Evidence of a Square Two-Dimensional Solid of Methane Physisorbed on the (100) Surface of Magnesium Oxide

J. P. Coulomb, K. Madih, and B. Croset
Faculté des Sciences de Luminy, Département de Physique, 13288 Marseille Cedex 9, France

and

H. J. Lauter
Institut Laue-Langevin, 38042 Grenoble Cedex, France

(Received 10 September 1984)

The structure of CD_4 films adsorbed on a highly homogeneous MgO(100) surface has been probed by neutron diffraction. Both the monolayer and the bilayer crystallize in a commensurate square $c(2\times2)$ superstructure. This is the first clear evidence of a two-dimensional condensation of a solid van der Waals film with square symmetry. An order-disorder transition is observed and appears to be a first-order melting.

PACS numbers: 68.20.+t, 61.12.Dw, 68.45.Da, 82.65.Jv

Previous studies on two-dimensional (2D) physisorbed phases have been restricted to the use of hexagonal substrates (graphite,[1] some lamellar halides,[2] and the boron nitride[3]). Indeed, only these materials present the very homogeneous surfaces which are required for the observation of 2D phases. Moreover, most of the theoretical work has been done for hexagonal substrates because the hexagonal symmetry is the higher one in two dimensions: As a matter of fact only two elastic constants are needed for this symmetry while three are needed in the case of square symmetry.[4,5]

Recently, Coulomb and Vilches have succeeded in the preparation of a new substrate of cubic symmetry: MgO.[6] The high homogeneity of their powder sample (100) surface is indicated by the observation of two successive 2D phase transitions during the condensation of a rare-gas monolayer.[7] The gas quantities, adsorbed on the same MgO powder of H^2S grade (highly homogeneous surface), are different at monolayer completion for Ar, Kr, Xe,[7] N_2, and CH_4,[8] suggesting that these 2D films (with the exception of at most one) are incommensurate with the MgO(100) surface. Structural studies of Kr/MgO[9] and of ^{36}Ar/MgO[10] carried out by x-ray and neutron diffraction have shown that the respective 2D solid phases crystallize in incommensurate close-packed structures. We note that the MgO powders used in these experiments seemed to have a weak surface homogeneity.

In two dimensions, the close-packed structure of spherical molecules is of hexagonal symmetry. Hence for the case of a square surface, as for MgO(100), a commensurate phase undergoes not only squeezing (or expansion) of the interatomic size, but in addition a drastic change in symmetry. CD_4 appears to be the most suitable adsorbate for the observation of a commensurate (2D) solid; as a matter of fact its bulk lattice parameter a ($a=4.18$ Å for the temperature $T=60$ K[11]) matches the MgO parameter a_0 very well ($a_0=4.21$ Å).

We present here a neutron-diffraction characterization of CD_4 films adsorbed on MgO powder (H^2S grade). Both the monolayer and the bilayer are commensurate solids over a wide temperature range ($2 < T < 80$ K). Previous structural studies of methane films adsorbed on uniform lamellar substrates such as graphite[12] or $NiCl_2$[13] have pointed out that the CH_4 monolayer structure is hexagonal close packed.

The experiment was performed on the D1B two-axis spectrometer at the high-flux reactor of the Institute Laue Langevin (ILL) ($\lambda=2.52$ Å, $\Delta q/q=10^{-2}$). The sample was prepared according to the method described by Coulomb and Vilches.[6] After combustion of magnesium ribbons, the MgO powder was baked for twelve hours at 950 °C in a quartz cell and transferred under vacuum into a 50-mm-high, 16-mm-diam aluminium cell. It was baked again at 400 °C after transport to the ILL.

Figure 1 shows isotherms of CD_4 and Kr measured on this sample. The substep in the Kr isotherm after the first step is our test to verify the quality of surface homogeneity. During the whole experiment, equilibrium pressures were in agreement with a set of isotherms previously measured.[8] Finally, the cleanliness of the sample was checked after the diffraction experiment. The quality criterion was still satisfied. The diffraction spectra were obtained by the difference between those of the substrate plus the adsorbate and those of the bare substrate. The mean counting time was 10 h, except for the bare substrate and the complete monolayer at 10 K, for which it was 20 h.

We shall discuss the structure of the physisorbed film for different coverages θ at low temperature. For $\theta=0.78$ and $\theta=1.0$, a strong "sawtooth" peak is observed at $q=1.50$ Å^{-1}, Figs. 2(a) and 2(b). This peak

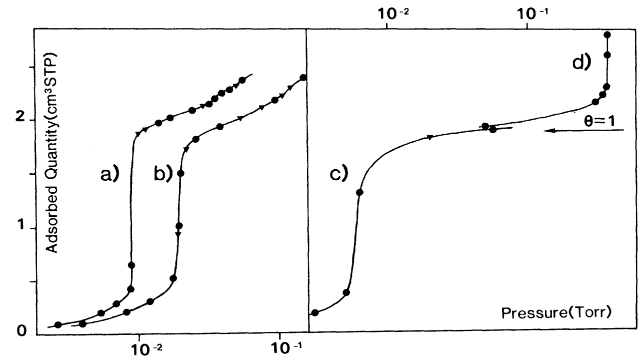

FIG. 1. Adsorption isotherms of Kr on MgO [at $T = 77.0$ K (curve *a*) and $T = 79$ K (curve *b*), respectively, before and after the neutron diffraction experiment] and of CD_4 on MgO [at $T = 78.3$ K (curve *c*) and $T = 76.5$ K (curve *d*)]. Experimental points are measured when adsorbing (circles) or when desorbing (triangles).

position is very different from those already obtained for diffraction by a CD_4 monolayer adsorbed on uniform hexagonal surfaces ($q = 1.71$ Å^{-1} for CD_4/graphite[12] and $q = 1.75$ Å^{-1} for $CD_4/NiCl_2$[13]). A second weak sawtooth peak is clearly visible at $q \simeq 2.1$ Å^{-1} in the long-counting time spectra (20 h), Fig. 2(b). Clear evidence for the existence of this peak is given by a least-squares-fit procedure employing no constraint on position or intensity. The calculated positions of the (10) and (11) diffraction peaks for a commensurate $c(2\times2)$ monolayer are $q = 1.49$ Å^{-1} and $q = 2.11$ Å^{-1} respectively, for the MgO(100) surface. These values are in excellent agreement with our experimental results and allow us to conclude that for a coverage $\theta \leqslant 1$, the CD_4 film is a square $c(2\times2)$ solid.

In order to compare the experimental peak shapes with calculated ones, we must make assumptions on the orientations of the CD_4 molecule in the unit cell. We have tested several possible orientations (molecule standing on a tripod with or without cylindrical symmetry, molecule rotating with spherical symmetry, and molecule standing on a dipod, i.e., on two hydrogen atoms). We noticed that the orientation of the molecule has little influence on both the peak shapes and their hierarchy. The calculated curves shown in Figs. 2(b) and 2(c) have been drawn with the molecules oriented in the unit cell as in Fig. 3(a) which gives the best fit between experimental and calculated profiles. The profile used was the one proposed by Ruland and Tompa.[14] We took into account the structure factor by direct multiplication. For a coverage of 2, the diffraction spectrum is quite different. While the (10) peak seems to be deformed and moved towards high q, the (11) peak is at the same position but is narrower and is strongly enhanced with respect to the (10) peak, Fig. 2(a). To understand such a diffraction spectrum, we must remember that the high-q part of a sawtooth peak is due to q vectors not parallel to the surface and that it may be strongly modified by the structure factor of the solid bilayer. This effect of modification of the peak shape (and even the apparent position) is much stronger in our case than in previous observations on graphite because of two reasons: Firstly, our substrate is a nonoriented powder and secondly, the symmetry of the solid bilayer is different, leading to a "forbidden" (10) peak for a diffraction vector parallel to the surface. The computa-

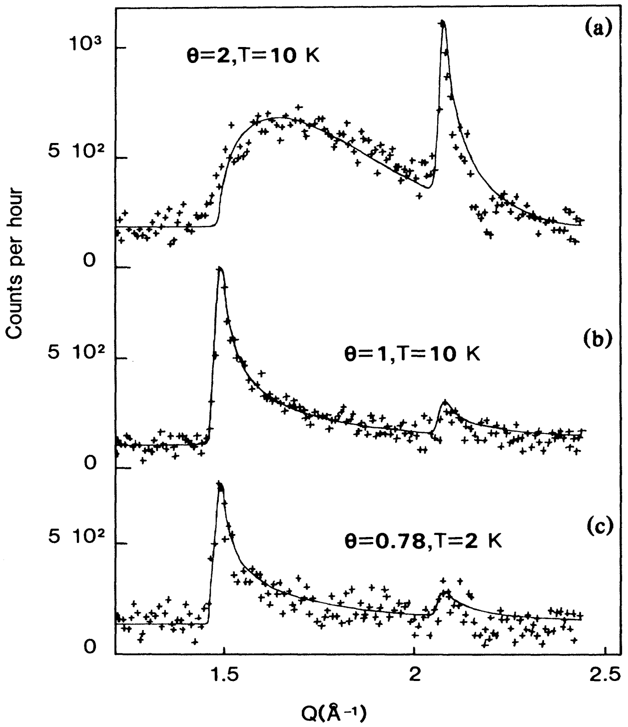

FIG. 2. Coverage dependence of the diffraction spectra for CD_4 films adsorbed on MgO at low temperatures. Crosses correspond to the experimental points and the full lines represent the calculated diffraction profiles. The experimental results are well fitted by solidlike profiles (with $q_{10} = 1.49$ Å^{-1}, $q_{11} = 2.11$ Å^{-1}, and a coherence length $L = 500$ Å).

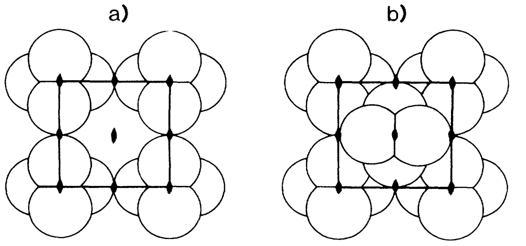

FIG. 3. Structure of the CD_4 films: (a) projection of the CD_4 molecules on the 2D unit cell; (b) same projection for the bilayer unit cell.

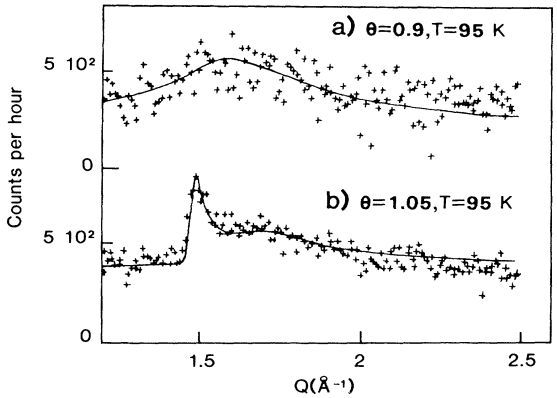

FIG. 4. Coverage dependence of the diffraction spectra for CD_4 films adsorbed on MgO at $T = 95$ K. (a) Liquidlike profile (with $q = 1.57$ Å^{-1} and $L = 10$ Å). (b) Sum of a solidlike profile (with $q = 1.5$ Å^{-1}, $L = 500$ Å) and of a liquidlike profile (with $q = 1.71$ Å^{-1}, $L = 15$ Å, and a proportion of 25%).

tion that we have done for different molecular orientations shows that the main features have little dependence on molecular orientation. The best agreement is obtained for $d = 2.25$ Å and the unit cell drawn in Fig. 3(b). The main result of our diffraction study is that both the bilayer and the monolayer are commensurate with a square $c(2\times2)$ structure.

We shall now present the spectra obtained for higher temperatures. For a submonolayer coverage $\theta = 0.78$, the square solid is stable below $T = 80$ K. At $T = 85$ K, we observe the vanishing of long-range order. The spectra are similar to that shown in Fig. 4(a) and are well fitted by a liquidlike peak at $q \simeq 1.57$ Å^{-1} with a coherence length $L = 10$ Å. For coverages greater than one monolayer, the $c(2\times2)$ solid structure still exists at $T = 95$ K. Even more interesting is the observation of the monolayer solidification, as coverage increases, where a phase coexistence between the commensurate solid and a disordered phase occurs at $T = 95$ K, Fig. 4(b). This is strongly suggestive of a first-order transition; however, other interpretations are not ruled out as a result of the statistical scatter and the use of a powder sample. Our study is still in progress and more detailed results will be published elsewhere.[15]

In conclusion, this study has established that deuterated methane adsorbed on high-quality magnesium-oxide powder forms a commensurate $c(2\times2)$ square structure. This commensurate structure persists through completion of the first layer; the bilayer is still commensurate at least at 10 K. In spite of the wide range of temperature and coverage explored, no evidence of an incommensurate solid phase was found. The orientation of the molecule which corresponds to the best fit of the diffraction data is rather surprising but is consistent with the square symmetry of the structure. Unlike the case of krypton on graphite, there is no commensurate-incommensurate transition. This may be simply explained by the fact that the $c(2\times2)$ square structure is very close to the structure of the (100) plane of bulk CD_4.[11] A film growing toward the bulk may well preserve the $c(2\times2)$ superstructure for several layers.

Considering the melting of the commensurate phase, several points appear. Firstly, the transition appears to be first order. Secondly, since the transition from liquid to solid is obtained by an increase in coverage, we must conclude that the liquid is less dense than the commensurate solid. While this fact is usual in melting transition, we must notice that the commensurate solid is 16% less dense than a compact one. Therefore the liquid phase is of abnormal low density. As a supplementary proof, the liquid ring is around 1.57 Å^{-1} for CD_4 on MgO while it is around 1.71 Å^{-1} for CD_4 both on $NiCl_2$[13] and on graphite.[12] This low-density liquid should be explained by an influence of the substrate potential.

Lastly, the existence of a commensurate phase allows isotherms of CD_4 on MgO to be used as standards for the measure of specific surfaces of this substrate.

We wish to thank the ILL staff who supported us during all this work: Mr. K. Bensaidane, Mr. P. Mangin, Mr. J. Pannetier; and Professor M. Bienfait and Professor J. Suzanne for careful reading of this paper. Faculté des Sciences de Luminy is equipe de recherche No. 899 associé au Centre National de la Recherche Scientifique.

---

[1] A. Thomy and X. Duval, J. Chim. Phys. **67**, 1101 (1970).

[2] P. Robert and Y. Larher, Phys. Rev. Lett. **40**, 1275 (1978).

[3] J. Regnier, A. Thomy, and X. Duval, J. Colloid. Interface Sci. **70**, 105 (1979).

[4] D. R. Nelson and B. I. Halperin, Phys. Rev. B **19**, 2457 (1979).

[5] L. D. Landau and E. M. Lifshitz, *Theory of Elasticity* (Pergamon, New York, 1970).

[6] J. P. Coulomb and O. E. Vilches, J. Phys. (Paris) **45**, 1381 (1984).

[7] J. P. Coulomb, T. S. Sullivan, and O. E. Vilches, Phys. Rev. B **30**, 4753 (1984).

[8] K. Madih and J. P. Coulomb, to be published.

[9] J. L. Jordan, J. P. McTague, L. Passel, and J. B. Hasting, Bull. Am. Phys. Soc. **28**, 870 (1983).

[10] H. J. Lauter, C. Tiby, H. Wiechert, and C. Knopp, to be published.

[11] W. Press, J. Chem. Phys. **56**, 2597 (1972).

[12] P. Vora, S. K. Sinha, and R. K. Crawford, Phys. Rev. Lett. **43**, 704 (1979).

[13] C. Tessier, thesis, Université de Nancy I, 1983 (unpublished).

[14] W. Ruland and H. Tompa, Acta Crystallogr. A **24**, 93 (1968).

[15] J. P. Coulomb, K. Madih, and B. Croset, to be published.