Diffusive motions in HD films physisorbed on graphite

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Abstract

High-resolution quasielastic neutron scattering was used to study diffusive motions in two-dimensional (2D) liquid and solid phases of deuterium hydride (HD) submonolayers adsorbed on graphite. For the first time it could be unambiguously clarified that the novel reentrant fluid (RF) phase at the commensurate-incommensurate (C-IC) transition has the character of a viscous fluid.

Key words: Thin films of quantum systems; hydrogen properties; phase transitions; diffusion

One of the most fascinating phase transitions in two-dimensional (2D) matter is the transition from the commensurate (C) to the incommensurate (IC) phase which due to the quantum nature of the hydrogen isotopes adsorbed on graphite is spread out over a much broader coverage range than in classical adsorbate systems (eg., Kr), and, hence, can be investigated in great detail [1–4]. Fig. 1 depicts a part of the phase diagram of HD on graphite in the vicinity of the C-IC transition obtained from heat-capacity measurements [1,4]. At coverages below one monolayer (ρ=1 ML is defined as the most complete $\sqrt{3}$-structure), the system condenses into a commensurate $(\sqrt{3} \times \sqrt{3})$ R30^o phase, whose order-disorder transition occurring at 19.32 K was shown to belong to the three-state Potts universality class [1]. When the coverage of HD exceeds 1.07 ML, the C-IC transition takes place and at low temperatures an intermediate phase appears which was identified as a solid striped domain-wall phase (SIC) [2–4]. At about 8.5 K this phase undergoes a transition to the reentrant fluid (RF) phase which beyond 18 K gradually transforms into an isotropic 2D fluid.

The reentrant fluid (RF) is an unusual, well-correlated state of matter not known in the bulk. According to theory [5] the weak IC phase should be unstable to the spontaneous creation of free dislocations and, hence, should be a fluid. This result was supported by molecular-dynamics simulations [6], which found a network of temporally meandering domain walls, a "domain-wall fluid". From diffraction experiments [1–4] it was concluded that this phase is an oriented, well-correlated fluid. However, this interpretation of the data was not unambiguous, because the microstructure of the RF phase could also be described by a distribution of static disordered patches of the striped domain-wall phase or by an amorphous phase [7]. In order to clarify the nature of the RF

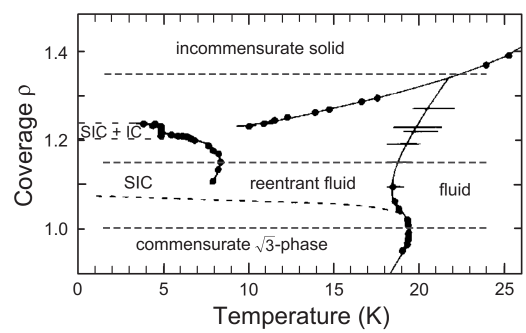

Fig. 1. Part of the phase diagram of HD on graphite in the vicinity of the C-IC transition [1,4]. The dashed lines indicate the trajectories of EISF-scans (see Fig. 3).

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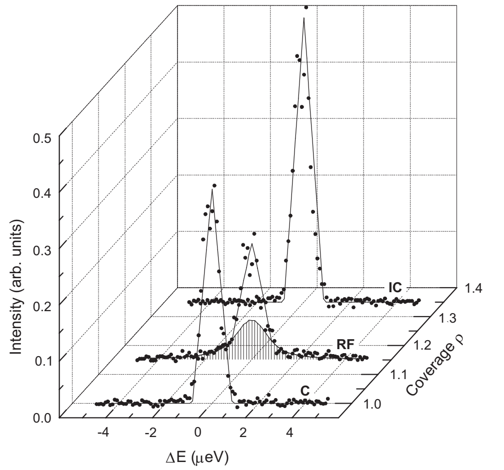

Fig. 2. Representative QENS spectra of HD physisorbed on graphite at Q=1.031 Å^{-1}, T=10 K and coverages 1.0, 1.15 and 1.35 ML. The solid lines represent total fits to the data including solid and liquid components, the hatched area is a powder-averaged Lorentzian fit to the mobile part of the film. The instrumental resolution function was considered in the fits.

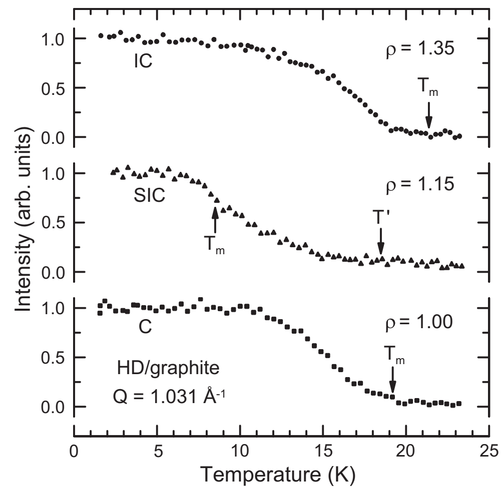

Fig. 3. Elastic incoherent scattering (EISF) intensity versus temperature for three coverages ρ of HD on graphite. Considerable mobility of HD molecules is evident well below the melting temperatures, T_m, and the transition temperature, T'.

phase and to explore molecular mobility in the various phases, quasi-elastic neutron scattering (QENS) measurements were carried out.

The experiments were performed at the ILL (Grenoble) on the cold neutron backscattering spectrometer IN10 designed for very high energy resolution ($\Delta E \approx 0.9\,\mu$eV). The system chosen was HD on graphite which due to its large time-independent incoherent neutron-scattering cross-section is the most favorable case.

Fig. 2 displays QENS spectra recorded at momentum transfer Q=1.031 Å^{-1}, at the fixed temperature T=10 K and at three coverages: ρ=1 in the C phase, ρ=1.15 in the RF phase and ρ=1.35 in the IC phase. The data were reduced by the background scattering. The figure reflects the dramatic evolution of the spectra with coverage. At 10 K spectra taken in the C and IC phases exhibit only resolution limited elastic peaks (solid lines), and thus these phases can be regarded as completely solidified. However, in the RF phase at ρ=1.15 the strongly reduced intensity of the peak and the appearance of wings indicated by the hatched area are first clear signatures of the liquid-like character of this phase. From line shape fits to the data (see Fig. 2) the QENS line-width was extracted. Data taken at different coverages and temperatures showed a progressive quasielastic broadening with raising temperature due to increasing mobility of the molecules.

This feature could also be confirmed by temperature scans of the elastic incoherent neutron-scattering intensity (EISF) at Q=1.031 Å^{-1} and the same three coverages (see Fig. 3). The arrows mark the melting temperatures T_m of the various phases and T' the transition temperature from the RF to the fluid phase. The decrease of intensity reveals that, surprisingly, molecular mobility in the C and IC phases already starts to wake up about 8 K below the melting temperatures. These precursors of melting correlate well with the long low-temperature wings of heat-capacity peaks [1,4] which are related to thermal fluctuations of the adsorbate. This effect is less pronounced for the SIC phase ($\approx$ 2 K) and the decrease of intensity continues gradually over a broad temperature range up to $T' \approx$ 18.5 K where the isotropic fluid phase is reached.

The analysis of the Q-dependence of the QENS spectra gave important insights into the microscopic mechanisms of diffusion occurring in the various phases which will be reported elsewhere.

In conclusion, the QENS measurements presented here provide the first unambiguous proof for the liquid-like nature of the reentrant fluid phase.

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References

[1] H. Wiechert, Physica B**169** (1991) 144.

[2] J. Cui, S.C. Fain, Jr., Phys. Rev. B**39** (1989) 8628.

[3] H. Freimuth, H. Wiechert, H.P. Schildberg, H.J. Lauter, Phys. Rev. B**42** (1990) 587.

[4] H. Wiechert, H. Freimuth, H.J. Lauter, Surf. Sci. **269/270** (1992) 452.

[5] S.N. Coppersmith, D.S. Fisher, B.I. Halperin, P.A. Lee, W.F. Brinkman, Phys. Rev. Lett. **46** (1981) 549.

[6] F.F. Abraham, S.W. Koch, W.E. Rudge, Phys. Rev. Lett. **49** (1982) 1830.

[7] H.J. Lauter, H. Godfrin, V.L.P. Frank, P. Leiderer, in: Phase Transitions in Surface Films 2, H. Taub et al. (eds.), Plenum Press, New York (1991) p. 135.