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Brief Reports

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Molecular-dynamics study of two-dimensional liquid K intercalated in graphite

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Following previous work on Rb intercalated in graphite, a molecular-dynamics study of potassium intercalated in graphite has been performed using an experimentally determined host-intercalant modulation potential. The circularly averaged static structure factor $S(q)$, the transform of the number density $\langle \rho_q \rangle$, the anisotropic liquid $S(\mathbf{q})$ at 300 and 200 K, and the angular modulation of the diffuse scattering are calculated. Excellent quantitative agreement with the experimental data is obtained.

The alkali metals are donor-type intercalants in graphite and at room temperature form an ordered stack of two-dimensional (2D) liquids uncorrelated from layer to layer that are incommensurate with the in-plane spacing of the graphite host lattice.[1] The structure of potassium intercalated in graphite ($\sim C_{24}K$) is similar to rubidium intercalated in graphite ($\sim C_{24}Rb$), with some notable differences. The potassium atom is smaller than rubidium and the spacing between the intercalated carbon layers is therefore shorter for K (5.4 Å) than for Rb (5.7 Å). As a consequence the potassium atoms are more strongly influenced by the host potential. In addition, the modulation potential for potassium[2] shows enhanced local minima over the carbon atoms; these minima are not present for rubidium[3] where the modulation potential could be well represented by a set of six simple sinusoidal terms (along the six equivalent directions of the hexagon).

The present molecular-dynamics (MD) simulation was performed following the procedure of Fan *et al.*[4] The critical input in the MD is the graphite-K modulation potential noted above, which was furnished by Kan *et al.*[2] though a careful x-ray scattering measurement of the K contribution to the *HK.L* graphite Bragg peaks. This potential will, in general,[5] take the form

$$V_m(r)=\sum_{H,K} V_{HK}e^{i\mathbf{q}_{HK}\cdot\mathbf{r}} ,$$

where q_{HK} is reciprocal-lattice vector of the graphite. The contribution to the potential due to the K-K repulsive interaction is the Vischer-Falicov repulsive screened potential[6] adapted by Plishke[7] for 2D liquids,

$$V_p(r)=\frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{r}-y(r)\right],$$

where $y(r)$ is the screening contribution; ϵ_0 is the effective dielectric constant that may be retained as the single adjustable parameter in our calculation aside from the in-plane density. (The familiar core-core repulsive term is not experienced by these partially screened ions.)

The MD simulation and all the structure calculations (Fourier transforms) were carried out on a Sun 4 computer using a periodic rhombic box of 36×36 graphite cells. The time step in the simulation was $\Delta t = 0.04$ ps. The total number of configurations used to calculate the statisti-

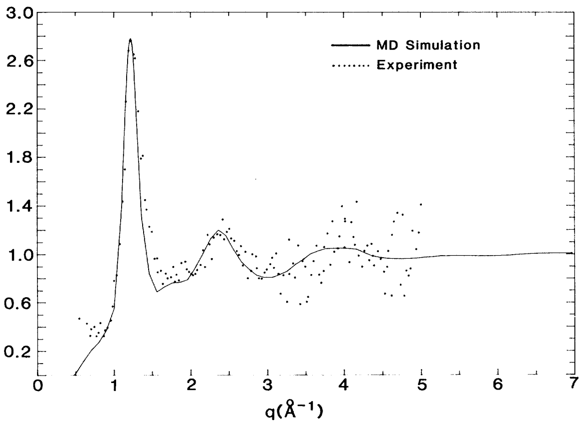

FIG. 1. Comparison of the circularly averaged liquid structure factor $S(q)$ obtained by MD simulation with the experimental data obtained for stage-2 K in HOPG (Ref. 8). The position of the first sharp peak is at $q = 1.22$ Å^{-1}. The experimental graphite Bragg peak (10.0) peak at 2.94 Å^{-1} has been removed along with the (11.0) peak at ~ 5.0 Å^{-1}; in the calculation these peaks were removed analytically.

TABLE I. Comparison of experimental and MD determinations of the Fourier transform of the potassium number density $\langle \rho'_{q_{HK}} \rangle$ at two in-plane densities.

HK	Experimental (Ref. 2)	MD ($KC_{11.52}$)	MD ($KC_{11.02}$)
10	0.52±0.03	0.48	0.46
11	0.31±0.03	0.31	0.31
20	0.25±0.03	0.21	0.20
21	0.08±0.03	0.07	0.06
30	0.11±0.03	0.09	0.09
22	0.02±0.03	0.03	0.03

cal average for both the circularly averaged static liquid structure factor $S(q)$ and the anisotropic liquid structure factor $S(\mathbf{q})$ is $N=280$. The time separation between two successive configurations was $100\Delta t$. As noted above, the adjustable parameters were the dielectric constant ϵ_0 and the alkali in-plane density ρ_0. Both of these parameters were chosen to fit the first sharp diffraction peak (FSDP) in the experimental $S(q)$ at $q=1.22$ Å^{-1}.

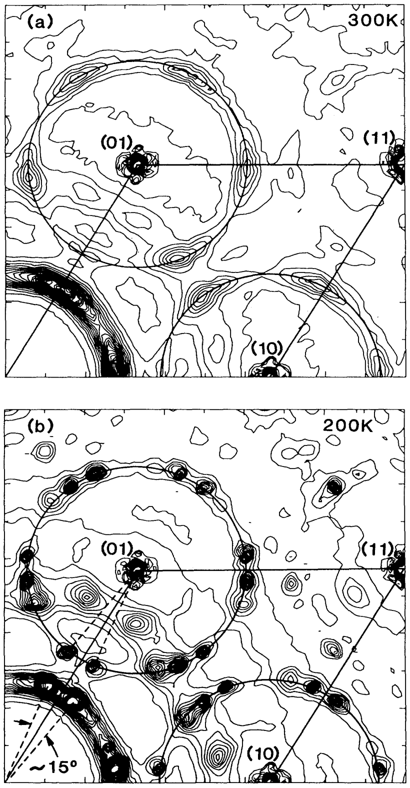

FIG. 2. (a) Anisotropic structure factor $S(\mathbf{q})$ via MD simulation at room temperature (300 K). The characteristic features of the liquid pattern are (i) contribution of K at the {10} graphite Bragg peaks, (ii) anisotropic modulated liquid scattering, and (iii) modulation halos about the {10} positions indicated by circles; there is also a weaker halo about {11}. (b) $S(\mathbf{q})$ by MD simulation at 200 K. On cooling, the diffuse scattering in the first ring concentrates into a pair of diffuse spots rotated by an angle of ~7.5° with respect to the graphite ⟨10.0⟩ directions.

Figure 1 shows the comparison between the calculated $S(q)$ and the experimental x-ray scattering data[8] obtained from a sample of highly oriented pyrolytic graphite (HOPG) intercalated to $\sim C_{24}K$. As in Ref. 4 the Bragg contributions have been analytically removed. The FSDP is fit very well, but for larger q, while the calculation appears to go through the data, the experimental accuracy is not good enough to make any real comparison. At this time, unfortunately, these are the only experimental data for $S(q)$ that are available. The value of the dielectric constant was fixed at $\epsilon_0=1.8$ and the in-plane density was set, through several trials, at $C_{11.02}$ K corresponding to 235 atoms of K in the rhombic graphite box.

In Table I we present the calculated values of the Fourier transform of the number density $\langle \rho' q_{HK} \rangle$, where

$$\langle \rho'_{q_{HK}} \rangle = \frac{1}{N} \left\langle \sum_i e^{i\mathbf{q}_{HK}\cdot\mathbf{r}_i} \right\rangle$$

for two different in-plane densities $C_{11.02}$ K and $C_{11.52}$ K and compare them with the experimental values obtained by Kan *et al.*[2] While the MD values of $\langle \rho'_{HK} \rangle$ for $C_{11.52}$ K are in slightly better agreement with the experiment, we have chosen the $C_{11.02}$ K concentration because it fits the data better for $S(\mathbf{q})$. (The experimental value[2] for this in-plane density was also $C_{11.52}$ K.)

The anisotropic structure factor $S(\mathbf{q})$ is calculated for liquid K in graphite at 300 K [Fig. 2(a)] and at 200 K [Fig. 2(b)] in which, as in Ref. 4, the Bragg contributions are now left in place. Certain features emerge from these contour plots. At 300 K, the characteristic diffuse scattering from the alkali liquid around the origin (00)

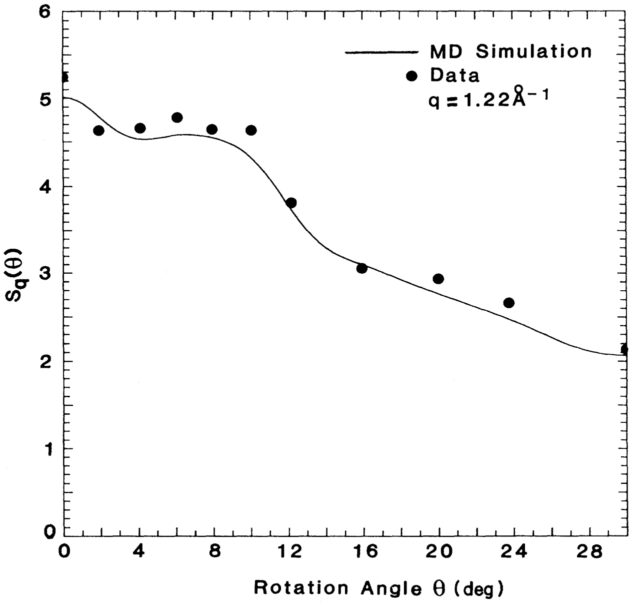

FIG. 3. Comparison of the MD-calculated angular modulation of the 300 K diffuse scattering in the first sharp peak at $q=1.22$ Å^{-1} with the experimental data (Ref. 11); the rotation angle θ is from the ⟨10.0⟩ direction in graphite.

and the anisotropy in this diffuse scattering are clear. Figure 2(a) shows a 90° segment of the (averaged) reciprocal lattice in which two of the six peaks in the modulation intensity, roughly in the $\{10.0\}$ direction, are noticeable. Also present are (anisotropic) halos of diffuse scattering about the (10) and (01) graphite positions, roughly reproducing the liquid scattering about the origin as predicted[5] and observed in a $C_{24}Rb$ crystal.[4] That this halo also appears weakly about (11) is a consequence of the magnitude of the Fourier coefficient V_{11} (compared to V_{10}). In the Rb compound[3] the ratio $V_{10}/V_{11}=7.5$; in the present K compound[2] it is $V_{10}/V_{11}=2.2$. Inasmuch as the halo intensity is roughly proportional to V_{HK}^2 (Ref. 5), we would expect a significant enhancement of the (11) halo in $C_{24}K$ over $C_{24}Rb$. While for $C_{24}Rb$ there is no observable halo about (11), in the present calculation it is clearly discernible.

In Fig. 2(b) at 200 K, the diffuse scattering on the principal ring forms two separate maxima about each $\{10.0\}$ direction and the angle between them is $\sim 15°$, corresponding to $\sim 7.5°$ rotation angle of the alkali structure with respect to the graphite lattice, in agreement with the experimental value of Mori *et al.*[9] and Rousseaux *et al.*[10] for the solid phase. We have also calculated the angular modulation of the diffuse scattering around the first diffraction ring at 300 K and Fig. 3 shows a comparison of the computed profile with the experimental data of Rousseaux and co-workers.[11] We may see that the intensity maxima are centered about the $\langle 10.0 \rangle$ graphite direction for K as already pointed out by Rousseaux *et al.*,[10] instead of the $\langle 11.0 \rangle$ graphite direction as in Rb,[12] and the agreement between the two curves is quite satisfactory. In other words, for K the intensity is a maximum along $\langle 10.0 \rangle$ while for Rb it is a minimum in that direction.

In summary, we have presented a MD calculation for $\sim C_{24}K$ to compare with the experimental determination of $\langle \rho'_{q_{HK}} \rangle$, $S(q)$ for HOPG and $S(\mathbf{q})$ for single crystals. The agreement is quite good in most of the details, although the in-plane K density required for this agreement is slightly greater than experimentally observed ($C_{11.02}$ K versus $C_{11.52}$ K). This comparison for 2D liquid potassium in graphite is important because the graphite-potassium modulation potential as determined by Kan *et al.*[2] differed substantially from the graphite-rubidium potential in Moss *et al.*[3] We should, however, note here that on further cooling the 2D potassium layer appears to freeze into a distorted hexagonal structure, which does not agree in detail with the experimental findings.[8-10] This inclination is already revealed at 200 K in Fig. 2(b), where all of the diffuse peaks do not fall exactly on the modulation circle or halo.

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