Room-temperature ferromagnetism of Cu-doped ZnO films probed by soft X-ray magnetic circular dichroism

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Introduction

Spintronics, which exploits the spin property of electrons, is an emerging paradigm for the next-generation electronic devices. Diluted magnetic semiconductors (DMS) combine the electronic functionality of conventional semiconductors and the non-volatility of ferromagnetism, representing one of the most promising routes to the realization of room-temperature spintronic devices. However, the lack of direct experimental evidence for the intrinsic ferromagnetism in DMS to date has rendered the nature of the observed magnetic phenomenon highly controversial. The element-specific soft x-ray magnetic circular dichroism (SXMD) is regarded as the litmus test for any intrinsic ferromagnetism.

I. Experimental

- Samples: Cu doped ZnO thin films (50 nm) were grown by PLD using mixed ZnO and CuO powder (99.99%)
- Sample 1: undoped ZnO (reference)
- Sample 2: 2 at% ZnO:Cu at O rich pressure (1×10⁻⁶ torr)
- Sample 3: 2 at% ZnO:Cu at O poor pressure (5×10⁻⁶ torr)

- Characterizations:
  - Crystal Structure and morphology: XRD, TEM, SEM, EDS, SIMS
  - Electronic Structure: XPS, XAS, PL, Raman
  - Magnetic Properties: SQUID, SXMD

II. Film Structure and Morphology

Good film crystallinity and homogeneous distribution of all elements.

III. Characterization of Defects

- Significant amount of oxygen vacancies (\(V_O\)) present in sample 3 (O-poor).
- Regular Cu²⁺ (\(U_p\)) is dominant in sample 2 (O-rich), while Cu⁺ (\(U_{as}\)) is dominant in sample 3 (O-poor) due to the doping effect of V_O.

IV. SXMD

- Strong XMCD signals occur at both Cu L-edge and O K-edge only for the FM sample 3—consistent with SQUID.
- The XMCD at Cu L-edge centralizes only at the 935 eV peak (Cu⁺:O₉), while at the regular Cu²⁺ site is negligible.
- Antiparallel alignment of the magnetic moments between Cu and O sites.
- The XMCD signal at O K-edge closely resembles the shape of XAS, indicating close correlation of magnetism and O₉ orbital.

V. Theoretical Calculations & Model

- Innovated First-principle calculations with disorder visualize the large sized \(V_O\) orbital residing within the host band gap and reveal incomplete spin polarization in the Cu 3d bands.
- The local magnetic moments of Cu in the vicinity of the \(V_O\) orbital are ferromagnetically coupled through a "double-exchange" like effect mediated by the overlapping vacancy orbitals.

Conclusions

- Cu (2%) doped ZnO under O-deficient condition displays ferromagnetism with \(T_C\) of 750 K.
- The intrinsic band polarization in Cu-doped ZnO is successfully probed by the SXMD at both Cu and O states.
- The observed FM is proposed to originate from the alignment of the localized large moments of Cu in the vicinity of oxygen vacancies mediated by the large-sized vacancy orbitals through an indirect "double-exchange" like effect mediated by the overlapping vacancy orbitals.