non-electron interaction $\hat{\omega}_{TO}$ is expressed as[4]

$$\hat{\omega}_{TO}^2 = \omega_{TO}^2 - \frac{4g}{(2\pi)^3}\int_w^0 \left(\frac{\hbar D^2}{2MNa^2}\right)\frac{\rho(E)dE}{E_G+2E}, \quad (4)$$

where w is the bandwidth. This equation indicates that the $\hat{\omega}_{TO}^2$ can most easily become negative near $E_G = 0$. This means that T_{c0} peaks at around $x = 0.47$ and coincides exactly with T_b.

In summary, an anomalous increase in Raman intensity due to unscreened LO phonons was observed at both temperatures T_c and T_b which correspond to the displacive phase transition and the band inversion, respectively. It is shown that the electron-soft-TO-phonon interaction plays an important role in the displacive phase transition in PbSnTe.

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[1]N. Kristoffel and P. Konsin, Phys. Status Solidi 21, K39 (1967).

[2]L. J. Brillson, E. Burstein, and L. Muldawer, Phys. Rev. B 9, 1547 (1974).

[3]E. R. Cowley, J. K. Darby, and G. S. Powley, J. Phys. C 2, 1916 (1969).

[4]K. L. I. Kobayashi, Y. Kato, Y. Katayama, and K. F. Komatsubara, Phys. Rev. Lett. 37, 772 (1976), and Solid State Commun. 17, 875 (1975).

[5]L. Brillson and E. Burstein, Phys. Rev. Lett. 27, 808 (1971).

[6]G. S. Powley, W. Cochran, R. A. Cowley, and G. Dolling, Phys. Rev. Lett. 17, 753 (1966).

[7]C. R. Hews, M. S. Adler, and S. D. Senturia, Phys. Rev. B 7, 5195 (1973).

[8]J. O. Dimmock, I. Melngailis, and A. J. Strauss, Phys. Rev. Lett. 16, 1193 (1966).

[9]J. R. Dixon and R. F. Bis, Phys. Rev. 176, 942 (1968).

[10]G. W. Pratt, Jr., and A. Das, J. Phys. Chem. Solids, Suppl. 32, 279 (1971).

[11]R. T. Bate, D. L. Carter, and J. S. Wrobel, in *Proceedings of the Tenth International Conference on the Physics of Semiconductors, Cambridge, Massachusetts, 1970*, edited by S. P. Keller, J. C. Hensel, and F. Stern, CONF-700801 (U. S. Atomic Energy Commission, Division of Technical Information, Springfield, Va., 1970), p. 125.

Structural Phase Transition in Epitaxial Solid Krypton Monolayers on Graphite[(a)]

M. D. Chinn and S. C. Fain, Jr.[(b)]
Department of Physics, University of Washington, Seattle, Washington 98195
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Lattice-constant measurements of epitaxial solid krypton monolayers adsorbed on the basal plane of graphite reveal an apparently second- (or higher-) order structural phase transition from an in-registry $(\sqrt{3}\times\sqrt{3})30°$ structure to an out-of-registry compressed structure. Measurements as a function of equilibrium vapor pressure were made with a high-resolution, low-energy-electron diffraction apparatus for three temperatures near 57 K. Indirect evidence for spatial modulation of the compressed structure by the substrate potential is presented.

We show here that a solid Kr layer adsorbed on the basal plane of graphite undergoes an apparently second- (or higher-) order phase transition from an in-registry, $(\sqrt{3}\times\sqrt{3})30°$ structure to an out-of-registry, compressed structure as the Kr pressure above the substrate is increased. This transition was first inferred from vapor-pressure isotherms,[1] but was not observed in an earlier low-energy-electron diffraction (LEED) investigation.[2] We observe this transition with high-resolution LEED[3] and report the first detailed measurements of mean overlayer lattice constant as a function of the equilibrium vapor pressure P. Our observations are inconsistent with the first-order, in-registry to out-of-registry transition recently proposed for Kr on graphite.[4] However, our results show remarkable agreement with a one-dimensional dislocation model of monolayer epitaxy.[5] The data provide a unique opportunity to test theories of monolayer epitaxy[5-8] in a case where the forces involved are fairly well known.

Kr monolayers were condensed on a cleaved, natural graphite crystal mounted in an ultrahigh-vacuum system.[3] The Kr pressure was increased in small increments while monitoring the LEED pattern. Parameters for the normal-incidence electron beam were 144 eV, 3 nA, and 0.2 mm diam. Electrons backscattered within 30° of nor-

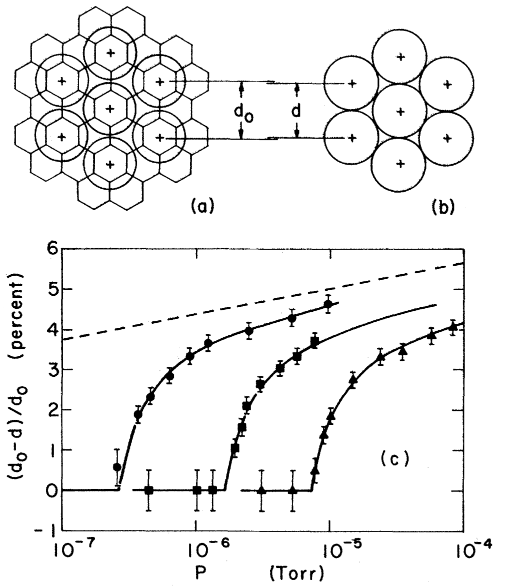

FIG. 1. (a) Kr atoms (circles) in a registered $(\sqrt{3}\times\sqrt{3})30°$ structure on the graphite basal plane. Carbon atoms are located at the vertices of the hexagonal net. $d_0=0.426$ nm. (b) Compressed Kr overlayer with nearest-neighbor distance d. (c) Mean misfit $(d_0-d)/d_0$ vs equilibrium vapor pressure P at 54 K (circles), 57 K (squares), and 59 K (triangles). The same solid line is drawn through each set of experimental data. The dashed line represents the natural misfit at 54 K for a Kr monolayer on a smooth graphite substrate (see Ref. 17).

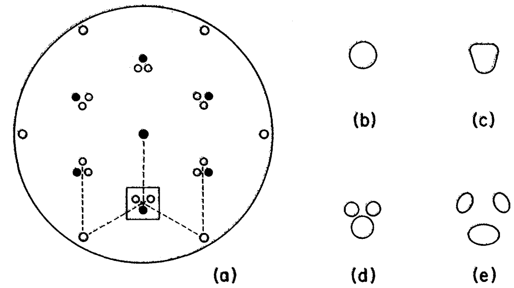

FIG. 2. (a) Idealized LEED pattern for a Kr overlayer compressed with respect the registered $(\sqrt{3}\times\sqrt{3})30°$ structure. Diffraction beams represented are the specular (center closed circle), first-order graphite (peripheral open circles), first-order krypton (six closed circles), and graphite plus krypton (remaing twelve open circles). Some of the Kr reciprocal-lattice vectors are shown as dotted lines. Actual pattern observed inside the box area is shown at right for mean misfits of (b) 0%, (c) 2%, (d) 3%, and (e) 5%.

mal were amplified and imaged by a flat channel-electron-multiplier plate and phosphor screen. Positions and shapes of the diffracted beams were measured from 35-mm transparencies projected onto a screen or magnified with a traveling microscope. Changes in temperature and relative pressures were measured to within ±0.3 K and ±5%, respectively. (Absolute values are known to within ±1 K and a factor of 2 in pressure.)

Figure 1(a) represents a $(\sqrt{3}\times\sqrt{3})30°$ registered layer of Kr atoms centered in the potential minima of the hexagonal graphite mesh.[9,10] Figure 1(b) shows a close-packed Kr monolayer. The mean overlayer lattice constant is presented in Fig. 1(c) as the mean misfit $(d_0-d)/d_0$ between the registered-layer nearest-neighbor distance d_0 and the mean distance d. The mean misfit is plotted for three temperatures versus the equilibrium vapor pressure of the layer. Zero misfit on the graph indicates no detectable change from the registered-layer LEED pattern consisting of the graphite-substrate pattern plus the six first-order Kr spots.[3] Past a critical pressure the Kr spots begin to change shape until at high enough pressure each Kr spot has separated into three distinct spots. This pattern is shown schematically in Fig. 2(a) and in a previously published photograph.[3]

The origin of the spots within the square in Fig. 2(a) can be explained by multiple scattering. The brightest spot, the filled spot in Fig. 2(a), is the first-order scattering by a compressed Kr layer from both the incident beam and the graphite specular reflection. Because the mean lattice spacing is smaller than in the registered layer, the Kr reciprocal-lattice vector lengthens and this spot is displaced radially outward. The other two spots are due to Kr scattering from the graphite first-order diffraction beams.[3] Some of the reciprocal-lattice vectors of the Kr layer are represented as dotted lines in Fig. 2(a). For the registered layer the Kr spots [Fig. 2(b)] are the same size as the substrate spots. Past the critical pressure, a radial elongation of the spots is observed. When the spots have a definite triangular shape [Fig. 2(c)], the misfit is inferred by assuming three overlapping spots of the same size and intensity as at 3% misfit [Fig. 2(d)]. At 5% misfit [Fig. 2(e)] the spots are elongated in a manner consistent with a spread in rotational alignment between substrate and overlayer as observed in other incommensurate epitaxial systems.[11,12]

Auger-electron spectroscopy measurements made using a 342-eV, 0.2-μA incident beam showed an increase in Kr coverage of about 30%

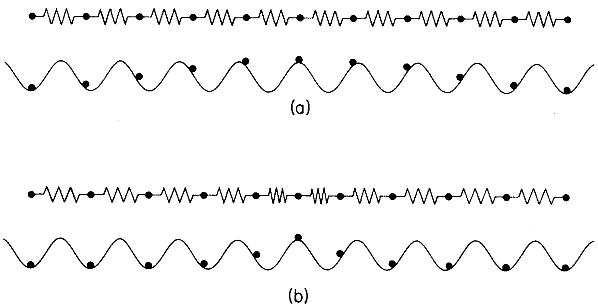

FIG. 3. (a) Chain of uniformly spaced adatoms and the corresponding potential energy for each adatom is a sinusoidal substrate potential. (b) Modulation of the adatom spacing by a misfit dislocation resulting from a strong substrate potential (from Ref. 5 with $l_0=3$).

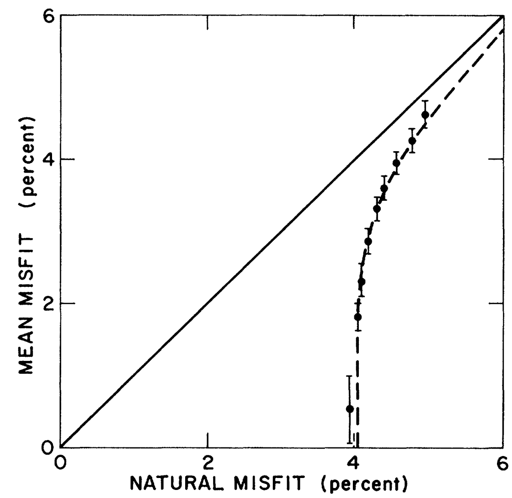

FIG. 4. Dashed line showing the mean misfit $(d_0-d)/d_0$ vs the natural misfit for the 1D model of Ref. 5 with $l_0=16$. Data points at 54 K are plotted using the natural misfit given by the dashed line in Fig. 1(c).

from monolayer condensation to onset of second-layer condensation, which occurred at 5.6% misfit.[13] These observations are consistent with vapor-pressure isotherms taken at 77 K which show distinctive layer-by-layer growth up to 3–5 layers.[1]

The model of Price and Venables (PV) for this in-registry to out-of-registry transition assumes that the out-of-registry overlayer is uniformly compressed [as in Fig. 3(a)], planar, and of infinite lateral extent.[4] With these assumptions PV found the Kr-graphite potential to be independent of lateral and orientational positioning of the overlayer on the substrate and predicted a first-order transition from an in-registry to an out-of-registry overlayer.[14] The lattice constant as a function of T and P for the out-of-registry phase was calculated for an overlayer on a hypothetical graphite substrate with no lateral periodicity. The most extensive results were presented for a multiparameter Kr-Kr potential[15] with (MPSP) and without (MP) a correction for the substrate polarizability.[16] The misfit calculated from the lattice constant of the out-of-registry overlayer (called natural misfit in Refs. 5, 6, and 8) varies with $\ln P$ qualitatively as shown by the dashed line in Fig. 1(c).[17] The difference between these calculations and experiment is greater than errors in the Kr-Kr potential, which largely determines the slope of the dashed line.

We believe that the discrepancy is due to modulations of the overlayer structure (misfit dislocations[5]) by the substrate potential.[18] For small misfits the Kr atoms can lower the Kr-graphite potential by relaxing toward the substrate potential wells [Fig. 3(b)]. As the Kr-Kr potential energy becomes greater at larger misfits, the overlayer distortion becomes less and the assumptions of PV become more valid. One-dimensional (1D) dislocation models have been proposed[5,7,8] in which the mean misfit of a chain of adsorbed atoms to a sinusoidal substrate potential (Fig. 3) is obtained as a function of the natural atom spacing in absence of the sinusoidal substrate. The results of Frank and van der Merwe[5] for a weak substrate potential are plotted in Fig. 4 as a dashed line, for their parameter $l_0=16$. The experimental mean-misfit points at 54 K are also plotted using the natural-misfit results from PV [dashed line in Fig. 1(c)]. The agreement may be fortuitous, due in part to our procedure for positioning the dashed line in Fig. 1(c).[17] However, the value of the parameter l_0 used for Fig. 4 is essentially the same as we deduce for the 1D model from calculated values for the adatom-adatom[15] and adatom-substrate[9,10] potentials.

Ying's more complete solution to the model of Frank and van der Merwe shows first-order transitions for strong substrate potentials.[7] For the weak substrate potential needed for Fig. 4, there is little difference between the solutions of Refs. 5 and 7.[19] Experimentally we cannot rule out a discontinuity in lattice constant of less than 1% at the transition (see Fig. 1). But our data clearly show a more gradual transition than the simple first-order transition of Ref. 4.

The nature of the commensurate-incommensurate transition for a 2D monolayer on the graphite basal plane has not been studied theoretically. However, Novaco and McTague have shown that orientational epitaxy of the incommensurate monolayer can result from 2D dislocation networks.[20]

Periodic networks of dislocations would produce additional LEED beams whose location and intensity will depend on the period and amplitude of the structural modulation.[21] The amplitude of the modulation is largest close to the transition,[5] where the extra beams will be very close to the original beams. Though we have not yet resolved such superlattice reflections for Kr on graphite, they could contribute to the radial elongation observed for misfits less than 2%.

The orientational epitaxy[20] and the apparently second- (or higher-) order nature of the in-registry to out-of-registry phase transition of Kr on graphite together provide strong evidence that the out-of-registry overlayer contains misfit dislocations as first discussed by Frank and van der Merwe.[5] We hope that the results presented here will stimulate an interest in realistic 2D dislocation models applicable to rare-gas–graphite epitaxy.

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[(b)]Corresponding author.

[1]A. Thomy, J. Regnier, and X. Duval, Colloq. Int. CNRS 201, 511 (1972).

[2]H. M. Kramer and J. Suzanne, Surf. Sci. 54, 659 (1976).

[3]M. D. Chinn and S. C. Fain, Jr., J. Vac. Sci. Technol. 14, 314 (1977).

[4]G. L. Price and J. A. Venables, Surf. Sci. 59, 509 (1976).

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

[6]J. H. van der Merwe, J. Appl. Phys. 41, 4725 (1970).

[7]S. C. Ying, Phys. Rev. B 12, 4160 (1971).

[8]J. A. Snyman and J. H. van der Merwe, Surf. Sci. 42, 190 (1974), and 45, 619 (1974).

[9]W. A. Steele, Surf. Sci. 36, 317 (1973).

[10]G. L. Price, Surf. Sci. 46, 697 (1974).

[11]*Epitaxial Growth*, edited by J. W. Matthews (Academic, New York, 1975), Pt. B, pp. 555, 593.

[12]P. I. Cohen, J. Unguris, and M. B. Webb, Surf. Sci. 58, 429 (1976).

[13]S. C. Fain, Jr. and M. D. Chinn, to be published.

[14]The possibility of such a transition for adsorbed monolayers was previously pointed out by G. D. Halsey, in *Fundamentals of Gas-Surface Interactions*, edited by H. Saltsberg, J. N. Smith, Jr., and M. Rogers (Academic, New York, 1967), p. 334.

[15]J. A. Barker *et al.*, J. Chem. Phys. 61, 3081 (1974).

[16]R. Wolfe and J. R. Sams, J. Chem. Phys. 44, 2181 (1966). [See Ref. 4 for discussions on the multiparameter potential (MP) and on the multiparameter potential with a correction for the substrate polarizability (MPSP).]

[17]The slope $db/d(\ln P)$ at a given lattice constant b is slightly different for the MP and MPSP models of Ref. 4. The slope of the dashed line is the mean value; the line was positioned in P so that the measurements appear to approach it asymptotically. The resulting position is intermediate between predicted positions for the two models in Ref. 4.

[18]The importance of misfit dislocations was first suggested to us by J. A. Venables, who has modified the theory of Ref. 4 to include this idea (private communication).

[19]Ref. 7, p. 4165, and S. C. Ying, private communication. $l_0=16$ is equivalent to $\sqrt{u}=0.06$ in Ref. 7.

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

[21]A. Guinier, *X-Ray Diffraction*, translated by P. Lorrain and D. S. Lorrain (Freeman, San Francisco, 1963), p. 216.