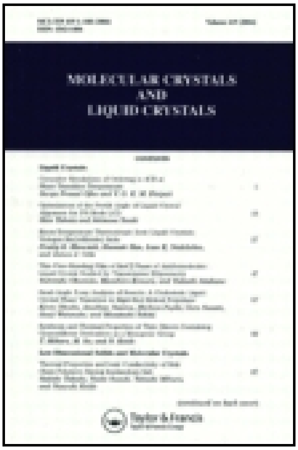

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Electronic Structure of Graphite Intercalated with U

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U-graphite intercalation compound (GIC) was prepared in-situ by deposition of U metal onto single-crystalline graphite(0001) and subsequent annealing. The samples were studied by angle-resolved photoemission (PE) and resonant PE at the $5d \rightarrow 5f$ excitation threshold. From a comparison of the experimental data with results of our LDA-LCAO calculations, the electronic structure of the GIC may be understood in a first approach by a charge transfer from the U atoms to unoccupied π_0^* orbitals of graphite. The latter is related to a shift to higher binding energies of all graphite-derived PE features and appearance of an additional rather narrow feature at the Fermi energy upon intercalation. This Fermi-level peak is superimposed by a sharp U 5*f* signal, that reveals no trace of multiplet splitting. Since our results give clear evidence for a localized character of the U 5*f* states, we assume that U is mixed-valent in this compound.

Keywords: photoemission; intercalation compounds

Actinides are characterized by the filling of the 5*f* shell, that is less localized than the 4*f* shell of the lanthanides allowing the 5*f* states to contribute to chemical bonding. Particularly in U systems the 5*f* states behave, therefore, usually itinerant. Many attempts have been done to localize the U 5*f* states by increasing the interatomic U-U distances by alloying, but up to now the effect of a reduced *f-f* overlap was almost always compensated by an increase of 5*f*-valence band hybridization. Really promising candidates for 5*f* localization, therefore, are graphite intercalation compounds (GIC's), where large interatomic distances of the intercalated species are combined with weak chemical interaction between the intercalant and the carbon matrices [1]. In the case of lanthanides, GIC's could easily be grown under UHV conditions by thermal deposition of the pure metals on graphite(0001) and subsequent annealing [2-4].

In the present paper we report on an angle-resolved photoemission PE and resonant PE study of the electronic structure of graphite intercalated *in-situ* with U. The PE data are compared with results of band-structure calculations. It is found that the intercalation leads to a shift of all graphite-derived PE structures toward higher binding energies (BE's) and the appearance of an additional narrow feature at the Fermi energy (E_F). This E_F peak is superimposed by a sharp U 5*f* signal that reveals no trace of multiplet splitting. Since both our experimental and theoretical results give clear evidence for a localized character of the U 5*f* states, we assume that U behaves mixed-valent in this compound.

The measurements were performed at the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY) using radiation from the SX/700 II beamline. Angle-resolved valence-band PE spectra and resonant PE spectra at the U 5*d*→5*f* excitation threshold were taken with a hemispherical electron energy analyzer (ARIES-VSW) tuned to an energy resolution of 150 meV and an angle resolution of 1°. Band-structure calculations were carried out in the framework of the local-density approximation (LDA) employing the method of linear combination of atomic orbitals (LCAO) in its fully relativistic version [5]. Since a transition from bandlike to localized behavior of the 5*f* states may be expected in U-GIC, we assumed also localized 5*f* configurations in our calculations.

Similar to the previous studies of RE-GIC's [2-4] *in-situ* intercalation of U was achieved by thermal deposition of relatively thick layers of the intercalant (100 Å) onto the clean graphite surface followed by a step-by-step annealing. The deposition at room temperature resulted in nonordered interfaces. Several stages of annealing (up to 1100 K) of the „as deposited" system led to a recovering of crystalline order with a sharp RE-GIC-like $(\sqrt{3}x\sqrt{3})R30°$ reconstruction of the LEED pattern [2-4]. The observed overstructure points to a UC_6 surface stoichiometry for the grown layers. A proper determination of the bulk composition, i.e., the stage of intercalation was not possible from the LEED experiment. Therefore, we have performed band-structure calculations for different stacking sequences of U- and graphite-derived layers. According to our results 1st stage intercalation leads to a larger charge transfer per C atom than that in a 2nd-stage GIC. This is reflected by the energy position of the π-symmetry graphite-derived bands, which play the role of electron acceptors. For a hypothetical UC_6 composition no agreement with the measured energy distribution curves (EDC's) could be obtained. In contrast to that the calculated electronic structure of a 2nd-stage GIC (UC_{12}) is in good correspondence to the experimental data [3].

Two sets of PE spectra for pristine graphite and U-GIC, which were

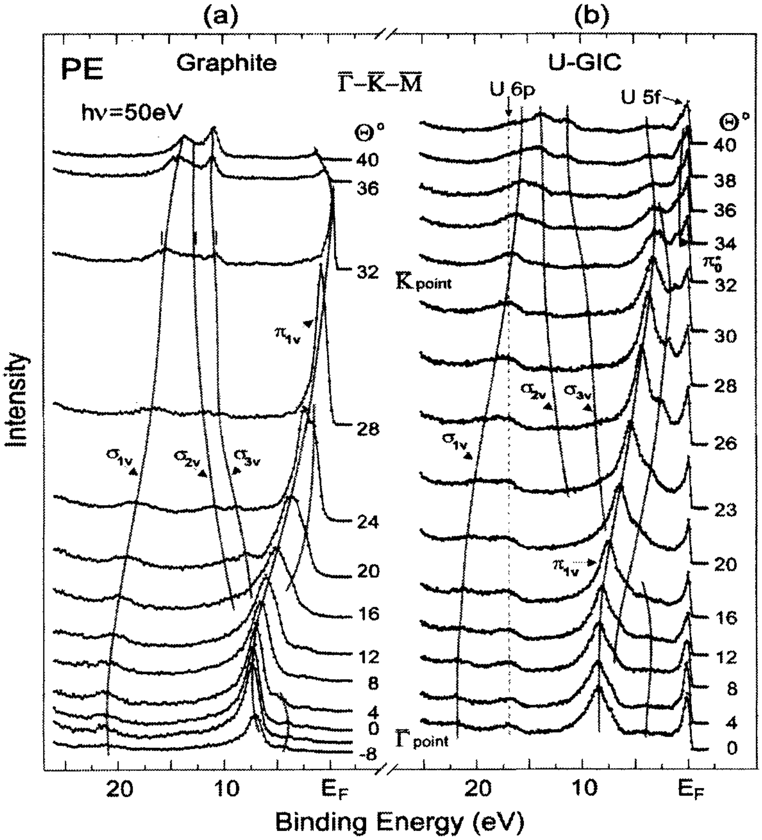

FIGURE 1 PE spectra taken for (a) graphite and (b) U-GIC.

taken at various polar angles Θ's, are shown in Figs. 1(a) and 1(b), respectively. In accordance with the results of earlier studies [3,6,7] angle-resolved EDC's of graphite are characterized by four main bands (π_{1v}, σ_{1v}, σ_{2v}, and σ_{3v}). At small Θ's the π_{1v}-symmetry band reveals highest PE intensity. Its PE weight considerably decreases in the second Brillouin zone (BZ). The latter can be explained by BZ selection rules based on the interference of outgoing photoelectron waves from two nonequivalent C atoms in the unit cell [8]. Two σ-symmetry bands of low intensity (σ_{2v} and σ_{3v}) are degenerated at the $\bar{\Gamma}$ point. With increasing wave vector these bands, which have $2p_{x,y}$ character, move toward higher BE's. Close to the border of the BZ the $2p_{x,y}$ bands overlap the 2s-originating band (σ_{1v}) giving rise to sp^2 hybrids characteristic for hexagonally arranged graphenes (marked by bars). According to the selection rules mentioned above the PE intensities of all three σ-symmetry bands grow in the second BZ.

The spectra of the GIC [Fig. 1(b)] reveal the same features as observed for graphite [Fig. 1(a)] but shifted toward higher BE's. The triplet structure of the sp^2 hybrids is preserved in the compound and the obtained characteristic variations of intensities of the π- and σ-originating features across the border of the BZ [8] show that the structure of the graphenes is retained. The important difference between the EDC's shown in Fig. 1(a) and 1(b), however, is a new intense peak that is located directly at E_F in the U-GIC. Related features were observed for all studied alkali- and RE-GIG's [2-4,9]. In contrast to these other compounds, in the U-GIC this structure reveals similar intensities for all angles of analyzing.

In RE-GIG's the structure at E_F was assigned mainly to a π_0^*-derived unoccupied band of graphite [3,4], which becomes filled in GIC's. Close to the border of the BZ of graphite this π_0^* band is pulled below E_F, while in the inner part of the BZ it is still situated above the Fermi energy. The nonconsistent behavior of the Fermi-energy peak in Fig. 1(b) suggests an alternative nature of this feature, namely, U 5*f* states. To discriminate 5*f*-derived PE features from carbon-derived bands angle-resolved resonant PE [10] at the

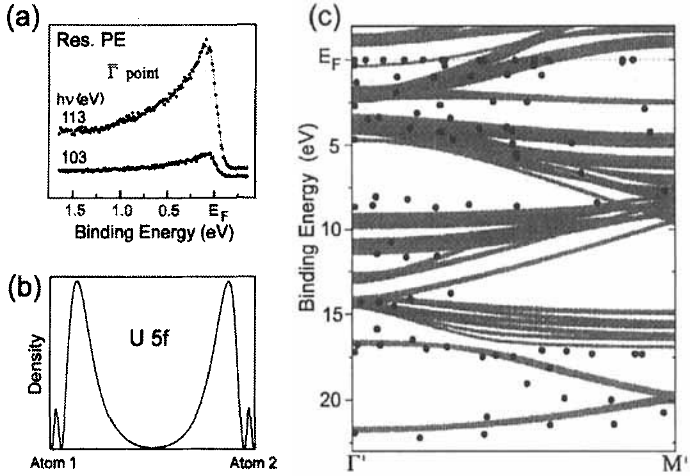

FIGURE 2 UC_{12}: On-resonance (113 eV) and off-resonance (103 eV) PE spectra; (b) U 5*f* radial contribution into atomic charge density; (c) projected band structure with experimental data points.

$5d \to 5f$ excitation threshold was applied. Particularly, we analyzed the resonant contribution of the 5*f* states to the PE spectra measured along the Γ - A and $\overline{\Gamma}$ - $\overline{M}$ directions in the BZ of graphite (not shown). In all cases an observed strong enhancement of the signal indicates the 5*f* origin of the E_F feature. Corresponding on- and off-resonance PE spectra taken close to the $\overline{\Gamma}$ point are shown in Fig. 2(a). The 5*f*-derived Fermi-energy peak reveals no fine structure or multiplet splitting. For all Θ's the maximum of the PE intensity remains pinned at E_F within the instrumental resolution and no evidence for a 5*f* band dispersion could be found. The latter favors a rather localized behavior of the 5*f* s in the obtained compound.

In contrast to U metal, where intersite hybridization of *f* states were concluded[11], there is no direct overlap between 5*f* orbitals in the U-GIC [Fig. 2(b)]. As follows from our band-structure calculations, also the overlap between 5*f* and π_0^* graphite-derived orbitals is in the same order as that between the

4*f* and π_0^* states in Eu-GIC, where the 4*f* states are known to be strongly localized [3]. The obtained *f* bands are extremely narrow giving further support for a localized character. From the band-structure calculations we obtain 5*f* occupation of 1.82 indicating that U is almost tetravalent ($5f^2$ configuration) in UC_{12}. In fact, for non-*f*-derived states only slight differences between bands calculated for bandlike 5*f* states and a localized $5f^2$ configuration are monitored. Fig. 2(c) shows the band structure of the stage-2 U-GIC ($5f^2$ configuration) calculated within the Γ′A′L′M′ plane in the BZ of GIC, which is projected onto the Γ′-M′ direction and compared to the experimental data.

In a localized picture, a 5*f* occupation of 1.82 indicates a mixed-valent character of the 5*f* states caused by weak $5f^1$ (and possibly $5f^3$) admixtures to a $5f^2$ ground state. For such a scenario, the PE signal would mainly consist of a single spin-orbit splitted $5f^1$ final state located just at E_F. Since the $^2F_{7/2}$ component of this final state is of negligible intensity for a $5f^2 \rightarrow 5f^1$ transition [12], in fact, no significant multiplet structure is expected.

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