"bare" surface tension σ_0 is used in Eq. (2), with

$$\sigma_0 = \sigma + (3/16\pi) k_B T k_{\max}^2. \tag{4}$$

In this case, theory predicts (with $k_{\max} = 2\pi/t_w$) $\sigma_0 = 18.8$ erg/cm^2 and $t_w(\text{erf}) = 6.67$ Å at 90 °K, which when subtracted from the experimental value leaves an intrinsic component $t_i(\text{erf}) = 4.8 + 0.6$ Å, increasing to 11.3 Å at 120 °K.

Computer simulation[9-11] can handle only a small number of atoms, with, consequently, a small surface dimension. With a surface dimension of $5d$, Ref. 9 finds $t = 1.7d$, while Ref. 10 with a surface dimension of $4d$ finds $t = 1.3d$. Simulations which vary the area of the surface[9] find a slow increase in the thickness as the surface dimension increases, and give support to the suggestion of an intrinsic plus a wave contribution. Kalos, Percus, and Rao[11] have found transverse correlations in their simulated interface, which appears rough rather than uniform.

In summary, the ellipsometry study reported here provides for the first time a measurement on a simple liquid to compare with theory, and it is evident that further theoretical work is needed to clarify the nature of, and the interaction of light with, the liquid-vapor interface.

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[1] F. P. Buff, R. A. Lovett, and F. H. Stillinger, Phys. Rev. Lett. 15, 621 (1965).

[2] R. A. Lovett, P. W. De Haven, J. J. Vieceli, and F. P. Buff, J. Chem. Phys. 58, 1880 (1973).

[3] B. Widom in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1972), Vol. 2.

[4] J. D. Weeks, J. Chem. Phys. 67, 3106 (1977).

[5] H. T. Davis, J. Chem. Phys. 67, 3636 (1977).

[6] F. F. Abraham, Phys. Rep. 53, 93 (1979).

[7] J. Lekner and J. R. Henderson, Physica (Utrecht) 94A, 545 (1978).

[8] J. Lekner and J. R. Henderson, Mol. Phys. 34, 333 (1977).

[9] G. A. Chapela, A. Saville, S. M. Thompson, and J. S. Rowlinson, J. Chem. Soc., Faraday Trans. 2 73, 1133 (1977).

[10] F. F. Abraham, D. E. Shreiber, and J. A. Barker, J. Chem. Phys. 62, 1958 (1975).

[11] M. H. Kalos, J. K. Percus, and M. Rao, J. Stat. Phys. 17, 111 (1977).

[12] C. V. Raman and L. A. Ramdas, Philos. Mag. 3, 220 (1927); C. Bouhet, Ann. Phys. (Paris) 15, 5 (1931); V. A. Kizel, Zh. Eksp. Teor. Fiz. 29, 658 (1955) [Sov. Phys. JETP 2, 520 (1956)].

[13] S. N. Jasperson and S. E. Schnatterly, Rev. Sci. Instrum. 40, 761 (1969).

[14] P. Drude, *The Theory of Optics* (Dover, New York, 1959).

[15] A. C. Sinnock and B. L. Smith, Phys. Rev. 181, 1297 (1969).

[16] F. Abelès, Ann. Phys. (Paris) 5, 596 (1950).

[17] P. J. Castle and J. Lekner, to be published.

[18] D. Stansfield, Proc. Phys. Soc., London 72, 854 (1958).

Positional and Orientational Correlations in the Graphite Intercalate $C_{24}Cs$

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An x-ray study of the Cs layers in $C_{24}Cs$ is presented. The Cs layer has a uniform 2-d liquidlike structure at 300 K not in registry with the graphite layers. A crossover to 3-d interlayer correlation is observed at 165 K. Single-crystal measurements show that the Cs layers rotate relative to the graphite ⟨100⟩ directions. An orientational ordering between two positionally disordered phases occurs at 228 K and a new transition to a mixed registered phase at 50 K is reported.

There have been several recent studies[1-5] of alkali-metal graphite intercalates showing an interesting variety of ordering phenomena associated with the intercalant atoms. These systems provide a unique arena for studying the melting of layers of metal atoms under varying degrees of interlayer coupling as the intercalation "stage," n, is varied (n = number of carbon layers between intercalant layers). This Letter describes a detailed x-ray study of the structure and temperature dependence of such intercalant layers in a higher-stage ($n = 2$) compound, $C_{24}Cs$. We will show that *orientational* correlations of the intercalant interatomic bonds, which have been ignored in previous studies, are very important for a complete description of the physical properties of some of the higher-stage cesium intercalates.

X-ray diffuse scattering experiments were carried out on samples prepared from two forms of graphite, namely, highly oriented pyrolytic graphite (HOPG) and natural single crystals of Madagascar graphite. In both cases, the samples were intercalated to stage 2, with use of the method of Hérold,[6] and sealed in Pyrex ampoules. X-ray intensities were measured on a Picker four-circle diffractometer fitted with a closed-cycle helium refrigerator. The x-ray source was a Rigaku 12-kW rotating-anode generator.

In contrast to C_8Cs, the intercalant layer in $C_{24}Cs$ is disordered[1] at 300 K. The in-plane structure factor $S(k)$ ($k \equiv 4\pi \sin\theta/\lambda$) is shown in Fig. 1(a). Sharp reflections from the graphite host were subtracted from the raw data and corrections were made for polarization, absorption, and Compton scattering. Note that $S(k)$ has the appearance of a simple close-packed liquid-metal structure factor. We will show later that interlayer positional correlations are effectively absent at 300 K and hence that a two-dimensional (2-d) analysis is appropriate here. The planar radial distribution function (RDF) [$\equiv 2\pi r\rho(r)$, $\rho(r)$ = areal atomic density], shown in Fig. 1(b), was obtained by performing a Fourier-Bessel inversion:

$$2\pi r\rho(r) = 2\pi r\rho_0 + r\int_{k=0.6\ \text{Å}^{-1}}^{k=15\ \text{Å}^{-1}} k[S(k)-1]J_0(kr)\,dk, \qquad (1)$$

where ρ_0 is the average areal density and $J_0(kr)$ is the zeroth-order Bessel function.

The important features of Fig. 1(b) are, firstly, the series of peaks at multiples of roughly 6 Å and, secondly, the area under the first peak which returns a first-shell coordination number of 6 ± 0.25. The integral RDF over the measured range of $r \leq 30$ Å is within 1% of the value calculated if we assume a mean *layer* stoichiometry of $C_{12}Cs$, indicating that the stoichiometry of our sample is accurately $C_{24}Cs$. Also, taking the areal density of Cs as 3.18×10^{-2} atoms/Å^2, corresponding to the above layer stoichiometry, and assuming a uniform, close-packed Cs layer, we calculate a 6.02-Å mean separation of Cs atoms which is close to the figure we obtain directly from the RDF. These facts together show that the Cs layer is *uniform, disordered, and has triangular short-range order* [see inset of Fig. 1(a)]. The nearest-neighbor Cs-Cs distance of 5.95 ± 0.1 Å is *not* related to a simple multiple of the distance, a_0, between carbon-hexagon centers [the closest such multiple would be $(7)^{1/2}a_0 = 6.51$ Å] and thus we conclude that, on average, the Cs atoms do not occupy sites over the center of carbon hexagons. This observation is contrary to a widely held view in the literature[1,7,8] that registry of the intercalant atoms with the graphite host (e.g., 2×2 for C_8Cs, $(12)^{1/2} \times (12)^{1/2}$ for $C_{24}Cs$ [7]) is required to explain the well-defined stoichiometries of these compounds.

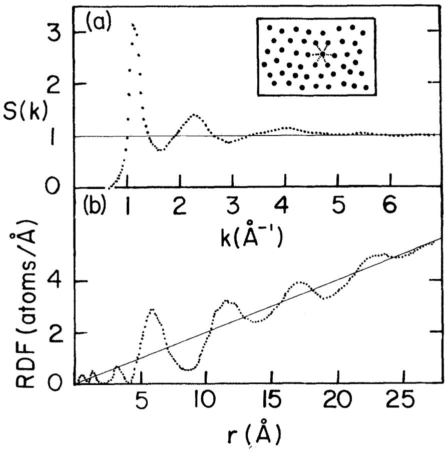

FIG. 1. (a) Structure factor $S(k)$ for the Cs layer in an HOPG sample of $C_{24}Cs$ at 300 K. Our data extend to 15 Å^{-1} but are not shown here. (b) Radial distribution function from $S(k)$ in (a) (The small ripples at $r < 3.5$ Å are finite-k artifacts.) Inset: short-range order of Cs layer.

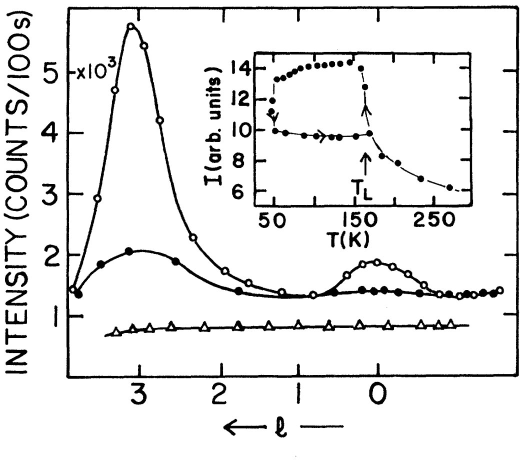

FIG. 2. Scans parallel to c^* with the projection of the diffraction vector on the Cs layer held constant at 1.158 Å^{-1} (for the same sample as in Fig. 1). Solid lines are guides to the eye. Open triangles, 300 K; closed circles, 170 K; open circles, 130 K. Inset: temperature dependence of intensity of the in-plane Cs peak at $q_0 = 1.158$ Å^{-1}, $l = 0$. (See text for discussion.)

We now turn to the positional ordering of the disordered Cs layer. In Fig. 2 (inset) is plotted the peak intensity of the first peak of the in-plane $S(k)$ shown in Fig. 1(a). It is seen that at a temperature $T_L = 165$ K there is a sharp inflection in the temperature dependence of this peak intensity. At approximately the temperature T_L an anomaly has been observed[9] in the electrical resistivity of $C_{24}Cs$ and it had been supposed that this anomaly was associated with the 3-d ordering of the intercalant layers.[1,9] However, we do not observe true Bragg scattering below T_L, with peaks of resolution-limited width, but rather in-plane linewidths which continue to become narrower on cooling below T_L, indicating temperature-dependent intralayer correlations.

To understand the significance of the temperature T_L, it is necessary to probe the interlayer correlations of Cs atoms. Figure 2 shows a series of scans along the reciprocal row line $(10l)$, corresponding to the first peak in $S(k)$. It is seen that the intensity is constant parallel to the reciprocal c axis, c^*, at 300 K, indicating no significant Cs interlayer correlations. However, as T_L is approached, intensity starts to build up around the (103) position signaling the growth of 3-d correlations in the sample. It is thus seen that T_L marks not the onset of traditional long-range order within the Cs layers but a crossover in the dimensionality of the system to 3-d interlayer coupling below T_L. A further feature of Fig. 2 is that, along c^*, the peaks are rather broad below T_L. A comparable broadening has been observed[3] in $C_{24}K$ and was interpreted as being due to stacking faults introduced into the graphite host by the intercalation process. In our case, the mean size of unfaulted regions along the c axis is calculated[10] to be ~40 Å and interlayer positional correlations are limited to this extent in $C_{24}Cs$.

Referring to the peak intensity shown in Fig. 2 (inset), we also draw attention to a new phase transition which we have observed to occur at approximately 50 K. The transition is strongly discontinuous with pronounced thermal hysteresis and seems to be associated with a breaking up of the uniform incommensurate Cs layer into macroscopic (>500 Å) 2×2 and 3×3 commensurate regions. On cooling, several reflections from the 2×2 superlattice start to appear at approximately 140 K, the upper stability limit of this mixed phase. Thus, we see that at sufficiently low temperatures the graphite potential dominates the ordering of the Cs layer.

In the intercalated HOPG samples, which were used to obtain data on the positional correlations described above, the a and b axes of the graphite host are powder averaged. Consequently, information on the orientational order within the basal planes is lost. In order to obtain this information, single-crystal samples must be used. At temperatures below T_L the in-plane diffraction pattern[1,10] of $C_{24}Cs$ single crystals consists of rings of 12 reflections from the cesium layer grouped around each graphite reciprocal-lattice point. A schematic of the primary ring of cesium reflections, each with wave-vector transfer $q_0 = 1.16$ Å^{-1} corresponding to the first peak in $S(k)$, is shown in Fig. 3 [inset (b)]. We can explain all of the main features of the in-plane diffraction pattern on the basis of a uniform Cs layer, with triangular symmetry which is incommensurate with the graphite bounding layers. The structure of the Cs layer will be modulated by the graphite potential having a fundamental reciprocal-lattice vector $\vec{q}_G$, where $q_G = 2.94$ Å^{-1}. The strain associated with the misfit (about 22% in our case) of the intercalant layer with respect to the graphite layers gives rise to a static-distortion wave (SDW)[11] which manifests itself in the appearance of satellite reflections having wave vectors $\vec{q}_0 \pm \vec{q}_G$, for example. Given the large misfit, the satellite reflections are unusually intense.[12] However, the Cs atoms are loosely packed in $C_{24}Cs$. Their interionic distance is 6.0

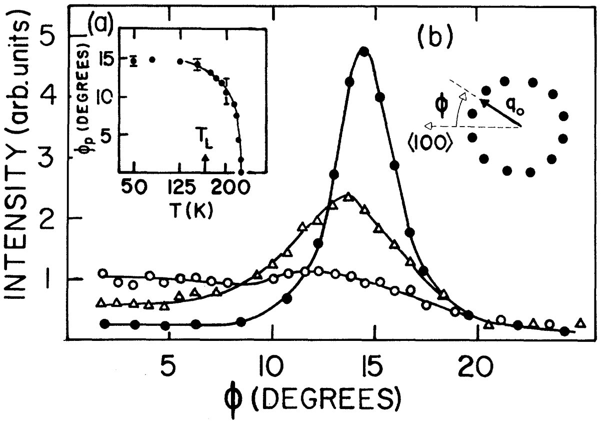

FIG. 3. Temperature dependence of one of the 12 primary $q = q_0$ sidebands in a single-crystal sample of $C_{24}Cs$. Closed circles, 148 K; open triangles 169 K; open circles, 185 K. Inset (a): Temperature dependence of the angular position of the sideband, φ_p, relative to a graphite ⟨100⟩ direction. The solid line is a power-law fit to the data (see text). Inset (b): geometry of χ scans used to obtain data in the figure.

Å at 300 K while the corresponding distance in bulk liquid Cs is 5.4 Å. Therefore the unregistered $C_{24}Cs$ structure is highly susceptible to SDW modulations even at 22% misfit.

For the simpler case of a rare-gas monolayer physisorbed onto a graphite substrate, Novaco and McTague[11] have shown that SDW terms in the free energy of the overlayer lead to a rotation, φ, or so-called "orientational epitaxy" of the overlayer relative to the graphite substrate. The effect was first observed in low-energy electron diffraction studies of incommensurate Ar overlayers on graphite.[13] In those studies domains were observed in which rotations occurred in both positive and negative senses from the graphite high-symmetry axes, leading to two counterrotated sixfold diffraction patterns. When superposed, these result in a pattern with six pairs of spots similar to the one shown in Fig. 3(b).

Figure 3 shows a series of χ scans (in the usual four-circle terminology) taken with a fixed diffraction vector $q_0 = 1.158$ Å^{-1} lying in the basal plane of intercalant atoms. The crystal is rotated about the basal-plane normal to record the intensity modulations around $k = q_0$ diffraction ring shown in Fig. 3(b). We have observed that, below $T_L = 165$ K, the angular width of the sideband shown in Fig. 3 is constant at approximately 3.5° and is not related to the in-plane mosaic of the graphite structure (0.4°) consistent with our conclusion that the Cs layer is not registered with the graphite layers. More importantly, Fig. 3 shows that the angular position of the peak, φ_p, is observed to shift continuously towards a graphite $\langle 100 \rangle$ direction as the temperature is increased and at $T_u = 228 \pm 3$ K [Fig. 3, inset (a)] becomes centered on $\langle 100 \rangle$. This preferred orientation, about the graphite $\langle 100 \rangle$ direction, persists up to at least 300 K and reflects the influence of the graphite potential on the orientation of the disordered Cs layer. Note that as the temperature increases, the sideband becomes broader and its peak intensity decreases, the integrated intensity remaining approximately constant throughout the whole temperature range.

The temperature dependence of φ_p shown in Fig. 3(a) suggests that an orientational ordering of the Cs layer sets in below the temperature T_u. We may picture the Cs-Cs bond directions as being distributed over two counterrotated Ising-like states, $\pm \varphi_t$. With this analogy φ_p would be the order parameter for the transition. We have measured the temperature exponent of φ_p to be $\beta = 0.46 \pm 0.07$ within a reduced-temperature range $0.03 \leq t \leq 0.30$ $[t \equiv (T_u - T)/T_u]$. This value presumably reflects the 3-d nature of the orientational ordering of the Cs-Cs bonds, as is evident from our observation of the well-defined preferred orientation described above.

Another possible explanation for the transition at T_u is the case proposed recently by Halperin and Nelson[14] in which melting proceeds via a liquid-crystal–like "hexatic" phase with relatively long-range orientational order, to the isotropic liquid. Their theory is derived fro a 2-d continuum. In view of the 3-d nature of the orientational order and the clear indications that interactions with the graphite bounding layers are very important for the orientational transition at T_u, it is unlikely that such a theory will be applicable to our case.

Finally, Onn, Foley, and Fischer[9] have observed a resistivity anomaly at approximately 236 K in $C_{24}Cs$, in addition to the one at T_L discussed above, which was associated with the growth of 3-d positional correlations. The former temperature is close to that at which we have observed the orientational transition at T_u.

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[1] G. S. Parry, Mater. Sci. Eng. 31, 99 (1977).

[2] R. Clarke, N. Caswell, and S. A. Solin, Phys. Rev. Lett. 42, 61 (1979).

[3] J. B. Hastings, W. D. Ellenson, and J. E. Fischer, Phys. Rev. Lett. 42, 1552 (1979).

[4] W. D. Ellenson, D. Semmingsen, D. Guérard, D. G. Onn, and J. E. Fischer, Mater. Sci. Eng. 31, 137 (1977).

[5] Per Bak and Etan Domany, to be published.

[6] A. Hérold, Bull. Soc. Chim. Fr. 187, 999 (1955).

[7] W. Rüdorff and E. Schulze, Z. Anorg. Chem. 277, 156 (1954).

[8] F. J. Salzano and S. Aronson, J. Chem. Phys. 42, 1323 (1965).

[9] D. G. Onn, G. M. T. Foley, and J. E. Fischer, Mater. Sci. Eng. 31, 271 (1977).

[10] R. Clarke, N. Caswell, S. A. Solin, and P. M. Horn, to be published.

[11] A. D. Novaco and J. P. McTague, Phys. Rev. Lett. 38, 1286 (1977).

[12] P. W. Stevens, P. Heiney, R. J. Birgeneau, and P. M. Horn, Phys. Rev. Lett. 43, 47 (1979).

[13] C. G. Shaw, S. C. Fain, Jr., and M. D. Chinn, Phys. Rev. Lett. 41, 955 (1978).

[14] B. I. Halperin and D. R. Nelson, Phys. Rev. Lett. 41, 121 (1978).

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, $hk0$ 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 ($hk0$) (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 $hk0$ 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