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Journal of Alloys and Compounds 401 (2005) 145–149

Journal of ALLOYS AND COMPOUNDS

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# The influence of the concentration of Sb ions onto the local crystal and electronic structures of $CuCr_{2-x}Sb_xS_4$ ($x = 0.3$, 0.4, 0.5) studied by XANES and EXAFS measurements and LAPW numerical calculations

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Received 12 June 2004; received in revised form 10 January 2005; accepted 20 January 2005
Available online 23 May 2005

**Abstract**

The X-ray absorption K-edges of sulfur in $CuCr_{2-x}Sb_xS_4$ ($x = 0.3$, 0.4, 0.5) have been measured and compared to linearized augmented plain wave (LAPW) numerical calculations. The near edge region is generated by magnetically polarized and hybridized S 2p energy levels and shows small change with increased Sb content, which can be attributed to the movement of Cr 3d spin-down states up on the energy scale. The LAPW result confirms this effect. Moreover, the calculations show that the antimony in those spinels is rather in +3 than in +5 valence state. The calculated magnetic moment on Cr equals to $2.72\mu_B$. In EXAFS, there is no visible change between $x = 0.3$ and 0.5 spectra, which indicates that the local structure does not change significantly.
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*Keywords:* Spin glasses; XAFS; LAPW; Spinel; Band structure; Crystal structure; Chromium

## 1. Introduction

The compounds under study belong to a large family of chromium based spinels ($ACr_2X_4$, where A = Zn, Cd, Hg, Cu and X = S, Se, Te) which have been analyzed during the last decades due to their interesting electric and magnetic properties like a large Seebeck effect and colossal magnetoresistance [1–3].

In the case of $CuCr_{2-x}Sb_xS_4$, the magnetic behavior evolves from ferromagnetic p-type metals ($x = 0.3$, 0.4) to antiferromagnetic semiconductors ($x = 0.5$). The compositions with $x = 0.3$, 0.4 reveal at lower temperatures (140 K) spin glass behavior and giant magnetoresistivity [1].

It has been shown earlier [4,5] that the occurrence of the spin-glass state in spinels with chromium can be attributed to the competition between two predominant magnetic interactions: a superexchange (antiferromagnetic) and a double exchange (ferromagnetic), which produces a spin frustration in the magnetic subarray.

Considering a simple model of a compound with formula $A^{2+}Cr_2{}^{3+}S_4{}^{-2}$, it follows that changing the atom on the site A to monovalent one (as $Cu^{1+}$) implies the following change to a formal valence of chromium $Cu^{1+}(Cr^{4+}Cr^{3+})S_4{}^{-2}$. As a result, the presence of $Cr^{4+}$ ions in a $Cr^{3+}$ array increases the double exchange coupling.

In our study, we have substituted chromium with antimony (we assumed $Sb^{+5}$ valence state), which in turn should decrease the ferromagnetic component in two ways:

(a) by breaking the magnetic paths $Cr^{3+}$–S–$Cr^{4+}$;

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doi:10.1016/j.jallcom.2005.01.060

(b) by changing the $Cr^{4+}$ ions back to $Cr^{3+}$ state (from the formal valence point of view or even possibly $Cr^{3+}$ to $Cr^{2+}$).

As a result, the double exchange ferromagnetic interactions should be significantly weaker.

However, there are already indications that the copper cations on A site rather create holes in anion band than change $Cr^{3+}$ into $Cr^{4+}$ valency state giving as a result $Cu^{1+}Cr_2{}^{3+}S_4{}^{-1.75}$ [6–9].

Since the double exchange and the super exchange are transferred through sulfur atoms, we have chosen to measure the sulfur K X-ray absorption edge as a probe for a local electronic structure. Moreover, the first shell around sulfur consists of all cation atoms (Cu, Cr and Sb). This makes the quantitative analysis of EXAFS oscillations very difficult but the qualitative comparison can detect any changes in all interatomic distances.

## 2. Experimental

The samples under study have been obtained with the aid of the solid-phase synthesis from the stoichiometric mixture of constituents. The process details have been described elsewhere [10].

The room temperature measurements for the powder polycrystalline samples have been carried out on the DRX1 beamline at the DAFNE-Light synchrotron radiation source in the Laboratori Nazionali di Frascati, INFN in transmission mode using a channel-cut Si (1 1 1) monochromator [11]. The ionisation chambers (19 cm active length) were filled with argon gas and the pressures were equal to 11 mbar ($I_0$) and 110 mbar (I). The entrance slit (before monochromator) was 2 mm-vertical × 1 cm-horizontal and the exit one 1 mm × 1 cm.

The polycrystalline samples has been finely powdered in a mortar and deposited on a film assuring the proper homogeneity as required by absorption experiment [12]. The chosen sample thickness gave step of absorption at the edge between 0.3 (for $x = 0.4$) and 1 ($x = 0.5$).

The XANES spectra were collected from 2460 to 2500 eV with 0.17 eV increment 2 s per point ($x = 0.4$ and 0.5) and 0.13 eV increment with 1 s ($x = 0.3$) per point.

The XANES region was averaged from two runs, reduced and normalized for a comparison with the numerical calculations according to the procedure, which was already used earlier [13].

Fig. 1 shows the XANES results on the absolute energy scale which were normalized in the following way:

- background was subtracted,
- the minimum of absorption was brought to 0 and the maximum to 1.

The EXAFS region was scanned from 2460 to 2860 eV with 1 eV/1 s speed (up to 10 $Å^{-1}$ in *k*-space). The EXAFS signal for the composition with $x = 0.4$ was too weak due to small quantities of the sample and was rejected from further analysis. The spectra were recorded at least twice for each setup.

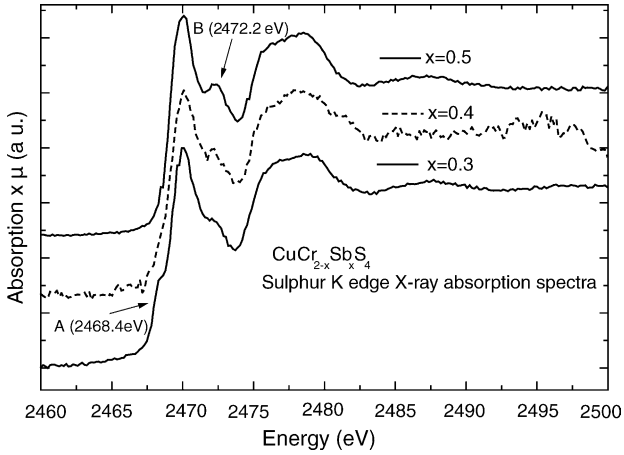


Fig. 1. Experimental spectra of X-ray absorption edges of sulfur for $CuCr_{2-x}Sb_xS_4$ ($x = 0.3$, 0.4, 0.5).

The EXAFS data have been processed with the aid of the IFEFFIT/FEFF6.02L/Artemis/Athena package [14]. The results of analysis were checked for both available runs for each compound with different background removal functions and Fourier transform settings.

## 3. Results and discussion

### 3.1. XANES and LAPW

It is known that the K-edge absorption spectrum probes the p-like density of unoccupied states [15]. When the Cr 3d states are split in an octahedral environment into $t_{2g}$ and $e_g$ subbands, the $t_{2g}$ levels can hybridize with sulfur 2p states. So, it is possible to detect changes in the transition metal state by investigating the sulfur K-edge. We have successfully used such approach earlier for analysis of S K-edges of transition metal monosulfides [13].

With increasing Sb content one could expect the following effects, which affect the XANES and EXAFS spectra:

(1) the appearance of new electronic states generated by Sb ions hybridized with sulfur p-like states (XANES);
(2) the change of the existing band structure due to:
   - the change of the chromium valency ($Cr^{2+}$, $Cr^{3+}$, $Cr^{4+}$) (XANES);
   - the deformation of the local crystalline structure (EXAFS).

In our results, the two effects can be clearly distinguished when Sb content increases, namely:

(a) the disappearance of a pre-edge structure A;
(b) the appearance of a new peak B on the right-hand shoulder of the main edge.

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