A study of $Cu_2FeSn_{3-x}Ti_xS_8$ ($0 \leq x \leq 3$) thiospinels Using X-ray Absorption Near-Edge Spectroscopy

John R. Hayes and Andrew P. Grosvenor

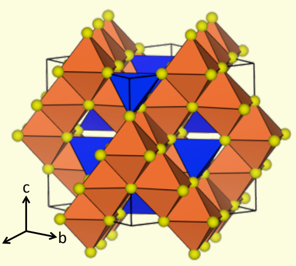
Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan S7N 5C9

Abstract

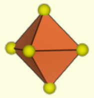
Spin-crossover (SCO) transitions are an interesting phenomena found in some materials, and occur when the metal centres switch from a low-spin to a high-spin electron configuration [1]. This transition may be induced by perturbing the system via irradiation with UV/VIS light, changing the atmosphere or pressure, or changing the temperature, and these materials may have applications for use as sensors and as materials for memory storage devices [2]. While well-known in molecular compounds, few studies have investigated SCO phenomena in crystalline materials, where long-range magnetic ordering may impact the SCO transition. A series of $Cu_2FeSn_{3-x}Ti_xS_8$ ($0 \leq x \leq 3$) compounds have been studied using temperature-dependent X-ray Absorption Near-Edge Spectroscopy (XANES). These materials adopt a spinel-type structure, where the octahedrally coordinated Fe^{2+} (d^6) may undergo a transition from a high-spin to a low-spin state [3]. As the Ti content is varied, substantial changes in the pre-edge and main-edge regions of the Fe K-edge spectra are observed. The main-edge excitations of the Fe K-edge spectra are found to change as the temperature is decreased from room temperature to 50 K. These results indicate that the Ti content and Fe spin state both influence the Fe–S bond environment. S K-edge spectra from the thiospinels have been collected to understand how the covalency of the Fe–S bond changes with the Fe spin state.

$Cu_2FeSn_{3-x}Ti_xS_8$ Structure

- As Ti content increases: *a* lattice parameter 10.33 Å → 10.00Å
  M–S bond distance 2.52 Å → 2.44 Å



Cu tetrahedral site



M = Fe, Sn, Ti
octahedral site

Experimental Methods

Synthesis:

$$2Cu(s)+Fe+(3-x)Sn+x(Ti)+8S \rightarrow Cu_2FeSn_{3-x}Ti_xS_8 \ (0 \leq x \leq 3)$$

- Heated in evacuated fused silica tubes; 6 days; 50 °C

Density of States (DOS) Calculations:

- Partial DOS calculated using LMTO-ASA package, 490 *k*-points [4]

XANES:

Fe K-edge

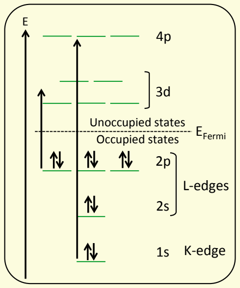
Beamline:	Soft X-ray Microcharacterization Beamline (CLS)
Data Collection:	Total Electron Yield (TEY)
Calibration:	Fe metal foil, 7112.0 eV [5]

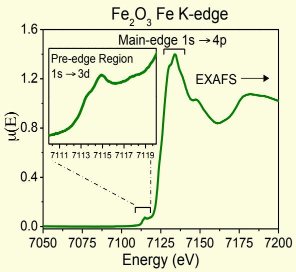
S K-edge

Beamline:	PNC/XSD-CAT 20-BM beamline (APS)
Sample Stage:	Liquid He cyrostat with Be windows
Data Collection:	13 element Ge Detector (PFY), Transmission mode
Calibration:	Fe metal foil, 7112 eV [5]

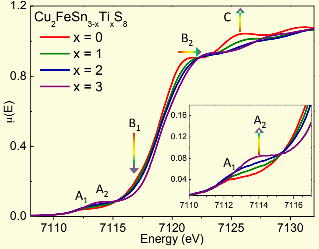
What is XAS?

- Spectra are divided into two regions: The near-edge region (XANES) and the post-edge oscillations (EXAFS)
- The near-edge region:
  - is subject to the dipole selection rule (Δl = ±1), and
  - provides information on the coordination and charge of the probed atom





Room-temperature Fe K-edge



Five features in Fe K-edge:

Pre-edge

- A_1 Fe 1s → Fe 3d t_{2g}
- A_2 Fe 1s → Fe 3d e_g^*

Main-edge

- B_1 Fe 1s → Fe 4p/Sn 5p
- B_2 Fe 1s → Fe 4p/Ti 4p
- C Fe 1s → Fe 4p multi-scattering resonance (MSR)

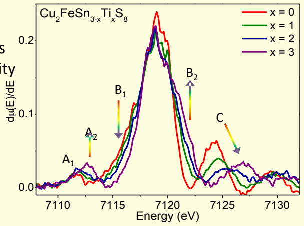
Derivative of Fe K-edge Spectra

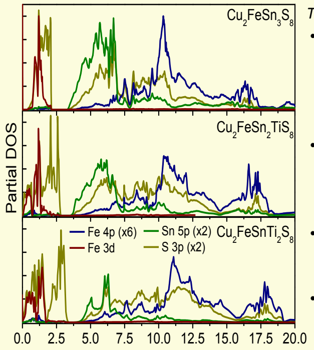
- Edge energy does not shift
  - Change caused by simultaneous changes in B_1 and B_2 intensity

Summary of Changes

With increased Ti Content

- A_2 intensity increases
- B_1 intensity decreases
- B_2 intensity increases
- C intensity decreases
- C shifts to higher energy



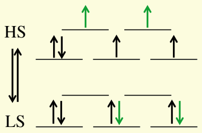


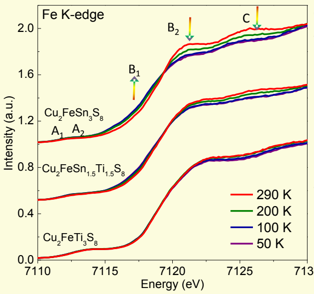
The reasons for the changes:

- A_2: Decreased Fe–S bond distance allows for better overlap of Fe 3d–S 3p orbitals
  - Increases dipolar character of excitation
- B_1: Decreased interaction between Fe 4p, Sn 5p
  - Reduced number Sn 5p states as Ti replaces Sn
- B_2: Fe 4p–S 3p–Ti 4p interactions replace Fe 4p–S 3p–Sn 4p interactions
- C: Ti has lower scattering power than Sn, substitution reduces MSR

Temperature-dependent Fe K-edge

- $Cu_2FeSn_{3-x}Ti_xS_8$ undergoes an SCO transition
  - Fe switches from a high-spin (HS) to low-spin (LS) state with decreasing temperature
  - Transition temperature is 215 K in $Cu_2FeSn_3S_8$ (T where %HS=%LS) [3]
- Use T-dependent XANES to investigate





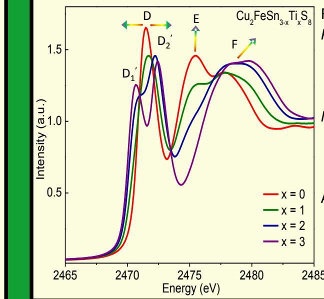
Changes in Fe K-edge spectra as T is lowered:

- A_1, A_2: No change
- B_1: Increases in intensity
- B_2: Decreases in intensity
- C: Decreases in intensity

Magnitude of change decreases as Ti content is increased

- Number of Fe^{2+} undergoing SCO transition decreases [3]
- Can't compare the absolute number of HS Fe^{2+} between different compositions.

S K-edge



Features in the S K-edge:

Pre-edge:

- D : S 1s → S 3p/Sn 5s
- D_1': S 1s → S 3p/ Ti 3d t_{2g}
- D_2': S 1s → S 3p/ Ti 3d e_g^*

Main-edge:

- E: S 1s → S 3p/Sn 5p
- F: S 1s → S 3p/Ti 4p &
  S 1s → S 3p/Fe 4p

As Ti replaces Sn:

- Less S-Sn 5s states, more S-Ti 3d states, pre-edge splits
- Less S-Sn 5p states, E decreases
- More S-Ti 4p states, F increases

Conclusions

In the $Cu_2FeSn_{3-x}Ti_xS_8$ thiospinels:

- The Fe–S bonds become more covalent as the Ti content is increased
- A Fe 3d–S 3p–Sn 4p interaction has been observed
- As Ti content increases, the number of Fe^{2+} that undergo an SCO transition decreases
- S K-edge results support the Fe K-edge results and describe the electronic structure of the materials

References

[1] Gütlich, P.; Goodwin, H.A. *Top. Curr. Chem*. **2004,** 233, 1-47. [2] Kahn, O. *Science* **1998**, *279*, 44-48. [3] Womes, M.; Reibel, C.; Mari, A.; Zitoun, D. *J. Solid State Chemistry* **2011**, *184*, 753-763. [4] Anderson, O.K.; Jepsen, O. *Phys. Rev. Lett*. **1984**, *53*, 2571. [5] Thompson, A. et al. *X-Ray Data Booklet* Lawerence Berkeley National Laboratory: Berkeley, 2009.

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