X-ray scattering from a two-dimensional liquid modulated by its periodic host

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We present a treatment of the x-ray scattering from a two-dimensional (2D) liquid modulated by its periodic host. While this is general for all fluids within (or upon) periodic lattices, we concentrate on alkali metals intercalated in graphite to reveal the origin of the following: (a) the alkali-metal contribution to the graphite Bragg peaks, (b) the replication of the alkali-metal liquid scattering about the graphite reciprocal-lattice points, and (c) the anisotropic sixfold angular modulation of the normally isotropic 2D liquid scattering. While the first is linear in the relevant Fourier coefficients of the modulation potential, the latter two appear to second order. Finally we indicate a method for accurately evaluating the above Fourier coefficients from graphite Bragg peak intensities in the disordered (liquid) state of the intercalated alkali-metal species, which includes corrections for correlations in the liquid.

I. INTRODUCTION

In the study of intercalate and overlayer systems we encounter two-dimensional (2D) fluids in, or adsorbed on, a periodic host crystal with which they interact. These fluids or liquids exist basically in a disordered state at high temperature only weakly perturbed by the host potential. As the temperature is lowered, the in-plane correlations increase, along with substrate effects, leading eventually to often complex ordering in two dimensions with the third dimension entering, in the staged intercalates, as a weak perturbation. In the alkali-metal—graphite intercalation systems with which we will be mainly concerned, there is ample evidence of the two dimensionality of these liquids.[1-4] They are distinguished by the following observations.

(1) At room temperature in stage $n \geq 2$, where n is the number of graphite basal planes separating the periodically spaced alkali-metal layers, the liquid structure has a basic in-plane spacing incommensurate with its graphite host and it cannot be treated as a simple disordered lattice gas.[5-7]

(2) The circular average of the liquid structure factor of all the alkali metals studied shows a familiar liquidlike diffuse scattering associated with an alkali-metal spacing of about 5.90—6.10 Å and a coordination number of six.[3,5]

(3) The liquid scattering pattern observed in a single crystal, first by Parry[8] in $C_{24}Cs$ and more recently by Rousseaux, Moret, and co-workers in $C_{24}K$ (Refs. 9 and 10) and $C_{24}Rb$ (Ref. 10), shows clearly that the circularly averaged diffuse scattering measured in highly oriented pyrolytic graphite (HOPG) is actually anisotropic; the 2D liquid is perturbed by its periodic host into a pronounced sixfold angular intensity variation whose maxima appear roughly along [11.0] for $C_{24}Cs$ (Ref. 8) and $C_{24}Rb$ (Ref. 10) and along [10.0] for $C_{24}K$ (Ref. 9). In addition, the anisotropic liquid pattern appears to be repeated as halos about the set of six {10.0} graphite reciprocal-lattice points; it does not seem, however, to have been observed about {11.0} and higher positions. Figure 1 presents the room-temperature x-ray photos of Rousseaux *et al.*[9,10] in

which these substrate effects on the 2D liquid may be seen. Schematic summaries of the effects are included.

(4) The disordered alkali-metal atoms make a pronounced contribution to the graphite Bragg peak intensities.[11] This has been confirmed in a set of recent experiments[4,12] in which this contribution was treated as evidence of either partial registry[4] or host modulation of the 2D liquid.[12]

(5) The alkali-metal liquid and the ordered state at lower temperature both demonstrate a dynamical response, as determined by incoherent inelastic neutron scattering, characterized by a two-peak frequency distribution (phonon density of states) which is not very temperature dependent.[13] The liquid also shows diffusional behavior typical of both a (registered) hopping solid and a (unregistered) diffusing liquid,[14] where the solidlike behavior dominates at lower temperature as ordering proceeds.

Clearly a theoretical perspective is needed. The present treatment analyzes the variety of diffraction data from the standpoint of a 2D alkali-metal liquid modulated by its graphite host. It is a detailed development of the theory sketched briefly in Ref. 12. Other theoretical treatments include Bunde and Dieterich,[15] who introduced a sinusoidal perturbation into a one-dimensional Percus-Yevick liquid to demonstrate modulation effects including Bragg peak contributions. Plischke[16] carried out a detailed study of the unmodulated 2D liquid, and Plischke and Leckie[17] performed Monte Carlo simulations in the presence of a simple (sinusoidal) substrate potential to study both the liquid and its freezing. Our own treatment develops the scattering formalism far enough to extract realistic modulation potentials from available diffraction data and shows clearly both the origin and form of the (static) structure effects discussed above.

II. THEORY

A. Bragg contributions

We begin with a 2D alkali-metal liquid layer in its graphite host. We choose Rb as we shall wish to make exper-

(a)
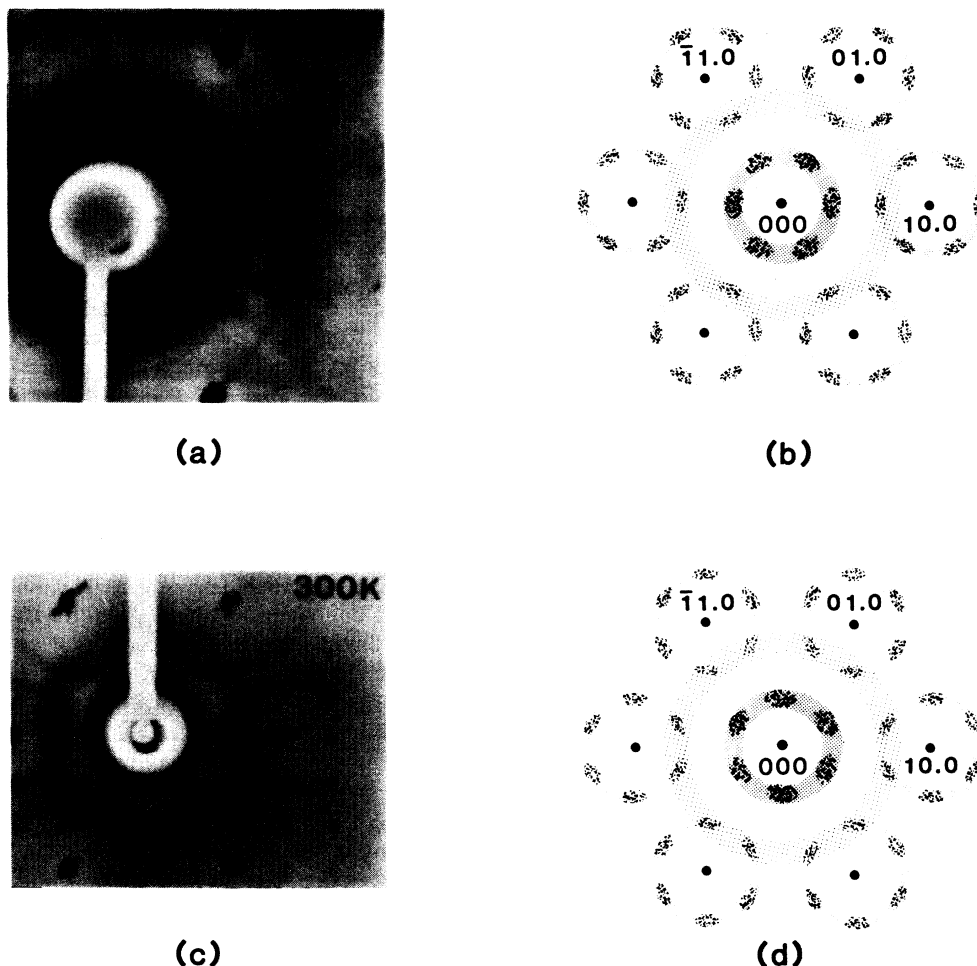

(b)

(c)

(d)

FIG. 1. (a) and (c), single-crystal x-ray photos from Rousseaux *et al.* (Refs. 9 and 10); (b) and (d), schematic representation of the principal effects including angular variation of the diffuse scattering and halos. The distortion in the data, due to cylindrical film geometry is not reproduced in (b) or (d). (a) and (b): $C_{24}K$ with peaking roughly in [10.0]; (c) and (d): $C_{24}Rb$ with peaking roughly in [11.0].

imental comparisons with $C_{24}Rb$.[12,18] The formalism, of course, applies equally well to all species that intercalate, or for that matter, exist as monolayer liquids on a periodic substrate surface.[19] Because the Rb layers are uncorrelated, we need only treat a single layer subject to the perturbing potential of the bounding graphite sheets. These sheets are known to be positioned directly over each other[1] which greatly simplifies the treatment. The perturbing potential may be written

$$V(\mathbf{r}) = \sum_i v(\mathbf{r} - \mathbf{R}_i) , \tag{1}$$

where $\mathbf{r}$ is a continuous position vector in the alkali-metal layer, $\mathbf{R}_i$ are the lattice vectors of the graphite, and $v(\mathbf{r})$ is the effective interaction potential for a single pair of intercalate and graphite atoms. If $\mathbf{R}_{\parallel}^i$ is any in-plane component of a graphite lattice vector,

$$V(\mathbf{r} + \mathbf{R}_{\parallel}^i) = V(\mathbf{r}) , \tag{2}$$

whereby the potential has the periodicity of the 2D graphite lattice. It therefore may be expanded as

$$V(\mathbf{r}) = \sum_{H,K} V_{HK}(z) e^{2\pi i (H\mathbf{b}_1 + K\mathbf{b}_2)\cdot\mathbf{r}} , \tag{3}$$

where z is the out-of-plane coordinate and $q_{HK} = 2\pi(H\mathbf{b}_1 + K\mathbf{b}_2)$ is a graphite reciprocal-lattice vector. We will assume for simplicity that only the $H=0$, $K=0$ term has a significant z dependence, and obtain

$$V(\mathbf{r}_{\parallel}, z) = V_0(z) + \sum_{H,K} V_{HK} e^{2\pi i (H\mathbf{b}_1 + K\mathbf{b}_2)\cdot\mathbf{r}_{\parallel}} . \tag{4}$$

$V_0(z)$ confines the alkali metal in the plane. The z dependence of the V_{HK} that we have neglected introduces a coupling between the z motion and the (x,y) motion. In the absence of this coupling, the density matrix for the system factors into a product of density matrices for the z and (x,y) configurations and the coefficient V_{HK} may be regarded as the average of the $V_{HK}(z)$ over the density matrix for the z coordinates. This interpretation is strictly correct for the calculations we will present that are first order in the V_{HK}, but it is not exact for the higher-order calculations. In as much as these higher-order terms will

be important, then, one must regard the V_{HK} as effective parameters related in a nontrivial, although calculable, way to the actual Fourier coefficients of the potential in (3). Because, however, the scattering experiments measure precisely this effective potential averaged over the z displacements, we choose to leave the factoring into parallel and perpendicular contributions as indicated, even when the first-order (linear) treatment breaks down.

The Hamiltonian for the Rb atoms may be expanded in the small displacements in the z direction, and we obtain a Hamiltonian for the system that describes a two-dimensional liquid, modulated by the potential given by the second term in (4), and a set of oscillators describing the motion in the z direction. The z motion then leads only to an experimentally determined Rb Debye-Waller factor. The perturbation of the 2D fluid by the graphite potential produces static density waves in the fluid at the graphite reciprocal-lattice wave vectors which give a Rb contribution to the Bragg peaks at these wave vectors. The amplitude of these density waves, assuming the perturbing potential is not too strong, can be obtained initially from linear-response theory, treating the liquid classically.

Let $q = q_{\|} + q_{\perp}$. We wish to calculate the Fourier transform of the number density $\langle \rho_q \rangle$ where

$$\rho_q = \sum_i e^{i q \cdot r_i}$$

and the r_i are the locations of the Rb atoms. The Hamiltonian with which we calculate the average, given the approximations described, is $H = H_{Rb}^{2D} + H_{Rb}^{\perp} + H_{GRb}$ where H_{Rb}^{2D} describes the 2D fluid. It is not likely that the interaction between the intercalate atoms bears much resemblance to the potential between these atoms in the 3D liquid state as there is significant charge transfer to graphite layers. In fact, the calculations by Plischke[16] of this potential suggest that it may be purely repulsive. $H_{Rb}^{\perp}$ gives the out-of-plane motion and H_{GRb} is the modulation potential,

$$H_{GRb} = \sum_i \sum_{H,K} V_{HK} e^{-i q_{HK} \cdot r_i} .$$

q_{HK} are the graphite reciprocal-lattice vectors as noted above. To first order in the modulation, the distribution of the $r_{\|}^i$ is given by the density matrix, which we will denote by D,

$$D = \frac{e^{-\beta(H_{Rb}^{2D} + H_{Rb}^{\perp})}}{Z_{Rb}^{2D} Z_{Rb}^{\perp}} (1 - \beta H_{GRb} + \cdots) , \qquad (5)$$

where $\beta \equiv 1/k_B T$. If we denote the average over the noninteracting density matrix, given by the first term in (5), by $\langle \ \rangle_0$ and the average over D by $\langle \ \rangle$, then

$$\langle \rho_q \rangle = \langle \rho_q (1 - \beta H_{GRb} + \cdots) \rangle_0$$

$$= \sum_i \langle e^{i q_{\perp} z_i} \rangle_0 \langle e^{i q_{\|} \cdot r_{\|}^i} (1 - \beta H_{GRb} + \cdots) \rangle_0 . \qquad (6)$$

Since, for the noninteracting fluid, the density is uniform,

$$\sum_i \langle e^{i(q_{\|} \cdot r_{\|}^i)} \rangle_0 = N \delta_{q,0} ,$$

where the δ function should be regarded as a Kronecker δ. (One actually gets the Fourier transform of the sample shape here.) The average of the second term is

$$-\beta N \sum_{H,K} V_{HK} \delta_{q,q_{HK}} \left[1 + \rho \int e^{i q_{HK} \cdot r} g(r_{\|}) dr_{\|} \right] , \qquad (7)$$

where $g(r)$ is the in-plane pair correlation function for particles separated by r, and ρ is the number of particles per unit area. The term within large parentheses would be the familiar static structure factor $S(q)$ if $g(r)$ were replaced by $g(r) - 1$. At normal values of q it makes no difference and at $q = q_{HK}$ they are identical and nearly equal to 1.0. In $C_{24}Cs$, for example, Clarke et al.[3] present a circularly averaged $S(q)$ in which $S(q_{10}) \simeq 0.87$ at $q_{10} = 2.94$ Å^{-1}. At $q_{11} = 5.09$ Å^{-1}, $S(q_{11}) \simeq 1.0$. The near equivalence of $S(q)$ to unity is due to the fact that the rubidium atoms are much larger than the carbon spacing so that the first peak or maximum in the liquid $S(q)$ comes at $q_{max} \simeq 1.2$ Å^{-1} while $q_{10} = 2.94$ Å^{-1} comes well beyond the second liquid peak. To the extent that $S(q_{HK}) \neq 1.0$, a correction can be applied using the method developed in Appendix A which requires as input the measured $S(q)$. This correction includes exactly the two-particle correlations, but it neglects higher-order correlations. It is appropriate particularly when the linear approximation of Eq. (5) is not valid.

The rubidium atoms in $C_{24}Rb$ are stacked in sandwich layers with three layers to a unit cell. The full structure factor for a single sandwich layer of two graphite planes with Rb between has been presented for the case of $C_{24}Rb$ with the Rb atoms in (partial) registry.[4] Our case requires merely that the N in Eq. (7) be replaced by the number of Rb atoms per unit cell for a single carbon sandwich where each carbon sandwich contributes four atoms to this unit cell. We then may use (7) for the Rb amplitude, together with the previously derived carbon contribution, to give below the full layer structure factor, F_L, where f_C and f_{Rb} are scattering factors for the carbon and rubidium atoms, C_1 is the ratio of the sandwich or gallery spacing to the C axis, and X' gives the deviation of the Rb concentration from $C_{24}Rb$ ($X' = 1$ corresponds to $C_{24}Rb$). The stacking of the alkali-metal—graphite sandwiches in the sequence ABC/ABC affects only the structure factor selection rules:

$$F_L = 4 f_C e^{-M_C(q_{\|}) - M_C(q_{\perp})} \{ \cos[\tfrac{2}{3} \pi(H + 2K)] \cos(\pi L C_1) \}$$

$$+ \frac{X'}{6} f_{Rb} e^{-M_{Rb}(q_{\perp})} (\delta_{q_{\|},0} - \beta \delta_{q_{\|}, q_{HK}} V_{HK}) . \qquad (8)$$

This expression has recently been used[12] to obtain preliminary values of the V_{HK}'s from the measured intensities and energy dependences of the Bragg peaks in disordered $C_{24}Rb$.

If $\beta V_{HK} \ll 1$ is not satisfied, it is necessary to go to higher orders in βV_{HK}, or to go beyond perturbation theory altogether. The general expression that replaces (6) is

$$\langle \rho_q \rangle = \sum_i \langle e^{i q_{\perp} z_i} \rangle_0 \langle e^{i q_{\|} \cdot r_{\|}^i} e^{-\beta H_{GRb}} \rangle_0 / \langle e^{-\beta H_{GRb}} \rangle_0 . \qquad (9)$$

The perturbation expansion of (9) involves higher-order

correlation functions of the 2D fluid, evaluated at the wave vectors of the graphite reciprocal lattice. Given, as noted above, that there is a large mismatch in size between the alkali-metal atoms and the graphite spacing, we neglect, for the moment, alkali-metal correlations in evaluating the Bragg peak contributions. In this case we may perform the integrals associated with a complete numerical evaluation of Eq. (9) which then becomes

$$\langle \rho_q' \rangle = \langle \rho_q \rangle / N e^{-M_{Rb}^{\perp}}$$

$$= \frac{\int_0^a \int_0^a e^{i\mathbf{q}\cdot\mathbf{r}} \exp\left[-\beta \sum_{H'K'} V_{H'K'} \exp(i\mathbf{q}_{H'K'}\cdot\mathbf{r})\right] d^2\mathbf{r}}{\int_0^a \int_0^a \exp\left[-\beta \sum_{H'K'} V_{H'K'} \exp(i\mathbf{q}_{H'K'}\cdot\mathbf{r})\right] d^2\mathbf{r}}$$

$$= F_1(\mathbf{q})/F_1(0) , \qquad (10)$$

where the integration in the numerator is evaluated at $\mathbf{q}=\mathbf{q}_{HK}$ and the denominator is associated with $q=0$. The term N, the number of Rb atoms, and $e^{-M_{Rb}^{\perp}}$ appear in Eq. (8) as $X'/6$ and $e^{-M_{Rb}(q_\perp)}$ and need not concern us here. The set of $\langle \rho_{q_{HK}}' \rangle$'s are the measured quantities from which a complete set of βV_{HK}'s can be extracted through an iterative solution of (10). When $\beta V_{HK} \ll 1$, $\langle \rho_{q_{HK}}' \rangle = -\beta V_{HK}$. The integrals are, in principle, performed over a planar graphite repeat (or unit) cell of length "a" but symmetry permits a significant reduction of this task. These calculations are currently being performed with our experimental data and will be reported in a separate publication.[18] The results indicate that the linear approximation of Eq. (5) is inappropriate.

Correlations can be included in Eqs. (9) or (10) by making a cluster expansion and neglecting three-particle and higher cumulants. The result, derived in Appendix A, is

$$\langle \rho_q' \rangle = [F_1(\mathbf{q})/F_1(0)] e^{[F_2(\mathbf{q})-F_2(0)]} , \qquad (11)$$

where

$$F_2(\mathbf{q}) = \sum_{q_{H'K'}} F_1(\mathbf{q}_{H'K'}) F_1(-\mathbf{q}+\mathbf{q}_{H'K'})$$

$$\times [S(\mathbf{q}_{H'K'})-1]/F_1(0)F_1(\mathbf{q}) . \qquad (12)$$

Typically, $S(\mathbf{q}_{H'K'})-1$ is only significant for the $\{10\}$ star, and is the same for every wave vector in the star. $F_2(\mathbf{q})$ is then proportional to an average of the values of F_1 on the star surrounding the point $\mathbf{q}$ of the reciprocal lattice, divided by the value at $\mathbf{q}$. It may easily be checked that, if all V_{HK} are sufficiently small, the linear approximation for $F_1(\mathbf{q})$ is valid and Eq. (11) reduces to

$$\langle \rho_q' \rangle = \delta_{q,0} - \beta V_{HK} S(q_{HK}) , \qquad (13)$$

a result that is derivable directly from linear-response theory and which appears in Eq. (7).

As noted in Appendix A, the procedure developed for the evaluation of βV_{HK} is applicable not only to the alkali metals and acceptors in graphite but to species adsorbed on graphite and other surfaces. The above correction will become increasingly important as the ratio of adsorbate to substrate spacing decreases.

B. Modulation of the liquid pattern: halos

In addition to producing an alkali-metal contribution to the host, or substrate, Bragg scattering, the coupling discussed here also changes the diffuse scattering pattern from that of an isotropic 2D liquid to a modulated liquid pattern and produces "halos" of this anisotropic liquid scattering about the graphite reciprocal-lattice points. Both effects have been seen experimentally and are reproduced in Fig. 1. The angular variation in the diffuse scattering pattern about $q=0$ is clear. Its ghost (halo) about all graphite $\{10.0\}$ reciprocal-lattice points is weaker but evident as well. To lowest order, the change in the diffuse scattering for $q\neq0$ is

$$\delta[\langle \rho_q \rho_{-q} \rangle - |\langle \rho_q \rangle|^2] = \sum_{H,K} (\beta V_{HK})^2 \langle \rho_q \rho_{-q} (\rho_{q_{HK}} \rho_{-q_{HK}} - \langle \rho_{q_{HK}} \rho_{-q_{HK}} \rangle) \rangle , \qquad (14)$$

where there is no first-order term in (14) because of the translational invariance of the fluid in the absence of the interaction. In Eq. (14), $\langle \rho_q \rho_{-q} \rangle$ is the familiar transform of the pair correlation function while $|\langle \rho_q \rangle|^2$ is the Bragg peak intensity contribution from the alkali-metal atoms, neglecting the normal carbon contribution and the attendant carbon—alkali-metal cross terms. The diffuse scattering is then formally associated with the difference $\langle A^2 \rangle - \langle A \rangle^2$ where A is a scattering amplitude. This familiar statement is noteworthy here because an analysis of the 2D diffuse liquid scattering which neglects it will be in error. Indeed, as the experimental system is cooled and the alkali metal makes an increasingly greater contribution at the graphite reciprocal-lattice points, there will be less alkali metal left for the diffuse scattering pattern. Finally, in a fully registered lattice gas

state, the alkali-metal scattering available for the eventual ordering or superlattice reflections will be given by the Laue monotonic term, $Nx(1-x)$, where N is the number of alkali-metal atoms and x is the ratio of alkali-metal atoms to total available hexagon sites.[7]

The quadratic term above involves a four-particle correlation function given explicitly by

$$\sum_{i,j,m,n} \langle \exp\{i[\mathbf{q}\cdot(\mathbf{r}_i-\mathbf{r}_j)+\mathbf{q}_{HK}\cdot(\mathbf{r}_m-\mathbf{r}_n)]\} \rangle . \qquad (15)$$

The terms for which $m=i$ and $n=j$, or vice versa, contribute

$$\sum_{i,j} \langle e^{i(\mathbf{q}\pm\mathbf{q}_{HK})\cdot(\mathbf{r}_i-\mathbf{r}_j)} \rangle . \qquad (16)$$

This is the familiar liquid structure factor, or transform

of the pair correlations, but shifted by $\pm q_{HK}$. That is, these terms produce liquid halos about each graphite reciprocal-lattice point. (We will show in Appendix B that the terms for which $m \neq i$, $n \neq j$, which must therefore be higher order in the density, lead primarily to an angular dependence of both the central ring and the halos.) It follows, then, that the relative total intensity of the modulation halo about a particular Bragg point compared to that about the origin, at $q=0$, is $(\beta V_{HK})^2$. This provides an independent check of the measured coefficients and explains why the halos about $\{11.0\}$ are not readily observed in the x-ray photos.[8–10] In principle the halos, being a second-order effect, should be more difficult to see than the intercalate contribution to the Bragg peaks which is a first-order effect. On the other hand, the halos appear by themselves in the diffuse alkali-metal pattern so that, while their strength enters proportional to $(\beta V_{HK})^2$, they are not necessarily a less "visible" effect of the substrate perturbation than the first-order Bragg peak contribution. They will, nonetheless, fall off much faster with q_{HK}, as noted.

C. Angular dependence of the liquid scattering

To see the effect of the interaction on the angular dependence of the diffuse scattering about $q=0$ (and in the halos about the other reciprocal-lattice points) requires a calculation of the four-particle correlation function and we do not know any simple way of doing this. At the densities and temperatures of the experiment, the simplest way that we have found of calculating the four-particle correlation function is based on a linear integral equation derivable from the Percus-Yevick equation. Since we wish primarily to show how the effect arises, rather than develop a detailed comparison with experiment, we will give a simpler derivation based on a low-density perturbation expansion of the pair correlation function. The basis of both calculations is the observation that, to second order, the effect of the substrate on the pair correlation function of the fluid is the same as that of an effective, angular-dependent, two-particle potential. We note that the change in the pair correlation function, $\langle \rho_q \rho_{-q} \rangle$, due to a change in the pair potential of the interacting intercalate atoms of the form

$$\delta H = \sum_{r_1, r_2} \delta V(r_1 - r_2) = \sum_{r_1, r_2} \sum_{H,K} e^{i q_{HK} \cdot (r_1 - r_2)} \delta V'_{HK}$$

$$= \sum_{H,K} \delta V'_{HK} \rho_{q_{HK}} \rho_{-q_{HK}} \qquad (17)$$

would be, to first order,

$$\delta \langle \rho_q \rho_{-q} \rangle = - \sum_{H,K} \beta \delta V'_{HK} \langle \rho_q \rho_{-q} (\rho_{q_{HK}} \rho_{-q_{HK}}$$

$$- \langle \rho_{q_{HK}} \rho_{-q_{HK}} \rangle) \rangle . \qquad (18)$$

That is, the effect of the substrate on the diffuse scattering to second order in the interaction with the substrate, as in (14), is determined by the same correlation function that arises to first order from an effective change in the pair potential of the fluid. Note that $\delta V'_{HK}$ should be chosen to be $-\beta V^2_{HK}$ to make the diffuse scattering identical, to lowest order, for the two cases of a substrate with modulated fluid (14) and an effective free fluid (18). *Thus the effective potential is always attractive.* This can be partly understood by noting that in a periodic potential of whatever shape, the fluid energy will be lowered, since the ions spend more time at the minima of the potential. Consequently the effective two-body interaction that reproduces the perturbed configurations must, on average, be attractive. The actual result is a bit stronger, in that all the Fourier coefficients, $\delta V'_{HK}$, of the effective modulation potential are negative. This, however, places no restraint on the actual V_{HK}'s. One can, therefore, determine the correlation function in (18) by differentiating the pair correlation function with respect to the potential. The pair correlation function, $g(r)$, is related to the two-particle density function

$$P(r_1, r_2) = \rho^2 g(r_1 - r_2) ,$$

and to $\langle \rho_q \rho_{-q} \rangle$ by

$$\langle \rho_q \rho_{-q} \rangle = N \left[1 + \rho \int e^{i q \cdot r} g(r) dr \right] = N[1 + \rho g(q)] .$$

$$(19)$$

Thus,

$$\frac{\partial \langle \rho_q \rho_{-q} \rangle}{\partial V'_{HK}} = -\beta \langle \rho_q \rho_{-q} (\rho_{q_{HK}} \rho_{-q_{HK}} - \langle \rho_{q_{HK}} \rho_{-q_{HK}} \rangle) \rangle$$

$$= N\rho \frac{\partial g(q)}{\partial V'_{HK}} \bigg|_{V'_{HK}=0} , \qquad (20)$$

where we think of $g(q)$ as a function of the effective pair potential. An integral equation for $\partial g / \partial V'_{HK}$ can be derived by differentiating one of the self-consistent approximate equations for the pair correlation function. We give in Appendix B the result for the Percus-Yevick equation. Here, we use the leading terms in a density expansion of the pair correlation function:

$$g(r_1 - r_2) = e^{-\beta V(r_1 - r_2)} \left[1 + \rho \int dr_3 (e^{-\beta V(r_1 - r_3)} - 1)(e^{-\beta V(r_3 - r_2)} - 1) \right] . \qquad (21)$$

Then,

$$\frac{\partial g(r_1 - r_2)}{\partial V_{HK}} = -\beta e^{i q_{HK} \cdot (r_1 - r_2)} g(r_1 - r_2) - 2\rho\beta e^{-\beta V(r_1 - r_2)} \int dr_3 g_0(r_1 - r_3) e^{i q_{HK} \cdot (r_1 - r_3)} [g_0(r_3 - r_2) - 1] . \qquad (22)$$

The first term contributes $-\beta g(\mathbf{q}+\mathbf{q}_{HK})$ to the Fourier transform. It is large when $\mathbf{q} \simeq -\mathbf{q}_{HK}$, and produces the halo at $-\mathbf{q}_{HK}$.

Let us consider the effect of the second term in (22) on $\delta\langle\rho_q\rho_{-q}\rangle$. The values of δV_{HK} that correspond to equivalent positions in the reciprocal lattice must be the same. Let us divide the sum over all reciprocal-lattice vectors into sets $\{H_iK_i\}$, which include all the vectors in the equivalent class; that is, vectors that transform into themselves under the actions of the symmetry group of the lattice. For example, in $\{1,0\}$ we would have $(1,0)$, $(0,1)$, $(\bar{1},0)$, $(0,\bar{1})$, $(1,\bar{1})$, $(\bar{1},1)$ which arise because the 2D hexagonal reciprocal space properly requires a three-vector specification using H, K, $-(H+K)$. Then the second term contributes

$$-\beta\rho\sum_i \delta V'_{H_iK_i} \sum_{\{H_i,K_i\}} e^{-\beta V_0(\mathbf{r}_1-\mathbf{r}_2)}\frac{1}{(2\pi)^2} \int e^{i\mathbf{q}\cdot(\mathbf{r}_1-\mathbf{r}_2)}g_0(\mathbf{q}-\mathbf{q}_{H_iK_i})[g_0(\mathbf{q})-\delta(\mathbf{q})]d\mathbf{q} \; . \tag{23}$$

This term leads to an angular variation with $\mathbf{r}=\mathbf{r}_1-\mathbf{r}_2$, and hence to an angular variation of $\delta\langle\rho_q\rho_{-q}\rangle$ with q. This angular variation must have the sixfold symmetry of the graphite lattice. To see this, observe that if $\mathbf{r}'=R\mathbf{r}$, where R is a rotation by 60°, then $\mathbf{q}\cdot\mathbf{r}'=R^{-1}\mathbf{q}\cdot\mathbf{r}=\mathbf{q}'\cdot\mathbf{r}$. Changing variables from $\mathbf{q}$ to $\mathbf{q}'$, and noting that g_0 depends only on the magnitude of q, we get for the integral in (23),

$$f(\mathbf{r}')=\frac{1}{(2\pi)^2}\sum_{\{H_iK_i\}} \int e^{i\mathbf{q}\cdot\mathbf{r}}g_0(R\mathbf{q}'-\mathbf{q}_{H_iK_i})$$

$$\times[g_0(\mathbf{q}')-\delta(\mathbf{q}')]d\mathbf{q}' \; . \tag{24}$$

However, $|R\mathbf{q}'-\mathbf{q}_{H_iK_i}| = |\mathbf{q}'-R^{-1}\mathbf{q}_{H_iK_i}|$ and $R^{-1}\mathbf{q}_{H_iK_i}=\mathbf{q}_{H_iK_i}$. Since the sum is over all H_iK_i, the two integrals are identical, and $f(R\mathbf{r})=f(\mathbf{r})$. This term is thereby responsible for the six-fold modulation of the liquid scattering pattern in Fig. 1.

We note that if we write the leading contribution as

$$\delta\langle\rho_q\rho_{-q}\rangle \simeq N(\beta V_{10})^2 a_1(q)\cos(6\theta) \; , \tag{25}$$

the sign of the coefficient $a_1(\mathbf{q})$ determines whether the pattern peaks in the [10.0] directions, $a_1(\mathbf{q})>0$, or in the [11.0] directions, $a_1(\mathbf{q})<0$. Both patterns occur in practice as in Fig. 1. In view of the fact, demonstrated in Appendix B, that $a_1(\mathbf{q})$ is given by multiple integrals of $g(\mathbf{r})$ and $e^{-\beta V_0(\mathbf{r})}$ against Bessel functions, the possible sign variation is not surprising, as the integrals oscillate rapidly over most of the domain of integration. While it is not transparent either in (25) or in Appendix B, this sign is controlled primarily by the relative size of alkali metal to graphite spacing and thus by the in-plane density in these compounds.

The halos, it should be noted, are also modulated. This arises from higher-order terms in the perturbation expansion and can be treated by solving the integral equation in Appendix B.

III. SUMMARY

The major effects that arise in the x-ray scattering from a 2D alkali-metal liquid modulated by its periodic graphite host include the following.

(a) Alkali-metal contributions to the graphite Bragg peaks which appear as a first-order effect. Assisted by the fact that the alkali-metal size is considerably greater than the carbon spacing in graphite and, therefore, that the alkali-metal liquid scattering, $S(\mathbf{q})$, is nearly featureless at the graphite reciprocal-lattice points (q_{HK}), we present an accurate and useful method for extracting the Fourier coefficients, V_{HK}, of the modulation potential evaluated at the alkali-metal layer which includes corrections for the actual liquid pair correlations. Because this modulating potential is appreciable compared with k_BT, the linearized treatment presented in Eqs. (5)–(8) and used earlier in a preliminary calculation,[12] will be a poor approximation.

(b) Replication of the alkali-metal liquid scattering pattern as halos about the graphite reciprocal-lattice points. This effect arises only to higher order in the V_{HK}'s and is associated with four-particle correlation functions. It falls off with increasing q_{HK}, proportional to $(\beta V_{HK})^2$. While it is thus a second-order effect, it appears by itself rather than under the graphite scattering and is quite visible in Fig. 1 around the $\{10.0\}$ positions.

(c) Development of anisotropy both in the 2D liquid scattering and in its halos about the graphite Bragg peaks. This anisotropy also arises only to higher order in βV_{HK} and clearly is due to the anisotropy of the impressed potential. Its explicit dependence on angle, however, while possible to demonstrate, is not easy to calculate, since it involves complex integrals against higher-order Bessel functions. We do note that the sign of the angular dependence of the liquid structure factor can produce a maximum in the 2D reciprocal lattice along either [10.0] directions or [11.0] directions and both are observed. This effect is higher order in the intercalate density than the appearance of the halos.

It is fortunate that a principal result of this theoretical study are useful expressions, Eqs. (10) and (11), for the extraction of a set of V_{HK}'s, and thus a realistic $V(\mathbf{r}_{\parallel})$, from measurements of Bragg peak intensities and/or their energy dependence.[4,12] This will be presented in a forthcoming paper.[18]

APPENDIX A

We present here a method of including the correlations in the liquid into the determination of the intercalant-substrate potential. Inasmuch as three-particle and higher-order correlations are not experimentally available, they will be neglected in the cumulant expansions we use. It is required to calculate, as in Eq. (9),

$$\langle \rho'_q \rangle = \langle \rho_q \rangle / N e^{-M\frac{1}{Rb}}$$

$$= \left\langle e^{i\mathbf{q}\cdot\mathbf{r}_1} \prod_{i=1}^{N} e^{-\beta V(\mathbf{r}_i)} \right\rangle \Big/ \left\langle \prod_{i=1}^{N} e^{-\beta V(\mathbf{r}_i)} \right\rangle , \quad \text{(A1)}$$

where the average is over the unperturbed liquid and $V(\mathbf{r})$ is the intercalant-substrate potential. If we regard $i\mathbf{q}\cdot\mathbf{r}_1 - \beta V(\mathbf{r}_1)$ as the variable X_1, $-\beta V(\mathbf{r}_i) = X_i$, $i > 1$, the

averages in (A1) can be written as

$$\left\langle \prod_{i=1}^{N} e^{X_i} \right\rangle = \exp \left[\sum_i K_1(X_i) + \sum_{ij} K_2(X_i X_j) + \cdots \right] , \quad \text{(A2)}$$

where

$$e^{K_1(X_i)} = \langle e^{X_i} \rangle ,$$

$$e^{K_2(X_i, X_j)} = \langle e^{X_i} e^{X_j} \rangle / \langle e^{X_i} \rangle \langle e^{X_j} \rangle , \quad \text{(A3)}$$

and we will neglect all higher-order terms in the expansion. K_2 can be determined from the pair correlation function. The denominator in (A1) is obtained from the numerator by setting $q=0$. We have, therefore, using the fact that the particles are identical,

$$\langle \rho'_q \rangle = \frac{\exp[K_1(X_1) + (N-1)K_1(X_2) + (N-1)K_2(X_1,X_2) + \frac{1}{2}(N-1)(N-2)K_2(X_2,X_3)]}{\exp[NK_1(X_2) + \frac{1}{2}N(N-1)K_2(X_2,X_3)]} \quad \text{(A4)}$$

or

$$\langle \rho'_q \rangle = \frac{\exp[K_1(X_1) + (N-1)K_2(X_1,X_2)]}{\exp[K_1(X_2) + (N-1)K_2(X_2,X_3)]} . \quad \text{(A5)}$$

Now

$$K_2(X_1 X_2) = \ln \left[1 + \frac{\langle e^{X_1} e^{X_2} \rangle_C}{\langle e^{X_1} \rangle \langle e^{X_2} \rangle} \right] , \quad \text{(A6)}$$

where

$$\langle e^{X_i} e^{X_j} \rangle_C = \langle e^{X_i} e^{X_j} \rangle - \langle e^{X_i} \rangle \langle e^{X_j} \rangle .$$

Noting that the two-particle probability distribution for the liquid can be written as $(1/V^2)g(\mathbf{r}_1 - \mathbf{r}_2)$, where $\int g(\mathbf{r}_1 - \mathbf{r}_2) d\mathbf{r}_2 = V$, we have

$$\langle e^{X_i} e^{X_j} \rangle_C = \int d\mathbf{r}_i \int d\mathbf{r}_j \frac{1}{V^2} [g(\mathbf{r}_i - \mathbf{r}_j) - 1] e^{X_i} e^{X_j} . \quad \text{(A7)}$$

Since the function $g(\mathbf{r}) - 1$ is integrable, the integral is proportional to $1/V$, and we have, therefore,

$$(N-1)K_2(X_i, X_j) = \frac{\rho}{V} \int d\mathbf{r}_i \int d\mathbf{r}_j [g(\mathbf{r}_i - \mathbf{r}_j) - 1]$$

$$\times e^{X_i} e^{X_j} / \langle e^{X_i} \rangle \langle e^{X_j} \rangle . \quad \text{(A8)}$$

If we define

$$[S(\mathbf{q}) - 1] = \rho \int e^{i\mathbf{q}\cdot\mathbf{r}} [g(\mathbf{r}) - 1] d\mathbf{r} , \quad \text{(A9)}$$

we have

$$\rho[g(\mathbf{r}) - 1] = \frac{1}{V} \int e^{-i\mathbf{q}\cdot\mathbf{r}} [S(\mathbf{q}) - 1] d\mathbf{q} . \quad \text{(A10)}$$

Since $V(\mathbf{r} + n\mathbf{a}) = V(\mathbf{r})$, where $\mathbf{a}$ is a primitive vector of the graphite cell, we have

$$e^{-\beta V(\mathbf{r})} = \sum_{H,K} e^{-i\mathbf{q}_{HK}\cdot\mathbf{r}} F_1(\mathbf{q}_{HK})$$

and   (A11)

$$\frac{1}{V} \int d\mathbf{r} e^{i\mathbf{q}\cdot\mathbf{r}} e^{-\beta V(\mathbf{r})} = \frac{1}{V_c} \sum_{q_{HK}} F_1(\mathbf{q}_{HK}) \delta_{\mathbf{q},\mathbf{q}_{HK}} ,$$

where V_C is the volume of a single primitive cell of the graphite lattice. Thus

$$(N-1)K_2(X_1,X_2) = \sum_{q_{HK}} F_1(\mathbf{q}_{HK})F_1(-\mathbf{q}_{HK}+\mathbf{q})[S(\mathbf{q}_{HK})-1]/F_1(\mathbf{q})F_1(0) \equiv F_2(\mathbf{q}) , \quad \text{(A12)}$$

while

$$(N-1)K_2(X_2,X_3) = \sum_{q_{HK}} F_1(\mathbf{q}_{HK})F_1(-\mathbf{q}_{HK})[S(\mathbf{q}_{HK})-1]/[F_1(0)]^2 \equiv F_2(0) \quad \text{(A13)}$$

and hence

$$\langle \rho_q' \rangle = \frac{F_1(\mathbf{q})}{F_1(0)} e^{[F_2(\mathbf{q})-F_2(0)]} \ . \tag{A14}$$

Equations (A12) through (A14) thereby provide a correction to Eq. (10) of the text and give us an expression for the measured alkali-metal contribution to the peak intensities in terms of the coefficients in the potential which enter F, and the value of the diffuse scattering from the unperturbed liquid evaluated at the graphite Bragg peaks. We note that the $S(\mathbf{q})$ that enters the theoretical expression is not actually accessible experimentally, since the measured values include the effect of the substrate on the

pair correlations whereas the theory uses the unperturbed liquid structure factor. This is not a serious drawback for small values of βV_{HK}, since the corrections to the measured $S(\mathbf{q})$ are second order in βV_{HK}. It would present a problem of interpretation if the observed intensity in the halos and the depth of the angle-dependent intensity modulation were comparable to that of the liquid diffuse scattering. With this proviso, the intercalant-graphite potential may be obtained from the measured data by standard fitting procedures. In fact, the methods which we have obtained here, once the appropriate corrections given above are made, apply to a wide variety of intercalant and overlayer systems.

APPENDIX B

We wish to provide an integral equation for $\partial g(\mathbf{r})/\partial V_{HK}'$ that can be used to calculate the diffuse scattering pattern when the density is too high to make Eq. (21) appropriate. We begin from the Percus-Yevick equation,[20]

$$g(\mathbf{r}) = e^{-\beta V(\mathbf{r})} \left[1 + \rho \int d\mathbf{r}' g(\mathbf{r}-\mathbf{r}')(1-e^{\beta V(\mathbf{r}-\mathbf{r}')})[g(\mathbf{r}')-1] \right] \ . \tag{B1}$$

Letting $V(\mathbf{r}) = V_0(|\mathbf{r}|) + \delta V_{HK}' e^{i\mathbf{q}_{HK}\cdot\mathbf{r}}$, we find

$$\frac{\partial g(\mathbf{r})}{\partial V_{HK}'} = -\beta e^{i\mathbf{q}_{HK}\cdot\mathbf{r}} g(\mathbf{r}) - \beta\rho e^{-\beta V(\mathbf{r})} \int d\mathbf{r}' g(\mathbf{r}-\mathbf{r}') e^{\beta V(\mathbf{r}-\mathbf{r}')}[g(\mathbf{r}')-1] e^{i\mathbf{q}_{HK}\cdot(\mathbf{r}-\mathbf{r}')}$$

$$+ \rho \int d\mathbf{r}' \frac{\partial g(\mathbf{r}-\mathbf{r}')}{\partial V_{HK}'}(1-e^{\beta V(\mathbf{r}-\mathbf{r}')})[g(\mathbf{r}')-1] + \rho \int d\mathbf{r}' g(\mathbf{r}-\mathbf{r}')(1-e^{\beta V(\mathbf{r}-\mathbf{r}')}) \frac{\partial g(\mathbf{r}')}{\partial V_{HK}'} \ . \tag{B2}$$

A consistent iteration of these equations as a density expansion leads to Eq. (21) of the text. Note that the modulation of the rings requires that a pair of particles be affected by the angular-dependent potential of a third particle and hence is a higher-order effect in the density than the appearance of the halos. For example, it might at first seem that we can extract all of the angular-dependent factors simply by noting that, to lowest order,

$$g(\mathbf{r}) = \exp\left[-\beta \left[V_0(\mathbf{r}) + \sum_{H,K} \delta V_{HK}' e^{i\mathbf{q}_{HK}\cdot\mathbf{r}} \right] \right] \ . \tag{B3}$$

Because the exponent contains an angular varying part, $g(\mathbf{r})$ varies with $q_{HK}\cdot\mathbf{r} \propto \cos\theta$. By expanding (B3) and transforming it, however, we see that this angular dependence produces only the halos and *not* the desired angular variation about the origin of the principal liquid pattern in Fig. 1.

To evaluate more explicitly the expression in Eq. (23) in order to obtain the leading term in the angular variation of the structure factor, we rewrite, dropping the subscript 0,

$$\sum_{\{H_i,K_i\}} g(\mathbf{q}-\mathbf{q}_{H_iK_i}) = \sum_{n=1}^{\infty} g_n^i(q)\cos(6n\theta) \ , \tag{B4}$$

where θ is the direction of $\mathbf{q}$, with respect to $\mathbf{q}_{10}$. Then, using

$$g(\mathbf{q}) = \int e^{i\mathbf{q}\cdot\mathbf{r}} g(\mathbf{r})d\mathbf{r}$$

and the expansion

$$e^{i\mathbf{q}\cdot\mathbf{r}} = \sum_{n=1}^{\infty} 2i^n J_n(qr)\cos(n\theta) + J_0(qr) \ , \tag{B5}$$

we have

$$g_n^i(\mathbf{q}) = \frac{1}{\pi} \int_{-\pi}^{\pi} \cos(6n\theta) \left[\sum_{\{H_i,K_i\}} \int e^{i(\mathbf{q}-\mathbf{q}_{H_iK_i})\cdot\mathbf{r}} g(\mathbf{r})d\mathbf{r} \right] d\theta$$

$$= 4n_i\pi \int dr\, r J_{6n}(qr)J_{6n}(q_{HK}r)g(r) \ , \tag{B6}$$

where n_i is the number of wave vectors in the set $\{H_iK_i\}$. Inasmuch as $J_{6n}(q_{HK}r)$ is rapidly varying on the scale of $g(r)$, the sign of this coefficient is indeterminate.

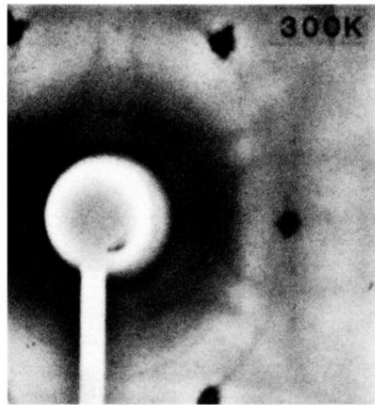We have, then, for the contribution of the angular-dependent term

$$\delta g(\mathbf{r}) = \sum_{H,K} \frac{\partial g(\mathbf{r})}{\partial V_{HK}'} \delta V_{HK}' = -\beta\rho \sum_{i,n} \delta V_{H_iK_i}' e^{-\beta V_0(\mathbf{r})} \frac{1}{(2\pi)^2} \int e^{i\mathbf{q}\cdot\mathbf{r}} g_n^i(q)\cos(6n\theta)[g(\mathbf{q})-\delta(\mathbf{q})]d\mathbf{q}$$

$$= -\beta\rho \sum_{i,n} \delta V_{H_iK_i}' e^{-\beta V_0(\mathbf{r})} \frac{(-1)^n}{2\pi} \int J_{6n}(qr)g_n^i(q)[g(q)-\delta(q)/2\pi q]q\, dq\, \cos(6n\phi) \ , \tag{B7}$$
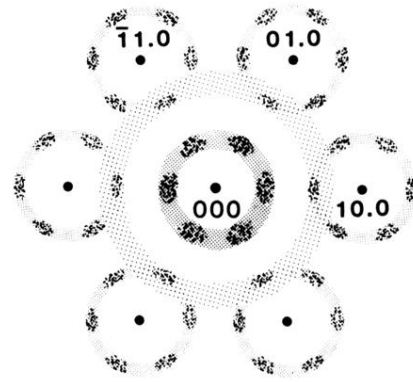
where ϕ is the direction of r with respect to the graphite $\langle 10.0 \rangle$ direction (along the real axis). Finally, upon Fourier transforming and using the relation $\delta V'_{HK} = -\beta V^2_{HK}$ we obtain

$$\delta \langle \rho_q \rho_{-q} \rangle = \sum_{i,n}^{N} \rho^2 (\beta V_{H_i K_i})^2 \int J_{6n}(qr) e^{-\beta V_0(r)} J_{6n}(q'r) g_n^i(q') [g(q') - \delta(q')/2\pi q'] \cos(6n\theta) q' r \, dq' \, dr \ . \tag{B8}$$
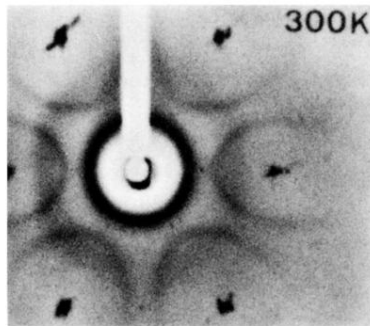
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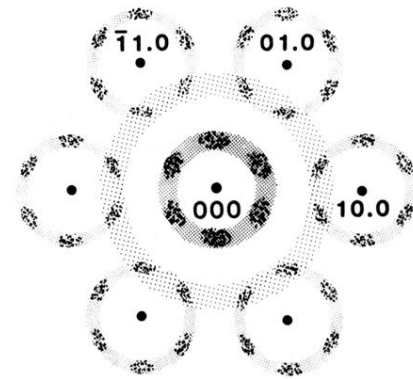
FIG. 1. (a) and (c), single-crystal x-ray photos from Rousseaux *et al.* (Refs. 9 and 10); (b) and (d), schematic representation of the principal effects including angular variation of the diffuse scattering and halos. The distortion in the data, due to cylindrical film geometry is not reproduced in (b) or (d). (a) and (b): $C_{24}K$ with peaking roughly in [10.0]; (c) and (d): $C_{24}Rb$ with peaking roughly in [11.0].