Observation of a Fano Resonance in Photoemission

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We report on the observation of a Fano resonance in normal emission ultraviolet photoelectron spectra of Cu or Ag impurities embedded in a Xe monolayer on highly oriented pyrolytic graphite. We show that Brillouin-zone folding resulting from the relatively weak perturbation by the $(\sqrt{3} \times \sqrt{3})R30°$ commensurate Xe overlayer couples K-point electrons with Γ-point electrons of pure graphite. Interference between this continuum of states and the discrete Cu 4s or Ag 5s states in the initial state leads to a typical Fano line profile in the spectra. This finding provides a new and promising avenue for the detection and characterization of impurities or small clusters at surfaces. [S0031-9007(99)08842-0]

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When a discrete electronic level interferes with a broad continuum of states, a Fano resonance phenomenon occurs giving rise to characteristically asymmetric peaks in excitation spectra [1]. These resonances have been found in atomic physics, e.g., in the photoionization continuum of rare gases [2], in solid state physics, e.g., in resonant photoemission of rare earths [3], and in surface physics, e.g., in scanning tunneling spectra of a single magnetic atom on a metal surface [4,5]. Because the parameters governing the line shape of the resonance are intimately linked to the nature of the quantum interference, i.e., the ratio of the transition probabilities for the discrete state and the band of unperturbed continuum states [1], such studies have contributed considerably to a detailed understanding of the electronic structure in atomic and condensed matter.

Recently, in angular resolved photoelectron spectra on copper and silver surfaces taken in normal emission geometry, the asymmetric line shape of the direct-transition peak derived from the nearly free-electron-like Ag sp states has been interpreted to originate from an interference between the outgoing electron waves from the direct transition and surface emission in the final state, a phenomenon which has been tentatively associated with the physics underlying a Fano resonance [6,7].

However, no measurement has been reported so far which reveals the manifestation of a typical Fano resonance profile in valence band photoemission spectra. A favorable situation to observe such an interference with the characteristic dips associated with it is given when a localized state couples weakly with a broad continuum of states. In order to observe the interference in the spectrum, transitions from both the localized and the extended states need to be allowed. This situation has been realized in the present experiment in the following way: We have chosen matrix-isolated atoms of Cu or Ag embedded in a commensurate Xe monolayer (ML) on highly oriented pyrolytic graphite (HOPG) as a model system. The Brillouin-zone folding resulting from the relatively weak perturbation by the $(\sqrt{3} \times \sqrt{3})R30°$ overlayer couples K-point electrons with Γ-point electrons of pure graphite. This renders the former K-point states of pure graphite observable under normal emission with ultraviolet photoemission spectroscopy (UPS). Because of its dispersion normal to the graphite layers, the bands near the Fermi energy, E_F, give rise to smooth emission in the energy range between E_F and 2 eV. In contrast to Fano's paper [1] where the localized state is in the final state, in the present experiment these are the localized Cu 4s and Ag 5s initial state orbitals which mix with the continuous band of states, and this is followed by a transition into the continuum of states of the outgoing photoelectron. These conditions result in a relatively sharp resonance with a pronounced Fano line shape. This finding provides a new and promising avenue for a "Fano spectroscopy" of impurities or small clusters at surfaces.

The experiments were performed in an ultrahigh vacuum chamber with a base pressure of 2×10^{-10} mbar employing *in situ* characterization of the sample by low-energy electron diffraction (LEED) and UPS. Satellite-free photoelectron spectra were measured using the He I (21.2 eV) and He II line (40.8 eV) of a high-intensity gas discharge lamp (Gammadata) combined with a homebuilt monochromator [8]. All spectra are obtained in normal emission geometry by collecting the photoelectrons with a hemispherical electron analyzer (HA 150 from VSW). The total instrumental energy resolution was set to 50 meV and the angular resolution was $\pm 2°$. The HOPG crystal was cleaved in air and subsequently transferred into the vacuum chamber on a cold finger held at 50 K by a closed-cycle helium refrigerator. A retractable electron gun allowed for rapid heating to 1200 K of the substrate for cleaning and annealing [9]. The sample temperature of $T = 50(5)$ K was measured with a precision of $\pm 5\%$ using a W$-$26% Re/W$-$5% Re thermocouple spot-welded to the sample holder. Xe was introduced into the vacuum by a leak valve and was adsorbed at low temperature on the clean HOPG substrate. The thickness of the Xe film was determined from the characteristic Xe $5p$ photoemission signal [10,11]. Subsequently, Ag or Cu impurities were deposited from a directly heated tungsten filament or by using a mass-selected cluster beam [12] where the amount of the deposited material was determined by monitoring the beam current on the sample.

Figures 1(a) and 1(b) are LEED images of the clean HOPG substrate displaying its characteristic hexagonal structure [13] and the substrate after adsorption of 1 ML Xe taken at $T = 50(5)$ K [11], respectively. Heating the sample above $T = 65(5)$ K causes a sudden extinction of the inner spots indicating desorption of the Xe film from the surface [14]. The commensurate $(\sqrt{3} \times \sqrt{3})R30°$ Xe adlayer on graphite implies that the reciprocal lattice vector $\Gamma\Gamma$ associated with the Xe adlayer matches exactly the vector ΓK of the graphite Brillouin zone [see Fig. 1(c)], a very important property for what follows.

Figure 2 presents UP spectra taken with He II radiation from the clean HOPG substrate [2(*a*)] and covered with a Xe ML [2(*b*)]. The observation [2(*a*)] of a weak conduction band below the Fermi level (E_F), a σ band at 4.5 eV, a π band at 8 eV, and another σ band at 20 eV confirms earlier experimental and theoretical findings [15–17]. After adsorption of Xe [2(*b*)], the Xe $5p$ states between ≈6 and 7.5 eV, characteristic for the presence of exactly one ML of adsorbed Xe [10,18,19], as well as emission from the atomic Xe $5s$ states at about 17 eV binding energy [20], become visible. In addition to the now slightly reduced emission (due to the Xe overlayer) from the HOPG valence band states [2(*a*)], three new spectral features can be discerned at ≈1.8, 11, and 14 eV binding energy in 2(*b*) where the spectral intensity changes in a spectacular way between E_F and about 2 eV binding energy. This additional intensity near E_F after Xe adsorption is also clearly visible in the photoemission spectra obtained with He I excitation [Fig. 3(*a*)]. The inset [3(*d*)] shows the Xe $5p$ excitations and, for comparison at the same vertical scale [3(*e*)], the featureless emission from uncovered HOPG.

Subsequent deposition of 0.1 ML Cu atoms impinging from a cluster beam with 6 ± 4 eV kinetic energy on the Xe film or, alternatively, Cu vapor deposition leads to the

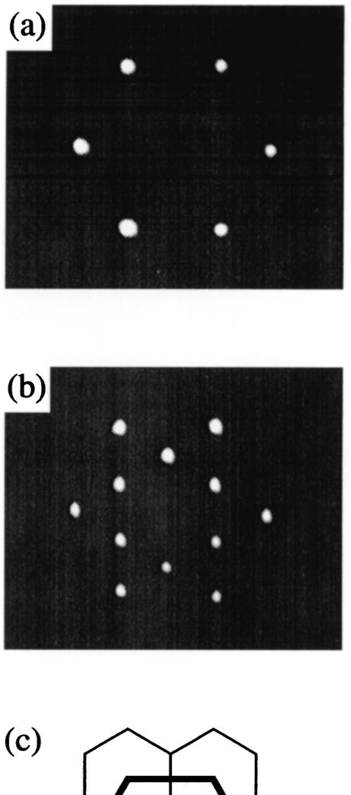

FIG. 1. Hexagonal LEED ($E_p = 184$ eV) patterns at $T = 50(5)$ K of (a) HOPG and (b) a commensurate $(\sqrt{3} \times \sqrt{3})R30°$ Xe ML on HOPG. (c) Resulting Brillouin zones for Xe (thin) and HOPG (bold line).

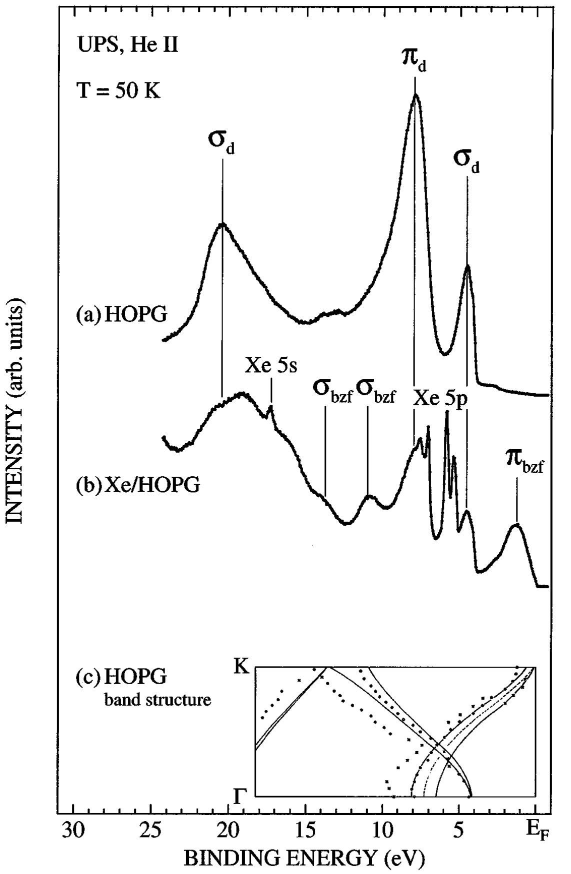

FIG. 2. UP spectra (He II) of (*a*) clean HOPG and (*b*) after adsorption of 1 ML Xe at $T = 50(5)$ K. Positions of the σ and π bands after Ref. [16]; lower indices d (bzf) for direct (Brillouin-zone folded) transition corresponding to emission from the Γ (K) point of the first Brillouin zone of graphite. Inset (*c*): HOPG band structure from Ref. [16].

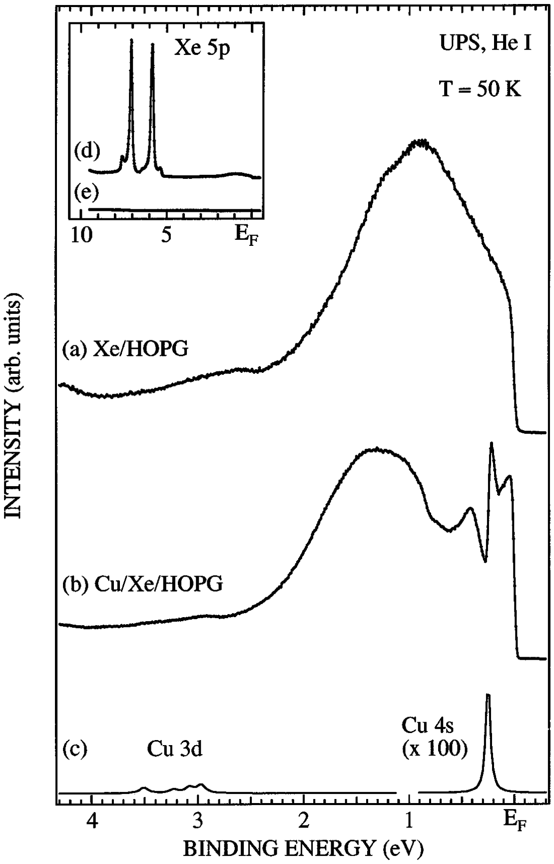

FIG. 3. UP spectra (He I) $T = 50(5)$ K of (*a*) 1 ML Xe on HOPG; (*b*) Cu on the Xe ML; (*c*) gas phase spectrum of Cu after Ref. [26]. Inset: (*d*) Xe $5p$ excitations and (*e*) uncovered HOPG in a wider binding energy range.

second surprising observation in the normal emission spectra, the appearance of a clear Fano line profile at 250 meV below E_F [Fig. 3(*b*)]. We note that the Fano signal is present for He I and also at a somewhat weaker intensity for He II excitation pointing to an initial state effect. The resonance signal increases with Cu coverage becoming first visible at about 2% ML Cu. A concomitant broadening and a binding energy shift of the resonance from about 100 to 250 meV below E_F is observed which implies an interaction with the Xe matrix [21]. This finding is corroborated by the fact that the Xe $5p$ levels also broaden and shift with increasing Cu concentration. We note that after deposition of Ag and Cu the Xe-overlayer structure persists in the observed LEED pattern. Rotating the sample by 10° from the surface normal leads to the extinction of both the additional intensity in the Xe covered HOPG spectrum near E_F and the Fano resonance. The Fano signal is only observable when Cu or Ag are deposited after Xe adsorption on HOPG. Deposition of Cu(Ag) directly on HOPG leads to a spectrum characteristic for the metallic state [22,23] indicating island formation due to the high mobility of Cu on HOPG even at 50 K. The same behavior is observed after deposition on the Xe film and subsequent thermal desorption ($T \geq 65$ K) of the Xe monolayer. Thus, we can safely conclude that the Fano resonance signal is related to the presence of isolated Cu(Ag) impurities in the adsorbed Xe film [24] and that the outermost bound electrons of the impurity atoms play a decisive role in the formation of the resonance. Gas phase photoemission spectra of Ag and Cu [25,26] indicate that after adsorption on a substrate a binding energy of the $5s$ ($4s$) levels just below E_F can be expected [27]. In Fig. 3(*c*), the $4s$ level in the Cu gas phase spectrum [26] has been aligned with the Fano resonance showing also that the atomic Cu $3d$ excitations contribute weakly to emission between 3 and 4 eV in the spectrum of Fig. 3(*b*). The remarkable amplification of the $4s$ signal by roughly a factor of 100 indicates an interesting and new Fano resonance phenomenon observed with photoemission techniques which we rationalize in the following paragraph.

The considerable increase in spectral density near E_F after adsorption of a Xe monolayer cannot be caused by Xe because the nearest level ($6s$) is located above E_F. Even if this level may be partly occupied due to interaction with the substrate [28], this effect is far too small to explain our observations. In addition, the interaction between Xe and graphite is weaker than between Xe and a metallic substrate [29]. Rather, the geometry of the commensurate Xe adlayer on graphite contains the clue to the experimental observations. Figure 1(c) shows that the reciprocal lattice vector, $\Gamma\Gamma$, associated with the Xe adlayer matches exactly the vector ΓK of the graphite Brillouin zone. In other words, the Brillouin-zone folding resulting from the relatively weak perturbation by the Xe $(\sqrt{3} \times \sqrt{3})R30°$ overlayer couples K-point with Γ-point electrons of pure graphite (Fig. 2). This symmetry argument explains why states with a wave vector around the K point of the unperturbed graphite may become observable under normal emission ($k_{\|} = 0$) with UPS. If the overlayer is looked at as a perturbation, one may say that bound Bloch waves as well as photoelectrons emitted from graphite with $k_{\|} \approx K$ can be scattered into $k_{\|} = 0$. A comparison between the energy positions of the newly observed spectral features with the known band structure of graphite [16] (see inset of Fig. 2) remarkably confirms this reasoning and explains the observed sensitivity of the spectra with respect to off-normal emission. Because of their dispersion normal to the graphite layers, the π_{bzf} bands ($_{\text{bzf}}$ for Brillouin-zone folding) near E_F give rise to smooth emission in the energy range between E_F and 2 eV. The Cu $4s$ and Ag $5s$ atomic levels couple relatively weakly with this π_{bzf} band. These conditions necessarily lead to quantum interference which results in the photoemission intensity I from the zone-folded and the atomiclike transitions,

$$I \propto |M^{\text{folded}} + M^{\text{atomic}}|^2, \tag{1}$$

and which causes a pronounced Fano profile in the excitation spectra. A Fano line shape analysis of the narrow spectral structure, including a Fermi function cutoff, captures the essential physics of this resonance phenomenon (see Fig. 4). We obtain a resonance energy $E_0 = 0.25$ eV

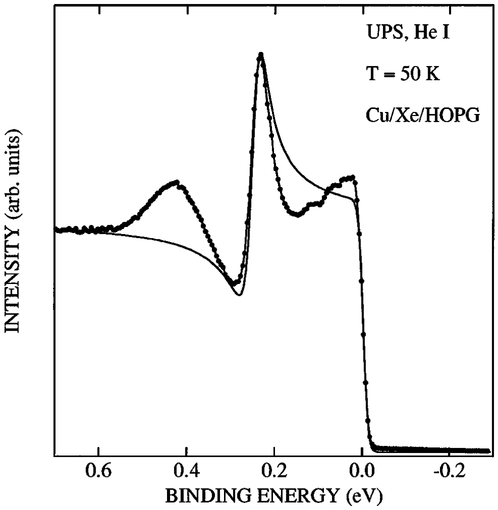

FIG. 4. He I excited UP spectra (dots) and Fano line shape analysis (full curve) of the resonance in a narrow region below the Fermi energy (see text).

and a Fano parameter $q = 1.5$, i.e., the ratio of the transition matrix elements between the modified, localized states and the unperturbed extended states which is of the order of 1 [30]. We note that, in contrast to Ref. [1], in the present experiment the localized orbital mixes with the continuous band of states in the initial state, followed by a transition into the continuum of states of the outgoing photoelectron.

This study has shown the presence of two new effects which previously have not been considered when analyzing angle resolved photoemission spectra. First, Brillouin-zone folding between adjacent commensurate layers may lead to unexpected spectral intensities in a certain energy range of the valence band spectra. Second, interference with localized levels of impurities present in the same energy window may then lead, provided favorable coupling between extended and localized states occurs in the initial state to unconventional line shapes in photoemission, in the present case to a characteristic Fano profile. These findings may bear some relevance for the study of low-dimensional systems, of heavy Fermions, and of high-T_c materials.

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