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Phases and Phase Transitions of D_2 on Graphite obtained by variable ^{4}He Pressure

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Abstract

Phases and phase transitions of D_2 on graphite have been investigated using ^{4}He as 2-dimensional pushing-gas. A quite unusual path in the D_2 phase diagram is followed when the 2-dimensional D_2-lattice is compressed due to the ^{4}He adsorption as the temperature is lowered: starting in the commensurate phase, passing through the domain wall liquid phase, ending in the striped superheavy domain wall phase.

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The phase diagram of a monolayer of D_2 on graphite is a typical example of a quantum gas on graphite like adsorbed ^{3}He[1]. However, the transition from the $(\sqrt{3}\times\sqrt{3})R30°$ commensurate phase (C-phase) to the incommensurate phase at low temperatures (T<7K) as a function of coverage exhibits more intermediate phases (see fig.1) than the transition of the other quantum gases. This is due to the less pronounced quantum character of D_2. The phase diagram has been defined by heat capacity measurements[2]. The structures were studied by neutron diffraction[3,4,5], LEED[5,6] and NMR[7]. The dynamics in the different phases was investigated with inelastic neutron scattering[8,13].

Here we want to concentrate on the C-, the α- and the β-phase which are depicted for the pure D_2-graphite system in fig.1. The diffraction peaks observed in the α-phase have been fitted with a model of superheavy striped domain walls[4,9]. The β-phase has a liquid-like structure factor (see the discussion of the scans of fig.2) but the same excitations as seen in the α-phase are maintained at least near the α-β transition[8] (in particular the transverse phonon which is characteristic of a solid phase). This means that this phase may be defined as fluid in the sense that the domain wall length is shortened with respect to the α-phase (this gives a liquid like line shape) thus allowing for a high mobility of the domain walls but still exhibiting the characteristic excitations of a solid. The dashed line between the C-phase and β-phase in fig.1 is just a guide to the eye connecting the high heat capacity peaks of the melting C-phase to the start of the α-β transition.

In heat capacity and neutron scattering experiments the study of phase transitions is usually done as a function of temperature: a certain amount of gas is filled into the sample cell to obtain a certain coverage and after an annealing procedure the data are recorded at constant coverage (corrected for thermal desorption if necessary) as a function of temperature. It is very difficult to study a phase transition at constant temperature as a function of coverage because thermodynamic equilibrium is reached very slowly (if at all) if the adsorption is done at low temperatures. However, another gas can be coadsorbed and, provided both gases do not mix, it can act as pushing gas (2-dimensional (2-d) piston), driving the host gas through phase transitions as a function of spreading pressure or density[10]. This effect is analogous to a coverage dependence for a pure adsorbate.

In our case we have used ^{4}He as pushing gas. It can adsorb or desorb without difficulty at e.g. T=6K. In this experiment we added the ^{4}He at a temperature where the D_2 is adsorbed in the fluid phase. During cooling down the D_2 becomes solid first, but also the ^{4}He adsorbs and increases the 2-d spreading pressure, thereby compressing the D_2. The vapor pressure of the 3-dimensional ^{4}He gas was recorded down to T=5K. From a series of ^{4}He adsorption isotherms the 2-d spreading pressure was calculated[11] (see fig.2).

The neutron diffraction pattern shown in fig.2 have been taken on the D16 spectrometer of the ILL on the cold source at a wavelength of 4.526 Å. The sample consisted of a stack of ZYX-graphite[12]. The coverage of a complete commensurate layer was 14.43 cm^3 STP (coverage $\rho=1$) deduced from the highest intensity of the diffraction peak of the D_2 commensurate layer out of a sequence of diffraction scans as a function of coverage at 4K[4].

The runs presented in fig.2 show the (10) diffraction peak of the D_2 adsorbed layer (the neutron cross section of ^{4}He is nearly 20 times smaller than the one of D_2). A first filling of 11.1 cm^3 STP D_2 was made. Then an amount of 8.0 cm^3 STP ^{4}He was added. The whole system was thermalized at 38K and slowly cooled down. For each neutron scan the system was kept at a constant temperature. By this technique different phases are crossed (see fig.1). In order to draw the points into the phase diagram of pure D_2 we used as definition of the coverage the deduced density of the D_2 alone:

- The two spectra, taken at 16.9K and 15.9K, exhibit liquid character. The coverage is taken to be the one of the pure system, because this phase is homogeneous and the ^{4}He is assumed to be in the second layer and above.
- At 13.9K the lattice spacing ($Q=1.703Å^{-1}$) is the one of the C-phase. The coverage can range from the previous value up to $\rho=1$. Within this range the peak position and shape does not change. The same holds for the next spectrum taken at 10.0K. Here the peak intensity has increased because the Debye-Waller factor increased. For T<10.0K the peak intensity drops and the width of the peak increases due to an effective density $\rho>1$ of the D_2 (the overfilling of the C-phase creates dislocations).
- Only at 8.0K a shift of the peak position, which evidences a compression of the adsorbate, indicates the transition to the β-phase (This may define the dashed line in fig.1 which is not seen in heat capacity measurements). At 6.0K a further compression is noticeable but the line shape still indicates the β-phase. Thus this point must be placed just below the transition line between the α- and β-phase.
- Further cooling brings about a decrease in the width of the peak and the appearence of satellites. The scan at 4K shows that the line shape can be well fitted with the model of a Monte-Carlo distribution of superheavy domain walls of the pure D_2-graphite system[4]. This fit gives a value of $\rho=1.116$ at which this scan is marked in fig.1. This is in agreement with the coverage-position of the scans at higher temperatures. It should be pointed out that the lineshape is identical to the ones calculated for the pure D_2 system. Thus the ^{4}He has no influence on the structure factor of the D_2 lattice and consequently we argue that it does not mix with the D_2.
- It is interesting to note that the spectra at 5.0K and 5.5K display a new kind of lineshape which cannot be fitted up to now. New satellites appear between the main peak and the satellite position of the α-phase. We interpret this effect as a particular part of the α-β transition not visible as a pronounced peak in the heat capacity.

The 2-d spreading pressure can be used to estimate the relaxation of a D_2-molecule in a superheavy domain wall (relaxation with respect to the adsorption site on the graphite[4]) neglecting the interaction with the D_2-molecules next to the domain wall. A value of 0.2Å is obtained if a spring force constant of 91 dyn/cm[13] (in-plane between D2 and graphite) is taken. This value has to be compared with the one of 0.68Å resulting from the calculation of the structure factor in the domain wall phase[4]. The two values have the same order of magnitude and the difference can be explained by the fact that the force constant taken is the one at the adsorption site and not the one at the relaxed position. The agreement between the two values of the relaxation deduced from two different experiments is very reasonable.

To conclude, we have shown for the first time that a compression of the D_2 monolayer on graphite by coadsorption of ^4He is possible. This permits to study delicate parts of the D_2 phases and its phase transitions and to get more valuable information about the domain walls. Here we presented a study which includes the transition from the commensurate phase to the domain wall liquid phase and from this phase to the striped superheavy domain wall phase.

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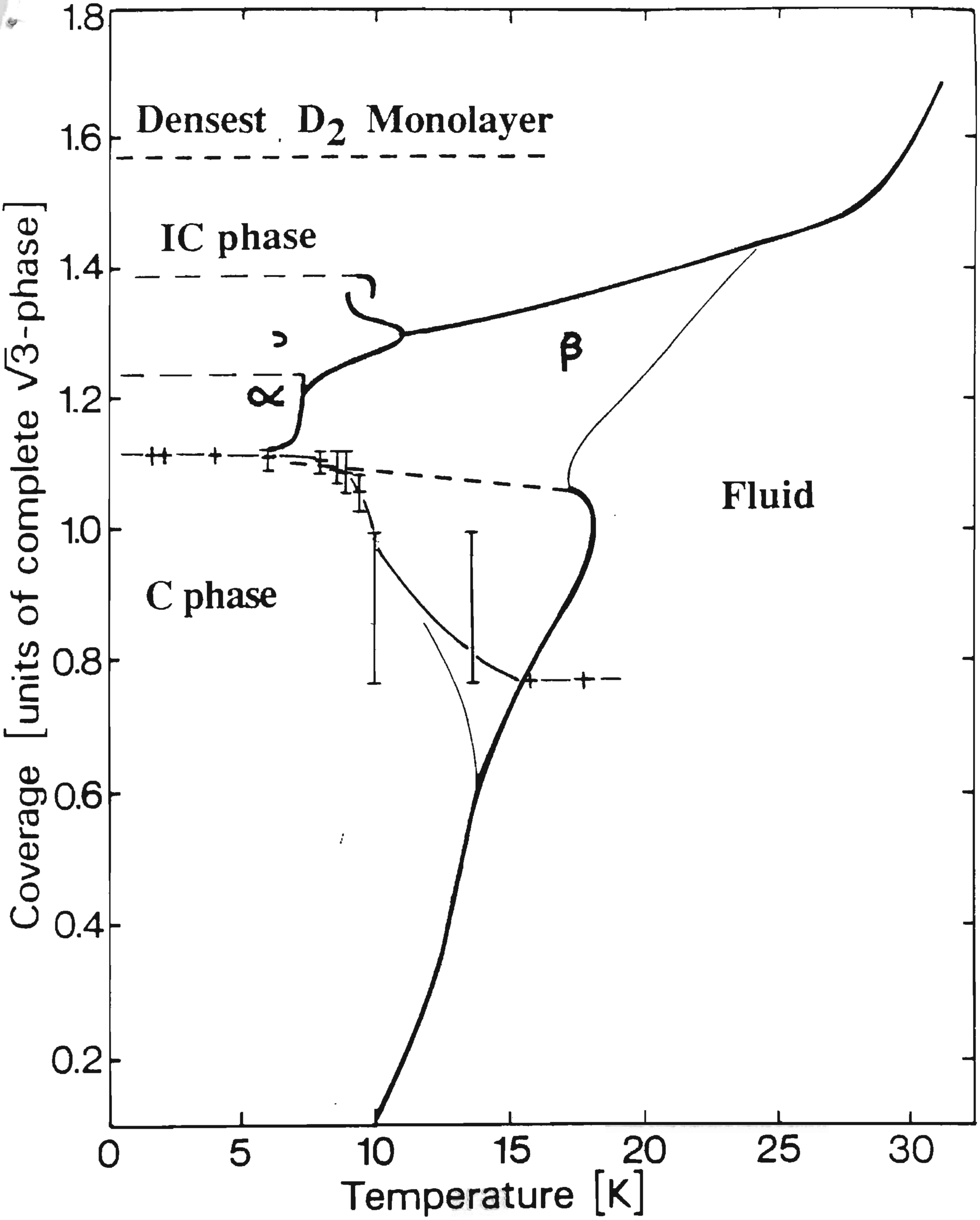
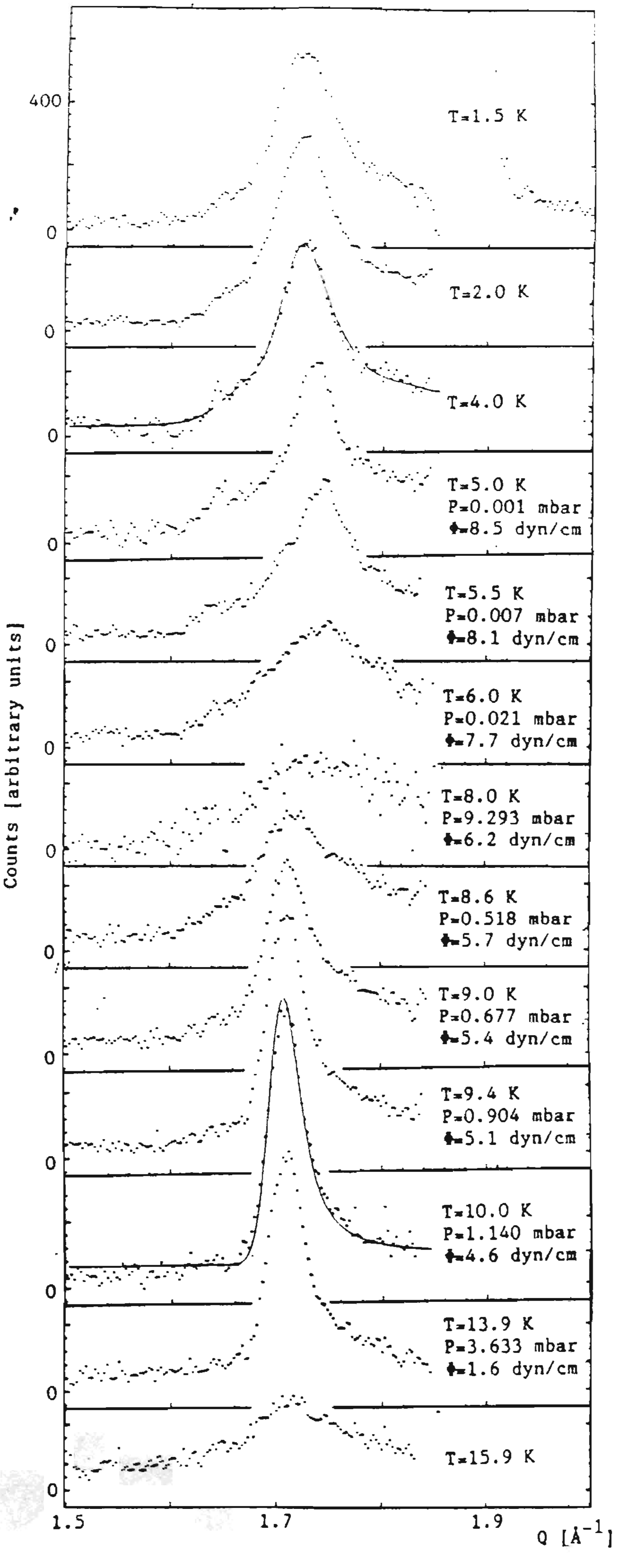
Figure captions

Fig.1: Monolayer phase diagram of D_2 on graphite. The phase transitions (solid lines) are given by heat capacity measurements[2]. The dashed line is a supposed transition between C- and β-phase and is discussed in the text. The meaning of C-, α-, β-phase is also explained in the text. The line through the points indicates the path in the D_2 phase diagram on graphite accomplished by compression due to the coadsorbed ^4He.

Fig.2: Sequence of neutron diffraction spectra as a function of temperature. The temperature at which each diffraction spectrum was taken, the measured 3-dimensional ^4He pressure and the calculated spreading pressure[11] are marked.


Densest D_2 Monolayer
IC phase
α
β
C phase
Fluid
Coverage [units of complete √3-phase]
Temperature [K]
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
5
10
15
20
25
30

F = 1


400
0
T=1.5 K
0
T=2.0 K
0
T=4.0 K
0
T=5.0 K
P=0.001 mbar
Φ=8.5 dyn/cm
0
T=5.5 K
P=0.007 mbar
Φ=8.1 dyn/cm
0
T=6.0 K
P=0.021 mbar
Φ=7.7 dyn/cm
0
T=8.0 K
P=9.293 mbar
Φ=6.2 dyn/cm
0
T=8.6 K
P=0.518 mbar
Φ=5.7 dyn/cm
0
T=9.0 K
P=0.677 mbar
Φ=5.4 dyn/cm
0
T=9.4 K
P=0.904 mbar
Φ=5.1 dyn/cm
0
T=10.0 K
P=1.140 mbar
Φ=4.6 dyn/cm
0
T=13.9 K
P=3.633 mbar
Φ=1.6 dyn/cm
0
T=15.9 K
0
Counts [arbitrary units]
1.5
1.7
1.9
Q [Å^{-1}]

FIG