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Phase transitions in monolayer hydrogen and deuterium on graphite

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Submonolayer phase transitions of parahydrogen and orthodeuterium on graphite have been investigated with positronium annihilation. It is shown that in contrast with conventional specific-heat measurements, quantitative assessments of gas in the mixed commensurate solid plus gas phases are possible, which will lead to a redrawing of the phase diagrams.

The study of physisorbed monolayers on smooth graphite surfaces is now a mature field. The adsorption of a range of gases, from hydrogen to xenon, has been well investigated with a variety of methods, including isotherms, specific heats, neutron scattering, low-energy electron diffraction, x-ray diffraction, and others. The nature of the two-dimensional (2D) phase transitions and the role of the underlying carbon substrate have been especially interesting.[1] H_2 and D_2 monolayers on graphite allow one to study ordering phenomena and phase transitions in quantum systems. In both cases at low coverages, a commensurate $(\sqrt{3}\times\sqrt{3})$ $R30°$ phase forms due to the corrugation of the carbon surface potential, and at coverages near monolayer completion an incommensurate triangular 2D solid phase is created. Specific-heat measurements on submonolayers have allowed phase diagrams to be drawn for H_2 (Refs. 2 and 3) and D_2 (Ref. 4) that describe the transitions from 2D gas to commensurate solid plus gas. These measurements, however, based on broad peaks, are not very informative. They do indicate differences between H_2 and D_2, which have been attributed to differing zero point motions of the quantum particles, but they cannot give quantitative descriptions of the mixed gas/solid phases.

In this paper we report on measurements with a new method employing positronium (Ps) formation, which offers the prospect of detailed examination of these phase transitions.

Positronium offers a unique means of studying the behavior of two-dimensional systems. It is well known that positrons injected into metals quickly thermalize by electronic and phononic excitations and may then diffuse to a surface to cause the emission of Ps by capturing a surface electron.[5] In the special case of graphite, Sferlazzo *et al.*[6] with a positron beam experiment observed that under normal conditions at room temperature little emission occurs. However, their 2-γ angular correlation study revealed that large amounts of Ps were emitted at high temperatures. The lack at low temperatures was attributed to the band structure of graphite,[7] which showed that parallel momentum conservation would forbid surface electrons at the top of filled bands participating in Ps formation, whereas at high temperatures the abundance could be explained with a mechanism in which momentum conservation was satisfied by the emission and absorption of phonons.[6]

The basal plane of graphite offers an ideally smooth substrate for the thermodynamic study of condensed gas monolayers: their creation and their phase transitions.[8] The exfoliated form of graphite, grafoil, is a leaflike structure (of typical dimension, 100 nm)[8] with basal plane surfaces of large specific adsorption area.[9] Gases easily permeate the internal spaces and condense on the (001) surfaces. At low temperatures, in the presence of graphite, the condensed gases will be parahydrogen and orthodeuterium.[10]

Positrons injected into grafoil will thermalize in the carbon and have a high probability of arriving at a (001) surface. We have previously observed that at low temperatures these positrons are capable of forming Ps if physisorbed atoms are present on the surface and that with Ar, N_2, and O_2 the amount depended on the monolayer coverage.[11] Measurements on similar systems have been reported.[12,13] A subsequent study on fluid-physisorbed methane[14] demonstrated that Ps production rises to a peak and then declines to zero as the coverage approaches completion. We suggested it was the recoil of molecules that conserves momentum and hence allows the formation of Ps, but that the recoil was prevented with 100% monolayer coverage.

The apparatus consisted of a 110-ml copper chamber mounted directly on the cold finger of an APD Displex closed-cycle helium refrigerator with temperatures controlled with an accuracy of 0.3 K. The pressure of the gas within the chamber was continuously monitored with an external Digiquartz gauge at room temperature. The 0.53 g grafoil (20 $m^2\,g^{-1}$) sample consisted of ten lavers each of area 130 mm^2 at the center of which was a directly deposited 30 μC ^{22}NaCl positron source. The technique adopted was to seal in a fixed quantity of H_2 or D_2 and then to record the spectra of annihilation photons emitted perpendicular to the basal planes with a germanium detector for sample temperatures declining from 300 to 8 K. The conventional $3\gamma/2\gamma$ parameter R (counts in the range 0–450 keV divided by counts in the 511 keV peak) indicates the ortho-Ps annihilation. About 60 runs were taken for D_2 and H_2, each with 40 measurement temperatures over 24 h.

Very similar curves are obtained for H_2 and D_2, but they differ in detail. As an example, Fig. 1 for D_2 shows the amount of ortho-Ps formed for seven various starting quantities of gas corresponding to final $\sqrt{3}\times\sqrt{3}$ coverages lying between 0.4 and 0.9. In all cases, as the temperature is lowered, condensation commences, and the Ps rises to a maximum $[R\sim 6.47]$. For the 5.1 Torr case, all the D_2 is condensed on the graphite by 35 K, at a 2D coverage of 0.41 $\sqrt{3}\times\sqrt{3}$, and the Ps production remains flat down to about 16

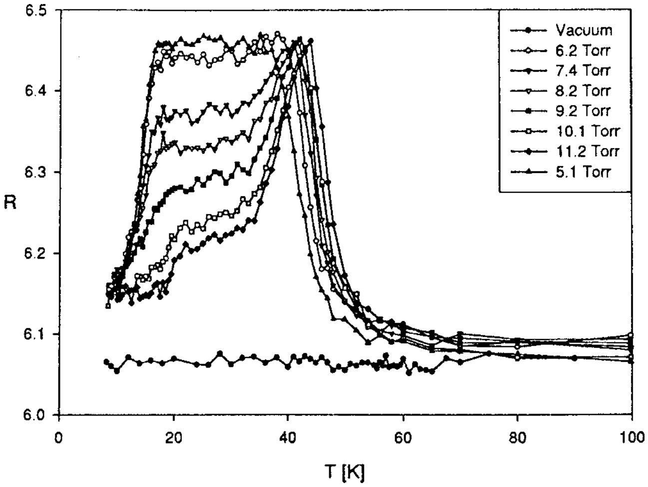

FIG. 1. Orthopositronium annihilation for condensed monolayers of deuterium with coverages ranging from 0.4 to 0.89 $\sqrt{3}\times\sqrt{3}$. The response with vacuum is also shown.

K. When more gas is present (e.g., 8.2 Torr≡0.65 coverage) the Ps production increases to a peak, then declines to the left of the maximum as more D_2 is laid down, only to plateau when all the gas is adsorbed.

The right-hand sides of the peaks depict the initial laying down of the gas and are well described by the Boltzmann approximation formula for ideal adsorbed 2D gases[8] relating pressure $P=(n/\beta\lambda)\exp(-\beta\varepsilon_0)$ with the areal coverage (n), ε_0 the adsorption energy, $\beta=1/kT$, and $\lambda=h/\sqrt{2\pi mkT}$. Values of pressure and temperature for a sequence of positronium peaks with hydrogen are shown in Fig. 2. The good optimum fit of the line to the data justifies the connection between Ps annihilation and monolayer gas coverage. The fit indicates a hydrogen/graphite binding energy of 490 K and common peak coverages (n) of 0.235, equivalent to 0.4 $\sqrt{3}\times\sqrt{3}$ commensurate coverages.

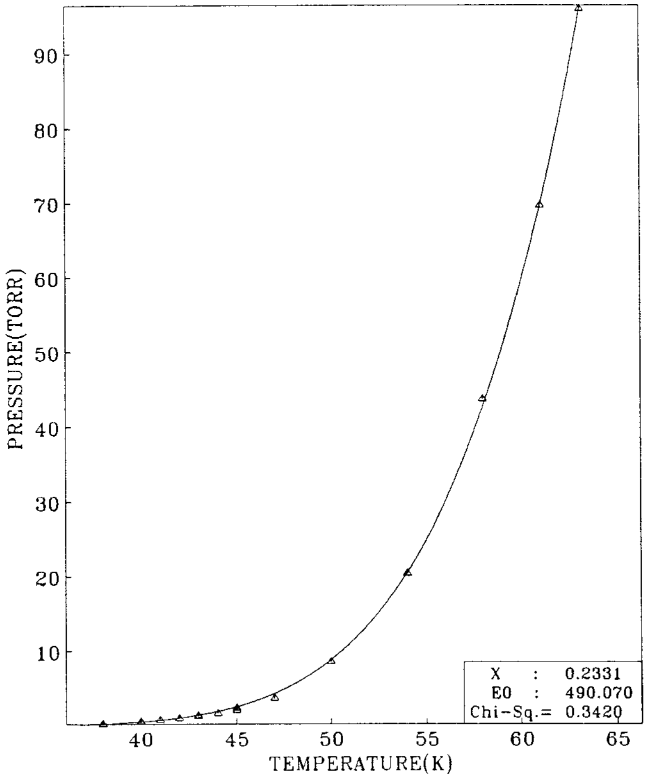

FIG. 2. A fit of the Boltzmann expression to the pressures and temperatures pertaining at the peaks of the Ps curves.

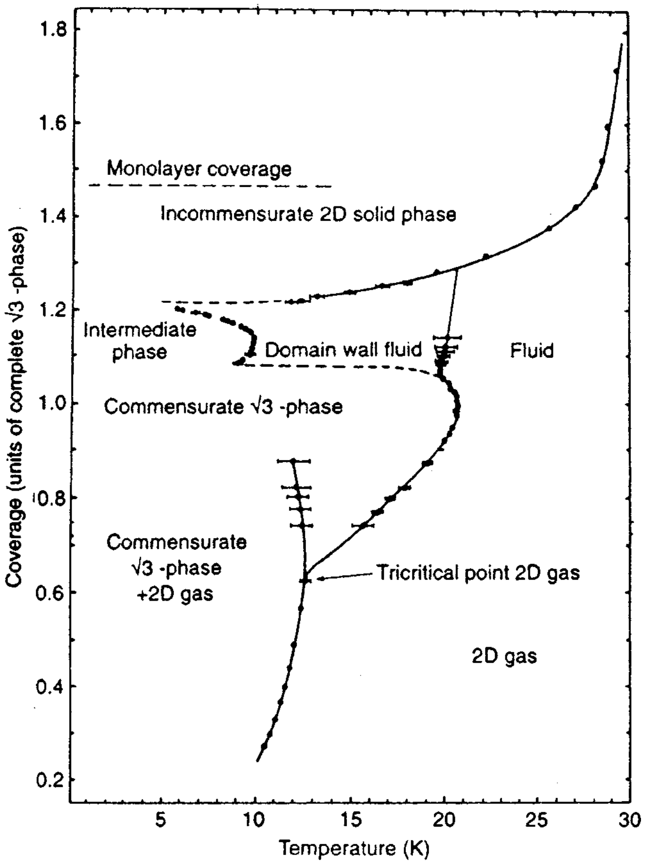

FIG. 3. The accepted phase diagram of H_2 on graphite. (Refs. 1 and 15). D_2 has a similar diagram (Ref. 15), but, while the line below 0.6 coverage is parallel to that for H_2, it lies about 1 K higher. And the right-hand fork for D_2 crosses that for H_2 at 14.5 K (Ref. 15).

The accepted phase diagrams for the submonolayer regions of D_2 and H_2 are similar but not identical. Figure 3 shows the H_2 diagram.[1,15] For both gases, below a coverage of 0.6 $\sqrt{3}\times\sqrt{3}$, a simple line, established from the broad peaks of the specific-heat curves,[3,4] represents the transition from gas to a mixed phase of commensurate solid plus gas. It is clear that the drops in Ps production below 20 K, seen for D_2 in Fig. 1, are associated with these phase changes. For the 0.41 $\sqrt{3}\times\sqrt{3}$ D_2 case, the boundary is encountered at 16 K; in the 11.2 Torr example (0.89 $\sqrt{3}\times\sqrt{3}$) the phase transition is seen to start at a higher temperature of 22 K. Below 10 K, the value of $R=6.14$ indicates the low level of Ps production when the 2D layer is essentially commensurate D_2 solid.

Above 0.6 $\sqrt{3}\times\sqrt{3}$, shoulders appeared with the specific-heat peaks, and these were interpreted as forks in the phase boundaries, the bifurcation being less pronounced for D_2 than for H_2. Thus in Fig. 1 the transition at 22 K may be associated with the right-hand fork; i.e., the transition at 0.89 $(\sqrt{3}\times\sqrt{3})$ coverage from a 2D gas to a commensurate solid. A comparison of Ps production for H_2 and D_2 is shown in Fig. 4 for two approximately equal coverages. At a H_2 coverage

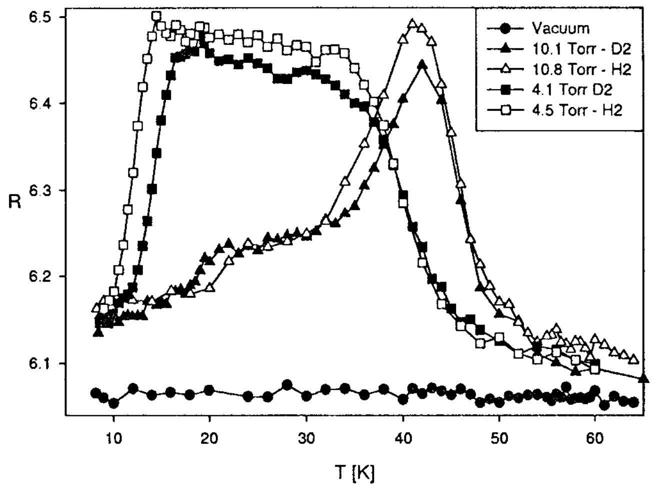

FIG. 4. Selected Ps curves for H_2 and D_2. The drops on the left-hand sides describe phase transitions, and they show that the relative temperatures of the transitions for H_2 and D_2 are reversed for the two different coverages. The difference in the magnitudes of the *o*-Ps annihilation (*R*) for D_2 and H_2 is a consequence of the differing zero point motions of the adsorbed quantum particles.

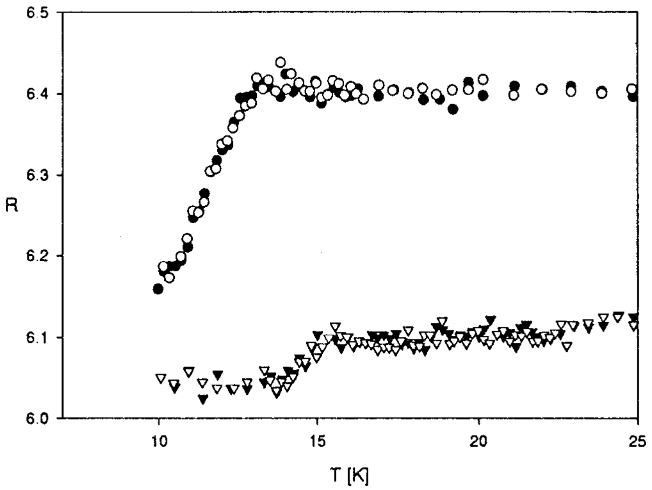

FIG. 5. High precision runs for H_2 at two coverages. The positronium parameter (*R*) is a function of the 2D gas present. The black points represent descending temperatures; the open points rising temperatures. The continuous transitions are quantified; there is no hysteresis. The top curve corresponds with a final coverage of 0.35 $\sqrt{3}\times\sqrt{3}$, the lower with a much higher coverage of 2.9 $\sqrt{3}\times\sqrt{3}$.

of 0.35 $\sqrt{3}\times\sqrt{3}$ (4.5 Torr), the Ps begins to drop at about 2 K below the D_2 curves, whereas for a higher coverage of 0.85 $\sqrt{3}\times\sqrt{3}$, the relative H_2 and D_2 transition temperatures are reversed in order, in accord with the respective right-hand forks in the phase diagrams.[3,4] However, the hypothesis implied by the fork is that if one imagines reducing temperature with a coverage of, say, 0.8 $\sqrt{3}\times\sqrt{3}$, a 2D hydrogen layer crosses via a second-order transition from a gas phase to a commensurate solid at 17 K and then to a mixed gas plus commensurate solid phase at 12 K, and similarly for D_2. This idea is not supported by the positronium evidence; the 10.1 Torr D_2 run (0.8 $\sqrt{3}\times\sqrt{3}$) starts to drop at 20 K, but if the transition were from a pure 2D gas to a pure commensurate phase the drop in *R* would be effectively vertical and not spread over >6 K.

The descent of the Ps parameter *R* as a phase crosses the boundary from gas to commensurate-solid-plus gas (Figs. 1 and 4) gives more information than can be obtained from specific-heat measurements. Our hypothesis is that the slopes actually reveal the proportions of gas in the 2D mixtures as a function of temperature.

We decided to examine in more detail the connection between the specific-heat peaks and our assessments of the *o*-Ps annihilation (*R*). For two H_2 coverages, we measured the Ps production with smaller steps first descending in temperature and then rising. Figure 5 shows the curves; to be noted is the absence of any hysteresis, confirming that the fractions of 2D gas present were in equilibrium at all temperatures. The top curve (final 0.35 $\sqrt{3}\times\sqrt{3}$ coverage) starts to drop at 13.2 K and reaches the minimum ($R = 6.15$) at 10.3 K. This mixed phase region of about 3 K should correlate with the well-known lever rule of statistical mechanics. It is important to note that the positronium shows that the solidification actually commences at 13.2 K, i.e., 2 K above the transition at 11.2 K indicated by the specific-heat peaks.[15] A better line on the phase diagram, for coverages below 0.6 $\sqrt{3}\times\sqrt{3}$, separating the gas phase from the mixed commensurate-solid-plus-gas phase would therefore be a line about 2 K above the accepted line.[15]

In conclusion, in this paper, we have demonstrated the clear connection between Ps production and the proportion of 2D gas in mixed commensurate solid and gas phases of H_2 and D_2. The results place a question mark over the presently accepted picture of H_2 and D_2 submonolayer phases. In the future, accurate measurements will allow quantitative assessments of these phase transitions to augment the relatively incomplete descriptions provided by specific-heat measurements.[1]

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[1] L. W. Bruch, M. W. Cole, and E. Zaremba, *Physical Adsorption: Forces and Phenomena* (Oxford Science Publications, Oxford, 1997).

[2] M. Bretz and T. T. Chung, J. Low Temp. Phys. **17**, 479 (1974); F. A. B. Chaves, M. E. B. P. Cortez, R. E. Rapp, and E. Lerner, Surf. Sci. **150**, 80 (1985).

[3] H. Freimuth and H. Wiechert, Surf. Sci. **162**, 432 (1985).

[4] H. Freimuth and H. Wiechert, Surf. Sci. **178**, 716 (1986).

[5] A. P. Mills, Jr., in *Positron Solid-State Physics*, edited by W. Brandt and A. Dupasquier (North-Holland, Amsterdam, 1983).

[6] P. Sferlazzo, S. Berko, K. G. Lynn, A. P. Mills, Jr., L. O. Roellig, A. H. Viescas, and R. N. West, Phys. Rev. Lett. **60**, 538 (1988).

[7] R. S. Tatar and S. Rabii, Phys. Rev. B **25**, 4126 (1982).

[8] J. G. Dash, *Films on Solid Surfaces* (Academic, New York, 1975).

[9] Grafoil is made by the Union Carbide Corporation.

[10] N. Davidson, *Statistical Mechanics* (McGraw-Hill, New York, 1962).

[11] P. Rice-Evans, M. Moussavi-Madani, K. U. Rao, D. T. Britton, and B. P. Cowan, Phys. Rev. B **34**, 6117 (1986).

[12] Y. C. Jean, C. Yu, and D. M. Zhou, Phys. Rev. B **32**, 4313 (1985).

[13] N. Hozhabri, S. C. Sharma, and S. J. Wang, Phys. Rev. B **39**, 3990 (1989).

[14] P. Rice-Evans and K. U. Rao, Phys. Rev. Lett. **61**, 581 (1988).

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