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Orientalional ordering of a cesium monolayer on graphite

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Orientalional ordering has been observed by low-energy electron diffraction for structures close to (2×2) in an overlayer of cesium absorbed on the graphite (0001) surface at liquid-nitrogen temperature. The relative orientation of the Cs overlayer to the graphite substrate varies from about 5° to 0° and the lattice misfit changes from about 27.6% to 0% as the coverage of Cs on the graphite surface is increased. For the same lattice-parameter misfit the rotation angles in the structure are almost half of those in the rare-gas physisorbed systems on graphite (0001), the Na chemisorbed on Ru(001), and the Cs planar layer intercalated in the high-stage graphite intercalation compounds. The (2×2) family of structures for the Cs-chemisorption-on-graphite system is consistent with the Novaco-McTague theory of orientational ordering, but there is a stronger bond strength between adatoms in the Cs/C overlayer than in the above other three systems.

INTRODUCTION

Orientalional epitaxy of an incommensurate structure refers to an overlayer lattice having a specific orientation and lattice misfit relative to the substrate lattice. Usually the angle between the two lattices is not a high-symmetry angle of the system. A number of incommensurate and rotated structures in adsorbed layers have been studied in the past including K on Cu(111) (Ref. 1) and Cu(100),² Xe on Pt(111),³ Br on Ag(111),⁴ Na and Cs on Pt(111).⁵ Since there are only a few detailed observations of orientational ordering, the relationship between orientation angles and lattice parameters is not well known. As a result, it is difficult to identify the conditions that impact the observed behaviors of the rotated structures, e.g., impurities, surface steps, and dislocations, which might lock in an incommensurate overlayer into a certain orientation.

The theory of Novaco and McTague^{6,7} (NM) predicts the rotational ordering phenomenon and shows that when the adsorbate-adsorbate interaction dominates in a competition with substrate adsorbate interactions, an incommensurate interfacial structure is formed on the substrate. As a result of periodic strains caused by the substrate field, the overlayer assumes a definite nonsymmetry angle relative to the substrate so as to lower the total energy of the system. Recently, Fuselier, Raich, and Gillis (FRG) have also described orientational ordering by the model of equilibrium configuration of coincident adsorbed monolayers.⁸ They pointed out that there are series of overlayer structures which minimize the free en-

ergy of the overlayer-substrate system and are periodic relative to the substrate but oriented away from simple symmetry directions of the substrate. These structures converge with increasing coverage to a high-symmetry commensurate structure. Both of the noted theories (NM and FRG) fit very well the experimental results for Ar and Ne physisorbed on the graphite basal plane.^{9,10} They also have been applied to orientational ordering recently observed in a strongly chemisorbed system, Na on the Ru(001) surface.¹¹ However, until now, all observed orientational ordering structures have been close to the $(\sqrt{3}x \times \sqrt{3})R 30^\circ$ commensurate structure on a hcp substrate.

This paper describes the observation of the orientational ordering phenomenon for Cs chemisorbed on the graphite (0001) surface with a series of structures close to the $p(2 \times 2)$ structure. The behavior of these Cs structures, defined as the $(2 \times 2)^*$ orientational phases, is consistent with the NM theory, but is not consistent with the FRG model.

EXPERIMENTAL

The experiment was undertaken in an ultrahigh-vacuum (UHV) chamber equipped with a four-grid low-energy electron-diffraction (LEED) optics also used for Auger electron spectroscopy (AES). A natural graphite crystal cleaved by the high-pressure nitrogen gas method¹² was mounted on a universal manipulator¹³ and cleaned by heating to 1000 K in an UHV. A cesium getter vapor source¹⁴ was installed in the chamber with

the amount of Cs exposure controlled by evaporation time and source current. Typically, the temperature of the cesium source was 900 K and the temperature of the graphite substrate was 80 K. The corresponding amount of adsorbed cesium was monitored by recording the AES peaks of Cs and C. All the experimental details have been described previously.¹⁵

The LEED patterns observed for the graphite surface upon increasing exposure of Cs clearly show that the cesium overlayer undergoes various transitions: short-range order to long-range order (commensurate), commensurate to commensurate order, commensurate to incommensurate order, and commensurate or incommensurate to disorder.¹⁵ At a coverage $\Theta=0.085$, a rotationally ordered incommensurate phase appeared. The angular orientation and lattice mismatch of the incommensurate Cs monolayer was measured from the LEED pattern at each stage of cesium exposure.

RESULTS AND DISCUSSION

As previously noted,¹⁵ the orientationally ordered structure appeared in the temperature range from 80 to 155 K and coverage range between about $\Theta=0.085$ –0.11 (where the coverage is defined by the ratio of the number of Cs atoms on the surface to the number of C atoms in the surface layer). This structure was close to the $p(2\times 2)$ structure and was thus denoted the $(2\times 2)^*$ structure. Figure 1 displays three of the LEED patterns obtained from the cesium incommensurate structure on graphite (0001). Their corresponding schematic diagrams are also shown in Fig. 1. In Fig. 1(a) the LEED pattern consists of six graphite first-order beams $\{\mathbf{G}\}$, six sets of quartets of spots around the $(0, \frac{1}{2})$ positions, and six sets of quartets of spots around the $(\frac{1}{2}, \frac{1}{2})$ positions. The cesium overlayer lattice is clearly incommensurate with its graphite substrate and is rotated with respect to the graphite lattice. As shown in Fig. 1, \mathbf{Q} is the vector of the cesium reciprocal lattice, \mathbf{G} is the graphite reciprocal vector, and ϕ indicates the rotation angle between the corresponding \mathbf{Q} and \mathbf{G} vectors which for Fig. 1(a) is 4° .

It should be noted, however, that the entire pattern about the origin in the (h,k) plane is not repeated about each graphite reciprocal lattice point. Six pairs of extra reflections located on the first circle near the origin are equal and each pair is split by a rotational angle 2ϕ , about the (10) directions. Each pair of this first set of extra order beams have the same LEED I - V curve characteristics, therefore, they may correspond to two equiprobability hcp domains of cesium rotated by $\pm\phi$ from either the (10) or the (01) axis of the graphite substrate.

The six dimers of spots defining the second set of extra order beams can be accounted for by double diffraction from the substrate lattice and the overlayer superlattice, and they have intensity-energy curves different from those of the first set of extra order spots. There are also six pairs of diffraction spots which exist around the first-order graphite beams as seen clearly in the LEED photograph in Fig. 1(b) and shown by the open circles in the corresponding drawing. They can be indexed as the third-order beams of the cesium overlayer. The six sets

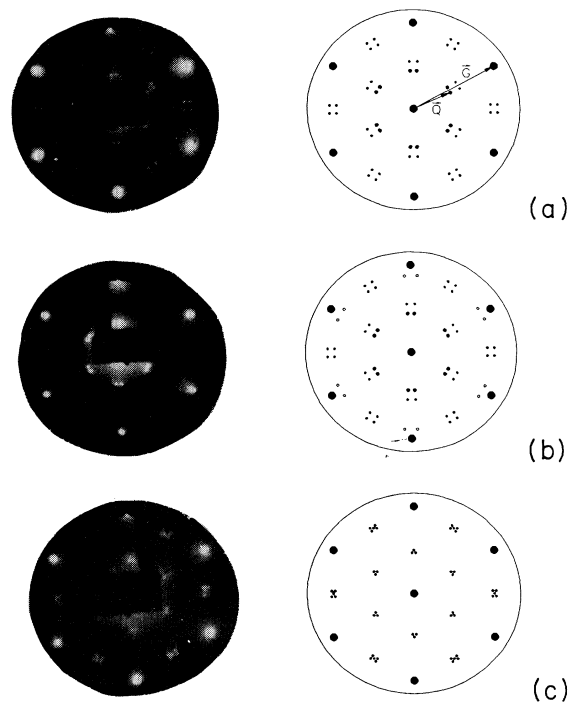


FIG. 1. LEED patterns and their schematics for $\text{Cs}(2\times 2)^*$ structures: (a) $\Theta=0.091$, $\phi=4.0^\circ$, $m=17.6\%$, twelve sets of quartets of first-order and second-order diffraction spots as a result of the Cs orientational phase ($E_p=74$ eV); (b) $\Theta=0.088$, $\phi=4.25^\circ$, $m=21.5\%$, twelve sets of quartets of spots and six dimers of spots (open circles) which are the third-order Cs overlayer diffraction beams ($E_p=74$ eV); (c) $\Theta=0.10$, $\phi=2.1^\circ$, $m=8.7\%$, the coexistence of $(2\times 2)^*$ and $p(2\times 2)$ phases at higher Cs coverage ($E_p=60$ eV).

of quartets of spots on the third and fourth circles in the LEED patterns of Fig. 1 are the second-order beams of the incommensurate cesium phase. Four spots in each set are at the symmetric position around the midpoint between the first-order beams of the graphite (0001). The double-diffraction beams would overlap with them.

As the evaporation time was increased, e.g., Cs coverage increased, the angle between the two oppositely rotated reciprocal lattices and the mean misfit of lattice parameter decreased. The misfit m is defined in terms of the deviation of the mean nearest-neighbor spacing from the commensurate $p(2\times 2)$ spacing $d_0=4.92$ Å as $m=(d_c-d_0)/d_0$, where d_c is the lattice constant in $(2\times 2)^*$ structure. Figure 1(c) is an example of a LEED pattern with smaller rotated angle $\phi=2.1^\circ$ than that in Fig. 1(a). The respective lattice misfit for Figs. 1(a) and 1(c) are $m=17.6\%$ and 8.7% . Figure 1(c) also shows the coexistence of the $(2\times 2)^*$ Cs structure with $p(2\times 2)$ Cs domains as a result of the high coverage of Cs ($\Theta=0.1$).

The compilation of experimental data for the ϕ - m relationship for the $(2\times 2)^*$ structure is shown in Fig. 2. With increased exposure the orientational angle changes from about 5° to 0° with the lattice misfit decreasing from about 27.6% to 0% . It is interesting to note that the

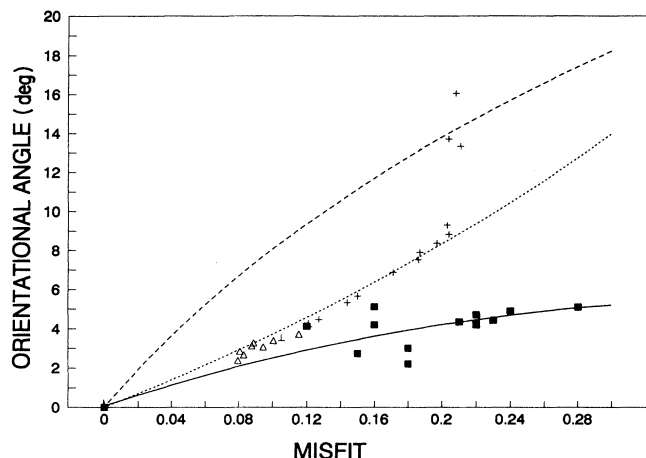


FIG. 2. Orientational ordering phenomena predicted by the NM model with $C_L/C_T=1.63$ (solid line) and with $C_L/C_T=\sqrt{3}$ (dotted line); by the trajectory method (Ref. 11) from $(\sqrt{7}\times\sqrt{7})R19.11^\circ$ to $p(2\times 2)$ (dashed line). Experimental data: Δ , Ar on graphite (Refs. 9 and 11); $+$, Na on Ru (Ref. 11); \blacksquare , this work. The lattice misfits and orientation angles for the Ar on graphite and Na on Ru systems are for deviations from $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure, whereas the Cs on graphite data are for the $p(2\times 2)$ structure.

maximum average Cs-Cs separation measured in this experiment is ≈ 6.1 Å, which is 7% larger than the average distance between atoms in Cs-liquid (5.61 Å), but close to the 6.045-Å lattice constant in the bcc unit cell of three-dimensional (3D) Cs metal. The Cs-Cs separation is also not related to a simple multiple of the 2.46 Å distance between the carbon hexagon centers in the graphite (0001) plane.

The data for Ar physisorbed on graphite and Na chemisorbed on Ru are also shown in Fig. 2 for comparison. It is seen that the rotation angles in the Cs $(2\times 2)^*$ structures are much smaller than those in the Ar on C and Na on Ru structures at the same misfit value. NM theory predicts that when the mismatch in lattice parameters of adsorbate and substrate is small, the equilibrium orientation is a particularly simple function of these lattice parameters and of the elastic constants of the adsorbate film. Rotation away from a symmetry angle will occur only if the transverse phonon branch is soft enough. The theoretical curves of this function are plotted in Fig. 2. It is obvious that our data are in excellent agreement with the theoretical predictions if the ratio of longitudinal and transverse sound velocities of the adlayer C_L/C_T is taken to be 1.63. The experimental data for Ar on graphite and Na on Ru, however, agree with predictions if $C_L/C_T=\sqrt{3}$. This difference may result from the possibility that there is relatively stronger bond strength (or weaker repulsive interaction) between Cs adatoms on graphite as compared to the rare gases on graphite and Na on Ru(001). This could be due to significant electron charge transfer from Cs adatoms to graphite and would cause a smaller C_L and a larger C_T in the Cs $(2\times 2)^*$ film.

In other words, agreement with NM theory would require the transverse branch in the rare gases on graphite and Na on Ru systems to be softer than in Cs $(2\times 2)^*$ on graphite systems.

Although there exist quite similar diffraction patterns for incommensurate alkali-metal phase in the planar structures of the high-stage alkali-metal-graphite intercalation compounds (AM-GIC's),¹⁶ the $(2\times 2)^*$ Cs overlayer structure has different properties from the planar structures of high stage AM-GIC's. In fact, several models have succeeded in describing the AM intralayer structure in high-stage AM-GIC's.¹⁶⁻¹⁸ They propose that the incommensurate planar structure is the result of a triangular AM lattice modulated by the graphite lattice (static distortion wave method),¹⁶ or that the graphite lattice is modulated by the rigid triangular AM lattice,¹⁷ or that the discommensurate domains cause the modulation.¹⁸ However, they result commonly in a simple trigonometric relationship between rotation angle ϕ and misfit m . This is quite similar to NM results with $C_L/C_T=\sqrt{3}$ in the small misfit region, but does not conform to the $(2\times 2)^*$ Cs on graphite experimental data. This might be because intercalated Cs atoms transfer more electron charge into both the carbon layers (above and below) and have stronger repulsive interaction than the Cs atoms adsorbed on top of the graphite. Besides, the entire diffraction pattern about the origin in the (h,k) plane is repeated about each graphite reciprocal lattice point in the high stage AM-GIC's. As discussed above, this is not the case for the $(2\times 2)^*$ Cs structure.

Alternatively, the equilibrium rotation angles and lattice constants of a monolayer in the $(\sqrt{3}\times\sqrt{3})R30^\circ$ Ar on C and $(\sqrt{3}\times\sqrt{3})R30^\circ$ Na on Ru systems are also described very well by the FRG model.⁸ In a way similar to that of the FRG model, we have obtained a series of possible structures for Cs overlayers on graphite as a function of coverage. These structures have very large periodicity. With increasing overlayer density the various branches of stable structures converge to a (2×2) structure. Our experimental data for Cs $(2\times 2)^*$ structures are consistent with one such branch. This branch, however, is not one of the high density branches relying on high-symmetry binding sites for the adatoms. As a result, the FRG model is not accepted as an appropriate model since high symmetry binding sites have been shown to be probable for Cs on graphite.^{19,20} Additional analysis, such as the calculation of the total free energy of this system, would shed more light on this evaluation.

As a final point, Doering and Semancik¹¹ have noted that the main branch of the FRG model is equivalent to a 30° trajectory curve, i.e., the overlayer is compressed from the $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure toward the (1×1) structure with atoms moving along straight lines, which they deduce from the Na on Ru data.¹¹ As described by the phase diagram for cesium adsorbed on the graphite (0001) surface,¹⁵ the graphite (0001)- $(2\times 2)^*$ Cs appears after additional cesium deposition on the graphite (0001)- $(\sqrt{7}\times\sqrt{7})R19.11^\circ$ -Cs structure. It could be possible that the cesium atoms moved linearly along the 40.9° trajectory from $(\sqrt{7}\times\sqrt{7})R19.11^\circ$ lattice sites to the $p(2\times 2)$ commensurate sites; however, this is not

borne out by the data in Fig. 2. The simple trajectory from $(\sqrt{7} \times \sqrt{7})19.11^\circ$ structure to the $p(2 \times 2)$ gives too large an orientation angle as compared to the experimental data of $\text{Cs}(2 \times 2)^*$ system and theoretical data from the other models.

CONCLUSION

The results of our experiments suggest that orientational ordering behavior in an adlayer is a general phenomenon. It can exist not only in physisorbed sys-

tems, and chemisorbed systems, but in structures close to both the $(\sqrt{3} \times \sqrt{3})R 30^\circ$ structure and the $p(2 \times 2)$ structure. It has also been shown that the C_L/C_T ratio is not universal for orientational ordering behavior and is probably affected by intralayer and interlayer charge transfer.

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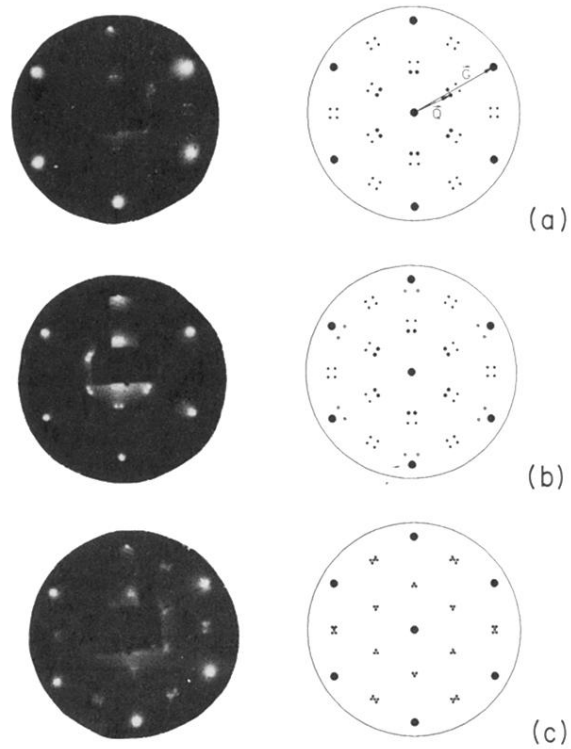


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