

## THE INFLUENCE OF THE CONCENTRATION OF $Sb^{5+}$ 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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The sulphur K edges XANES and EXAFS spectra of  $CuCr_{2-x}Sb_xS_4$  ( $x=0.3, 0.4, 0.5$ ) spinel type crystal solid solutions have been investigated in order to find the contribution of  $Sb^{5+}$  ions onto the local crystal and electronic structures. The measurements for the powder samples have been carried out on the DAFNE-Light synchrotron radiation source in the absorption mode using the channel-cut Si [111] monochromator.

The properties of the crystals under study evolve from the ferromagnetic  $p$ -type metals ( $x = 0.3, 0.4$ ) to the antiferromagnetic semiconductors ( $x = 0.5$ ). The compositions with  $x = 0.3, 0.4$  reveal at lower temperatures the spin glass behaviour and the giant magnetoresistivity.

It is known that the sulphur K edge absorption probe the  $p$ -like density of unoccupied states around sulphur. The latter are influenced by the hybridisation of the sulphur  $p$ -like electronic states with the electronic states of both the antimony and multivalent chromium ( $Cr^{3+}$ ,  $Cr^{4+}$ ) ions. Therefore one could expect the following effects which affect the XANES spectra:

- 1) the appearance of the new electronic states generated by  $Sb^{5+}$  ions,
- 2) the change of the existing band structure due to:
  - the increase of the  $Cr^{3+}/Cr^{4+}$  ratio,
  - the deformation of the local crystalline structure.

In our results two effects can be clearly distinguished, 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,

The comparison of our results with the sulphur K edge spectra for pure  $CuCr_2S_4$  compound suggests that the second effect can be originated by the Sb substitution. The first effect can be attributed to the change of the  $Cr^{3+}/Cr^{4+}$  ratio. In order to confirm both effects the Linearized Augmented Plane Wave method

has been used to calculate the density of states, the magnetic moments and the theoretical X-Ray absorption spectra for the chosen composition ( $x = 0.5$ ).

To determine the deformation of the local crystal structure in the case of the compositions  $x=0.3$  and  $x=0.5$  the EXAFS sulphur K edge spectra have been recorded with the 1 eV increment up to 400 eV above the edge. The data have been processed with the aid of the IFEFFIT/FEFF6 package. The scattering paths of the starting model has been prepared on the basis of the structure obtained from the single crystal X-ray diffraction measurements.

The experimental data have been processed in the following way:

1. The  $\mu_0$  contribution has been removed with the built-in Autobk function with  $Rbkg = 1.5$ .
2. The forward Fourier transform has been performed on  $k$ -weighted  $\chi(k)$  for  $k = 1.5$  to  $9 \text{ \AA}^{-1}$  with the use of the Hanning window with  $dk = 1$ .

The results of this procedure are presented in Figure 2.

The largest maximum (1.5 to 2.5  $\text{\AA}$ ) corresponding to the first neighbour region is generated by the single scattering paths leading to the nearest ions of either copper, or chromium or antimony. Further analysis of the scattering paths has shown that in the second neighbour region (from 2.5 up to 4  $\text{\AA}$ ) the single scattering events on the nearest sulphur ions dominate. One can see in Figure 2 a very good agreement of the two curves in the first neighbour region, whereas in the second neighbour region the two curves significantly differ. It seems that this effect is related to the fact that every anion in the spinel type compounds has in the crystal structure one free parameter, called the anion parameter.

To conclude, one can say that the substitution of chromium ions by antimony ions influences the electronic structure but not the local crystal structure.

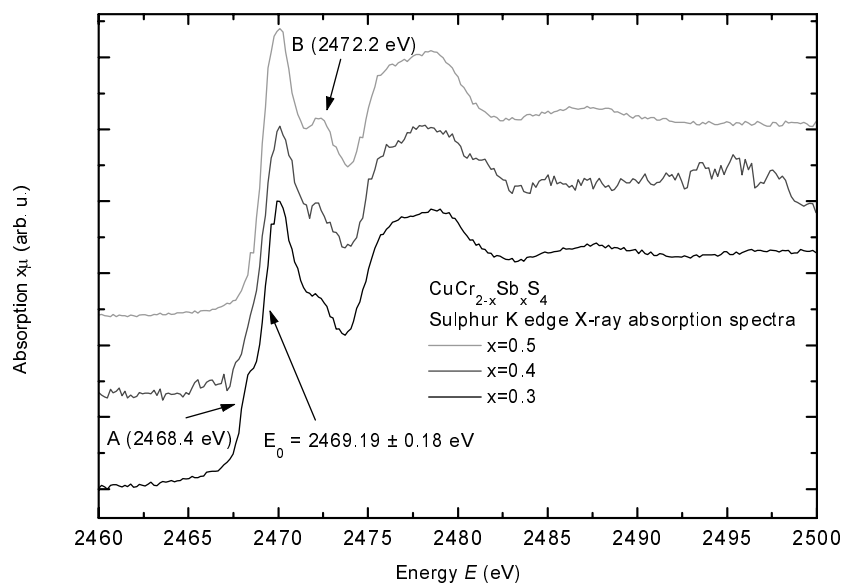


Figure 1.

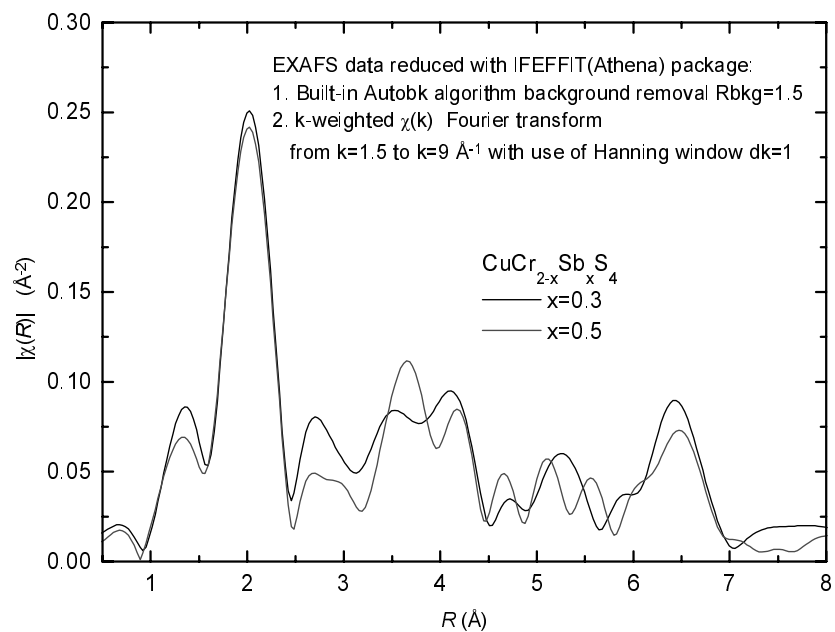


Figure 2.