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# VIBRATIONAL STATES AND PHASE DIAGRAM OF THE SUBMONOLAYER KRYPTON ADSORBED ON GRAPHITE BY THE LOW TEMPERATURE HEAT CAPACITY*

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ABSTRACT

Heat capacity measurements have been made for the krypton submonolayers physically adsorbed on the surface of graphite between 3 and 110 K for four coverages near the completion of a monolayer. The vibrational states at low temperatures for both "commensurate" and "incommensurate" phases are discussed with particular attention to the effect of corrugation of the surface potential. Finding of two anomalies in heat capacity below the melting point at a coverage close to the monolayer capacity for commensurate structure suggested two possibilities for the sequence of phases, i.e., either commensurate → incommensurate → commensurate or incommensurate → re-entrant fluid → commensurate with increasing temperature.

## INTRODUCTION

Over the years much attention has been given to the fundamentals of adsorption on graphite surfaces (ref. 1), and the adsorption of rare gas atoms on graphite is now understood reasonably well. A current theoretical work demonstrates (refs. 2 and 3), however, that further study is necessary to understand the characteristics of vibrational states in the adsorbed monolayer even of rare gases and also to be able to describe it in a quantitative manner. The heat capacity and its temperature dependence at low temperatures are very informative for this purpose as is the case for the bulk solids (ref. 4). The example we choose to illustrate the point is the krypton/graphite system for which we are also interested in the phase diagram in detail. The heat capacity at fixed coverages is again most sensitive to phase boundaries at fixed temperatures.

### The effect of surface corrugation

It would rather be simple to deal with vibrational states of the two-dimensional solid with no substrate underneath which is called as a floating monolayer (ref. 5). The invariance under lateral translations of the monolayer center of mass exists, which leads to normal modes with vanishing frequency at

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the Brillouin-zone center. The heat capacity may therefore obey the Debye's $T^2$ law at sufficiently low temperatures. In actual system of the adsorbed monolayer, however, the corrugation potential of the substrate plays an important role. It is necessary to take into account adatom-substrate interactions as well as adatom-adatom interactions. The most prominent effect is the realization of a "commensurate" phase: The commensurate-monolayer solid is in registry with the underlying substrate, whose structure is determined by the periodic components of the adatom-substrate potential. The normal mode frequencies near the zone center of the commensurate monolayer have a nonzero minimum value. In other words, there is a finite cut-off to the density of states at the low-frequency end of the vibrational spectrum. The heat capacity is thus exponential at low temperatures and given by

$$C \propto (h\nu_c/kT) \exp(-h\nu_c/kT) \tag{1}$$

where $\nu_c$ is the cut-off frequency (ref. 6). The gap is shown in model calculations for the commensurate monolayer of nitrogen on graphite (ref. 7).

According to Steele's Fourier decomposition (ref. 8), the adatom-substrate potential for a monatomic adsorbate is expressed as

$$V(\vec{r},z) = V(z) + \Sigma V_g(z) \exp(i\vec{g}\cdot\vec{r}) \tag{2}$$

where $\vec{r}$ is a vector in the plane of the surface, z is the distance between adatom and substrate, and the vectors $\vec{g}$ are the reciprocal-lattice vectors of the substrate surface. The gap or the cut-off frequency is directly related to the amplitudes $V_g$ of periodic components which play an important role for determining the stability of commensurate monolayers (ref. 9). The purpose of this paper is to obtain the size of $V_g$ for the commensurate krypton on graphite from the $\nu_c$ which can be obtained from the low temperature heat capacity.

## The phase diagram

The main feature of the phase diagram for krypton/graphite was obtained by isotherm measurements (ref. 10): At low coverages, the krypton forms a $(\sqrt{3}\times\sqrt{3})$ triangular commensurate solid at low temperatures, in which the nearest neighbor distance between the atoms is expanded by about 6 % compared with that for the bulk solid. As the coverage is increased, it transforms into an incommensurate but still triangular solid phase with the same interatomic distance as for the bulk. Heat capacity studies (refs. 11 and 12) were also successfully used to map the phase boundaries. More recently, however, a high-resolution x-ray diffraction study (refs. 13 and 14) demonstrated quite an exotic behavior near the completion of monolayer: The incommensurate phase cannot transform to the commensurate phase directly but through a re-entrant

fluid phase which exists between the two. On the other hand, as observed in the case of Xe/graphite at 73 K (ref. 15), a direct transition between commensurate and incommensurate might still be possible. Rather than exploring the entire phase diagram, we concentrate on the detection of those phase boundaries by heat capacity measurement, which is another purpose of the present work.

## EXPERIMENTAL

The calorimetric technique for measuring heat capacities has been described previously (ref. 16). The only change made in the system was the insertion of a new calorimeter vessel, which was equipped with a needle valve. The Grafoil MAT (7.67 g) with a specific surface area of 24 $m^2/g$ (ref. 17) was used as the substrate which was obtained from Union Carbide. It was heated to 400°C under vacuum before use. Krypton gas of research purity (99.99 %) was purchased from Takachiho Kagaku and was purified further by fractional distillation.

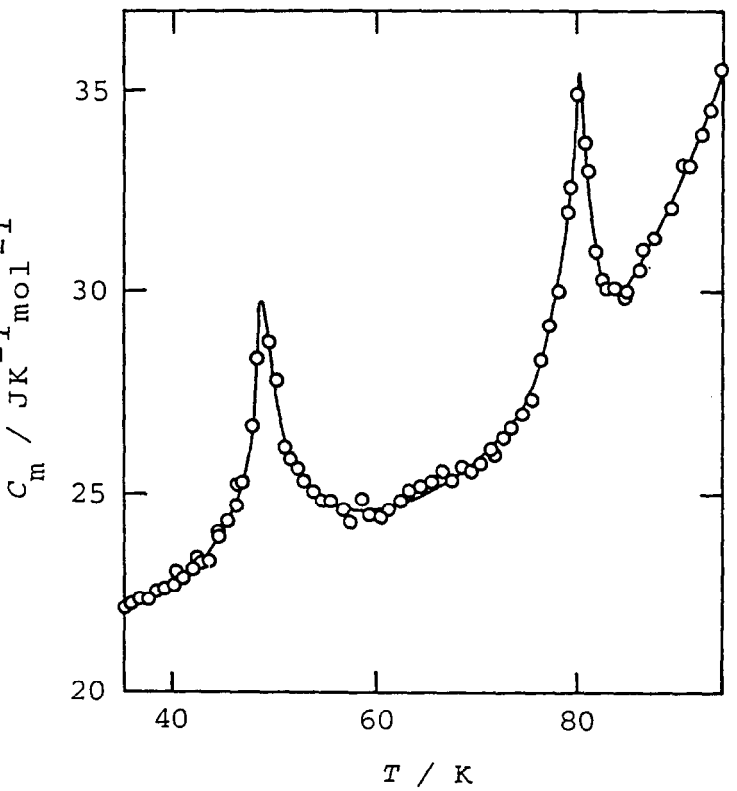


Fig. 1. Molar heat capacity of krypton adsorbed on graphite at a coverage close to the monolayer capacity for commensurate structure ($n_a$ = 2.00 mmol). The correction for desorption at higher temperatures is not applied.

Heat capacity measurements were made between 3 and 110 K for four coverages and up to even higher temperature for some coverages. The actual amounts of the gas introduced into the vessel were 1.42, 1.60, 2.00, and 2.20 mmol. While it is not easy to assess their absolute coverage accurately, the former two surely correspond to the commensurate coverage and the last to the incommensurate one at low temperatures as will be seen in the phase diagram. The coverage with the amount of 2.00 mmol seems to lie very close to the boundary between commensurate and incommensurate phases.

## RESULTS AND DISCUSSION

### The phase diagram

The most remarkable feature was obtained for $n_a$ = 2.00 mmol with respect to the phase diagram: Two small but sharp anomalies in heat capacity were found at 49.2 K and 80.5 K below the melting point (Fig. 1). As suggested in the previous section, there are two possibilities for the sequence of phases, either commensurate → incommensurate → commensurate or incommensurate → re-entrant fluid → commensurate with increasing temperature. An x-ray

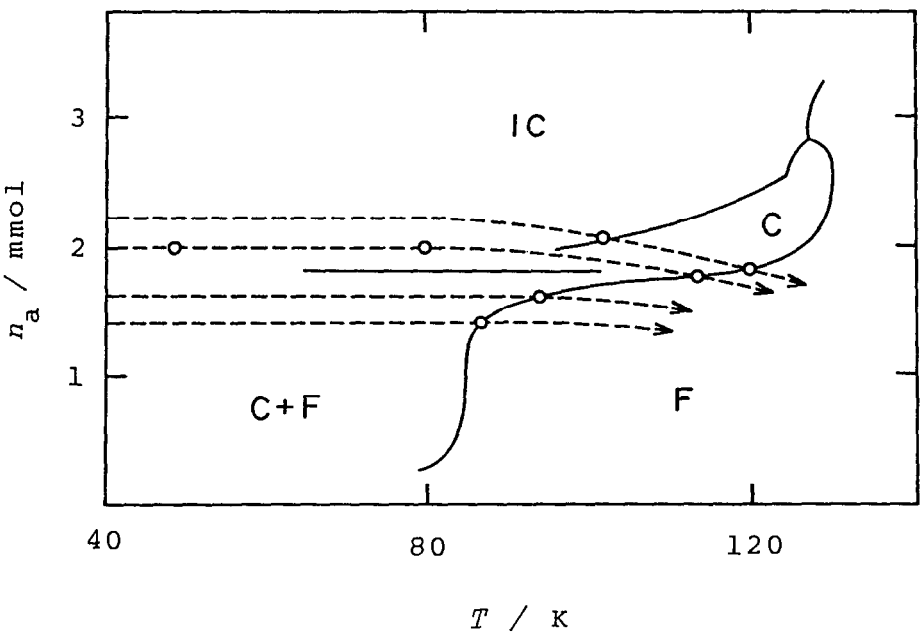


Fig. 2. The phase diagram of krypton adsorbed on graphite: C, commensurate solid phase; IC, incommensurate solid phase; F, fluid phase; -----, our measurement path; o, the peak in heat capacity observed by the present work. The coverage is adjusted by the phase boundary at the commensurate coverages determined by Butler et al. (ref. 12) (———).

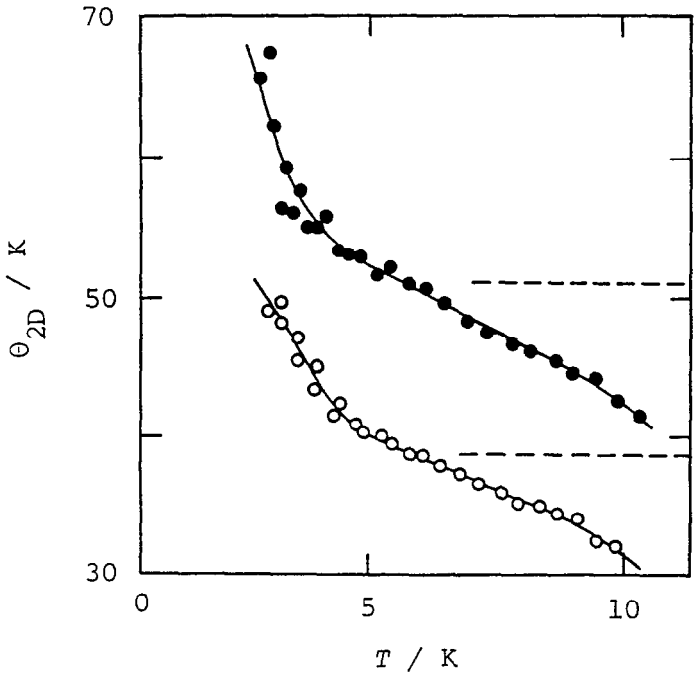


Fig. 3. Two-dimensional Debye temperatures calculated from the observed heat capacities: o, commensurate solid phase ($n_a$= 1.60 mmol); •, incommensurate solid phase ($n_a$= 2.20 mmol); -----, supposed behavior for the contribution from lattice vibrations.

diffraction study would easily discern which is the case. While our results are consistent with the phase diagram constructed by the previous heat capacity measurements by Butler et al. (Fig. 2), it is suspected that they missed the lower transition, or alternatively they may have hit the overlap region of the two transitions.

Vibration perpendicular to the surface

The heat capacities obtained at low temperatures were converted to the two-dimensional Debye temperatures, assuming 2N degrees of freedom for krypton adsorbed on graphite. The results are illustrated in Fig. 3 for $n_a$= 1.60 mmol (commensurate phase) and 2.20 mmol (incommensurate phase). The more rapid decrease above 6 K should come from contribution other than the Debye vibrations, i.e., the excitation of the vibrational motion perpendicular to the surface. The strategy which we normally adopt for obtaining the characteristic temperature for such a motion is to subtract such extra contribution to the heat capacity that arises from that motion so that the

Debye temperature remains constant at higher temperatures. We thus obtain 48 K Einstein characteristic temperature for both coverages, assuming that the mode has no dispersion. It is thus suggested that the vibrational motion perpendicular to the surface is not significantly affected by the surface corrugation in krypton/graphite system.

Amplitude of the surface corrugation

One of the simplest models of the phonon density of state for the commensurate solid would be the Debye-like model with a cut-off frequency $\nu_c$ as well as a Debye frequency $\nu_D$, which is shown in Fig. 4. The heat capacity data for $n_a$= 1.60 mmol were fitted to the model as illustrated in Fig. 5. The parameters we obtained from such a fitting are 10 K and 36 K for the $\Theta_c$ and $\Theta_D$, respectively, where $\Theta = h\nu/k$. The value of $V_g$ can be calculated from the $\Theta_c$ (or $\nu_c$) under certain approximation (ref. 2) and is given by

$$\nu_c = 2(-3V_g/m)^{1/2}/a \qquad (3)$$

where $m$ is the mass of a krypton atom and $a$ is the nearest-neighbor spacing (4.26 Å). From it we obtain $V_g$= -6.9 K, which value indicates that the krypton atoms sense a more strongly modulated potential than that calculated (-4.4 K) by the use of the potential and parameters of Steele (ref. 8). On the other hand, another theoretical consideration (ref. 9) demonstrates that even more

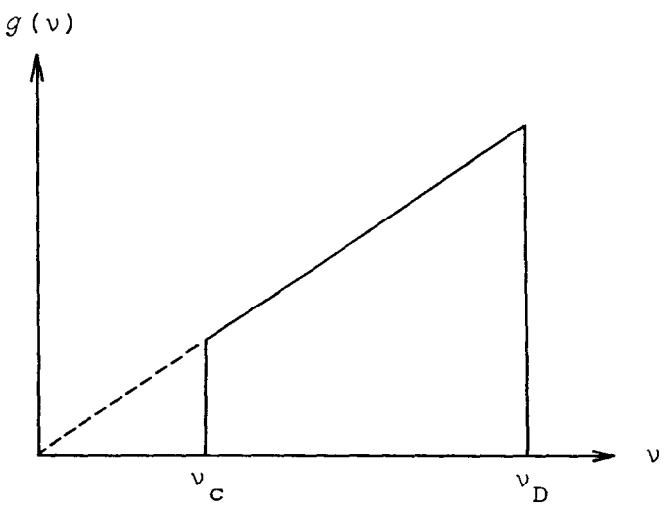


Fig. 4. Debye-like model of the frequency spectrum with two parameters used for fitting of the low temperature heat capacities.

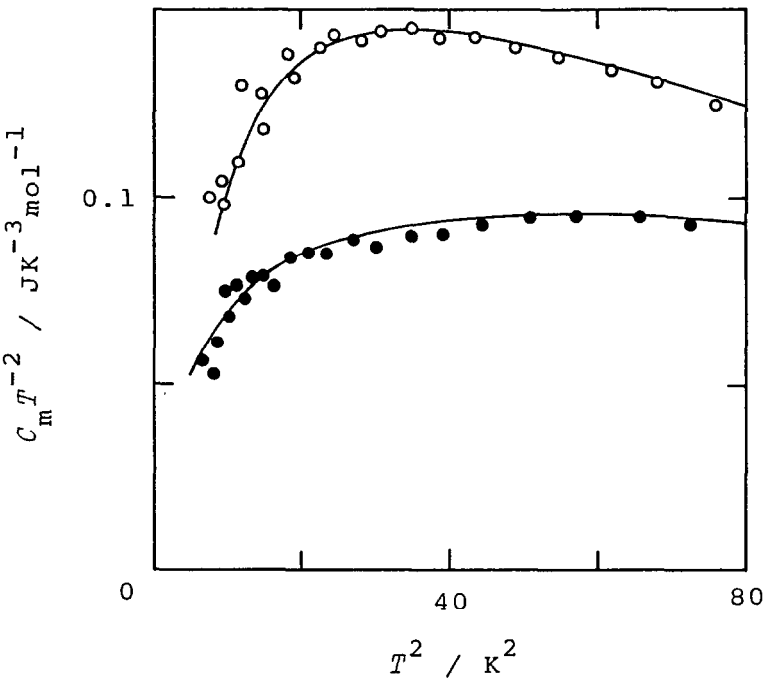


Fig. 5. A plot of $C/T^2$ against $T^2$ at low temperatures: o, commensurate solid phase ($n_a$= 1.60 mmol); •, incommensurate solid phase ($n_a$= 2.20 mmol); ———, fitting curves for both phases with the model. Contribution from the vibration perpendicular to the surface is subtracted from the observed heat capacities.

strongly modulated potential ($V_g \leq$ -11 K) would be neccessary to stabilize the ($\sqrt{3}$x$\sqrt{3}$) structure.

When such analysis is applied for the incommensurate phase (2.20 mmol), we obtain a finite value, $V_g$= -3.4 K (Fig. 5). The reason is that since it is not the floating incommensurate layer, the effect of surface corrugation can not completely be averaged out. Further heat capacity measurements at the lower temperatures would be advisable to ascertain the feature of vibrational states.

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REFERENCES


1 W.A. Steele, The Interaction of Gases with Solid Surfaces, Pergamon, New York, 1974.
2 T.M. Hakim, H.R. Glyde and S.T. Chui, Phys. Rev., B37 (1988) 974.
3 L.W. Bruch, Phys. Rev., B37 (1988) 6658.
4 R.H. Beaumont, H. Chihara and J.A. Morrison, Proc. Roy. Soc. London, 78 (1961) 1462.
5 L.K. Moleko, B. Joos, J.M. Hakim, H.R. Glyde and S.T. Chui, Phys. Rev., B34 (1986) 2815.
6 J.G. Dash, Films on Solid Surfaces, Academic Press, New York, 1975.
7 G. Cardini and S.F. O'Shea, Surf. Sci., 154 (1985) 231.
8 W.A. Steele, Surf. Sci., 36 (1973) 317.
9 R.J. Gooding, B. Joos and D.L. Bergersen, Phys. Rev., B27 (1983) 7669.
10 A. Thomy and X. Duval, J. Chim. Phys., 67 (1970) 1101.
11 D.M. Butler, J.A. Litzinger, G.A. Stewart and R.B. Griffiths, Phys. Rev. Lett., 42 (1979) 1289.
12 D.M. Butler, J.A. Litzinger and G.A. Stewart, Phys. Rev. Lett., 46 (1981) 1533.
13 D.E. Moncton, P.W. Stephens, R.J. Birgeneau, P.M. Horn and G.S. Brown, Phys. Rev. Lett., 46 (1981) 1533.
14 E.D. Specht, M. Sutton, R.J. Birgeneau, D.E. Moncton and P.M. Horn, Phys. Rev., B30 (1984) 1589.
15 H. Hong, C.J. Peters, A. Mak, R.J. Birgeneau, P.M. Horn and H. Suematsu, Phys. Rev., B36 (1987) 7311.
16 A. Inaba and H. Chihara, Can. J. Chem., 66 (1988) 703.
17 A. Inaba, Y. Koga and J.A. Morrison, J. Chem. Soc., Faraday Trans. 2, 82 (1986) 1635.