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## The interaction of Xe and Xe + K with graphene

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#### ABSTRACT

We have investigated the electronic properties of monolayer graphene with adsorbed layers of xenon or potassium, or a combination of the two. The formation of the first Xe layer is characterized by a dipole polarization which is quenched by a second Xe layer. By comparing K on Xe on graphene to K on bare graphene, we determine the K contribution to trigonal warping and mass renormalization due to electron–phonon coupling. The former is found to be small but significant, while the latter is shown to be negligible. Thus, previously determined values of electron–phonon coupling for K on graphene are shown to be intrinsic to doped graphene and not determined by the proximity of K ions to the graphene. Published by Elsevier B.V.

#### 1. Introduction

The doping-dependent properties of graphene, a single layer of carbon atoms in a graphite-like honey-comb lattice, are important both fundamentally and technologically [1]. We have previously shown that the doping can be readily accomplished by adsorbing K atoms, upon which we observed enhancements to the electron–electron and electron–phonon interactions [2]. In contrast, many studies have performed the doping through gating the graphene in a field-effect device geometry [3,4]. So it is important to understand whether any of the effects induced by potassium are related to the proximity of the dopant ions or are intrinsic to doped graphene.

Here we separate the effects of K atoms from the dopinginduced effects by comparing K adlayers on graphene with or without a film of Xe atoms condensed onto the graphene at low temperatures. We find that the doping of the graphene proceeds readily in either case as a function of K deposition, but when there is an interlayer of Xe atoms, we observe several interesting features: (1) the carbon bands are distinctly broadened due to scat-

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tering through the Xe layer; (2) the trigonal warping of the carbon bands is reduced, suggesting that some of the warping observed for graphene/K is due to the K Coulomb potential; (3) there is no detectable change in the mass renormalization of the graphene bands when Xe is present, suggesting that the anomalously large electron–phonon coupling previously reported [2,5] is not due to the influence of the K donor ions.

Although the motivation of this study is to explore the strong chemical interaction of graphene with K, the bonding of graphene to Xe is also interesting. Xe atoms are bonded only weakly to graphene through hybridization of Xe 5*p* and 6*s* states to the C  $\pi$  bands, ~-4eV below and 5eV above *E*<sub>F</sub>, respectively, with no ionic charge transfer between Xe and graphene [6]. The bonding to the substrate is weak, on the order of the interatomic Xe interaction, and the phase diagram of Xe on graphite is complicated and well-characterized [7]. As in bulk graphite and Xe crystals, a significant contribution to the bonding by van der Waals interaction could be expected; such interactions figure prominently in interfaces between organic conductors and metals, and are difficult to calculate [8]. The Xe on graphene system can therefore be a model for such weakly bonded systems.

Graphene was prepared at the surface of SiC(0001) by the usual UHV annealing method [9]. Our method of preparation and details of the clean and K-doped band structure (without Xe) are further





**Fig. 1.** A series of Xe 4*d* spectra for different coverages of Xe on graphene. (a) Spectra #1–22, which start from the clean surface and were obtained for  $P = 5 \times 10^{-10}$  T. (b) Spectra #23–48 which go up to ~1.77 layers and were obtained for  $P = 5 \times 10^{-9}$  T. Binding energy is relative to  $E_{\rm F}$ .

described in Refs. [2,5,10]. Such samples consist of a conductive graphene layer on top of a graphene-like, but insulating, buffer layer with  $6\sqrt{3} \times 6\sqrt{3}$  symmetry [9,11,12]. Samples at temperature T < 20 K were exposed to Xe gas to adsorb the initial rare-gas film, under which conditions three-dimensional Xe is known to condense in the related Xe/graphite system [7]. K was deposited from a commercial source (SAES Getters). Photoemission measurements were obtained at beamline 7.0 (Electronic Structure Observatory) of the Advanced Light Source synchrotron facility in Berkeley, CA, using 94 eV photons. Photoelectron spectra were obtained with a Scienta R4000 electron analyzer. The total instrumental energy resolution was about 0.03 eV. Band structures were obtained with momentum resolution better than 0.012 Å<sup>-1</sup>.

#### 2. Condensation of Xe film

Fig. 1 shows the Xe 4d core level spectrum acquired as a function of time during the condensation of the Xe rare-gas film. A total of forty eight spectra were acquired, starting from clean (spectrum #1) up to ~1.77 layers (#48), the latter thickness obtained assuming an electron escape depth of 3.5 Å at the kinetic energy used [13], a layer thickness of 3.6 Å for fcc Xe(1 1 1), and full coverage of the first monolayer. In addition to the core level spectrum, a valence band spectrum along the GKM direction of the graphene Brillouin zone was acquired for each dosing step. The initial Xe exposure (spectra #1–22, 0.24L total) was accomplished at Xe pressure  $5 \times 10^{-10}$  Torr while the remaining spectra (#23–48, 5.2L additional) were collected in a Xe pressure 10 times greater. Each cycle consisting of a core level and a valence band spectrum was acquired in 40 s.

Four selected core level spectra are plotted, together with leastsquares curve-fits, in Fig. 2. All the core-level spectra were fitted with Voigt lineshapes (Lorentzian peaks with Gaussian broadening) with fixed Gaussian width of 25 meV (representing the instrumental resolution), much smaller than the peak widths observed. Judging by the good quality of all the fits, it appears such a small Gaussian broadening is well justified, and that the lifetime of the Xe core levels is reflected by the Lorentzian widths, and not by any significant amount of inhomogeneous broadening.

Fig. 2 shows that in the initial phase of condensation (spectrum #11 of Fig. 1), the Xe is adsorbed mainly into a single species ("peak 1"). Compared to the spectra that follow, the core-level lifetime is relatively short, as indicated by a large Lorentzian width. We note that the peaks in this stage are slightly asymmetric to lower binding energy (BE), and that this asymmetry could be accounted for by a



**Fig. 2.** Selected Xe 4*d* core level spectra, numbered as in Fig. 1. The peaks are fitted to Gaussian-broadened Lorentzian lineshapes as discussed in the text. Binding energy is relative to  $E_{\rm F}$ .

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