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X-ray Study of Intercalate Order-Disorder Transition in $C_{24}K$

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Below $T_c = 122.9$°K, $C_{24}K$ shows a transition from the intralayer disordered state to an ordered state. For $T > T_c$, present diffuse scattering data from the potassium intercalate in graphite indicate a two-dimensional (2-D) character of the short-range order. As this 2-D scattering increases with decreasing temperature, *hk*0 superlattice reflections appear at T_c which have a true 3-D character that results from essentially simultaneous intralayer and interlayer ordering. This long-range order vanishes as $|T-T_c|^\beta$ with $\beta = 0.180 \pm 0.01$.

In recent years graphite intercalation compounds have attracted increasing interest because of their pronounced anisotropic [quasi two-dimensional (2-D)] properties.[1] In the pure stage-2 compounds, $C_{24}M$ (M=K, Rb, Cs), every second hexagonal graphite plane is followed by an alkali layer, regularly stacked together along the hexagonal *c* axis.[2,3] At high temperatures, the alkalais are sited within the graphite lattice possibly as a 2-D lattice gas which undergoes an order-disorder transition at a lower temperature as first explored by Parry and co-workers.[4] While many papers have dealt with the structure of the $C_{24}M$ compounds,[4] there has been until recently[5,6] little quantitative structural information on the phase transitions. Prior work[6,7] indicates that $C_{24}K$ actually undergoes two transitions, at ~124 and ~95 °K, and we shall concentrate here on the upper one.

We used highly oriented pyrolytic graphite (HOPG) with a *c*-axis mosaic spread of ~1°, which broadens to about 2° in the intercalation process. The hexagonal (*hk*0) (*hkl* refer to continuous reciprocal lattice variables) plane is thus explored as a 2-D powder pattern with cylindrical rather than spherical averaging. Sample preparation and characterization are described in detail elsewhere.[8] However, we note that the sample chambers were fitted with Be windows which permitted observation of weak diffuse K scattering otherwise obscured by the diffuse scattering from the commonly used glass containers. The stage of the sample was determined by the *c*-axis repeat distance which was 26.15 ± 0.03 Å compared to 26.2 Å for the ideal stage-2 compound $C_{24}K$.[3] In this study we used Mo $K\alpha_1$ radiation off a Johanne asymmetric-cut Ge(111) monochromator. All scans were carried out in the transmission-scattering geometry. For the low-temperature measurements a liquid nitrogen cryostat with resistance heater was used. Chromel-Alumel thermocouples were placed in a hole in the metal sample chamber and the temperature was maintained to better than ± 0.02 °K with an Atronix controller.

In the event that true 2-D translational long-range order (LRO) exists within the (uncorrelated) potassium layers, reciprocal lattice rods from the ordered structure are expected rather than 3-D reciprocal lattice points. For HOPG such rods become cylindrical shells of intensity extended in the direction normal to the *hk*0 plane. For the translational short-range order (SRO) preceding the LRO, the same considerations apply. X-ray step scans in different directions of the reciprocal lattice were carried out as noted in Fig. 1: Scan *A* corresponds to a θ:2θ scan in the

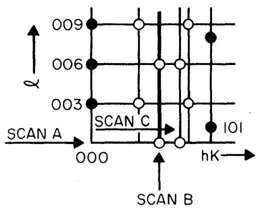

FIG. 1. Part of the reciprocal lattice projected on (hk) (Refs. 4 and 6). The filled circles refer to the fundamental reflections of graphite. The open circles refer to potassium superlattice reflections. The thick line indicates a reciprocal lattice rod for 2-D ordered K layers. The scans are described in the text.

cylindrically averaged $hk0$ plane; scan B, which is normal to the $hk0$ plane, probes the dimensionality of the intensity distribution due to LRO and SRO; scan C crosses the rod (cylindrical shell) parallel to the $hk0$ plane and permits us to separate 2-D SRO diffuse scattering from a 3-D Bragg peak below T_c.

In Fig. 2, the experimental results of scan A at room temperature are compared with those at 85 °K, 38 °K below the observed critical temperature, T_c, of 122.9 °K. The graphite reflections at $q(hk) = 2.94$ Å^{-1} and $q(hk) = 5.08$ Å^{-1} are not affected by the transformation. The "peak" at $q(hk) = 2.94$ Å^{-1} is due to the stacking-fault-smeared $101-10\bar{1}$ profile[6] and is not a 100 reflection which is forbidden. The main diffuse peak centered around $q(hk) = 1.26$ Å^{-1}, as well as its harmoinc at 2.40 Å^{-1}, gradually sharpens during cooling but shows no singularity at T_c. Above T_c, this diffuse scattering at 1.26 Å^{-1} does not fall off normal to the $hk0$ plane, thus indicating an intensity distribution attributable to truly planar potassium pair correlations with no correlations between planes. For $T < T_c$ additional superstructure reflections of the ordered potassium layers appear at $q(hk) = 1.70$, 2.18, 3.66, 3.86, and 4.22 Å^{-1}. While we concentrate in the following on the intensity distribution in the vicinity of the peak at 1.70 Å^{-1}, we note that the positions of the five reflections may be indexed with use of a $2\sqrt{3}a \times 2\sqrt{3}a$ supercell for the ordered layer where a is the graphite spacing. However, intensity calculations have yet to establish the true ordered structure.

The temperature dependence of the intensity distribution at the 1.70-Å^{-1} potassium reflection was measured in two directions of the reciprocal lattice, according to scan B and scan C in Fig. 1. Figure 3(a) shows two typical examples of scan B at $q(hk) = 1.70$ Å^{-1} along l above and below T_c. Above T_c, the Bragg-like intensity disappears leaving a flat background which consists mainly of SRO diffuse scattering. The diffuse scattering background alone seems to be independent of l in the low-temperature ordered phase. Whereas the Bragg peak reflects a 3-D ordering, the ridgelike diffuse scattering in directions normal to the $hk0$ plane indicates a 2-D SRO of the potassium atoms. Scan C in (hk) at $q(l) = 0.2$ crosses the ridge well away from the Bragg peak and thus reflects the in-plane SRO diffuse scattering alone. The peak in Fig. 3(b) was seen over a range of temperature from well below to well above T_c [see Fig. 4(c)]. It shows that the diffuse (critical) scattering has 2-D character above T_c because, as in Fig. 3(a), it is l independent. Projected in the $hk0$ plane it is centered at the same position as the 1.7-Å^{-1} superstructure peak below T_c and must be distinguished from the pronounced high-temperature scattering shown in Fig. 2(a). Because similar scans below T_c gave similar results, we tentatively conclude that the diffuse critical scattering at $T < T_c$ indicates 2-D fluctuations accompanying 3-D order.

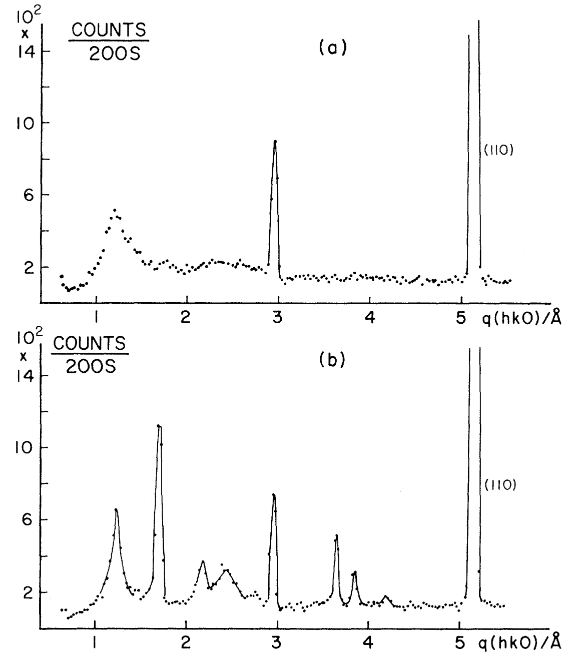

FIG. 2. Scan A of the powder-averaged ($hk0$) plane: (a) disordered phase at 292 °K; (b) ordered phase at 85 °K. The curves are drawn as an aid to the eye.

If one adopts here the language of classical phase transitions, the superlattice peak intensity on top of the ridge is proportional to the square

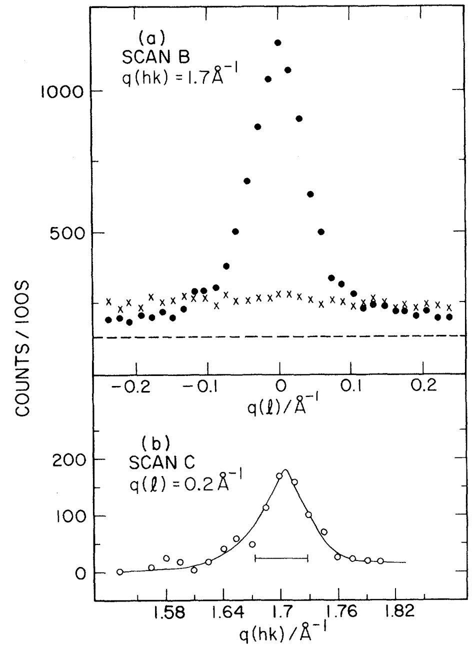

FIG. 3. (a) Scan *B*: data taken at T_c − 24.5° (filled circles), and T_c + 2° (crosses); the dashed line indicates background scattering, measured well away from $q(hk) = 1.7$ Å^{-1}. (b) Scan *C*: data taken at T_c + 0.2° (open circles).

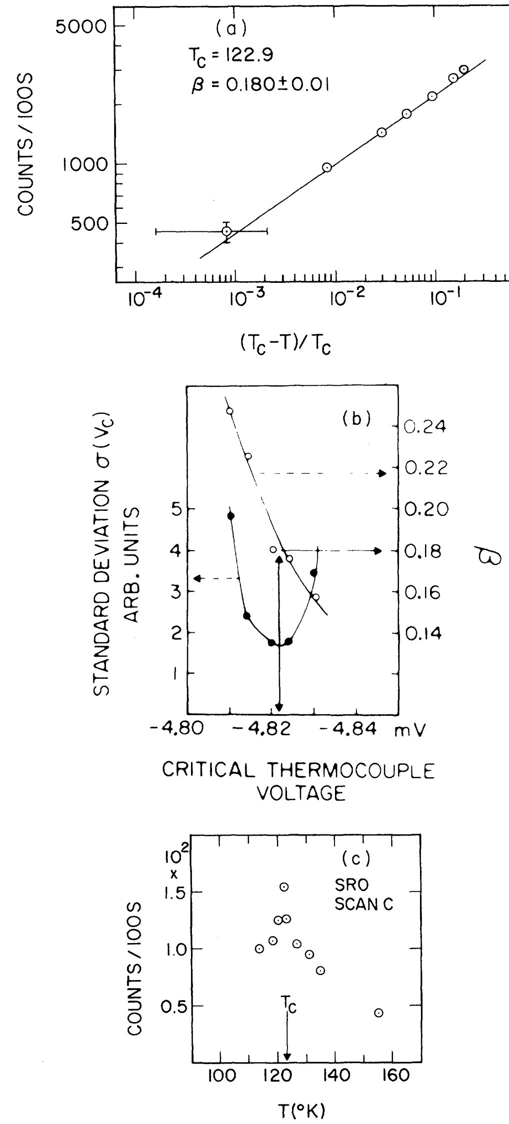

FIG. 4. (a) The $q(hk) = 1.70$ Å $q(l) = 0$ superlattice-peak intensity vs reduced temperature difference from the phase transition temperature of 122.9°K. The full line corresponds to the power law $I = a[(T - T_c)/T_c]^{2\beta}$ with the best-fit values $T_c = 122.9$°K and $\beta = 0.180$. (b) Standard deviation (closed circles) vs critical thermocouple voltage to determine the best critical voltage, V_c. From the upper plot of β (open circles) vs V_c, the appropriate β is then selected. (c) Peak intensity of the SRO diffuse scattering, measured with scan *C* [$q(l) = 0.2$ Å^{-1}] as a function of temperature.

of an assumed LRO parameter provided that the (flat) background is properly subtracted. The peak intensity was scanned in the *l* direction at $q(hk) = 1.70$ Å^{-1} and the background from $q(l) = \pm 0.24$ Å^{-1} to $q(l) = \pm 0.16$ Å^{-1} was averaged and subtracted from the peak intensity, which was determined from the maximum plus the two adjacent values summed to improve statistics. As the full width at half maximum does not change with temperature, the temperature dependence of the peak intensity so determined indicates a continuous or second-order phase transition, as noted in Ref. 6. We therefore performed a least-squares fit of our measured and corrected intensity, I_m, according to the power law $I_m = a(V - V_c)^{2\beta}$, and the final result in temperature units is shown in Fig. 4(a). V and V_c are the thermocouple voltages which are linearly related to the measured temperature and critical temperature, respectively, and β is the exponent for the assumed LRO parameter. By variation of V_c the standard deviation, $\sigma = \sum_i [I_m^i(V^i) - a(V^i - V_c)^{2\beta}]^2$, was minimized, as described by Als-Nielsen and Dietrich,[9] yielding the values $\beta = 0.18 \pm 0.01$ and $T_c = 122.9 \pm 0.5$ °K [see Fig. 4(b)]. Figure 4(c) shows that the *l*-independent peak maximum of the SRO diffuse scattering (scan *C*) becomes critical at the same T_c. In order to extract the corresponding critical exponents γ and ν, the line shape of the diffuse peak must be unfolded from the instrumental resolution function and this is currently underway.

These experiments show that the LRO is 3-D at T_c although SRO above and below T_c has a 2-D character. The critical temperature $T_c = 122.9$ °K is in reasonable agreement with earlier work.[6,7] No indication of a second phase transition at the lower resistivity anomaly at[6,7] 95 °K or at the transition temperature of 98 °K given by Nixon and Parry[4] could be detected in the $hk0$ x-ray scans. Thus, the 98 °K transition seems to result from additional interplane sequencing.[6]

The exponent $\beta = 0.18 \pm 0.01$ is certainly well removed from the Padé-approximant value of 0.312 for a 3-D Ising model.[10] It is slightly closer to the exponent for the 2-D antiferromagnets of the class[11] K_2NiF_4 for which the most recent determinations by Ikeda, Suzuki, and Hutchings[12] show true 2-D Ising behavior with $\beta \simeq 0.125$. Clearly a very anisotropic (essentially 2-D) interaction Hamiltonian is responsible for the intraplane ordering. Presumably a weak longer-range interaction between planes[13] results in simultaneous interplane and intraplane ordering with no apparent transition regime from 2-D to 3-D behavior.

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Nature of the Bond in Hydrogen Chemisorption on Ni, Pd, and Pt

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We describe a model of H chemisorption on Ni, Pd, and Pt in which both extended sp bands and the more localized d bands are appropriately incorporated. It is found that interaction between the H $1s$ level and the substrate d levels plays an important role which increases in the order $\mathrm{Ni} > \mathrm{Pd} > \mathrm{Pt}$. The results are in good accord with ultraviolet-photoelectron-spectroscopy data.

The chemisorption of hydrogen on such metals as Ni, Pd, and Pt has been extensively studied experimentally. Many theoretical calculations[1-5] exist on these systems but a clear insight into the nature of the bond still seems to be lacking.

Ultraviolet photoelectron spectroscopy (UPS) studies[6] on the Ni(111), Pd(111), and Pt(111) surfaces show a peak below the d band induced by H chemisorption, described in Anderson-model theories as a $1s$-d bonding state. This contrasts clearly with the much simpler H-jellium system, where first-principles calculations[7] reveal the