangle}{\sum_{i=1}^2 \frac{E_F + A_i}{\Gamma_i}} \int_0^{X_m} dX_m \frac{X^2 e^X}{(e^X - 1)^2}, \quad \dots (34)$$

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

where $q_{a1} \cong k_{F1}$, $q_{a2} \cong k_{F2}$. Inserting $v_c = 3.5 \times 10^3 \text{ m s}^{-1}$ and several values into eq. (34), and adjusting the values of A , B and P , we obtained a best set of these parameters:

$$A = 22, \quad B = 5.7 \times 10^{-6}, \quad P = 3.0, \quad \dots (35)$$

where inserting these values into eq. (33), it satisfies $R_c < 1$.

Fig. 6 shows the comparison between the observed and the calculation TEP, where the white circles ($\circ$) correspond to the observed values, S_{c-d} and S_{c-ph} represent the calculated values for the diffusion and the phonon drag TEP, respectively. And the total calculated c -axis TEP is $S_{c-cal} = S_{c-d} + S_{c-ph}$.

5. Discussion

Analytical results for TEP of stage-2 IBR-GICs shown in **Fig. 3** are

Fig. 7 Comparison of the theoretical calculation (solid line) and the observed TEP (●) for the stage-2 ICl-GICs. The dashed line (S_p) and the broken line (S_d) represent the calculated values for the phonon drag and the diffusion TEP²⁾.

Fig. 8 The temperature behavior of in-plane (●) and c -axis^{5),6)} (○) thermoelectric power of the stage-2 IBr-GICs, and in-plane²⁾ (◆) and c -axis⁴⁾ (◇) thermoelectric power of the stage-2 ICl-GICs.

compared with those of stage-2 ICl-GICs shown in Fig. 7²⁾. Carrier density of these specimens obtained from Hall effect measurements is almost identical to be about $8 \times 10^{26} \text{ m}^{-3}$ ^{7,8)} but S_d of IBr-GICs is considerably larger than that of ICl-GICs. This difference is derived from the difference in P_i values of Eq. (8) for these specimens and also considered to be due to the difference in E_F values: 0.55 eV for IBr-GICs and 0.77 eV for ICl-GICs.

Since boundary scattering ($1/t_b$) is dominant below 50 K, S_p is almost the same for these specimens at this temperature region. With increasing temperature, S_p of IBr-GICs increases and shows a clear peak at about 100 K. On the other hand, S_p of ICl-GICs decreases

gradually without showing a clear peak. This is because temperature sensitive Rayleigh scattering ($1/t_l$) as well as phono-phonon scattering ($1/t_p$) becomes more active in IBr-GICs than in ICl-GICs.

Fig. 8 shows experimental results of in-plane and c -axis TEP for both IBr-GICs and ICl-GICs. In-plane TEP is similar to each other for these specimens but c -axis TEP is significantly larger for IBr-GICs than for ICl-GICs. c -axis TEP results from hopping conduction along the conduction path present in c -axis direction⁹⁻¹²⁾ and the difference in S_d shown in Fig. 3 and Fig. 7 leads to this significant difference of c -axis TEP. The theory developed by Sugihara^{2),9)} is found to explain well TEP of interhalogen GICs.

6. Summary

The theory developed by Sugihara^{2),9)} explains well TEP of IBr-GICs by adjusting four parameters available in the theory. Below 170 K, $S_p > S_d$ for in-plane TEP, indicating that phonon drag carrier transport is more dominant than diffusion at this temperature region.

S_p increases in proportional to T^2 in accordance with eq. (19) at low temperatures because boundary scattering ($1/t_b$) is dominant and R in eq. (16) is temperature insensitive. With increasing temperature, other scattering processes become active and S_p increases linearly with temperature. S_p shows a clear peak against temperature at about 100 K and decreases above 100 K. Because of it is mainly increase of phonon-phonon scattering ($1/t_p$) that leads to this decrease of S_p above 100 K.

c -axis TEP of stage-2 IBr-GICs exhibits a deviation from T -linear dependence above 80 K and its slope decrease gradually with increasing T . The theory of c -axis TEP for GICs developed by Sugihara explains well the observed TEP of stage-2 IBr-GICs by adjusting parameters^{5),6)}.

Acknowledgements

The authors are grateful to Dr. A. Moore of Union Carbide Corporation for kindly supplying HOPG specimens, and also to Professor Takuro Tsuzuku and Professor Kiyoshi Kawamura for their interest and stimulating discussion.

We pray for the soul of the late Professor Ko Sugihara, one of the authors.

References

- 1) T. Enoki, Graphite Intercalation Compounds and Applications (T. Enoki, M. Suzuki and M. Endo, eds.) (2003) p.190, OXFORD, New York.
- 2) K. Kobayashi, H. Oshima, K. Sugihara and T. Tsuzuku, *J. Phys. Soc. Jpn.* **61** (1992) 596-601.
- 3) K. Kobayashi, K. Sugihara, H. Oshima and T. Tsuzuku, *J. Phys. Soc. Jpn.* **63** (1994) 4451-4455.
- 4) K. Kobayashi, K. Sugihara and H. Oshima, *J. Phys. Chem. Solids* **57** (1996) 931-933.
- 5) K. Kobayashi, S. Suzuki, H. Oshima and K. Sugihara, *J. Phys. Soc. Jpn.*

- 68 (1999) 2006-2009.
- 6) K. Kobayashi, S. Suzuki, H. Oshima and K. Sugihara, *Mol. Cryst. Liq. Cryst.* **340** (2000) 143-148.
- 7) Y. Ohta, K. Kawamura and T. Tsuzuku, *J. Phys. Soc. Jpn.* **57** (1988) 196-204.
- 8) M. Barati, P. K. Ummat and W. R. Datars, *J. Phys. Condens. Matter* **11** (1999) 5569-5576.
- 9) K. Sugihara, *Phys. Rev. B Condens. Matter* **28** (1983) 2157-2165.
- 10) K. Sugihara, *Phys. Rev. B Condens. Matter* **29** (1984) 5872-5877.
- 11) S. Shimamura, *Synth. Met.* **12** (1985) 365-370.
- 12) K. Sugihara, *TANSO*. **1988** [No.134] 198-210 [in Japanese].
- 13) J. Blinowski, N. Hy Hau, C. Rigaux, J.P. Vieren, R. Le Tollec, G. Furdin, A. Hérold and J. Melin, *J. Phys.* **41** (1980) 47-58.
- 14) L. Piraux, M. Kinany-Alaoui, J.-P. Issi, A. Perignon, P. Pernot and R. Vangelisti, *Phys. Rev. B Condens. Matter* **38** (1988) 4329-4332.
- 15) T. Tsuzuku and K. Sugihara, Chemistry and Physics of Carbon, Vol. **12** (P. L. Walker and P. A. Thrower, eds.) (1975) p. 109, Dekker, New York.
- 16) P. Carruthers, *Rev. Mod. Phys.* **33** (1961) 92-138.
- 17) K. Sugihara, *J. Phys. Soc. Jpn.* **29** (1970) 1465-1470.
- 18) K. Sugihara, T. Takezawa, T. Tsuzuku, Y. Hishiyama and A. Ono, *J. Phys. Chem. Solids* **33** (1972) 1475-1486.
- 19) J.-P. Issi, J. Heremans and M. S. Dresselhaus, *Phys. Rev. B Condens. Matter* **27** (1983) 1333-1347.
- 20) K. Sugihara, *J. Phys. Soc. Jpn.* **62** (1993) 624-633.