*Synthetic Metals*, *12* (1985) 33–38

# STRUCTURAL PHASE TRANSITIONS IN STAGE 1 POTASSIUM-GRAPHITE INTERCALATION COMPOUNDS AT HIGH TEMPERATURES

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## ABSTRACT

X-ray diffraction studies of melting and stacking transitions of K-layers in stage 1 K-GIC have been investigated as a function of temperature at a constant $p_K$, the vapor pressure of K. At high $p_K$, two successive phase transitions have been observed; the low-T αβγδ staking solid - αβ stacking solid - liquid phases. The melting transition shows some continuous natures at $T_m$, the melting temperature;no discontinuous change of the first peak wave-number, $q_o$, of K-liquid halo, the existence of correlated liquid having the same symmetry as solid, a remarkable growth of intra- and interlayer correlations just above $T_m$, and a continuous growth of ordering of solid below $T_m$. However a discontinuity in the correlation lengths at $T_m$ indicates that the melting is weakly first order. At low $p_K$, the αβγδ solid melts directly into liquid without appearance of αβ phase.

The analysis of Debye-Waller factor has revealed an anisotropic thermal displacement of K-atoms in solid at high temperatures.

## INTRODUCTION

The stage 1 alkaline metal graphite intercalation compounds(GIC) have the simplest crystal structure among GICs, and provides us a prototype of liquid-solid transition in quasi-two-dimensional system; the motion of an alkaline metal atom is confined in a gallery between two graphite layers. The transition is very interesting in relation to the low dimensional melting. In the real system alkaline layers have an interaction with neighboring alkaline layers, which leads to a stacking ordering, a three-dimensional ordering.

The phase diagram of stage 1 K-GIC was determined by Carton and Hérold[1], and Salzano and Aronson[2], who suggested the K-liquid phase at high temperatures. The diagram is shown in Fig.1, which was determined by recent stu-

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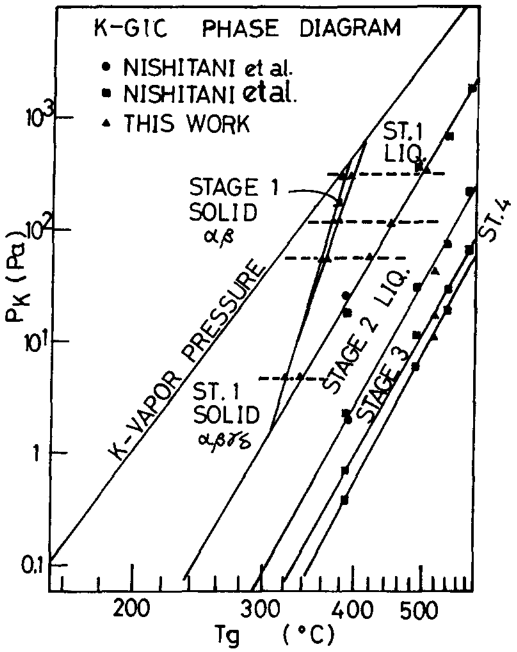


Fig. 1.

Phase diagram for K-GIC system. Dotted lines correspond to the constant $P_K$ sections studied. The data points, circles and squares are quoted from refs. 3 and 4, respectively.

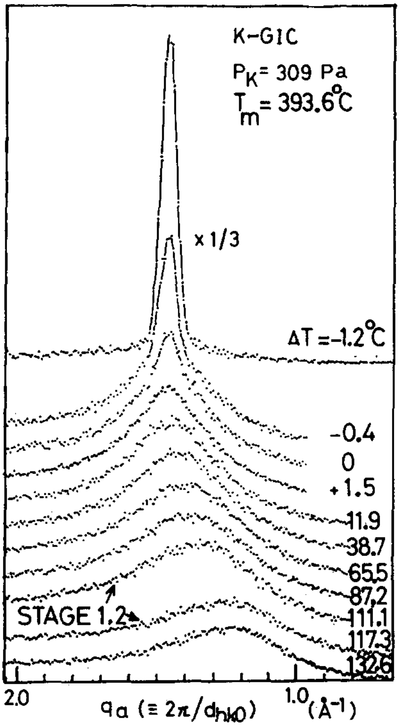
dies of high temperature X-ray diffraction[3]. Nishitani et al[4] studied the liquid-solid transition as a function of $p_K$, pressure of K, at a constant $T_G$, the temperature of compound, and revealed some remarkable natures of the continuous melting although it was concluded that the transition is weakly first order transition. In this work we studied details of its critical behavior as a function of $T_G$ along some sections of constant $p_K$.

## EXPERIMENTAL PROCEDURES

Samples were made from HOPG of a dimension of 3x3x0.2 mm. $T_G$ and $T_K$ were controlled independently to an accuracy of 0.1°C by means of a vertical two-zone furnace. The X-ray diffraction studies were carried out by an angle dispersion technique with use of MoKa radiation from a 12-kW rotating anode. The density of potassium was determined from the transmission intensity of X-rays through the sample[5].

## RESULTS

In the present work, we investigated the in-plane structure of K-layer, the stacking ordering, and the K-density at some constant $p_K$ sections. Fig.2 shows the (hk0) diffraction spectra of liquid phase at $p_K$ = 309 Pa as a function of $\Delta T$, where $\Delta T = T_G - T_m$, and $T_m$ = 393.6 °C for 309 Pa. The broad halo at $T_G > T_m$ corresponds to the first diffuse scattering from K-liquid layers. The peak wave-number of the halo, $q_o$, is small at $T_G \gg T_m$. As it approaches $T_m$, $q_o$ shifts to a larger value, the width of the halo becomes narrower, and the peak intensity grows up. These facts mean that the in-plane density of K-layer and also the in-plane correlation increase near $T_m$. At $T_G = T_m$ the Bragg reflection peak of the K-lattice (100) comes out and its intensity increases rapidly with temperature decreasing. As confirmed from the (hkl) reflections, this solid phase has the stacking order of two-layers period, $\alpha\beta$, and (2x2) in-plane superstructure. The most remarkable feature is that the Bragg peak of solid comes out right on top of liquid halo;that is $q_o$ changes continuously at $T_m$. These critical features are shown in Fig.3 as a temperature dependence of $q_o$. On the other hand the width $\Delta q_o$ in liquid decreases above $T_m$, but it changes discontinuously to that of solid at $T_m$.



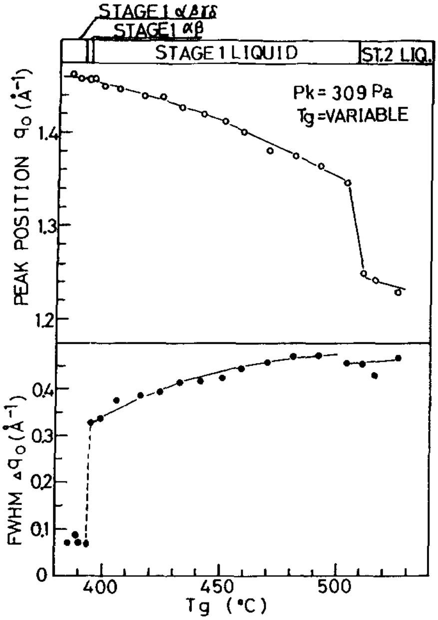


Fig. 2 (left). The variation of (hk0) diffraction spectra with $T_G$ at constant $p_K$(=309 Pa). $\Delta T = T_G - T_m$, where $T_m$ is melting temperature. A diffuse halo of liquid at $\Delta T>0$, and the Bragg peak (100) of K-solid($\alpha\beta$) at $\Delta T<0$ are observed.

Fig. 3 (right). The temperature dependences of the first peak wave-number of liquid halo, $q_o$, and its line-width, $\Delta q_o$.

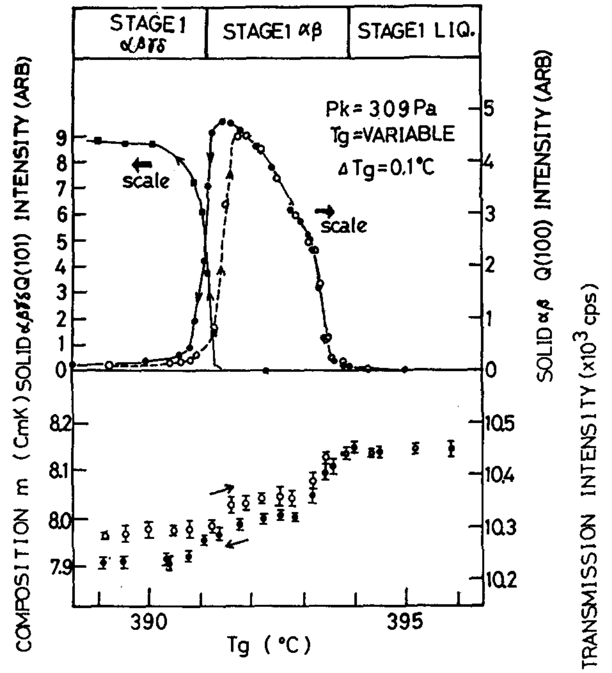


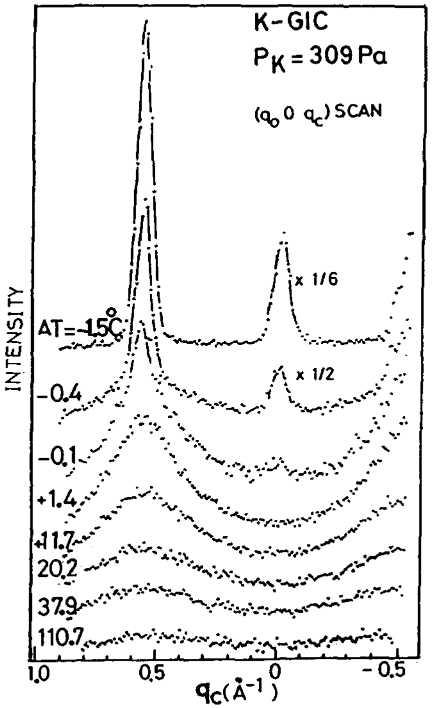
Fig.4. The temperature dependence of the Bragg peak intensity of solids and K-composition in $C_mK$.

The temperature dependence of order parameter of solid phase is evaluated from the intensity of the Bragg reflection as shown in Fig.4. The intensity increases continuously from $T_m$ and its temperature dependence shows no hysteresis. The drastic decrease of intensity at a lower temperature corresponds to the stacking transition of αβ to αβγδ phase. The stacking transition has a thermal hysteresis.

The composition m in $C_mK$ changes gradually at $T_m$, but there is no significant gap as shown in Fig.4. The gradual change suggests the 2nd order transition. We can expect such a gradual change in composition in the usual 1st order transition when there is coexistence of two phases. However we can rule out its possibility because the usual two-phase coexistence in the latter sense is not allowed in the present experimental conditions, infinite K-reservoir. The difference of m between the starting and final data at $T_G$= 389 °C in Fig.4 arises from increasing absorption of X-rays due to the glass tube which reacts with potassium. The small difference in m between αβ and αβγδ phases is possibly related to large thermal vibration of K-atoms at high temperatures:the observed Debye-Waller factor for αβ phase is larger than that of αβγδ phase.

The stacking correlation of K-layers also grows in liquid state near $T_m$. Fig.5 shows the $q_c$ scan at $q_a = q_o$, which reflects the stacking structure. At $T_G > T_m$ stacking correlation appears which has a two-layer period. This indicates that in liquid state the K-layer has an ordering with the symmetry of solid. As it approaches $T_m$ the peak intensity increases and simultaneously the width decreases. The correlation length along the c-axis grows up to about 20 A immediately below $T_m$(Fig.6). At $T_m$ the Bragg reflections of αβ solid come out right on the peaks of liquid. We can say that the stacking sequence in liquid is αβ , the same symmetry as that of high temperature solid phase as far as all the observed reflections are concerned. Such a growth of stacking correlation favors the second order melting. However, the correlation length changes discontinuously to the value of solid at $T_m$.

Summarizing these critical behaviors at $p_K$ = 309 Pa, the temperature dependences of $q_o$, the Bragg intensity of αβ solid,and composition of K show the continuous change at $T_m$, and the intra- and interlayer correlations, which has the same symmetry as that of solid, increases at $T_G \gtrsim T_m$. However the correlation lengths change discontinuously at $T_m$. We conclude that the melting is the weakly first order transition.



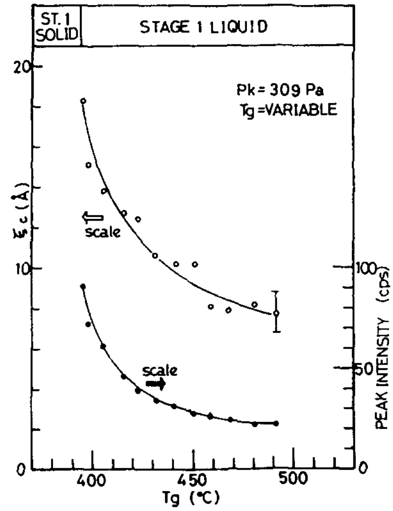


Fig. 5. The temperature dependence of the ($q_o$ ,0,$q_c$) spectra .
Fig. 6. The temperature dependence of correlation length of stacking, $\xi_c$ and the (101) peak intensity.

We studied similar experiments at $p_K$ = 120, 54 and 5.5 Pa. At lower $p_K$, $q_o$ and m show a discontinuous change at $T_m$, and the melting is clearly first order. The existing region of the αβ solid phase becomes narrower with $p_K$ decreasing, finally it disappears at $p_K$ = 5.5 Pa; namely the liquid changes into αβγδ solid directly. The transition of liquid to αβγδ solid is first order.

The $p_K$-dependence of the melting nature suggests that the continuous melting may occur at a higher $p_K$. Lee et al[6], Bak et al[8] and very recently Miyazaki et al[7] have studied the phase diagram of this system with use of the lattice-gas model, and Lee et al showed the second order transitions for a case of weak interaction between 2nd neighboring layers; liquid - (2x1)αβ solid - (2x2) αβγδ solid.

In solid phases at high temperatures we observed a large Debye-Waller(DW) factor for K-atoms. However the observed intensity of the (h,k,0) reflection,particularly in αβ phase can not be fitted to the intensity calculated on the basis of an isotropic DW factor. The analysis taking account of anisotropic DW factors gives a good agreement with the experimental results.The DW factors for αβ phase lead to the in-plane displacement of a K-atom of $u_1$ = 0.72 A in the (100) direction and $u_2$ = 0.45 A in the (110) direction at T = 392.5 °C, where u is the root mean square of the displacement. This is reasonable because a K-atom is packed closer in the (110) direction than in the (100) direction.

## ACKNOWLEDGMENTS

The authors wish to thank Dr. R. Nishitani for his stimulating discussion. The present work was supported partially by a Grant-in-Aid of scientific research from the Ministry of Education of Japan.

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