

Local Structure and Ligand State of Chevrel Phase Superconductor - 3d Metal Doping Effect

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Experiment:

We have used x-ray absorption spectrum (XAS) to study Chevrel Phase Superconductors $M_x\text{Sn}_{1-x}\text{Mo}_6\text{S}_8$. Mo *K*-edge extended x-ray absorption fine structure (EXAFS) and S *K*-edge x-ray near edge absorption spectrum (XANES) measurement were carried out at the 01C1/16A DCM beamline of NSRRC in Taiwan by transmission /fluorescence signal respectively. The superconductivity in these samples was checked by transport and magnetic properties and the pure phase was verified by x-ray diffraction.

Results and Discussions:

Figure 1 shows the sulfur *K*-edge XANES of host and 3d elements doped compound $\text{Sn}_{0.9}\text{M}_{0.1}\text{Mo}_6\text{S}_8$. Refer to host SnMo_6S_8 sulfur *K*-edge main peak, Fe, Co, and Ni doping induce sulfur *K*-edge shift to low energy side gradually from -0.34 to -0.78 eV and reverse shift from Cu doping -0.34 eV to Zn doping 0.27 eV to high energy side. If the main peak in figure 1 was aligned together for samples to see the p-d hybridization ligand state difference upon doping. Obviously, (Fe, Co, Ni, Cu)/Zn doped samples have low/high p-d hybridization between Mo and S ion and small/large crystal field splitting than that of host sample (see the area pointed by arrow).

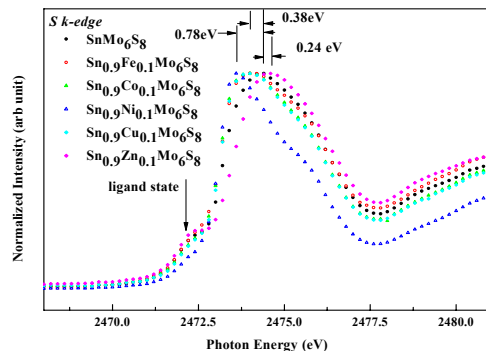


Figure 1. S *k*-edge, Normalized main peak to unit

Figure 2 and 4 show Mo *K*-edge EXAFS $k^3\chi$ transformation and Fourier transformation of $k^3\chi$. The EXAFS results show the magnitude of Fourier transformation and the Mo-S, and MO-MO bonding condition variation. Peak a and peak b in figure 3, show their bonding condition. The change of a/b ratio is consistent with the trend of peak shift in figure 1. The stronger p-d orbitals hybridization is correlated to the local structure distortion that was related to transport and magnetic properties. This result implied Mo valence in Fe, Co, and Cu doped

samples is more but is less in Zn doped sample than the valence of host compound.

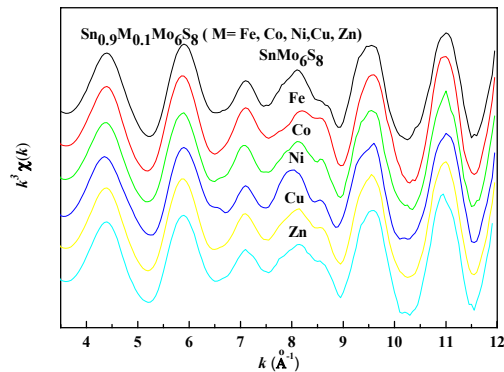


Figure 2. Mo *k*-edge EXAFS oscillation $k^3\chi$ data

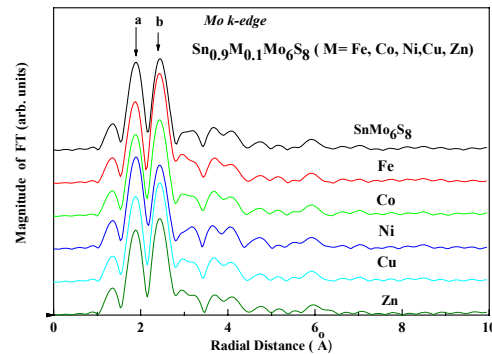


Figure 3. Fourier transform of $k^3\chi(k)$ spectra from $k = 3.5$ to 12 \AA^{-1}

Conclusion:

The S *K*-edge spectrum shows S unoccupied states were affected by the doping element (M). (Fe, Co, Ni) and (Cu, Zn) doped samples have low/high p-d hybridization and small/large crystal field splitting than that of host sample between Mo and S ion. Mo *L*-edge structure shows the consistent charge redistribution between Mo-S sites. We correlated transition temperature of superconductivity to the doping effect induced Mo 4*d*-S 3*p* hybridization ligand state change in conclusion. The p-d hybridization dominates the physical properties of these samples that were induced by the local structure no change.

Acknowledgment:

This work was supported by National Science Council, Taiwan, Republic of China under grant number; NSC-94-2112-M-014-003-