Zinc oxide is a wide band-gap semiconductor that has been recently attracting an increasing interest in the scientific community, especially for its promising applications in optoelectronics, spintronics, and catalysis [1–3]. In particular, the perspective of preparing a material combining both magnetic and semiconducting properties has prompted an intense research activity aimed at identifying a valuable and reliable transition metal dopant, in a so-called diluted magnetic semiconductor oxide with room temperature (RT) ferromagnetic properties [4–10]. Elements like Mn and Cu, that do not present secondary ferromagnetic phases due to partial clustering, are highly preferred. In addition, the Cu/ZnO system has been largely used as an excellent catalyst for the industrial methanol synthesis. However, key questions on the microscopic mechanism of the reaction are still open and the incorporation of Cu atoms into ZnO may play a role in determining the catalytic activity of Cu/ZnO [11,12].

Cu doping of ZnO has been previously achieved by either pulsed-laser ablation or high temperature diffusion (>1000 °C), resulting in Cu ions substituting lattice Zn ions [10,13]. Several studies based on photoluminescence experiments [14,15], electrical measurements [16,17], and on GGA + U calculations [18] have reported a deep acceptor state with the transition energy level (0, −1) high in the band gap. In this Letter we present a combined experimental and theoretical study of the Cu/ZnO system prepared by Cu deposition on ZnO single crystal surfaces. The high resolution electron energy loss spectroscopy (HREELS) data reveal that Cu can diffuse into bulk ZnO by a mild thermal treatment yielding an unusual donor state in ZnO. Theoretical modeling suggests that the shallow donor state results from the formation of interstitial Cu⁺ ions in ZnO.

All experiments were carried out in a HREELS system, as described in a previous work [19]. In short, the ZnO(0001) sample was prepared by repeated cycles of Ar ion sputtering and subsequent annealing at 850 K for 10 min. The Cu evaporator used in this work is a homemade setup with an electronic beam heating. The film thickness is measured by a quartz crystal with an experimental error of about 10%. The broadening (Δ) of the quasielastic peak in HREELS is derived according to the formula \( \Delta_{\text{app}}^2 = \Delta_{\text{tot}}^2 - \Delta_{\text{b}}^2 \) [19], where \( \Delta_{\text{app}} \) denotes the apparatus broadening.

The calculations have been performed within spin-polarized density-functional theory (DFT), using the hybrid B3LYP functional [20]. The Kohn–Sham orbitals were expanded in Gaussian type orbitals, as implemented in CRYSTAL06 package [21] [the all-electron basis sets are O 8-411(d) [22], Zn 8-64111(d411) [23] and Cu 8-6411(d41) [24]]. The bulk wurtzite ZnO has been modeled by a 192-atoms supercell \( 4 \times 4 \times 3 \) with optimized bulk lattice parameters: \( a = 3.278 \) Å, \( c = 5.287 \) Å. The reciprocal space was sampled in a \( 2 \times 2 \times 2 \) k-point mesh. We refer to a previous work for the detailed description of the theoretical approach to compute formation energies (\( E_{\text{form}} \)) and transition energy levels (\( e \)) [25,26]. Thermodynamic transition levels (\( e_{\text{therm}} \)) of defects in bulk materials can be directly compared to donor levels ionization energies, as determined with the experimental approach of this and previous work [19].

The polar O-ZnO(0001) surface is electrostatically unstable because of uncompensated surface charges and exhibits a complex surface structure [3]. The HREELS spectrum of the clean O-ZnO surface is characterized by intense Fuchs-Kliewer phonons at 68, 135 and 201 meV (see Fig. 1) [27]. After deposition of Cu up to 20 monolayers (ML) at RT, the surface phonons are fully screened by Cu layer. They reappear and increase in intensity with annealing the sample to higher temperatures. Upon heating to 825 K, the spectrum of Cu/O-ZnO becomes comparable with that of the clean O-ZnO (Fig. 1). We can first rule out the possibility of Cu desorption from the surface, as confirmed by the corresponding thermal desorption spectroscopy data (not shown). The present HREELS results could