Evidence for positronium formation at incommensurate monolayers of argon on graphite

2003 J. Phys.: Condens. Matter 15 L771

(http://iopscience.iop.org/0953-8984/15/50/L04)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **15** (2003) L771–L776 PII: S0953-8984(03)64558-3

LETTER TO THE EDITOR

Evidence for positronium formation at incommensurate monolayers of argon on graphite

R S Morton, D P van der Werf and P Rice-Evans

Physics Department, Royal Holloway University of London, Egham, Surrey TW20 0EX, UK

Received 10 June 2003
Published 3 December 2003

Abstract
Positronium formation has been studied at a graphite surface in the presence of a physisorbed monolayer of argon. In addition to the expected formation when a partial fluid monolayer is present, it is observed that formation is increased when the monolayer becomes an incommensurate solid.

The recent death of Martin Deutsch (16 August 2002) reminds us of his discovery in 1951 of positronium, the bound electron–positron system analogous to the hydrogen atom (Deutsch 1951). With anti-parallel spins Ps was expected to have a lifetime, against two-quantum annihilation, of 10^{-10} s and 10^{-7} s for the three quantum decay of the parallel case. When studying the spectra from positrons annihilating in a gas, Deutsch found that by adding NO, which has an odd number of electrons, to nitrogen he diminished the number of three-photon events, demonstrating the conversion of triplet states to singlets by electron exchange.

It also reminds us that we have only a poor understanding of the conditions which are conducive to the creation of Ps. In this paper we report evidence to indicate that Ps may be formed at graphite surfaces in the presence of incommensurate solid monolayers of argon.

Positronium production at bare graphite surfaces has been studied by Sferlazzo *et al* (1988) with a positron beam experiment. They observed that under normal conditions at room temperature little emission occurs. However their 2γ angular correlation study revealed that large amounts of Ps were observable at high temperatures. The lack at low temperatures was attributed to the band structure of graphite (Tatar and Rabii 1982), 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. The basal plane of graphite offers an ideally smooth substrate for the thermodynamic study of condensed gas monolayers, their creation and their phase transitions (Dash 1975). The exfoliated form of graphite, grafoil[1], is a leaflike structure (of typical dimension, 100 nm) with basal plane surfaces of large specific adsorption area. Gases easily permeate the internal spaces and condense on the (001) surfaces.

---

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

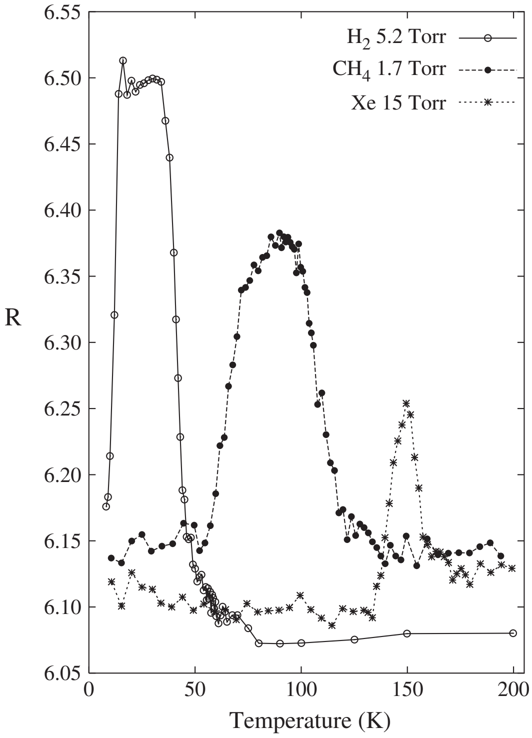

Figure 1. Typical plots of the parameter R (indicating *ortho*-positronium) for xenon, methane and hydrogen monolayers as they are condensed on a graphite surface by lowering the temperature.

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, LEED, x-ray diffraction and others. The nature of the two-dimensional phase transitions and the role of the underlying hexagonal carbon substrate have been found to be especially interesting (Bruch *et al* 1997). We have ourselves examined phase transitions in monolayer hydrogen and deuterium on graphite (Morton *et al* 2000).

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 (Rice-Evans *et al* 1986). Measurements on similar systems have been reported (Jean *et al* 1985, Hozhabri *et al* 1989). A subsequent study on fluid physisorbed methane (Rice-Evans and Rao 1988) 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.

For the present study, 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 10 layers of 130 mm^2 at the centre of which was

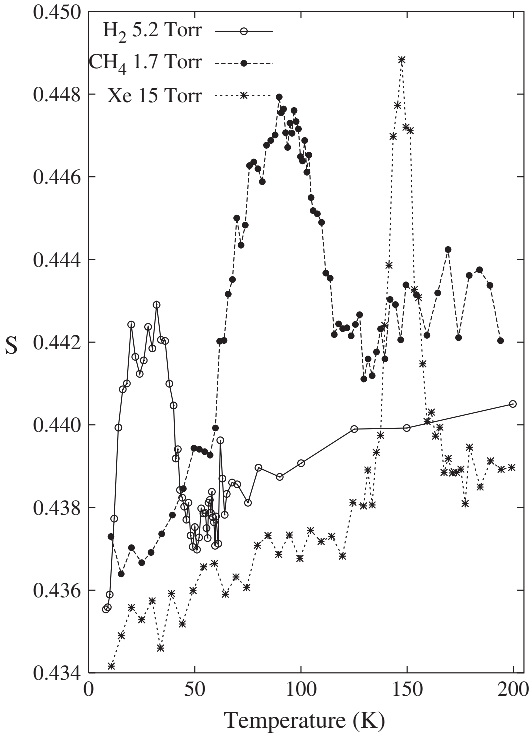

Figure 2. From the same data as in figure 1, plots of the Doppler parameter *S* (indicating *para*-positronium) for xenon, methane and hydrogen.

a directly deposited 30 μC ^{22}NaCl positron source. The technique adopted was to seal in a fixed quantity of argon 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) gives an indication of the amount of *ortho*-Ps annihilation; more three-gamma decays implies a rise. From the same spectral data one can also obtain the line-height parameter S which is a measure of the narrowing of the 511 keV peak; a rise in S means less Doppler broadening with orbital electrons and hence more 2γ events arising from *para*-Ps annihilation. This parameter S represents the counts in the central 11 channels of the 511 keV line divided by the number of counts in the whole line, after subtraction of the background (Chaglar *et al* 1981).

Figures 1 and 2 for hydrogen, methane and xenon are presented to illustrate the variety of responses one finds for different gases as the temperature of the grafoil is reduced. A single peak is commonly observed, indicating the rising amount of positronium that is created as more gas is adsorbed into the monolayer. The details of the peaks—i.e. the temperatures and shapes—depend on the adsorption energies and sometimes the two-dimensional phase changes. For example the curve for hydrogen at the lowest temperatures shows first a rise corresponding to increasing monolayer gas coverage, the plateau due to there being insufficient gas to increase the coverage further, followed by a sharp drop in the Ps formed due to the monolayer suffering a phase change to a mixed phase of commensurate solid plus gas (Morton *et al* 2000). One can also observe the differences in the proportions of *para*-Ps and *ortho*-Ps by comparing the relative heights of S and R in the two figures.

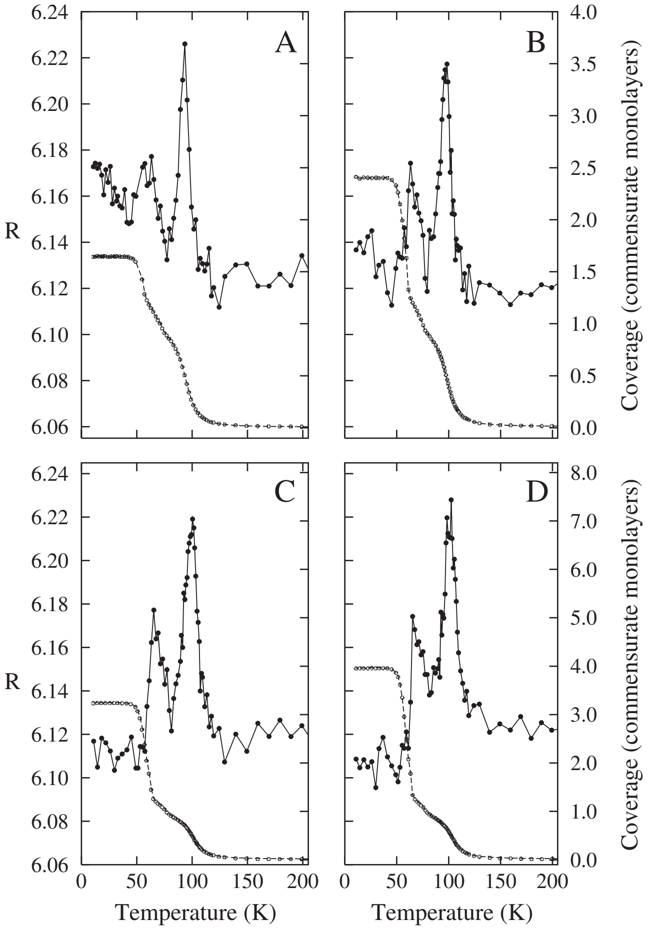

Figure 3. Four sets of values for *R* (*ortho*-Ps) for argon, corresponding to initial chamber gas pressures of (A) 20, (B) 30, (C) 40 and (D) 50 Torr. As the chamber temperatures are reduced, the simultaneous pressures are measured and resultant calculated monolayer coverages are plotted (open circles). The major peaks in *R* correspond to the condensation of the fluid argon monolayer, but the secondary (unexpected) peaks at lower temperatures are associated with the development of incommensurate solid monolayers as the coverage rises (from 1.0 to 1.3 equivalent commensurate monolayers).

It is important to note that the Ps created in our experiments is uniquely a consequence of the actual band structure of the carbon surface electrons. We demonstrated this with condensation of oxygen on silica and alumina powder for which very different results occur (Haynes *et al* 1994).

Figure 3 shows the production of positronium for sets of measurements with starting argon pressures in the sealed chamber of about 20, 30, 40 and 50 Torr. As the chamber temperatures are lowered, the simultaneous pressures are recorded from which the layer coverages are calculated. These are plotted. The *ortho*-positronium parameter *R* is seen to rise to a maximum but then to decline to yield a sharp peak. From the coverage rates one can associate the low point of the value with essentially a coverage of one commensurate layer, even though such a coverage is not thought to be solid in nature (Larese and Zhang 1990).

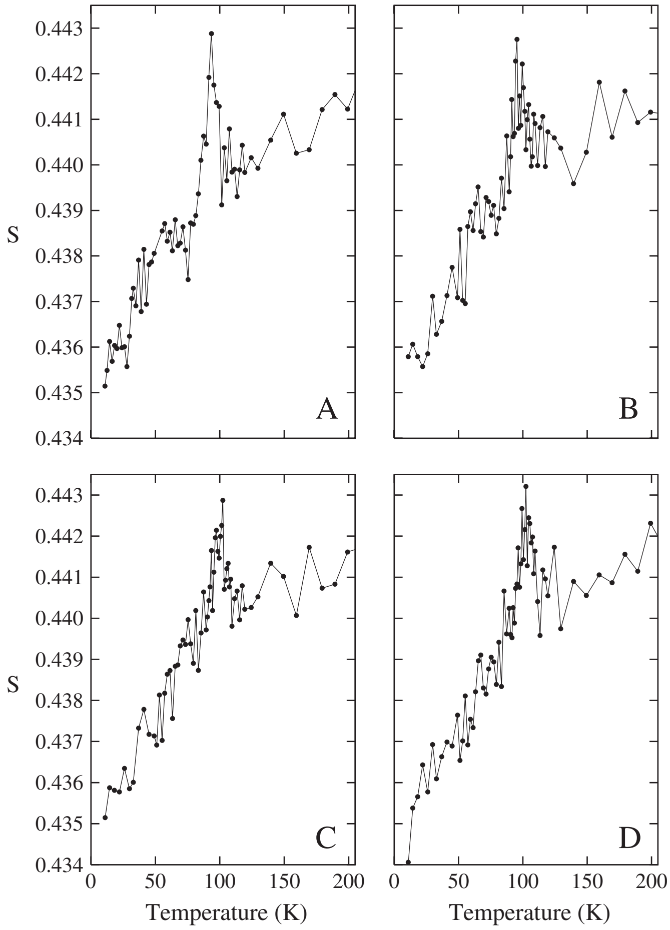

Figure 4. Corresponding sets of estimated values of S (*para*-Ps). Peaks are seen to appear at about 100 K, corresponding to the major peaks in R (figure 3).

The basic phase diagram of argon on graphite was proposed by Migone *et al* (1984), on the basis of heat-capacity scans. They concluded that the argon only formed a solid that was incommensurate with the underlying hexagonal lattice although the liquid phase appeared to be orientationally ordered below 54 K.

In figure 3, as one follows further reductions in temperature, these results for argon produce a new phenomenon: a second peak in *ortho*-positronium is seen. A careful scrutiny of the coverage curve reveals that this second peak coincides with a second point of inflexion which we take to indicate the development of the solid incommensurate layer. This is completed at a density of 1.3 commensurate monolayers (Larese and Zhang 1990). It is noticeable that the second peak continues to rise until this value is exceeded, when commencement of the bilayer inhibits the formation of positronium at the carbon surface.

Para-positronium is expected always to accompany the formation of *ortho*-Ps and figure 4, showing plots of the estimated line-height parameter (S), demonstrates this. The statistics in the calculation of S are not as robust as those for R, but nevertheless four clear peaks are seen to be associated with the four main peaks in R.

In figure 4, the poor statistics for S, and the sharply rising ‘background’ in the temperature region, corresponding to the second peaks in the parameter R, tend to obscure the possible existence of small peaks in S that would suggest accompanying *para*-positronium.

The results reported here extend the known circumstances that are propitious for the formation of positronium. The earlier ideas that the recoil of monolayer fluid molecules enabled the creation of Ps need to be extended to accommodate the irregular connection of the solid layer to the carbon substrate. This will provide a healthy challenge to theorists.

It is a pleasure for one of us (PR-E) to thank the Leverhulme Trust for the award of an emeritus fellowship. The early stages of the work were conducted with the support of the EPSRC (grant GR/J7 1984). We acknowledge the assistance of Miss D R Giles in the preparation of this paper.

References

Bruch L W, Cole M W and Zaremba E 1997 *Physical Adsorption, Forces and Phenomena* (Oxford: Oxford Science Publications)
Chaglar I, Rice-Evans P, El Khangi F A R and Berry A A 1981 *Nucl. Instrum. Methods* **187** 581
Dash J G 1975 *Films on Solid Surfaces* (New York: Academic)
Deutsch M 1951 *Phys. Rev.* **82** 455
Haynes C E, Rice-Evans P and El Khangi F A R 1994 *J. Phys.: Condens. Matter* **6** 2277
Hozhabri N, Sharma S C and Wang S J 1989 *Phys. Rev.* B **39** 3990
Jean Y C, Yu C and Zhou D M 1985 *Phys. Rev.* B **32** 4313
Larese J Z and Zhang Q M 1990 *Phys. Rev. Lett.* **64** 922
Migone A D, Li Z R and Chan M H W 1984 *Phys. Rev. Lett.* **53** 810
Morton R S, van der Werf D P and Rice-Evans P 2000 *Phys. Rev.* B **62** 17031
Rice-Evans P, Moussavi-Madani M, Rao K U, Britton D T and Cowan B P 1986 *Phys. Rev.* B **34** 6117
Rice-Evans P and Rao K U 1988 *Phys. Rev. Lett.* **61** 581
Sferlazzo P, Berko S, Lynn K G, Mills A P Jr, Roellig L O, Viescas A H and West R N 1988 *Phys. Rev. Lett.* **60** 538
Tatar R S and Rabii S 1982 *Phys. Rev.* B **25** 4126