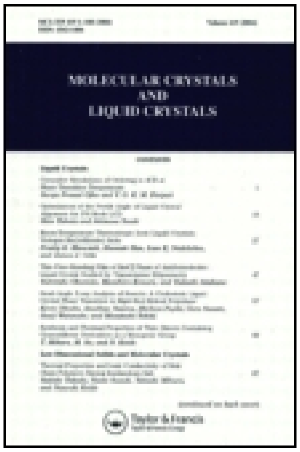

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Peculiarities of The Thermal Expansion of ICl Mono- and Hetero-Graphite Intercalation Compounds under Order-Disorder Phase Transitions

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Peculiarities of The Thermal Expansion of ICl Mono- and Hetero-Graphite Intercalation Compounds Under Order-Disorder Phase Transitions

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The temperature dependence of the thermal expansion coefficient α in highly oriented pyrolytic graphite (HOPG), first stage graphite intercalation compound (GIC) $C_{8.1}ICl_{1.1}$, second stage GIC $C_{16.3}ICl_{1.1}$, hetero-intercalated compounds $C_{12}FeCl_3(ICl)_{0.75}$ and $C_{10}CuCl_2(ICl)_{0.6}$ in the main crystallographic directions in the temperature range $40<T<350$ K has been investigated. It was shown that the Debye temperatures in plane and in the perpendicular direction are different in ICl graphite intercalation compounds.

Keywords: phase transition; graphite intercalation compounds

INTRODUCTION

The graphite intercalation compounds have a great number of different phase transition[1]. The investigation of phase transitions in GIC yields very important information about chemical and physical properties of these low dimensional systems. In the region of the phase transition the substance is in an unique state with anomalous values of heat capacity, dielectric constant, thermal expansion coefficient, conductivity, etc. The peculiarities of different physical properties of GIC in the region of the phase transition have not only theoretical but also a practical significance for application in electronics, optics, chemistry, etc. The aim of the present paper is to report upon the temperature dependence of the thermal expansion coefficient α in HOPG, low stage GIC in the main crystallographic directions in the temperature range $40<T<350$ K and peculiarities of electron-phonon interaction under phase transitions.

EXPERIMENTAL

The samples were synthesized by intercalation of HOPG. The pristine graphite is characterized by a basal-plane grain size of ~10^4 nm and an interlayer distance $d_0=0.3356$ nm. The misorientation angle of the grains with respect to the c-axis was less than 1°. GIC with ICl of the low stages were prepared by the vapour method in a two-zone ampoule, hetero-intercalated compounds $C_{12}FeCl_3(ICl)_{0.75}$ and $C_{10}CuCl_2(ICl)_{0.6}$ were synthesized in two steps. At first the second stage $C_{12}FeCl_3$ or $C_{10}CuCl_2$ were produced. The introduction of ICl resulted in the filling of all free interlayer distance and the formation of a corresponding first stage hetero-intercalated compounds $C_{12}FeCl_3(ICl)_{0.75}$ and $C_{10}CuCl_2(ICl)_{0.6}$. The conductivity along the c-axis and in a basal plane was determined by the four-contact method under DC conditions and by a contactless method at low frequency. The temperature dependence of the thermal expansion coefficient was measured with help of a precise dilatometric equipment with accuracy of 10^{-9} m. X-ray analysis was carried out on a diffractometer using Ni filtering Cu K_α irradiation.

RESULTS and DISCUSSION

The temperature dependence of the thermal expansion coefficient α in HOPG and the second stage $C_{16.3}ICl_{1.1}$ along the c-axis and in basal plane are shown in Fig.1 and Fig.2 respectively. The $\alpha(T)$ dependence for graphite is monotonous while for the intercalation compound $C_{16.3}ICl_{1.1}$ there are some

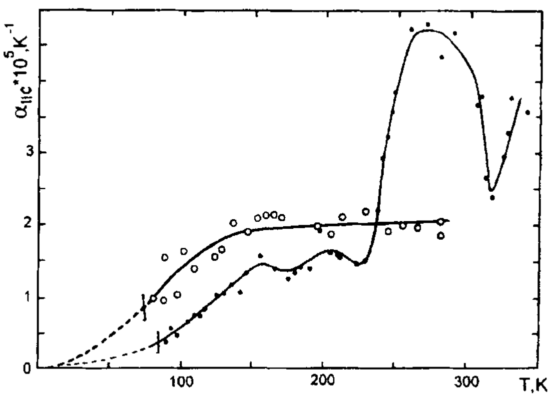

FIGURE 1 Temperature dependence of the thermal expansion coefficient α along the c-axis of pristine graphite (open circles) and the second stage GIC $C_{16.3}ICl_{1.1}$ (full circles).

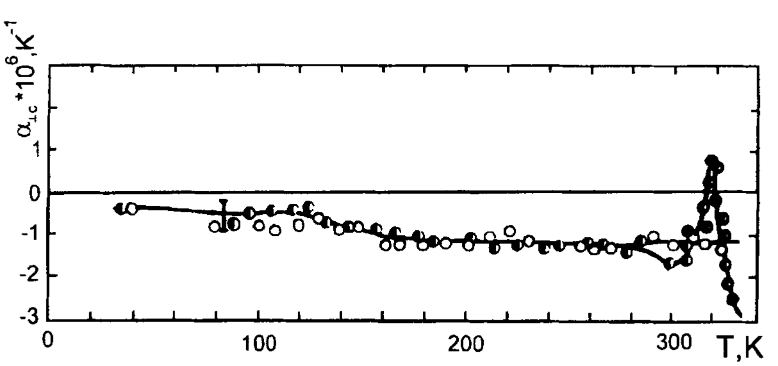

FIGURE 2 Temperature dependence of the thermal expansion coefficient α in a basal plane of pristine graphite (open circles) and the second stage GIC $C_{16.3}ICl_{1.1}$ (half full circles).

maximums in the dependence of the thermal expansion coefficient on temperature. It looks like the phase transition in the intercalation compounds goes through different stages. Heating and cooling dependencies do not coincide which is typical for the first order transition[2]. Probably molecules of ICl deintercalate under heating. At temperatures less than 70 K the α(T) dependencies for graphite and $C_{16.3}ICl_{1.1}$ (shown by dashed lines in Fig.1) exhibit the influence of the external pressure. The data in Fig.1 and Fig. 2 are shown for the pressure of 10^5 Pa. This temperature region will be discussed in the next publication. We pay attention to the fact that just near the phase transition temperature the coefficient α becomes positive.

In a basal plane the thermal expansion coefficient is negative. For HOPG the dependence of α(T) is monotonous while in $C_{16.3}ICl_{1.1}$ there is a λ-shape peculiarity near the temperature of the phase transition $T_c \approx 320$ K. The value of α in a basal plane for graphite and intercalation compound $C_{16.3}ICl_{1.1}$ coincides (see Fig. 2). It means that in-plane vibrations of the crystal lattice do not depend on the stage number. Thus the energy of interaction of carbon atoms in plane does not depend on intercalation. The X-ray measurements in low stages graphite intercalation compounds show that the distance between carbon atoms in layer almost independent on intercalation.

The peculiarities in the temperature dependence of the thermal expansion coefficient α along c-axis and in perpendicular direction were observed at different temperatures T_c. In the direction of the weak atomic bonds $T_c \approx 240°C$ while in plane $T_c \approx 280\text{-}300°C$. These data correspond to the well known different Debye temperatures along c-axis and in perpendicular direction in GIC.

As it was shown early[2,3] in hetero-intercalated compounds $C_{12}FeCl_3(ICl)_{0.75}$ and $C_{10}CuCl_2(ICl)_{0.6}$ there is a resistivity jump at the temperature of the phase transition. In this paper we report on the investigation of the temperature dependence of the interlayer distance d_i in hetero-intercalated graphite of acceptor-acceptor type. In Fig. 3 the dependence of $d_i(T)$ is shown. At the

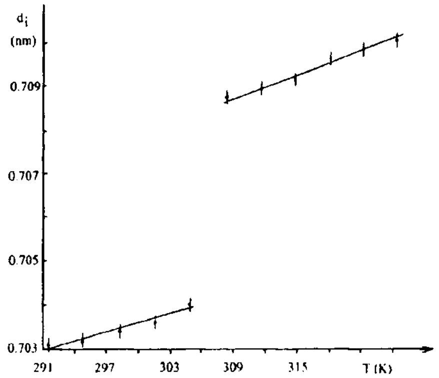

FIGURE 3 Temperature dependence of the interlayer distance d_i in hetero-intercalated GIC $C_{10}CuCl_2(ICl)_{0.6}$

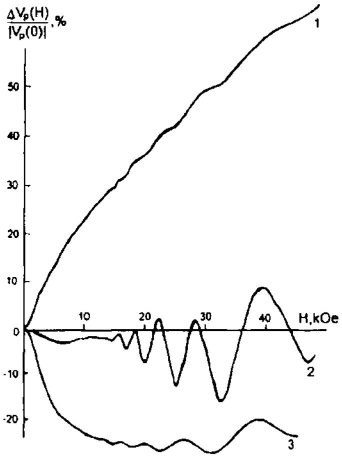

FIGURE 4 Dependence of the relative potential voltage on magnetic field H for sample $C_{9.3}AlCl_{3.4}$ at T=4.2 K. 1 - the sample in which there is no change in the sign of potential under phase transition, 2, 3- two different samples in which there is a change of sign of potential under the phase transition during cooling

temperature T_c of the phase transition a jump in d_i of about 0.005 nm was observed. The same jump in d_i was observed in the first stage GIC $C_{8.1}ICl_{1.1}$.

The jump in resistivity ρ_c along the c-axis and in derivative $\partial\rho_a/\partial T$ of in-plane resistivity ρ_a under phase transition is observed in other GIC[4]. It is worth to say that in the first stage GIC $C_{9.3}AlCl_{3.4}$ at the temperature of the phase transition T_c=203-210 K under DC measurements we observed the jump in the voltage from the potential contacts and even the change of sign of the potential. This phenomenon was accompanied by some features: 1) the value of potential jump varied from sample to sample. The temperature of transition T_c lied in the interval 203-210 K, but fixed for any sample. 2) Negative potential voltage changed the sign under the commutation of the current and increased linearly with the value of current. 3) There were a Shubnikov-de Haas oscillations at liquid helium temperature in all samples starting in magnetic fields about 1.5 T. 4) The frequency of oscillation does not depend on the value of the potential changes at the $T=T_c$ or the change of sign of potential. 5) When the potential changed the sign at $T=T_c$ monotonous part of magnetoresistance disappeared (curves 2, 3 in Fig. 4).

In conclusion we would like to note that the temperature of the phase transition of 2D melting type in GIC does not coincide with the temperature of the melting of the intercalated substance itself an depends on the chemical nature of the intercalate and its interaction with carbon matrix.

Acknowledgements

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