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Initial stages of Ca intercalation into natural graphite

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Introduction

The relatively high superconducting transition temperature of 11.5 K in the stage-1 Ca GIC (CaC_6) [1,2] has recently been attributed to the formation of a Ca-derived Fermi surface located in the vicinity of the K point [3]. This Fermi surface competes with a second Fermi surface related to the partially filled π* band, in the vicinity of the K point. The goal of our experiment was to trace the build-up of these two surfaces, as a function of the intercalation level.

Experimental

Angle-resolved photoelectron spectroscopy (ARPES) has been employed to study the effects of annealing of thin Ca films deposited onto the surface of natural graphite, and on the electronic properties of the resulting surface intercalation compounds, for different steps of the annealing process. Ultrathin Ca films of a thickness of 0.3±0.1 Å (sample A) and 3.6±0.3 Å (sample B) were prepared by direct sublimation of Ca metal onto the surface of single-crystalline, natural graphite.

Results

After the deposition of a small amount of Ca atoms, denoted (b) in Fig. 1, the presence of surface Ca atoms in a partially metallic state is manifested in the appearance of a small Fermi edge and of an increased feature at about 5.5 eV that is certainly related to the bottom of the free-electron-like 4s-p band of Ca metal. During an extended annealing for 30 min at 400 °C, denoted (d), significant shifts of about 2.0 and 1.2 eV towards lower binding energy are observed, for the Ca (3p)- and (4s-p)-related features, respectively. Simultaneous shifts indicate a different environment for the Ca atoms and complete intercalation at least below the uppermost graphene sheet.

Intercalation of larger amounts of Ca atoms as performed on sample (B) is time consuming and requires higher temperatures of up to 650 °C. As displayed in Fig. 2, in the final step, an extended annealing leads to large splitting of π-derived bands in the vicinity of the K point, with relatively high binding energies of about 1.3 and 2.7 eV at K. It is obvious that the band structure of the observed surface intercalation compounds is distinctively different from that of bulk CaC_6.

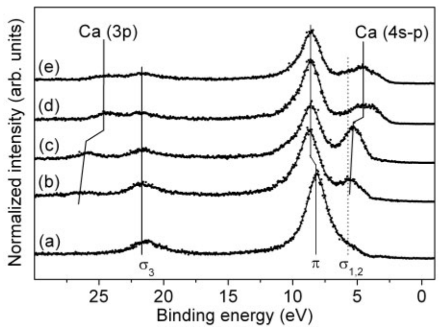

Fig. 1: Spectra (hν=70 eV) of sample A at the Γ point obtained *prior* (a) and after (b) Ca deposition, as well as after a short (5 min, (c)), extended (30 min, (d)) and long (90 min, (e)) annealing at 400 °C.

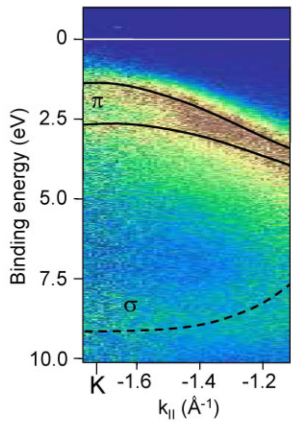

Fig. 2: Angle-resolved photoelectron intensity distribution (hν=50 eV) of sample B, after an annealing at 650 °C for about 120 min in total.

References

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