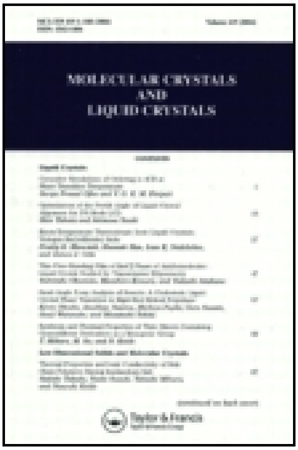

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Phonon Drag in GIC Based on Disordered Graphite

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Phonon Drag in GIC Based on Disordered Graphite

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The work presents the results of investigation and calculation thermopower in GIC's with $SbCl_5$ based on disordered graphite.

Keywords: graphite intercalation compounds; disordered graphite; diffusion thermopower; phonon drag thermopower; charge carrier scattering

INTRODUCTION

In nonmagnetic materials there are two mechanisms for thermopower generation: diffusion thermopower S_d is due to the spontaneous diffusion of the charge carriers caused by charge carrier energy redistribution around Fermi level in the presence of temperature gradient; and phonon drag thermopower S_{ph} involves the transfer of momentum from phonon system to charge carriers in the presence of temperature gradient. The total thermopower may be presented as a sum of diffusion thermopower S_d and phonon drag thermopower S_{ph}:

$$S = S_d + S_{ph} \qquad (1).$$

From the reported investigations in thermopower of graphite intercalation compounds (GIC's) based on highly-oriented pyrolytic graphite (HOPG) it is known that due to their peculiar electronic structure the effect of phonon drag of charge carriers can be observed in a wide temperature range. We have investigated thermopower in GIC's based on small-crystalline disordered pyrolytic graphite (DPG) and revealed that phonon drag effect plays an important role in these GICs.

EXPERIMENT

The samples of DPG (crystallite size L_a~$3\cdot10^{-8}$m, the distance between graphite layers d_{002}=$3.42\cdot10^{-10}$m, the parameter of prevailing orientation ~10^3) were intercalated by standard two-temperatures technique to the second stage. The thermopower was measured in the temperature range from 20K to 300K by use of automated arrangement based on IBM PC/AT. To register small voltages the method of digital synchronous detection was used. The measuring system was previously calibrated by using superconductive ceramics YBaCuO with the temperature of transition into superconductive state T_c=80K. This allowed us to reduce the error of thermopower measurements to 2%.

RESULTS AND DISCUSSION

The experimental dependence of thermopower S on temperature T for GIC with $SbCl_5$ based on DPG is given in Fig.1 (curve 1).

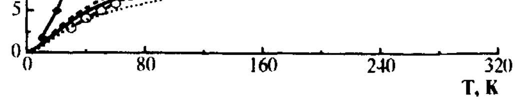

FIGURE 1 Temperature dependence of thermopower S(T): 1 - Gr-$SbCl_5$ based on DPG; 2 - GIC based on HOPG; 3 - the total S(T) calculated by taking into account the all mechanisms of charge carrier scattering; 4 - the calculated total S(T) at p=0; 5 - the calculated total S(T) at p=-0.5.

For comparison S(T) dependence for GIC based on HOPG[1] is also given in Fig 1 (curve 2). As it is seen from the figure the behavior of S(T) dependence for these materials is different.

It is known from the investigations in electrical resistivity and Hall coefficient for GIC that these compounds are single band conductors with conductivity of metallic type. The diffusion thermopower S_d for these materials depends linearly on the temperature[1]:

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

where k_b is Boltzmann constant, E_F is Fermi energy, p is the parameter which is determined by the prevailing type of charge carrier scattering. As it was shown earlier the thermopower for intercalation compounds based on both HOPG[1,2,3] and DPG[4,5] is described by the sum of two components: diffusion thermopower S_d and thermopower associated with the effect of phonon drag of charge carriers S_{ph} (equation (1)). The thermopower in GIC based on HOPG is satisfactorily described by equation (1) with the diffusion thermopower expressed by (2), while the thermopower in GIC based on DPG shows only qualitative agreement with the thermopower calculated by (1) with taking into account S_d component (2). K.Sugihara and other researchers showed in their recent calculations and the analysis of thermopower perpendicular to graphite plane measured for GIC with ICl based on HOPG in a wide temperature range[6,7] that if charge carrier scattering in the material is due to several mechanisms which have close values of relaxation time the parameter p must be determined not by the prevailing type of charge carrier scattering but by the contribution of all the mechanisms involved on account of their temperature dependences. According to these works:

$$p = \frac{\left\{\Gamma^{(DH)} + \Gamma^{(Io)} \cdot \left(1 + p^{(Io)}\right) + \Gamma^{(Ph)} \cdot \left(1 + p^{(Ph)}\right)\ \Gamma^2\right\}}{\left(1 + \frac{\Delta}{E_F}\right)\ \Gamma} \quad \Gamma = \sum_i \Gamma^{(i)} \quad \Delta = \frac{\gamma_1}{2} \qquad (3),$$

where γ_1 - is the overlap of electron wave functions of neighboring atoms in equivalent layers. $\Gamma^{(i)}$ is related to the collision time $\tau^{(i)}$ in basal plane by relation:

$$\Gamma^{(i)}(E)=\frac{\hbar}{2\tau^{(i)}}\propto E^{-p^{(i)}} \qquad (4)$$

where $p^{(i)}$ takes different values according to different scattering mechanism: $\Gamma^{(DH)}$ - boundary scattering: $p^{(DH)}=0$; $\Gamma^{(Io)}$ - ionized impurity scattering: $p^{(Io)}=1+2\Delta/E_F$; $\Gamma^{(Ph)}$ - in-plane phonon scattering: $p^{(Ph)}=0$ at low temperatures and $p^{(Ph)}=-1$ at high temperatures.

The phonon drag thermopower according to papers[2,3] can be presented as:

$$S_{ph}=\frac{\left\langle C_{ph}\,R(q)\right\rangle}{3e\,N} \qquad (5),$$

where C_{ph}- is the heat capacity of the phonon systems participating in the phonon drag effect, N is the density of carriers, $R(q)$-is a term characterizing relaxation processes for phonons participating in phonon drag effect:

$$R(q)=\frac{t(q)}{t_{c,p}},\quad \frac{1}{t(q)}=\frac{1}{t_{c,p}(q)}+\frac{1}{t_b}+\frac{1}{t_l(q)}+\frac{1}{t_p(q)} \qquad (6),$$

where $t_{c,p}$, t_b, t_l, t_p - are relaxation times on phonons due to scattering on charge carriers ($t_{c,p}$), on crystalline boundary (t_b), on phonons (t_p) and Rayleigh scattering associated with point defects (t_l). Except for t_b the phonon relaxation times are the functions of phonon momentum and temperature: $1/t_{c,p}=aq$, $1/t_b=v_s\,L$, $1/t_l=fq^3$, $1/t_p=BqT^3$, where a, f, B - are specific coefficients. The temperature dependence of phonon drag thermopower is completely determined by temperature dependence $\langle C_{ph}R\rangle$.

The temperature dependences for diffusion and phonon components of thermopower were calculated by formulas (2)-(6) for GIC based on DPG and GIC based on HOPG with crystallite sizes $L_a=5\cdot10^{-6}$m. The parameters of GIC based on HOPG required for calculations were chosen the same as in [3]. $E_F=0.4$eV that was used in the calculations of thermopower for GIC based on DPG was determined from the data on temperature dependence of electrical resistance and the value of sound velocity $v_s=6\cdot10^3$m/sec[4,5] was found experimentally for these compounds. The results of the calculations are given in Fig.2.

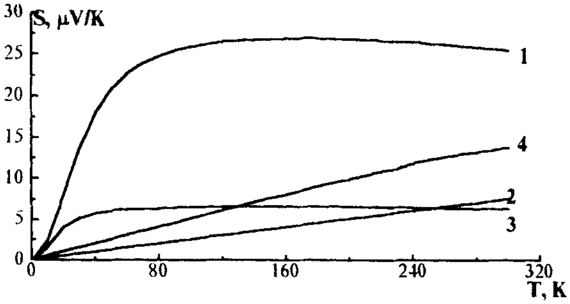

FIGURE 2 The calculated dependences of thermopower: 1- $S_{ph}(T)$ and 2- $S_d(T)$ in GIC based on HOPG; 3- $S_{ph}(T)$ and 4- $S_d(T)$ in GIC based on DPG.

As it is clear from the figure at the temperature >100 K the phonon drag thermopower in GIC based on HOPG is five times larger than the diffusion thermopower, while in GIC based on DPG the phonon and diffusion components of thermopower are very close in their values. That is, in contrast with GIC based on HOPG in which the temperature dependence of total thermopower is determined mainly by the temperature dependence of the phonon component, the thermopower in GIC based on DPG is determined equally by temperature dependence of both diffusion and phonon components of thermopower.

The analysis of the influence of p parameter on total thermopower for GIC based of DPG has shown that under the condition that p parameter in (2) is a constant the calculated total thermopower for these compounds does not correspond to the experimental thermopower in the whole temperature range from the low temperature to 300K. Fig. 1 shows the temperature dependence of total thermopower calculated with the assumption that p parameter is a constant and $p=0$ and $p=-0.5$ which corresponds to prevailing scattering on grain boundaries in different models of electronic structure in GIC (curves 4 and 5 respectively). As it is obvious from the picture this assumption gives the adequacy of the experimental temperature dependence S(T) and the calculated temperature dependences of thermopower only in a small temperature range: for p=-0.5 it is the interval of low temperature to 40K, and for p=0 it is the interval from 90K to140K. Fig.1 also presents the total thermopower for GIC based on DPG calculated by (2)-(6) on account of the diffusion component of thermopower including all mechanisms of charge carrier scattering (curve 3). As it is clear from the picture the temperature dependence of thermopower found experimentally is in good agreement with that calculated for the whole temperature range of investigations in spite of the fact that the parameters used in the calculations were determined only for GIC based on HOPG or just for HOPG.

Thus, the performed investigations showed that the thermopower in GIC based on structurally different carbon graphite materials is determined by the contribution of two components: diffusion thermopower and phonon drag thermopower, the relative contribution of each component into the total thermopower being determined by crystalline structure of initial graphite used for GIC. In GIC based on DPG the contribution of the diffusion and phonon components of thermopower into the total thermopower is approximately equal and in the calculations of diffusion component of thermopower the temperature dependence of all mechanisms of charge carrier scattering should be taken into account.

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