

Differences in XANES of isostructural and isoelectronic delafossites

When similar systems have different XANES

O. Šipr¹, F. Rocca², A. Šimůnek¹ and P. Fornasini³

¹: Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, CZ-162 53 Prague, Czech Republic

²: IFN-CNR, Istituto di Fotonica e Nanotecnologie del CNR, Sezione "FBK-CeFSA" di Trento, Via alla Cascata 56/C, I-38123 Povo (Trento), Italy

³: Dipartimento di Fisica, Università di Trento, Via Sommarive 14, I-38123 Povo (Trento), Italy

sipr@fzu.cz

http://www.fzu.cz/~sipr

Introduction

- Materials with similar structure and similar chemical properties are expected to have similar XANES.
 - Trigonal CuScO_2 and CuLaO_2 are isostructural and isoelectronic (Sc and La belong to the same column), hence their Cu K -edge XANES should be very similar.
- Delafossites may help in understanding XANES of other Cu oxides: possibility to study spectra of linearly coordinated monovalent Cu with O–Cu–O units pointing all in the same direction.

Motivation

Interesting and unexpected differences observed in Cu K -edge XANES of CuScO_2 and CuLaO_2 .

Aim of the study

- Analyze origin of these differences in terms of the polarization dependence of the spectra and of the scattering properties of atoms.
- Implications for the role of the pre-peak in other monovalent Cu compounds?

Experiment

- Fine powders on polytetrafluoroethylene membranes.
- Transmission measurements at Gilda beam-line at ESRF.
- See Ahmed *et al.* PRB **79**, 104302 (2009) for details.

Theory

- Ab-initio real-space calculations.
- Muffin-tin potentials taken from self-consistent calculations for clusters of 24–27 atoms embedded in a crystal.
- Energy-independent X_α potential with $\alpha=0.67$.

Alignment of the energy ranges

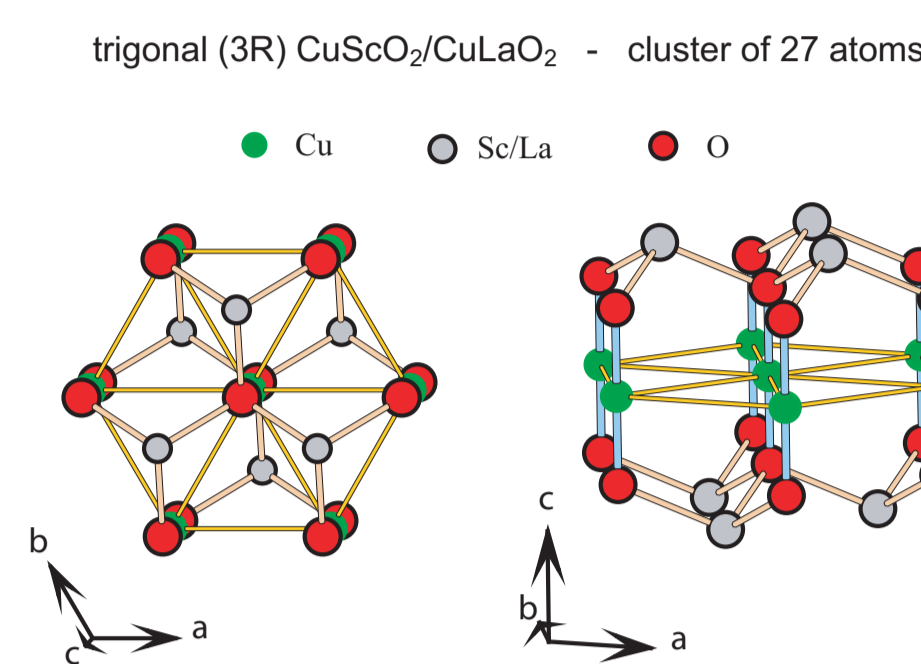
- Appropriate scaling of energy ranges suppresses differences in XANES which stem from different lattice constants.
- Features at E_1 and E_1' for one compound and at E_2 and E_2' for another compound, d_1 and d_2 characteristic distances:

$$(E_1 - E_1') d_1^2 = (E_2 - E_2') d_2^2 .$$

Conclusions

- Apparent chemical and structural similarity of compounds does not necessarily imply similarity of their XANES spectra.
- Differences between Cu K -edge XANES of CuScO_2 and CuLaO_2 can be understood if one focuses on the polarization-dependence of the spectra and on differences in Sc and La phase shifts.
- The pre-peak is connected with scattering of the photoelectron in the ab plane by at least seven Cu atoms and fourteen O atoms (analogous to the case of Cu K -edge XANES of Cu_2O).
- Further reading: O. Šipr *et al.* JPCM **21**, 255401 (2009).

Structure

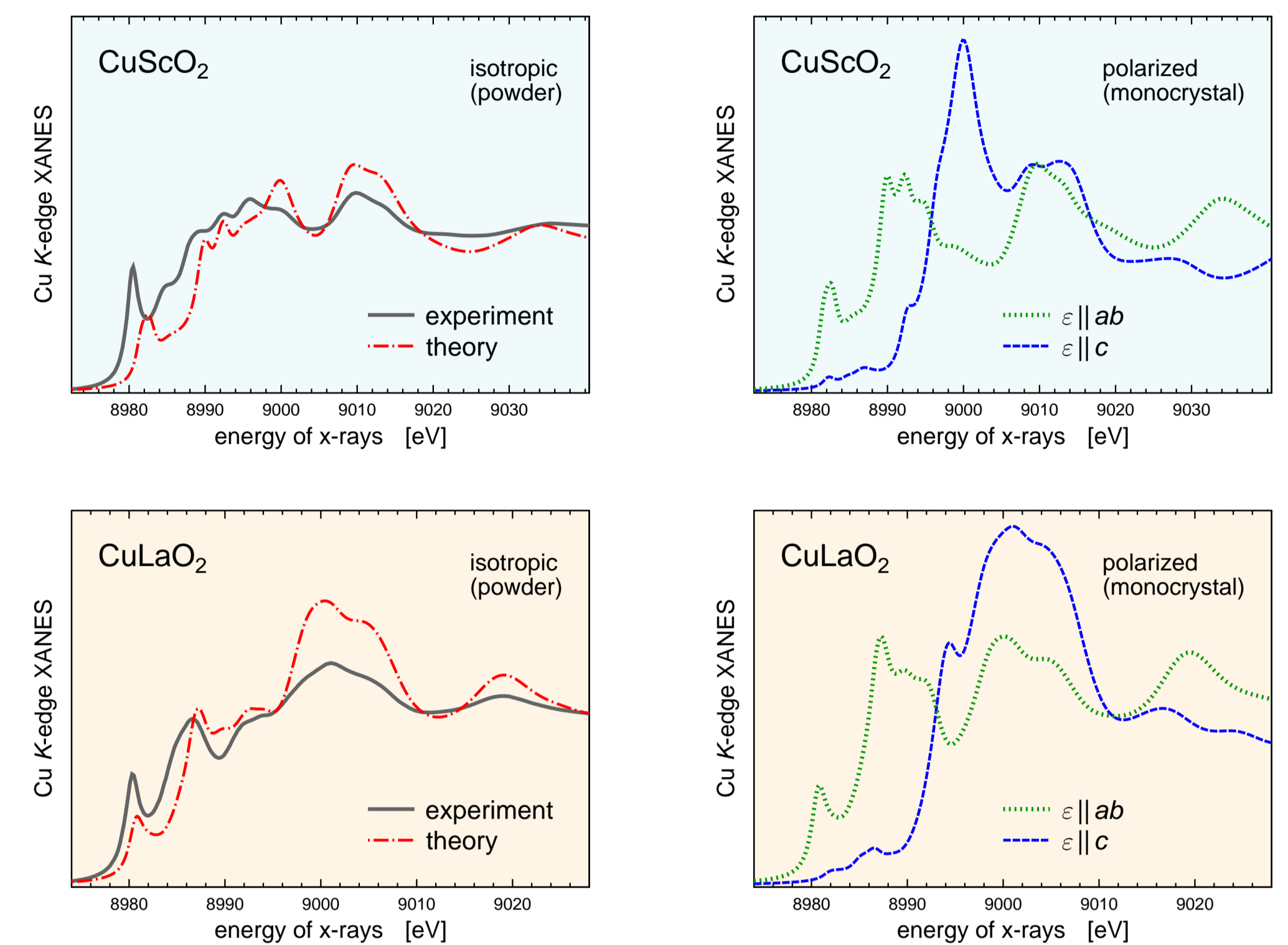


- Trigonal (rhombohedral) symmetry
- Distances along c axis nearly identical for CuScO_2 and CuLaO_2 , distances in the ab plane larger for CuLaO_2 by 20%

	N	CuScO_2	CuLaO_2	Cu_2O
Cu–O	2	1.80	1.85	1.85
Cu–Cu	6	3.22	3.83	3.02
Cu–M	6	3.40	3.61	3.02

Distances between Cu and its neighbors (in Å). The M atom is Sc in CuScO_2 , La in CuLaO_2 and Cu in Cu_2O .

Isotropic and polarized Cu K -edge XANES

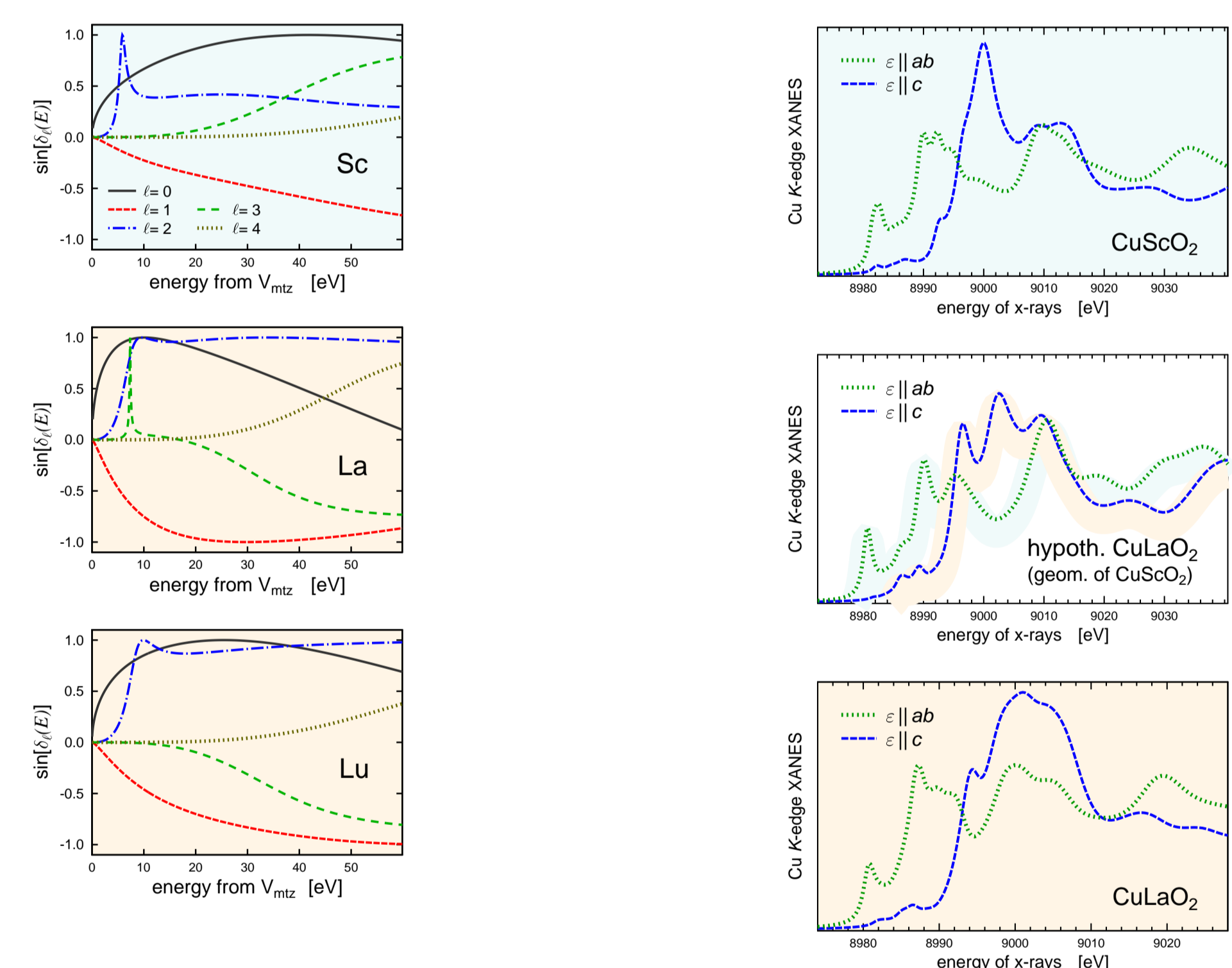


Left panels: Experimental and theoretical Cu K -edge XANES of powder CuScO_2 and CuLaO_2 .

Right panels: Theoretical polarized Cu K -edge XANES of CuScO_2 and CuLaO_2 monocrystals.

Scattering phase shifts of analogous atoms, Sc–La substitution

- Differences in phase shifts of Sc and La \Rightarrow differences in XANES of CuScO_2 and CuLaO_2 .
- Phase shifts for La and for Lu are similar \Rightarrow low-lying empty $4f$ states in La are *not* essential.
- Cu K -edge XANES of a hypothetical CuLaO_2 with the geometry of CuScO_2 :
 - $\epsilon || ab$ spectral component resembles the $\epsilon || ab$ component of true CuScO_2 (geometry dominates),
 - $\epsilon || c$ spectral component resembles the $\epsilon || c$ component of true CuLaO_2 (phase shifts dominate).

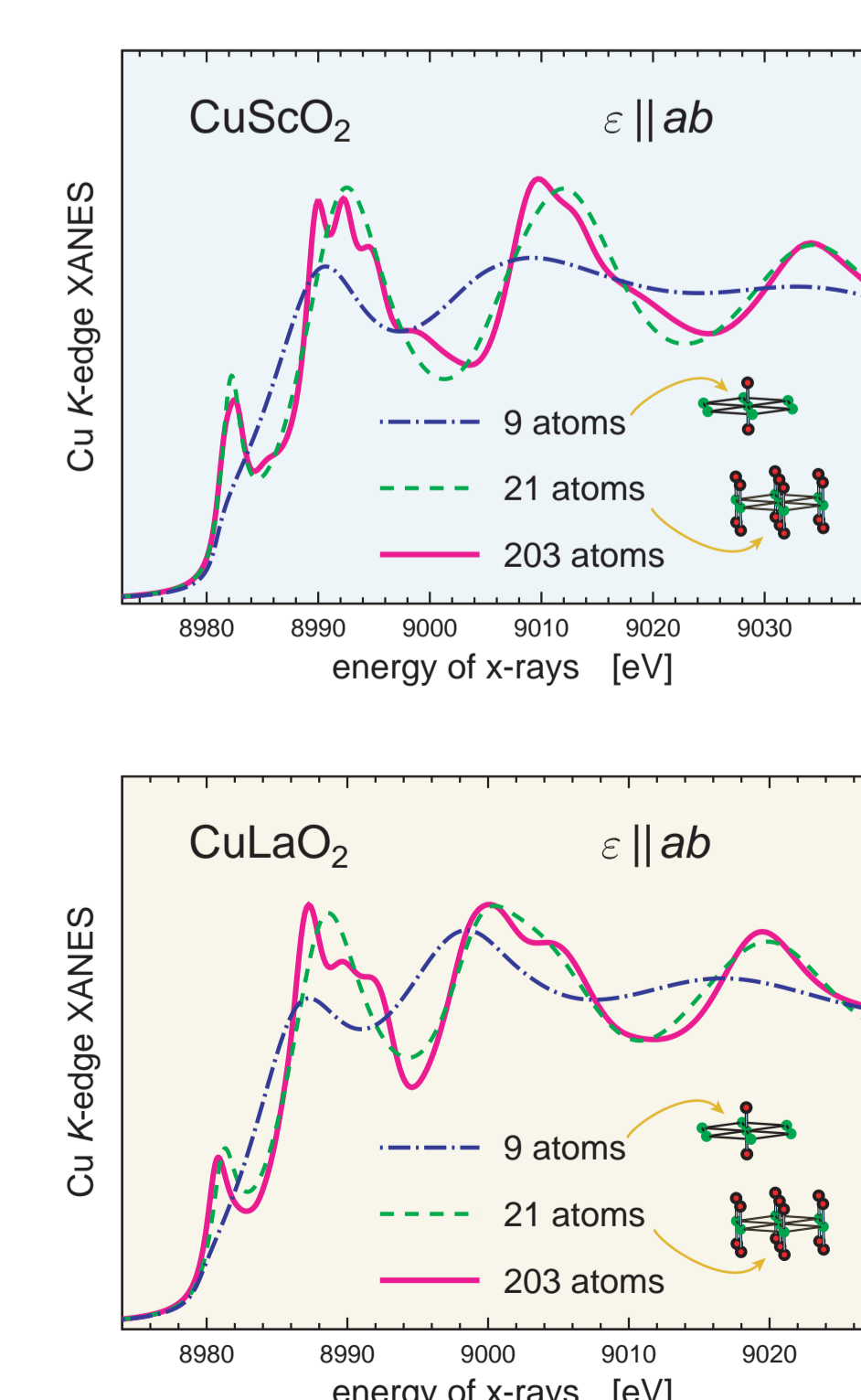


Phase shifts $\sin[\delta_\ell(E)]$ for Sc in CuScO_2 , La in CuLaO_2 and Lu in a hypothetical CuLuO_2 with geometry of CuLaO_2 .

Theoretical Cu K -edge XANES of a hypothetical CuLaO_2 with the geometry of CuScO_2 .

Role of specific groups of atoms, pre-peak issues

- Important features of the $\epsilon || ab$ spectrum can be reproduced for cluster of 21 atoms.
- Including the Sc/La atoms does not alter the $\epsilon || ab$ spectrum significantly.
- Pre-peak appears only for the $\epsilon || ab$ polarization.
 - Analogy with Cu_2O , where the pre-peak is connected with transitions perpendicular to the O–Cu–O axis.
 - O–Cu–O chains are parallel to each other in delafossites (unlike in Cu_2O) \rightarrow association between the pre-peak and states in the ab plane could be in principle demonstrated by experiment
 - Two kinds of pre-peak in monovalent Cu compounds?
 - * Pre-peak appears also in systems with linearly coordinated monovalent Cu with no Cu atoms in the ab plane — e.g., in $[\text{Cu}(xypz)]_2(\text{BF}_4)_2$.



Dependence of theoretical $\epsilon || ab$ component on the atoms included.

