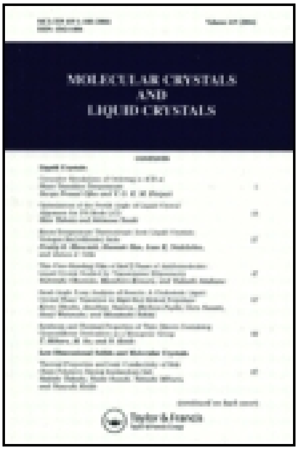

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Order-Disorder Phase Transition in Acceptor Type Graphite Intercalation Compounds

S. G. Ionov [a] , V. V. Avdeev [a] , V. A. Kulbachinskii [a] , S. A. Lapin [a] , E. A. Kamenskaya [a] & E. B. Udod [a]

[a] Moscow Lomonosov University, Chemical Department, 119899, Moscow, Russia

Version of record first published: 23 Oct 2006.

To cite this article: S. G. Ionov , V. V. Avdeev , V. A. Kulbachinskii , S. A. Lapin , E. A. Kamenskaya & E. B. Udod (1994): Order-Disorder Phase Transition in Acceptor Type Graphite Intercalation Compounds, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 244:1, 319-324

To link to this article: http://dx.doi.org/10.1080/10587259408050124

Mol. Cryst. Liq. Cryst. 1994, Vol. 244, pp. 319–324
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

ORDER-DISORDER PHASE TRANSITION IN ACCEPTOR TYPE GRAPHITE INTERCALATION COMPOUNDS

S.G.Ionov, V.V.Avdeev, V.A.Kulbachinskii, S.A.Lapin,
E.A.Kamenskaya, E.B.Udod
Moscow Lomonosov University, Chemical Department,
119899, Moscow, Russia

ABSTRACT A study was been made of the characteristic features of the electrical conductivity of some low stage acceptor type graphite intercalation compounds (GIC) near order - disorder phase transitions in intercalant layers of ICl, $AlCl_3$, $SbCl_5$. A change in the intercalant order of the iodine monochloride in graphite under pressure was detected.

INTRODUCTION

Intercalation of graphite increases the distance between the graphite layers by a factor of 2÷3, but alters only slightly the parameters of the crystal lattice in the basal plane. Intercalation of molecules in graphite produces monomolecular layers in which the intercalant molecules do not occupy strictly fixed positions, but form a two-dimensional liquid[1,2]. Cooling of GIC solidifies these layers which form either a periodic lattice (commensurate or incommensurate with graphite structure) or an amorphous glassy structure. The structure of intercalant layers is governed by the actual form of the intercalants and in some cases may be determined by X-ray analysis. The regular structure of the layer need not be associated with the regular distribution of charged centers, the number of which can vary quite widely, for example in GIC with $AlCl_3$. In present paper we report the study of order-disorder phase transition in quasi single crystals of low stage GIC of acceptor type $C_{9.3}AlCl_{3.4}$, $C_{24.5}SbCl_5$, $C_{8.3}ICl_{1.1}$, $C_{16.5}ICl_{1.1}$, $C_{24.8}ICl_{1.1}$ and hetero GIC $C_{12}FeCl_3(ICl)_{0.75}$.

EXPERIMENTAL

GIC samples of the acceptor type were obtained by intercalation of highly oriented pyrolytic graphite annealed at T=3300K. We synthesized GIC containing $AlCl_3$, ICl, $FeCl_3$ by the vapor phase method whereas $SbCl_5$ GIC were synthesized by the liquid phase method. The ICl was produced by synthesis from elements and purified by recrystallization from the melt, $FeCl_3$ and $SbCl_5$ were synthesized from the elements and refined by multiple distillations in a dry chlorine flow or in vacuum correspondingly. Synthesis of $AlCl_3$, ICl GIC took place in two-section glass ampoule in a chlorine atmosphere. The ampoule was sealed and placed in a tubular electric furnace. Variation of the temperature gradient between intercalant and graphite yielded GIC on different stochiometric compositions. The temperature gradient prevents also the condensation of an intercalant of the surface of samples.

The results of X-ray and chemical analyses of all the GIC on which physical measurements were carried out are listed in Table.1, where N is the stage number of GIC, d_i is the thickness of a layer filled with the intercalant, I_c is identity period in the direction of the trigonal axis, $I_c=d_i+(N-1)\cdot d_o$, $d_o=3.35Å$. The compound $C_{12}FeCl_3(ICl)_{0.75}$ was synthesized in two steps. At the beginning the second stage $C_{12}FeCl_3$ was produced. The introduction of ICl resulted in the filling of all free interlayer spacing. The sequence of layers in $C_{12}FeCl_2(ICl)_{0.75}$ are $C-FeCl_3-C-ICl$, $-C-FeCl_3-$... etc.

The electrical conductivity of the c-axis of GIC samples was determined by the four-contact method under DC conditions and also by a contactless induction method at a frequency of 100 kHz (in the a direction). Order-disorder phase transitions are easily registered by the discontinuity in resistivity ρ_c along the c-axis.

Hydrostatic pressures were created in a special chamber filled with dry oil.

Table.1 Chemical analyses and X-ray results

Chemical formula	N	d_i,Å	I_c,Å
$C_{9.3\pm0.1}AlCl_{3.4\pm0.1}$	1	9.54±0.02	9.54±0.02
$C_{12}FeCl_3(ICl)_{0.75}$	1	9.40±0.02	16.52±0.02
$C_{8.31\pm0.14}ICl_{1.10\pm0.03}$	1	7.13±0.02	7.13±0.02
$C_{16.5\pm0.5}ICl_{1.10\pm0.03}$	2	7.12±0.02	10.47±0.02
$C_{24.8\pm0.5}ICl_{1.10\pm0.05}$	3	7.12±0.02	13.82±0.02
$C_{24.5\pm0.5}SbCl_{5.0\pm0.1}$	2	9.36±0.02	12.71±0.02

RESULTS AND DISCUSSION

Order-disorder phase transitions in GIC samples which we investigated were accompanied by a strong reduction (by a factor of 2) of the resistivity ρ_c along the c-axis. Such a change exhibited a hysteresis on the temperature scale, typical of first order phase transitions. Fig.1 shows how ρ_c depends on temperature in $C_{24.5}SbCl_5$ (1) and $C_{9.3}AlCl_{3.4}$(2). A study of temperature and pressure induced structural and electronic changes in $SbCl_5$ intercalated graphite was done in [3-5].

Gravimetric, X-ray and chemical analyses showed that chemical composition and stage number did not change after some cycles of cooling. In the GIC of iodine monochloride order-disorder transitions occur for $T_c \simeq 310K$ (N=1), $T_c \simeq 312K$ (N=2) Fig.2. In GIC $C_{8.3}ICl_{1.1}$ with N>2 T_c does not depend on N and $T_c \simeq 313K$.

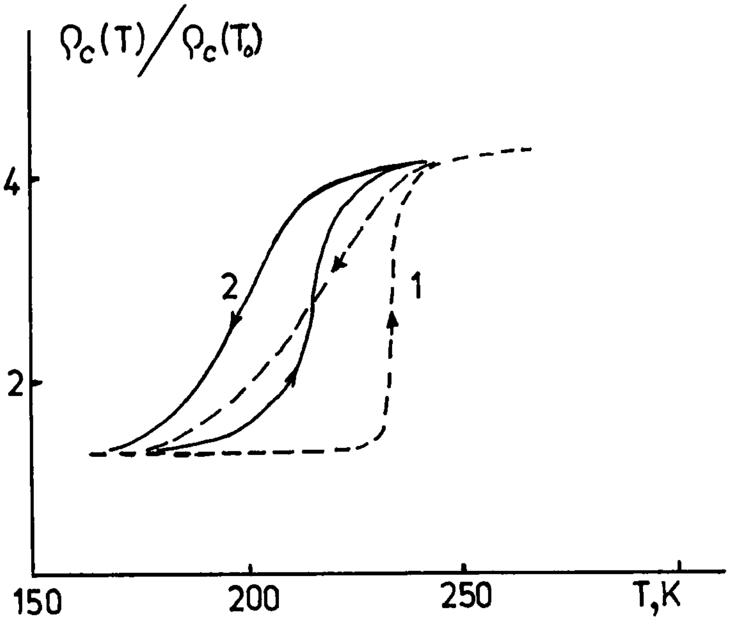

FIGURE 1 Temperature dependencies of the resistivity ratio $\rho_c(T)/\rho_c(T_o)$ for $C_{24.5}SbCl_5$(1) and $C_{9.3}AlCl_{3.4}$(2) $T_o=T_c-20K$, T_c - temperature of phase transition.

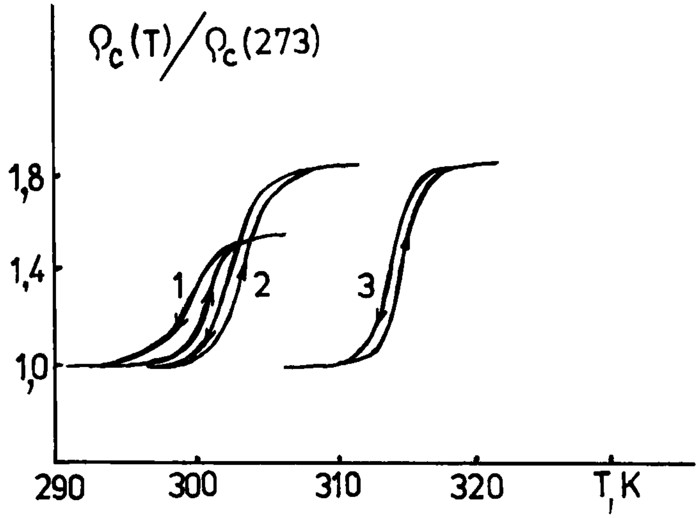

FIGURE 2 Relative change resistivity along the c-axis in the first stage GIC $C_{12}FeCl_3(ICl)_{0.75}$ (1), $C_{8.3}ICl_{1.1}$ (2) and $C_{16.5}ICl_{1.1}$ (3).

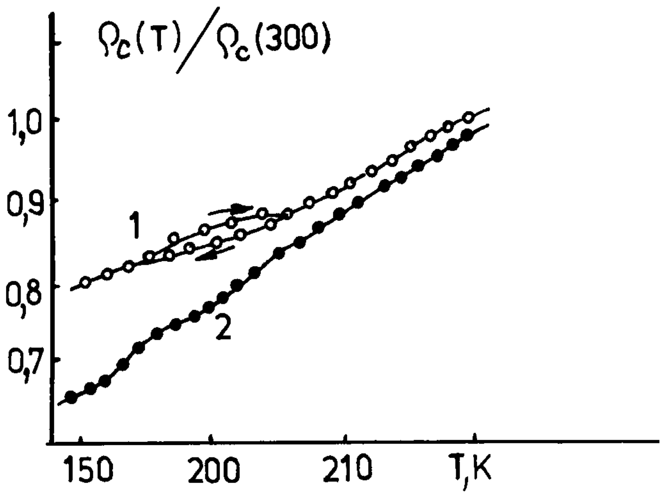

FIGURE 3 Temperature dependencies of the resistivity ratio $\rho_a(T)/\rho_a(300K)$ measured by a contactless method for $C_{24.5}SbCl_5$ (1) and $C_{9.3}AlCl_{3.4}$ (2).

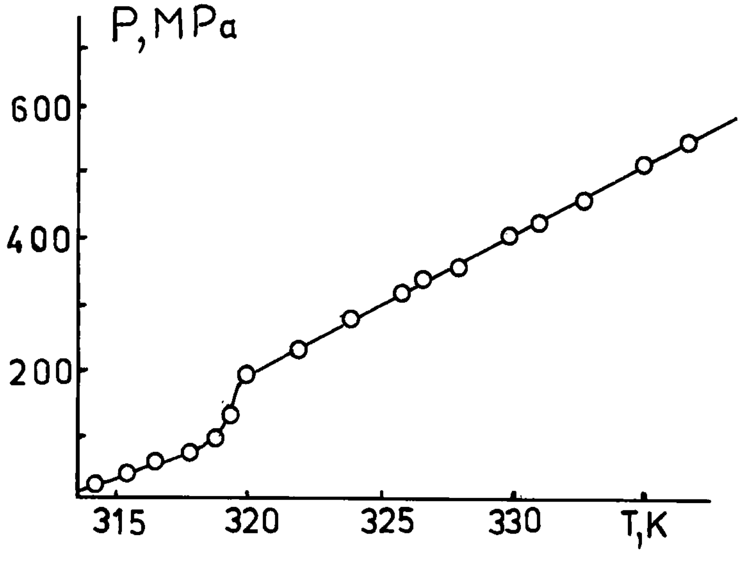

FIGURE 4 Pressure dependence of phase transition temperature T_c for $C_{16.5}ICl_{1.1}$.

In Fig.2 the relative change in the c-axis resistivity ρ_c is shown also for first stage hetero GIC $C_{12}FeCl_3(ICl)_{0.75}$. The temperature of the phase transition in this GIC T_c 302K is less than in $C_{16.5}ICl_{1.1}$ and the resistivity discontinuity for the transition is less by a factor 2. The temperature shift of the transition may be explained by the reduction of the interaction in the ICl layers in the hetero GIC as compared with pure ICl GIC.

The dependence of the resistivity ρ_a in a basal plane on T did not show strong anomalies (Fig.3), that is a concentration of carriers almost the same before and after the phase transition.

We investigated also pressure dependence of T_c in $C_{16.5}ICl_{1.1}$ (Fig.4). The value of T_c increases when pressure increases. The quantum oscillations of transverse magnetoresistance showed that a pressure induced phase transition occurs in the ICl GIC, accompanied by a change in the stage from the second to the third [6]. The characteristic features of the transition is the monotonic increase in the content of the third stage regions and a decrease in the content of the second stage regions in the specimen.

In investigated GIC, temperature of phase transition is different from the temperature of melting T_m of intercalated substances: $T_c \approx 203 \div 210K$ for $C_{9.3}AlCl_{3.4}$ ($T_m \approx 465.7K$), $T_c \approx 230 \div 240K$ for $C_{24.5}SbCl_5$ ($T_m \approx 275.9K$).

REFERENCES

1. Dresselhaus M.S., Dresselhaus G. - Adv.Phys., 1981, v.30, N2, p.181.
2. Bardhan K.K., Wu J.C., Chung D.D.L. - Synth. Metals, 1980, v.20, N1-2, p.371.
3. Morelli D.T. and Uher C.-Phys.Rev.B., 1983, v.27, N4, p.2477.
4. Lelaurain M., Mareche J.F., McRae E., Anderson O.E. and Sundqvist B. - J.Mater.Res., 1992, v.7, N11, p.2972.
5. Anderson O.E., Sundqvist B., McRae E., Mareche J.F., Lelaurain M.- J.Mater.Res., 1992, v.7, N11, p.2989.
6. Brandt N.B., Kuvshinnikov S.V. and Ionov S.G. - Pisma ZETF, 1983, v.38, N6, p.275.(Sov.Phys.JETP Lett, 1983, v.38, p.326).