# In-Plane Density of Potassium Liquid and Liquid-Solid Transitions in Potassium Graphite Intercalation Compounds

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An x-ray–diffraction study of in-plane structures in K-graphite has revealed a remarkable chemical potential ($\mu_K$) dependence of the in-plane density in pure stages 1 and 2, and some continuous nature of the stage-1 melting transition. A simultaneous growth of intralayer and interlayer correlations of K atoms in stage-1 liquid is observed as $\mu_K$ approaches the solidification point. This transition is weakly first order. A new stacking transition from $\alpha\beta$ to $\alpha\beta\gamma\delta$ K layers in stage-1 solid is also reported.

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Graphite intercalation compounds (GIC's) exhibit various types of ordering, i.e., staging and in-plane ordering of intercalants, and stacking ordering of both the graphite and the intercalant layers.[1,2] These orderings are governed by temperature and the chemical potential $\mu$ of the intercalant. At high temperatures intercalants melt between rigid graphite layers. Such a liquid-solid phase transition (LST) as observed in alkali-metal GIC's is very interesting to study from a viewpoint of the dimensionality of melting.[3–5] The nature of LST in stage-1 compounds has been investigated experimentally in Li,[6,7] K,[8] Rb,[9] and Cs GIC's,[10,11] and the transitions were found to be of first order. Theoretically Bak and Domany[12] and Lee, Aoki, and Kamimura[13] have predicted a three-dimensional (3D) melting of first order in alkali-metal GIC's while Bak[14] suggested the possibility of 3D continuous melting in stage-1 Eu, Yb, and Ba GIC's.

In this Letter, we report our investigation of the in-plane structures of K layers at elevated temperatures as a function of potassium vapor pressure $p_K$, i.e., chemical potential $\mu_K$, using x rays from synchrotron radiation (SR) and a rotating-anode generator. We have observed a remarkable $p_K$ dependence of the in-plane composition $m$ ($C_{n\times m}K$, $n$ being the stage number) in the purely staged regions of stages 1 and 2, and a continuous change in $q_0$, the in-plane wave number of the first diffraction peak, at the stage-1 LST point. Also observed in the liquid state was the simultaneous growth of the intralayer and interlayer correlations when approaching the critical $p_K$ of LST. It has also been shown that a stacking-order transition of K layers takes place in stage-1 solid.

*In situ* x-ray–diffraction studies of K GIC in equilibrium with $p_K$ were carried out complimentarily by either an energy-dispersive (ED)[15] or an angle-dispersive (AD) technique. Graphite (highly oriented pyrolytic graphite; $4\times4\times0.2$ mm$^3$) and K metal were sealed in a Pyrex glass ampoule. $p_K$ was controlled by the temperature of K ($T_K$), while the temperature of GIC ($T_G$) was held constant (scan *AB* in Fig. 1). $T_K$ and $T_G$ were controlled within ±0.1 °C. Diffraction patterns in the in-plane direction $[q_a,0,0]$ were measured by ED method using SR white x rays at beam line BL-4B of the Photon Factory. Each pattern was taken in 1000 sec, and two continuous measurements at each $T_K$ were made for confirmation of the equilibrium of the system. Measurements in the interplane directions $[0,0,q_c]$ and $[q_a,0,q_c]$ were made by AD method with use of Mo $K\alpha$ radiation from a 12-kW rotating anode. Corrections for SR source profile and absorption of the glass ampoule were made by measurements of air scattering and the Bragg intensities of $SnI_4$ powder sample in a similar ampoule.

Figure 1 shows the $p_K$ dependence of diffraction patterns along $[q_a,0,0]$ observed in stage-2 and stage-1 K GIC's at $T_G = 390$ °C. The observed broad peak is characteristic of a liquid structure of

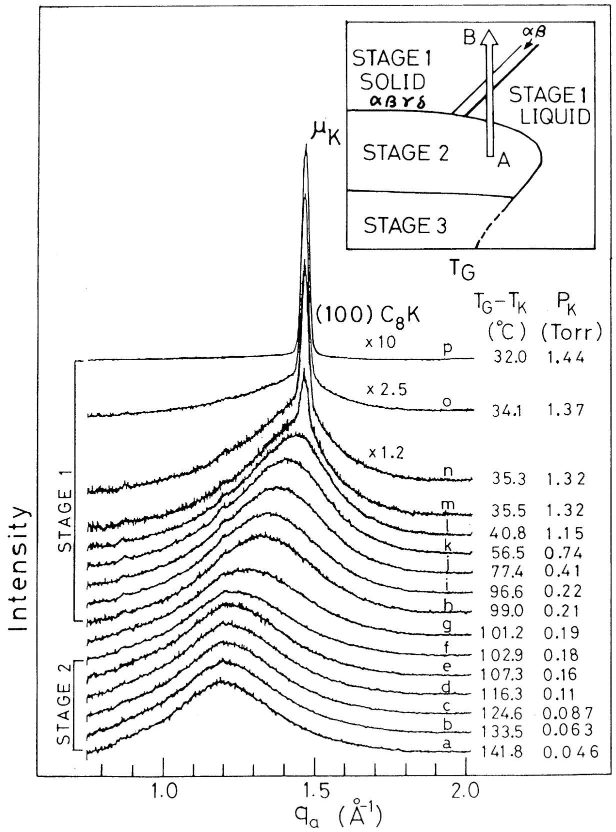

FIG. 1. Synchrotron-radiation x-ray diffraction spectra of stage-2 and stage-1 K GIC's measured along the $[q_a, 0, 0]$ direction as a function of $p_K$ at $T_G = 390\,°C$. Only the first halo peak of liquid K layers is shown. The (100) Bragg reflection of stage-1 solid appears above $p_K = 1.32$ Torr, superimposed upon the peak of the liquid halo. Inset: The schematic phase diagram and the scanning line.

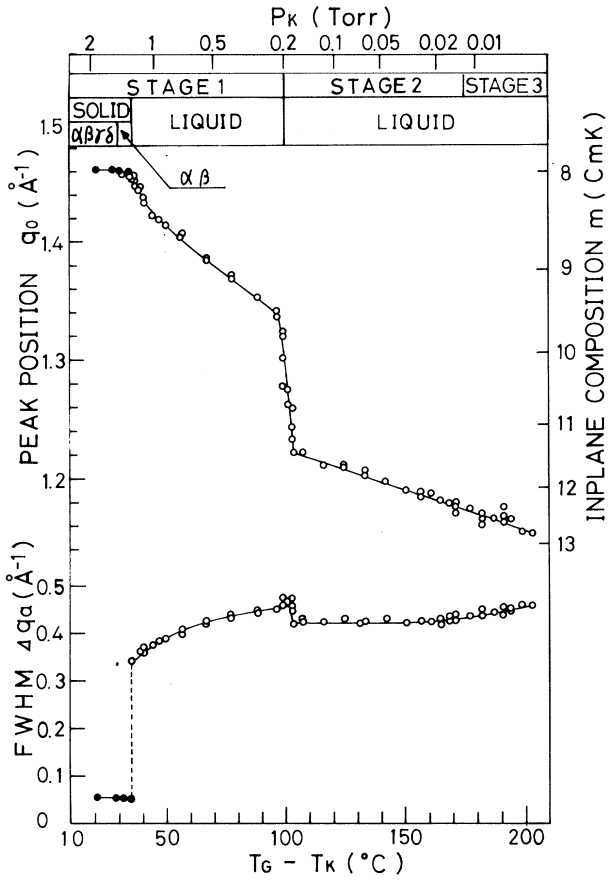

FIG. 2. The $p_K$ dependences of the peak position $q_0$ and peak width (full width of half maximum) $\Delta q_a$ of the first halo peak in the $(q_a, 0, 0)$ scan at $T_G = 390\,°C$. The stable regions of stages, phases, and stackings (listed at top) are determined independently from the $(0, 0, q_c)$ and $(q_a, 0, q_c)$ scans. The in-plane composition $m$ is calculated from $q_0$. Open and closed circles indicate liquid and solid phases, respectively. Solid lines are guides for the eye.

K atoms. The in-plane wave vector of the first peak $q_0$ shifts to a larger value with increasing $p_K$ even in the stable region of each stage. $q_0$ is plotted as a function of $T_G - T_K$ ($p_K$) in Fig. 2. A drastic increase of $q_0$ at $p_K = 0.18$–$0.21$ Torr, corresponding to Fig. 1, curves $f$–$h$, results from the stage transition from stage 2 to 1, which is directly detected in $(0, 0, q_c)$ and $(q_a, 0, q_c)$ scans (it took about 30 min to reach equilibrium at a given $T_K$ during this stage transition). The discontinuous change in $q_0$ indicates that the stage transition is of first order, which is in accord with previous works.[11,15] As $p_K$ increases, $q_0$ of stage 1 still increases gradually in the liquid state, until it reaches the critical value $q_0^S = 1.46$ Å$^{-1}$. Thus, $q_0$ shows a strong $p_K$ dependence in the purely staged regions of stages 1 and 2.

This change in $q_0$ infers that the in-plane density of K atoms depends on $p_K$ (and $\mu_K$). The in-plane composition $m$ (the chemical formula is $C_{n \times m}K$) is related to $q_0$ by the Ehrenfest relation,[16] $d = 2\pi R / q_0$, where $d$ is the K-K nearest-neighbor distance in liquid. $R$ is a configurational constant and is experimentally estimated as 1.14 under the assumption that the saturated compound of stage-1 liquid has the formula $C_8K$ at $q_0 = 1.46$ Å$^{-1}$. As shown in Fig. 2, the stable region is $11.47 < m < 12.41$ for stage 2, while $8.0 < m < 9.52$ for stage-1 liquid (this phase was reported as $C_{10}K$ by Salzano and co-workers[17]). The nonstoichiometric nature is consistent with the earlier work by Carton and Herold.[8] This variation of $m$ should have some crucial effects on in-plane structures in stage-2 heavy alkali-metal GIC's, such as the incommensurability and relative orientation,[18,19] and the domain structures[20-22] of alkaline layers, which are a matter of controversy.

When $q_0$ reaches the critical value $q_0^c$, the stage-1 liquid transforms into a 3D ordered solid with a $(2\times 2)$ in-plane superlattice and stacking order of $\alpha\beta$. In Fig. 1, curves $m-p$, a sharp Bragg peak of the solid comes out just on the broad peak of the liquid. This $q_0$ is confirmed to be equal to $q$ of the Bragg reflection of the $(2\times 2)$ commensurate lattice, $Q_K(100)=\frac{1}{2}Q_G(100)$, where $Q_K(hkl)$ and $Q_G(hkl)$ are the potassium and graphite reciprocal lattice vectors, respectively. The $\alpha\beta$ stacking phase is stable only in a very narrow region of $p_K$, and a slight increase in $p_K$ (an increase of 5 °C in $T_K$) drives another stacking-ordered phase, which has a four-layer period $\alpha\beta\gamma\delta$ and $(2\times 2)$ in-plane structure.[2,3]

The most noticeable feature concerning the critical behavior of the stage-1 LST is the fact that $q_0$ of liquid increases continuously up to that of solid, $q_0=Q_K(100)$. No discontinuous change in $q_0$ was observed at the LST point.[24] This feature is quite in contrast with the case of Cs GIC.[11] Figure 2 shows the $p_K$ dependence of the peak width (full width at half maximum) $\Delta q_a$ along $q_a$ in liquid. $\Delta q_a$ decreases gradually with increasing $p_K$ until $q_0=q_0^c$. This implies that the in-plane positional correlation of K atoms grows continuously in liquid near LST. However, $\Delta q_a$ remains finite at $q_0^c$, and it seems that the liquid halo still exists immediately above the critical $p_K$ (=1.362 Torr). It is not clear at present whether the coexistence[17] of the solid and liquid phases above LST is intrinsic or due to a trivial effect such as imperfections in the sample.

On the other hand, we observed a more remarkable growth of stacking correlation of K layers in liquid. The inset in Fig. 3 shows diffraction spectra observed along the $[q_0, 0, q_c]$ direction as a function of $p_K$. The diffraction spectrum in liquid shows broad intensity maxima at $q_c=\pm 0.58$ Å$^{-1}$ [a midpoint between $Q_G(101)$ and $Q_G(100)$]. This fact indicates the existence of stacking correlation of K layers even in liquid, such as $\alpha\beta\alpha\beta$. This is attributed to the repulsive interaction of K atoms which avoid the closest contact in the $c$ direction. As $p_K$ (and $q_0$) approaches the critical value, the peak width $\Delta q_c$ becomes narrower continuously and the peak intensity increases simultaneously. Figure 3 shows the $p_K$ dependence of the correlation length $\xi_c$ along the $c$ axis and the peak intensity in liquid near LST. $\xi_c$ is obtained from the best fit of a Lorentzian to the peak at $(q_0, 0, q_c=+0.58)$ under the assumption that the experimental resolution function including the mosiac spread of the sample is of Lorentzian shape. Steep increases of $\xi_c$ and intensity are observed upon approach of the critical $p_K$. However, they remain finite at the transition point instead of diverging. Thus, $\xi_c$ increases up to about 20 Å at the solidification point while $\xi_a$ is estimated as 20 Å.

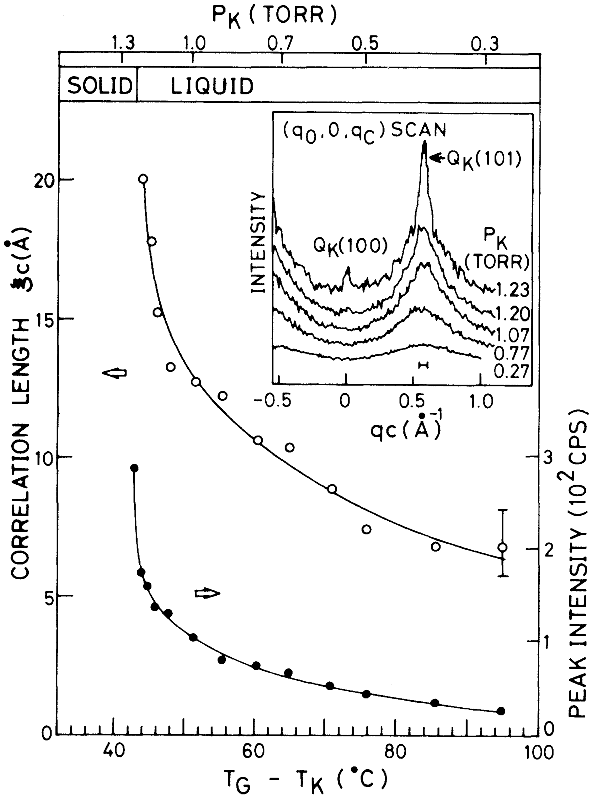

FIG. 3. The $p_K$ dependence of the correlation length $\xi_c$ along the $c$ axis and the $(q_0, 0, 0.58)$ peak intensity of stage-1 liquid at $T_G=395$ °C. Solid lines are guides for the eye. Inset: The diffraction spectra along $[q_a, 0, q_c]$ in stage-1 liquid and solid ($\alpha\beta$ stacking) phases as a function of $p_K$. Above $p_K=1.20$ Torr the Bragg reflection of the solid appears at $q_c=0$ [$Q_K(100)$] and $\pm 0.58$ Å$^{-1}$ [$Q_K(101)$]. The bar represents the experimental resolution.

Finally, the Bragg reflection of the solid phase comes out at both $q_c=0$ and $\pm 0.58$ Å$^{-1}$ above the critical $p_K$ of solidification. These points correspond to $Q_K(100)$ and $Q_K(101)$ of the stage-1 solid with the stacking $\alpha\beta$, respectively. No appreciable temperature hysteresis associated with LST was observed within the experimental accuracy of 0.5 °C. The continuous change of $q_0$, no hysteresis at the LST point, and the growth of positional correlation of K atoms in liquid phase indicate that the stage-1 LST is of second order. However, the nondivergent nature of the correlation length and the coexistence of the liquid and solid leads to the weakly first-order character of this transition.

These phase transitions in stage-1 K GIC have been understood by the earlier theoretical works based on the Landau-Ginzburg theory. Bak and Domany[12] showed that LST's in stage-1 alkali-metal GIC's could be of second order in principle because of the absence of the third-order term in the free-energy expansion. However, it should be a first-order transition in the case of the $\alpha\beta$ stacking solid because this transition is not driven by the fourth-order term but by a much higher-order one. This result may explain the weakly first-order transition in the present stage-1 K GIC. For the stacking transition in stage-1 solid Lee, Aoki, and Kamimura[13] used a lattice-gas model and predicted three possible orderings depending on the strength of interlayer interaction: (1) disorder-$(2\times1)\alpha\beta$-$(2\times2)\alpha\beta\gamma\delta$; (2) disorder-$(2\times2)\alpha\beta$-$(2\times2)\alpha\beta\gamma\delta$; and (3) disorder-$(2\times2)\alpha\beta\gamma\delta$. The present study clarifies that the phase transitions in K GIC correspond to the case (2), which leads to the second-neighbor interlayer interaction of K layers being much smaller than the first-neighbor one.

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