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Commensurate-incommensurate transition of solid krypton monolayers on graphite

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Low-energy electron-diffraction (LEED) data for the commensurate-incommensurate transition in solid krypton monolayers on graphite are reanalyzed and compared to recent x-ray diffraction data. For the temperature range 52 to 89 K, the mean misfit versus chemical potential change for both sets of data can be expressed as a power law with an exponent of about $\frac{1}{3}$. The critical pressure at which the transition occurs is consistent with $P_c(T) = (4.5 \times 10^{+9}\ \text{Torr}) \exp(-1990K/T)$ for $52 < T < 123$ K. Analysis of the LEED photographs at 52 K indicates that the krypton monolayer starts to rotate in an apparently second-order transition when the mean misfit exceeds two percent.

The hexagonal incommensurate krypton monolayer on graphite[1,2] can be characterized by the mean misfit m, which is defined in terms of the deviation of the mean nearest-neighbor spacing d from the commensurate $(\sqrt{3} \times \sqrt{3})30°$ spacing $d_0 = 4.26$ Å by

$$m = (d_0 - d)/d_0 \ . \tag{1}$$

If no vacancies, interstitials, or second-layer atoms are present, the mean density n for the experimental range of misfits $m < 5\%$ is given by

$$n \cong n_0(1 + 2m) \ , \tag{2}$$

where n_0 is the density of the commensurate monolayer. Volumetric isotherm measurements of the total adsorbed amount as a function of the Kr vapor pressure provided the first evidence for the commensurate-incommensurate transition.[3] However, the most accurate measurements of misfit are obtained from diffraction measurements[1,2] which do not require the corrections for second-layer adsorption and substrate heterogeneity[4,5] needed for isotherm measurements.

In Ref. 1 we compared our low-energy electron diffraction to the one-dimensional $T = 0$ Frank-van der Merwe theory.[10] A more detailed analysis of this data and the x-ray data[2] shows that the data are not consistent with this theory at misfits < 2%. Both sets of data are consistent with a power-law function of chemical potential change as proposed by Stephens *et al.*[2]

$$m = a(T \ln P - T \ln P_c)^\beta \ , \tag{3}$$

where T is the substrate temperature, P is the Kr vapor pressure, and P_c is a parameter chosen for best fit at each temperature. We present in Fig. 1 the LEED[1,6] and x-ray[2,7] data in a log-log plot of misfit versus chemical potential change. The straight line

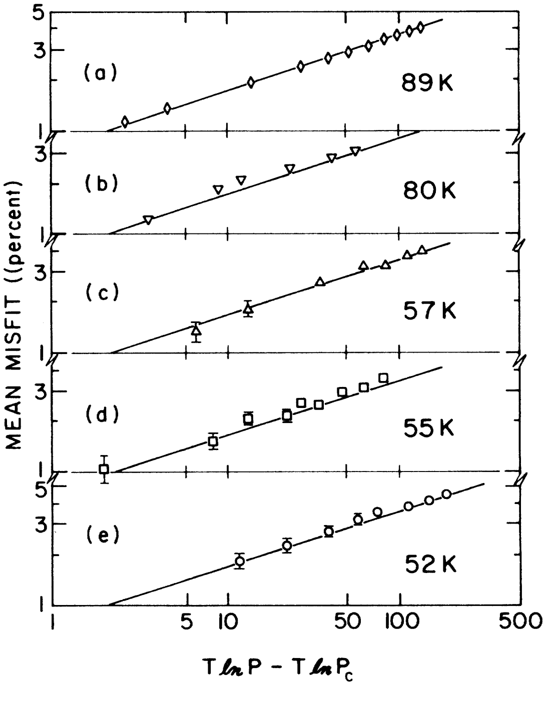

FIG. 1. Comparison of LEED and x-ray data for Kr on graphite with a power law in the mean misfit vs chemical potential change:

$$m = (d_0 - d)/d_0 = a(T \ln P - T \ln P_c)^\beta \ ,$$

where d is the mean nearest-neighbor spacing, $d_0 = 4.26$ Å is the d value for the $(\sqrt{3} \times \sqrt{3})30°$ structure, T is the substrate temperature, P is the Kr vapor pressure, P_c is a fitting parameter that depends on T, $a = 0.8\%$, and $\beta = 0.33$. The x-ray data [(a) and (b)] are from Ref. 2 and the LEED data [(c), (d), and (e)] are from Ref. 1 with a temperature correction applied (Ref. 6).

shown is our fit of the 89-K data to Eq. (3) with $a = 0.8\%$ and $\beta = 0.33$. (Stephens *et al.* found $\beta = 0.32 \pm 0.02$ for the 89-K data.[2]) From the quality of the fit in Fig. 1 we conclude that the diffraction data[7] are described by the same power law for $52 < T < 89$ K and $0.5\% < m < 5.0\%$.[8] No theory has yet been proposed that explains the power-law behavior of Eq. (3) with exponent $\beta \approx \frac{1}{3}$. (Several calculations predict an exponent $\beta = \frac{1}{2}$ for uniaxial domain walls,[13-15] which are not observed experimentally.[1,2])

The rounding of the transition at $m < 0.5\%$ shown in Refs. 2 and 9 is not described by the power law and may be due to finite-size effects. The x-ray measurements indicate that uniform regions of the commensurate phase for the "*ZYX*" substrate are about 600 Å in diameter.[2] In using domain walls to describe the incommensurate structure close to the transition,[10-16] this 600- Å length would contain only a few domain walls at 1% misfit and thus finite-size effects can be very important close to the transition. The single-crystal substrate used for the LEED measurements might have had larger uniform regions, but the apparatus resolution did not permit measurements for $m < 0.5\%$.

In Fig. 2 we show the pressure $P_c(T)$ at which the commensurate-incommensurate transition begins as obtained from volumetric isotherm measurements,[3,9] LEED,[6] x-ray[2] and transmission high-energy electron diffraction,[17] and heat-capacity measurements.[18] The solid line shown is a least-squares fit of the data from volumetric isotherm data ($72 < T < 96$ K)[3,9]

$$P_c(T) = P_0 \exp(-q/T) \; , \tag{4}$$

with $P_0 = (4.5 \pm 0.8) \times 10^{+9}$ Torr and $q = 1990 \pm 13$ K. This value of q is consistent with that deduced by Thomy *et al.* ($q = 1980$ K).[3] The deviation of the x-ray[2] values from this line could be due to undetected systematic errors. As mentioned in Ref. 4, there is no *a priori* reason why q should be temperature independent; the high-energy electron diffraction[17] and LEED[6] measurements are not sufficiently accurate to decide if Eq. (4) is precise near 55 K.

Structural modulations cause orientational ordering of incommensurate monolayers.[19,20] In Fig. 3 we present new measurements of the orientation angle of incommensurate Kr monolayers at 52 K. The LEED photographs of the original study[1,21] have been analyzed by comparison to spot profiles that were calculated by assuming two orientational domains[20] with overlapping Gaussian profiles. [A schematic drawing of the observed spots is shown in Fig. 2(e) of Ref. 1.] The results given in Fig. 3 indicate that rotation starts at about 2% mean misfit, and that rotation occurs in an apparently second-order transition. These two conclusions are in good agreement with Shiba's most recent calculation.[13] The

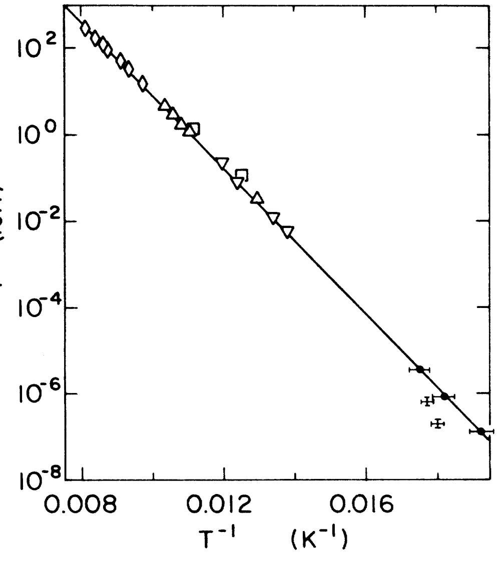

FIG. 2. Comparison of pressures P_c from different measurements with equation $P_c = P_0 \exp(-q/T)$, with $P_0 = 4.5 \times 10^{+9}$ Torr and $q = 1990$ K. Upright and inverted triangles are from volumetric isotherms (Refs. 3 and 9), squares from x-ray diffraction (Ref. 2), circles from LEED (Ref. 6), pluses from transmission high-energy electron diffraction (Ref. 17), and diamonds from heat-capacity peak correlation with vapor pressure (Ref. 18).

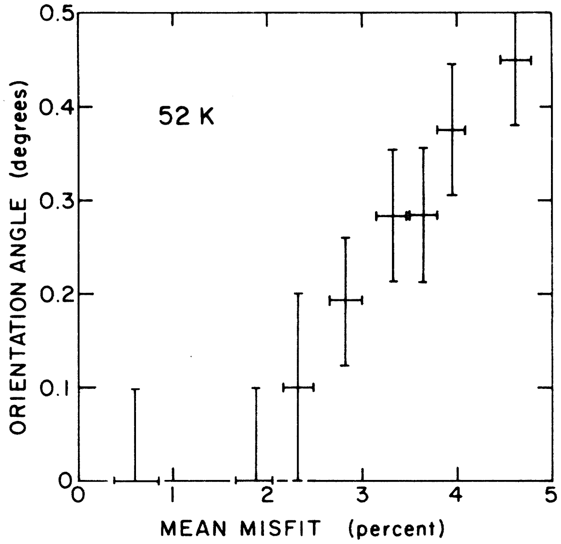

FIG. 3. Relative orientation angle between Kr monolayers at 52 K and the $(\sqrt{3} \times \sqrt{3})30°$ commensurate structure vs mean misfit $m = (d_0 - d)/d_0$, where d is the nearest-neighbor distance and $d_0 = 4.26$ Å. The elongated Kr spots [Fig. 2(e) of Ref. 1] have been analyzed assuming two orientational domains with overlapping Gaussian spot profiles.

maximum rotation of about 0.5° at 5% mean misfit is smaller by a factor of 2 or more than calculated by Shiba[13] or McTague and Novaco.[22] This difference at large misfits may be due to edge effects or to second-layer adsorption, effects invoked in explaining the deviation of argon rotation data from calculations at large misfit.[20]

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[1] M. D. Chinn and S. C. Fain, Jr., Phys. Rev. Lett. 39, 146 (1977).

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

[3] A. Thomy, J. Regnier, and X. Duval, in *Thermochimie, Colloques Internationaux du CNRS.* (CNRS, Paris, 1972), p. 511.

[4] S. C. Fain, Jr. and M. D. Chinn, J. Phys. (Paris) Colloq. 38, C4-99 (1977).

[5] G. D. Halsey, J. Phys. Chem. 81, 2076 (1977)

[6] Two corrections have been made to the LEED data from Ref. 1. The temperatures have been corrected downward by 2 K to account for a systematic error resulting from the method of mounting the thermocouple; this correction is certain to ± 1 K [C. G. Shaw, Ph. D. dissertation (University of Washington, 1979) (unpublished)]. The vapor pressures have been corrected downward by the necessary thermomolecular correction $(T/295)^{1/2}$ [C. G. Shaw and S. C. Fain, Jr., Surf. Sci. 83, 1 (1979)]. The pressure correction has no effect on the plot in Fig. 1; the temperature correction gives a small horizontal shift.

[7] X-ray data points with $0.5 \leq m \leq 1.0\%$ (1 at 89 K and 3 at 80 K) are consistent with the straight-line behavior in Fig. 1, but are not shown; due to the greater uncertainties in these points (see Fig. 3 of Ref. 2) they should not be weighted strongly in a power-law fit. Five x-ray data points ($m < 0.5\%$) and two LEED points ($m < 1.0\%$) are at pressures less than the critical pressures assumed for Fig. 1 and thus cannot be shown in such a plot.

[8] The misfit range from $\frac{1}{2}\%$ to 5% corresponds at 80 K to a range in "reduced" chemical potential $[T\ln(P/P_c)]/[T\ln(P_c/P_1)]$ from 6×10^{-4} to 0.7. The reference level of chemical potential $T\ln P_1$ chosen for this calculation was $P_1 = 1.0 \times 10^3$ Torr, the pressure of monolayer condensation at 80 K measured by Y. Larher, J. Chem. Soc. Faraday Trans. 1, 70, 320 (1974).

[9] Y. Larher, J. Chem. Phys. 68, 2257 (1978).

[10] F. C. Frank, and J. H. van der Merwe, Proc. Roy. Soc. A 198, 205, 216 (1949), and 200, 125 (1949).

[11] J. A. Venables and P. S. Schabes-Retchkiman, J. Phys. (Paris) Colloq. 38, C4-105 (1977), and Surf. Sci. 71, 27 (1978).

[12] P. Bak, D. Mukamel, J. Villain, and K. Wentewska, Phys. Rev. B 19, 1610 (1979).

[13] H. Shiba, J. Phys. Soc. Jpn. 46, 1852 (1979) and (unpublished).

[14] V. L. Pokrovsky and A. L. Talapov, Phys. Rev. Lett. 42, 65 (1979) and Zh. Eksp. Theor. Fiz. 75, 1157 (1978) [Sov. Phys. JETP 48, 579 (1978)].

[15] A. Luther, J. Timonen, and V. Pokrovsky, in *Phase Transitions in Surface Films*, edited by J. G. Dash and J. Ruvalds (Plenum, New York, 1980).

[16] J. Villain, in *Ordering in Strongly Fluctuating Systems*, edited by T. Riste (Plenum, New York, 1980), p. 214; M. B. Gordon and J. Villain, J. Phys. C 12, L151 (1979).

[17] P. S. Schabes-Retchkiman and J. A. Venables (private communication).

[18] D. M. Butler, Ph.D. thesis (University of Pittsburgh, 1979) (unpublished) and D. M. Butler, J. A. Litzinger, and G. A. Stewart, Phys. Rev. Lett. 44, 466 (1980).

[19] A. D. Novaco and J. P. McTague, Phys. Rev. Lett. 38, 1286 (1977) and J. Phys. (Paris) Colloq. 38, C4-116 (1977).

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

[21] M. D. Chinn, Ph.D. dissertation (University of Washington, 1977) (unpublished).

[22] J. P. McTague and A. D. Novaco, Phys. Rev. B 19, 5299 (1979).