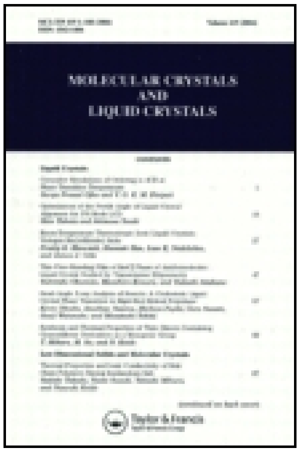

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The Contribution of Intercalate to the Electronic Structure and Transport Properties for Potassium-Oxygen-Graphite Intercalation Compounds

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The ultraviolet photoelectron spectra measurements for 1st and 2nd stage potassium-oxygen-graphite intercalation compounds (KO_x-GICs) were carried out for the electronic structure around the Fermi level E_F. The dependence of the photoelectron spectra upon the incident photon energy suggests the presence of the oxygen electronic states around E_F. The temperature dependence of the thermoelectric power (TEP) of KO_x-GICs reveals the positive TEP below around 150 K for 1st stage compound, which suggests the contribution of hole carriers to the transport properties in contrast to the expectation of negative TEP endorsed by the donor type character of KO_x-GICs. These experimental findings prove the contribution of intercalate to the electronic structure and transport properties.

Keywords: graphite intercalation compounds; photoelectron spectra; thermoelectric power; electronic structure

INTRODUCTION

Potassium-oxygen-graphite intercalation compounds ($C_{4n}KO_x$; stage number n=1, 2, $x \sim 2$) are expected to give a unique coexistence system of the oxygen magnetic moments and the graphitic conduction electrons due to the similarity of chemical composition of intercalate to that of pristine KO_2 having the magnetic moment S =

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1/2.[1] However, the temperature dependence of magnetic susceptibilities reveals the absence of localized magnetic moments.[2] At present the absence of magnetic moments is considered to arise from the delocalized electronic nature of intercalate oxygen, which is suggested from the self-consistent band calculation[3] and the considerations for the electronic structure based on the charge transfer per carbon atom.[2] It, therefore, is important to clarify the contribution of intercalate to the transport properties and electronic structure around the Fermi level. In this paper we present the results of the ultraviolet photoelectron spectra, and the thermoelectric power for 1st and 2nd stage potassium-oxygen-graphite intercalation compounds (KO_x-GICs).

RESULTS AND DISCUSSION

Figure 1 shows the dependence of the photoelectron spectra on the incident photon energy for 1st stage compound. The photoelectron spectra for 2nd stage compounds possess the similar dependence on the incident photon energy to those for 1st stage compound.[4] The relative intensities of UPS spectra above 1 eV to the intensity at the deeper binding energy decrease with decreasing the photon energy except the incident photon energy 34.8 eV for 1st and 2nd stage compounds. This dependence of UPS spectra on the incident photon energy suggests the existence of the atomic orbitals with the different dependence of the photoionization cross-section on the photon energy around E_F. Taking into account the dependence of the photoionization cross-section for carbon 2*p* orbital σ_{C2p} and oxygen 2*p* orbital σ_{O2p} on the incident photon energy, both of which decrease with increasing the photon energy and σ_{C2p} rapidly decreases than σ_{O2p}, the dependence of UPS spectra on the incident photon energy reveals the presence of oxygen states around the Fermi level. Thus, the electronic structure of KO_x-GICs around the Fermi level is clarified to consist of graphitic π bands and oxygen 2*p* bands as schematically shown in Figure 2.

The temperature dependence of the thermoelectric power (TEP) for 1st and 2nd stage compounds is shown in Figure 3(a) and 3(b), respectively. The TEP for 1st stage compound possesses the maximum around 75 K, and then, undergoes the change in the sign of TEP around 150 K, where the positive TEP turns into negative, while the TEP for 2nd stage compound possesses the negative TEP in the whole temperature range. The positive TEP below 150 K for 1st stage compound strongly suggests the contribution of hole carriers to the transport phenomenon. Meanwhile, the apparent hole carrier contributions to the in-plane transport are also observed in the Hall effect measurement, which gives the positive Hall coefficients R_H for both 1st and 2nd stage compounds over the whole investigated range from 1.7 K to room temperature.[4] Taking into account the oxygen states around E_F and the donor-type nature of KO_xGICs, the hole carriers

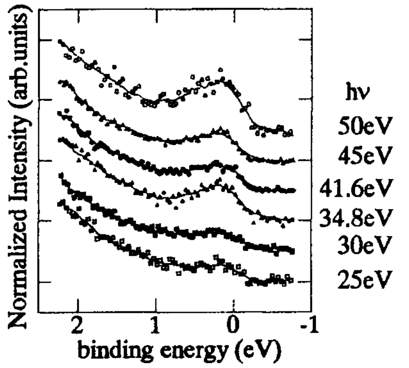

FIGURE 1 The dependence of photoelectron spectra upon the incident photon energy for 1st stage compound.

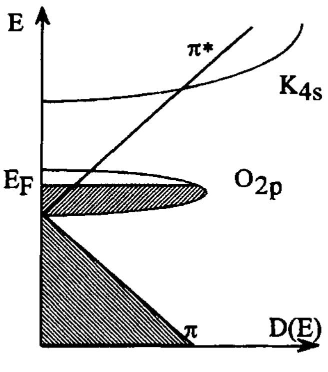

FIGURE 2 The schematic of the electronic structure for KO_X-GICs. The oxygen 2p bands lies around the Fermi level and form the hole carrier pocket.

are considered to originate from the intercalate oxygen.[4]

We, here, analyze the thermoelectric power (TEP) for 1st and 2nd stage compounds. The TEP for GICs consists of two terms[6, 7]; the contributions of the carrier diffusion S_d and the phonon drag effect S_p. The diffusion TEP S_d is related to the scattering process of conduction carriers and is proportional to the temperature given as following equation,

$$S_d = \frac{\pi^2 k_B^2}{3e} T \left[\frac{\partial \log \sigma}{\partial E} \right]_{E_F}, \tag{1}$$

where σ is the electrical conductivity including the carrier relaxation time associated to the scattering process, while the phonon drag TEP S_p is expressed as

$$S_p = \frac{\langle C_p R \rangle}{2en}, \tag{2}$$

where C_p is the specific heat for the phonon system which interacts with electrons and R and n are the momentum transfer ratio from phonon system to conduction carriers through the electron-phonon coupling and the carrier density, respectively. The momentum transfer ratio R[5] is given by

$$R = \frac{aq}{b + aq + fq^3 + BqT^3}, \tag{3}$$

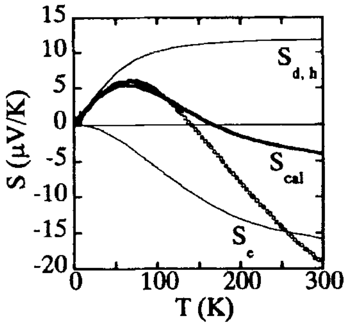

FIGURE 3(a) Temperature dependence of thermoelectric power (TEP) for 1st stage compound. The calculated TEP S_{cal} is the sum of S_e and $S_{d,h}$, where S_e and $S_{d,h}$ are the total electron TEP and the diffusion TEP for hole carrieres, respectively.

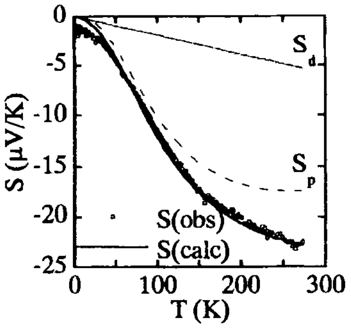

FIGURE 3(b) Temperature dependence of thermoelectric power (TEP) for 2nd stage compound. S_d and S_p stand for calculated contributions of the diffusion and the phonon drag to TEP, respectively.

where q is the wave number of phonon, and b, a, f and B are related to the scattering processes of phonon; domain boundary scattering, electron-phonon scattering, Rayleigh scattering and phonon-phonon scattering, respectively. The phonon drag TEP S_p tends to give the saturated TEP with maximum for acceptor-type GICs or minimum for donor-type GICs, where the temperature at the maximum (or minimum) is mainly influenced by the Fermi energy and the sound velocity of phonon.

First, we discuss the temperature dependence of TEP for 2nd stage compound. Since in the TEP for 2nd stage compound no apparent contribution of hole carriers is observed, we take only graphitic π bands into account for the analysis of TEP. In the calculation of TEP for 2nd stage compound[7, 8] we employed the Fermi energy E_F and the constant P_i associated with the energy dependence of the carrier relaxation time as the fitting parameters, where P_i is defined as $\tau = \tau_0 E^{P_i}$ for i-th band. Here, we neglect the difference in the scattering mechanism between the two graphitic π^* bands for simplicity, namely, $P = P_1 = P_2$. As for the other parameters for the momentum transfer ratio R, almost the same parameters for the pristine graphite and other GICs were employed.[6, 7, 9] The calculated TEP is in good agreement with the experimental TEP for 2nd stage compound as shown in Figure 3(b) and gives the estimation of the Fermi energy $E_F = 1.0 \pm 0.1$ eV and $P = -0.25 \pm 0.25$. The estimated $E_F = 1.0 \pm 0.1$ eV from TEP is relatively small compared to $E_F = 1.4$ eV from the in-plane C-C bond length change $\Delta d_{C\text{-}C}$[2,4] and the optical reflectivity[4]. As for the carrier scattering mechanism the quantities $P = -1, 0, 0$ are given by the scatterings due to the short range potential, the in-plane phonon through the electron-phonon coupling and theDaumas-Hérolddomain boundary, respectively.[10, 11] Thus, the estimated P=-0.25±0.25 reveals the predominant scattering mechanism of the in-plane phonon through the electron-phonon coupling and theDaumasHérold domain boundary.

Next, we discuss the temperature dependence of TEP for 1st stage compound, which displays the apparent contribution of hole carriers below 150 K. The TEP in the multicarrier system is expressed by

$$S = \frac{\sum_i \sigma_i S_i}{\sum_i S_i}, \tag{4}$$

where σ_i and S_i are the conductivity and TEP for i-th carriers, respectively. Thus, the contribution of hole carriers is given by the subtraction of the contribution of graphitic electron carriers to TEP S_e from the experimentally obtained TEP. The contribution of graphitic carriers to TEP S_e for 1st stage compound is estimated by employing the common parameters in the calculation of TEP for 2nd stage compound except the Fermi energy E_F. The subtraction of S_e from the experimentally obtained TEP proves the maximum in the resultant TEP around 100 K regardless of the employment of either E_F = 1.9 eV estimated from $d_{C\text{-}C}$[2, 4] or E_F = 1.4 eV, the latter of which is taken into account by smaller magnitude of estimated E_F from TEP compared with E_F from $d_{C\text{-}C}$ for 2nd stage compound as previously mentioned. If we regard the maximum around 100 K in TEP as the phonon drag effect for hole carriers, the TEP analysis for 2D-hole band $E=\hbar^2k^2/2m^*_h$ gives $E_{F,h}$ = 1.0±0.5 eV,[7] where m^*_h and $E_{F,h}$ are the effective mass of hole carrier $m^*_h \sim 3m_0$[4] and the Fermi energy for hole carrier defined as E_0-E_F, respectively, and E_0 is the energy at the top of the hole band. The estimated $E_{F,h}$ gives the hole carrier density $n_h = E_{F,h}\, D_I(E_F) = 10^{22\text{-}23}$ cm^{-3}, where $D_I(E_F)$ is the contribution of the intercalate to the density of states.[4] The estimated hole carrier density is largely inconsistent with the carrier density from the analyses of conductivity tensors $n_h \sim 10^{19\text{-}20}$ cm^{-3}.[4] Thus, the maximum in the contribution of hole carriers to TEP S_h is *not* explained by the phonon drag effect.

Next, we place the focus on the small concentration of hole carriers $n_h \sim 10^{19\text{-}20}$ cm^{-3}, which is obtained from the analyses of conductivity tensors.[4] The small carrier density $n_h \sim 10^{19\text{-}20}$ cm^{-3} and the partial density of states for the intercalate $D_I(E_F)$ give the Fermi temperature $T_F \sim 30$ K for the intercalate hole band. When $T > T_F$, we should treat the hole carriers as the non-degenerated metal, which obeys the Maxwell-Boltzmann statistics in contrast to the Fermi statistics for $T << T_F$. Thus, the temperature dependence of $S_{d,h}$ for the 2D hole band is linear for $T < T_F$, and then $S_{d,h}$ is saturated to $S_{d,h} = k_B/e$ = 86.14 mV/K.[11] Figure 3(a) shows the temperature dependence of calculated diffusion TEP for hole carriers $S_{d,h}$ and TEP for electron carriers S_e for 1st stage compound. The calculated $S_{d,h}$ from the carrier density $n_h = 4\times10^{20}$ cm^{-3} provides the agreement with the experimentally obtained TEP. However, at high temperatures the inconsistency between the calculated and experimentally obtained TEP become relatively large. This inconsistency probably arises from the employment of the same parameters for 2nd stage compound in the calculation of S_e for 1st stage compound and from the phonon drag effect, which is not accounted in the calculation of $S_{d,h}$ for hole carriers.

SUMMARY

We revealed the contribution of hole carriers to the in-plane transport phenomenon in addition to the contribution of electron carriers, which originate from graphitic π bands of donor-type KOx-GICs. Moreover, the hole carriers in TEP are considered to possess a non-degenerated nature due to the small concentration of hole carriers. Taking into account the oxygen electronic states around E_F, which is clarified by the dependence of the photoelectron spectra on the incident photon energy, we conclude that the intercalate oxygen has a delocalized nature and gives the contributions to the transport phenomenon with hole character.

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