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Positronium formation and the phases of two-dimensional oxygen physisorbed on graphite

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The connection between positronium formation at a graphite surface and the presence of physisorbed oxygen has been investigated. Unique measurements reveal the sensitivity of the positronium signal to the coverage and phase of the adsorbed layers. Below 38 K, the solid ζ_2 phase strongly promotes the creation of positronium and the temperature dependence of the intensity may be related to the tilt of the molecules on the substrate. In contrast, a fluid bilayer denies the observation of positronium probably due to the rapid formation of PsO_2.

Positronium (Ps) offers a unique means of studying the behavior of two-dimensional systems. This arises from a crucial experiment by Sferlazzo *et al.*[1] of Ps formation at an oriented graphite surface. It is well known that positrons injected into metals quickly thermalize and may then diffuse to a surface to cause the emission of Ps by capturing a surface electron.[2] In the special case of graphite, Sferlazzo *et al.*, 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,[3] 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.[1]

The basal plane of graphite offers an ideally smooth substrate for the thermodynamic study of condensed gas monolayers, their creation and their phase transitions.[4] The exfoliated form of graphite, grafoil, is a leaflike structure with basal plane surfaces of large specific adsorption area.[5] Gases easily permeate the internal spaces and condense uniformly on the (001) surfaces.

Positrons injected into grafoil will thermalize in the carbon by electronic and phononic excitations[2] 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.[6] Measurements on similar systems have been reported.[7,8] A subsequent study on fluid physisorbed methane[9] demonstrated that maximum Ps production occurred at 50% coverage. 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. On the other hand, we have found oxygen with its 1-eV electronic excited state to be a special case; copious Ps is still emitted at 100% coverage.[10]

Gases condense on substrates, layer by layer, as temperatures are lowered, due to the action of van der Waals forces. The case of two-dimensional oxygen has received detailed attention: isotherm,[11] heat capacity,[12] low-energy electron diffraction,[13] susceptibility,[14] neutron-[15] and x-ray-[16] diffraction measurements have suggested a rich phase diagram[13] with many liquid, fluid, and solid phases including two-phase coexistence regions; and the orientations of molecular axes[17] and the wetting behavior[18] have been reported. Recent interest has centered on the existence and nature of the solid phases. Toney and Fain[13] have found evidence with roughly a monolayer coverage for a new high-temperature solid θ phase that commences at 30 K and stretches at least up to 48 K. Guest *et al.*[19] have employed near-edge x-ray-absorption fine structure to examine the low-temperature solid phases; they found at 25 K that the flat δ phase had a mean molecular axis tilted 20° from the substrate surface, whereas the perpendicular ζ_2 phase was tilted at $53°\pm10°$. In this paper we report on positronium formation measurements with O_2 down to 8 K; the remarkable results reveal the significance of the solid ζ_2 melting boundary and a temperature dependence of the Ps production in the ζ_2 phase that may be related to the tilt of the molecules on the substrate.

The apparatus consisted of a 110-ml copper chamber mounted directly on the cold finger of an APD Displex closed-cycle helium refrigerator. 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 10 layers of 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 oxygen and then to record the spectra of annihilation photons, emitted perpendicular to the basal planes, with a germanium detector for sample temperatures declining from 350 to 8 K. The conventional $3\gamma/2\gamma$ parameter R (Ref. 9) (counts in the range 0–450 keV divided by counts in the complete 511-keV peak), which indicates ortho-Ps annihilation, and the customary 511-keV line-height parameter S (Ref. 9) (counts in central 15 channels of the 511-keV peak divided by the counts in the whole peak) which responds to the Doppler broadening of the e^+e^- system and hence is related to para-Ps annihilation, have been estimated from the spectra. In fact, the photopeaks contain Dopplerbroadened components corresponding to positrons annihilating in the graphite (empirically best fitted with a Gaussian and a parabola), in the oxygen, as fast para-Ps and as slow para-Ps, and a convolution analysis has been conducted to obtain the intensities of these components with due allowance for background and intrinsic detector resolution. Figure 1 illustrates a typical fit; we find χ^2/ν improves by a mean 20% for two Ps components (rather than one).

Figures 2(a) and 2(b) show that the parameters S and R are featureless for the grafoil in vacuum. With a particular starting quantity of O_2 in the chamber we see how the pressure declines due to adsorption in the grafoil as the temperature is reduced and how the amount of ortho-Ps (R) and para-Ps (S) rises. As we have shown before,[9] this may be described with the two-dimensional physisorption model with the Boltzmann approximation,[4] which gives a relation between coverage (n, mol m^{-2}) and pressure (P) of $P=(nkT/\lambda)\exp(-\varepsilon_0/kT)$, if $n\lambda^2 \ll 1$, where $\lambda = h/(2\pi mkT)^{1/2}$ and ε_0 is the binding energy of the molecule to the substrate. Our measurements have yielded 1070 K for ε_0, which agrees with 1050 K from isotherm studies.[11]

As the temperature is reduced to 60 K one observes a sharp drop in both R and S; i.e., in both ortho-Ps and para-Ps. The pressure measurements indicate that this is caused by adsorption in the region of bilayer coverage.[10] Incidentally, the spike in R at 65 K corresponds to a sharp drop in S and reflects the reduction in the conversion of ortho-Ps to para-Ps as the gas pressure declines, which tells us that the Ps is actually emitted into the gas and not trapped at the oxygen monolayer. Below 40 K we find a dramatic and quite unexpected rise in positronium emission.

In Fig. 3 we display data for six sets of measurements (columns A–F) for different starting quantities of O_2 gas. The top row indicates the unadsorbed gas in the chamber, obtained from the pressures. The steps indicate the completion of the first layer, which requires 0.0011 mol; A shows the case of many layers being deposited, B and C just over two layers, D less than two layers, E slightly more than one layer, and F less than half a monolayer.

In the convolution analysis two para-Ps Gaussian components emerge. One, the fast para Ps, not shown, declines in intensity with temperature gently from 7% at

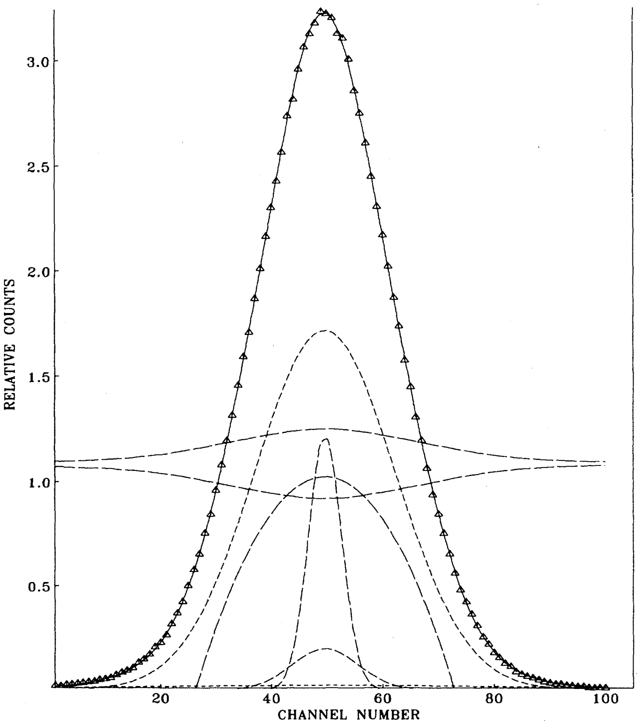

FIG. 1. At 102 K, an example of a fit of the 511-keV line into five Doppler components after prior subtraction of background. One channel represents a photon energy of 91 eV.

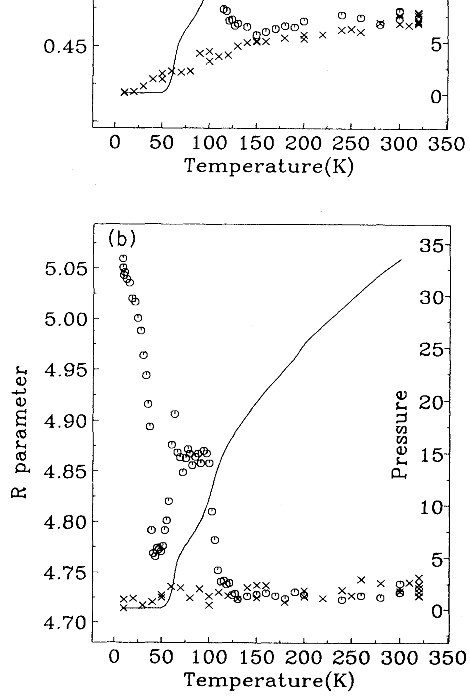

FIG. 2. Typical measurements for one quantity of sealed gas; the pressures in Torr indicate physisorption as temperatures are reduced (also seen in column C of Fig. 3). The vacuum results are also displayed as crosses. (a) The Doppler parameter (S) shows the rise, fall, and rise again of the para-Ps as the reducing temperature causes adsorption of O_2. (b) The $3\gamma/2\gamma$ (R) signals the simultaneous annihilation of ortho-Ps.

100 K to a few % at 50 K, and it appears unrelated to the physisorption. In the fourth row of Fig. 3 is plotted the intensity of the narrow (slow para-Ps) component, which is seen to be largely responsible for the variations in S. By combining the two para-Ps peak intensities with the $3\gamma/2\gamma$ data, row 5 has been calculated, giving the observed overall Ps intensity. This must be the quantity to be associated with the adsorbed layer. At the higher temperatures a steady 12% is found, which is entirely fast positronium.

In the case of a partial layer (column F) one notes that some Ps is observed as the oxygen is physisorbed but below 65 K it declines. In Toney and Fain's[13] diagram this temperature coincides with the start of the conversion from two-dimensional (2D) gas to 2D liquid, which suggests the liquid phase tends to diminish the observation of Ps. This would be similar to the finding for bulk liquid oxygen,[20] unlike 3D gas, for which the probable explanation is that the liquid phase encourages the creation of PsO_2,[21] which leads to fast pickoff of the Ps positron

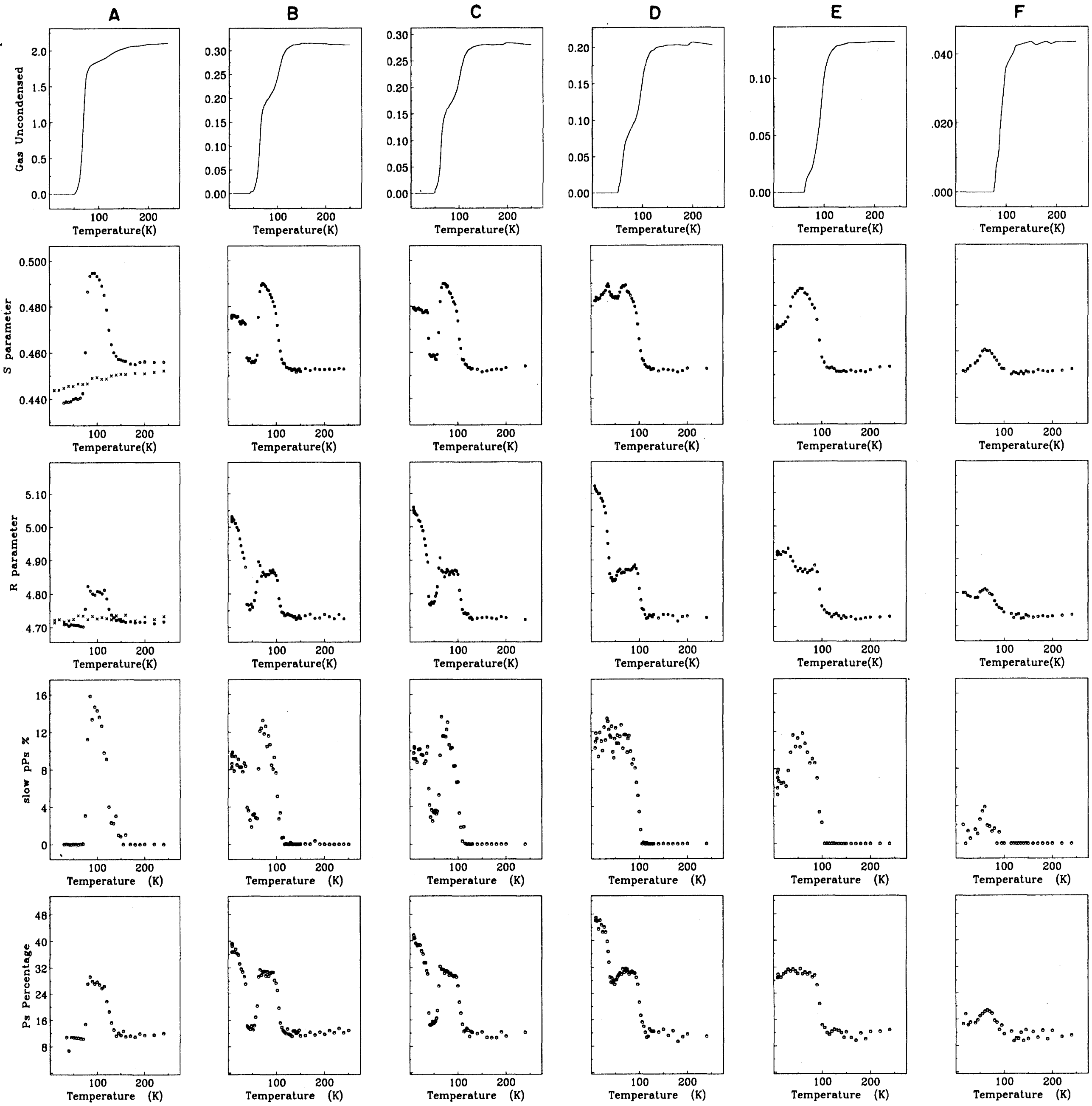

FIG. 3. Results for six quantities of sealed gas ($A \longrightarrow F$). The rows from the top show the unadsorbed gas (10^{-3}mol), S, R, the slow para-Ps% from convolution analysis, and the calculated total Ps.

by an oxygen electron, thus destroying the Ps signature.

The fifth column (E) represents a complete single monolayer, and the Ps production rises with adsorption from a steady 12% to 30%. The phase diagram for monolayer density is complex; the layer is solid in the flat δ phase below 38 K but above it may be fluid, although the solid θ phase is not excluded.[16] The plateau in Ps does not reveal the transition.

In contrast, the completion of the bilayer (column C) is associated with a dramatic drop in Ps at 65 K, little slow Ps between 65 and 38 K, and a sharp rise below 38 K. With only half a second layer (column D) the Ps formation below 38 K rises to an extraordinary 45% of total annihilations. As the bilayer is exceeded (column B) the Ps intensity below 38 K declines until, with a multilayer (column A), it disappears.

The Ps formation is at the carbon surface[9] and it is a function of the ability of the physisorbed layer to absorb surplus electron momentum. So the question is as follows: Why does Ps drop sharply on bilayer completion, only to rise again steeply at 38 K? At 65 K, the O_2 bilayer is a fluid[13] that appears to deny the observation of Ps, and we must conclude the Ps is captured to form PsO_2 and hence rapidly quenched.[21] The melting boundary occurs at 38 K (Ref. 16) below which the nearly perpendicular ζ_2 solid phase exists, and the results indicate that the solid bilayer promotes the emergence of Ps from the O_2 surface. Multilayers inhibit this.

It is important to note that at, say, 18 K the solid ζ_2 phase yields nearly double the slow Ps formation obtained with the δ phase. This must relate either to the ability of molecules to recoil or to the effective areal density of close contact between the differently tilted O_2 molecules and the carbon substrate. In the range 38–18 K, the temperature dependence of the Ps signal (roughly $-T^2$) in the ζ_2 phase is, we suggest, a consequence of the changing average tilt of the O_2 molecules and their dynamic qualities.[19] Below 18 K, the ζ_1 and ε phases provoke little change.

Oxygen is special: it has a complex two-dimensional phase diagram; it is paramagnetic; it has a triplet $^3\Sigma_g^-$ ground state with two unpaired electrons; and it has a 1-eV electronic state the excitation of which allows the recoil necessary for Ps formation, even when surrounded by other molecules.[10] Many questions, on both the mechanisms of Ps formation and absorption and on the nature of physisorbed phases, remain unanswered, but the richness of detail obtained with this unique approach suggests that further experimental refinement, coupled with theoretical exploration, points the way forward.

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