RA01

Cu K AND Cr K EDGES IN $CuCr_{2-x}Sb_xS_4$ (x = 0.3, 0.4, 0.5) - XANES SPECTRA AND LAPW CALCULATIONS

<u>P. Zajdel</u>[1*], M. Green[2,3], J. Warczewski[1], J. Konior[4], J. Krok-Kowalski[1], P. Gusin[1], M. Oboz[1], L.I. Koroleva[5], R.V. Demin[5], and S. Fiddy[6]

[1]*University of Silesia, Institute of Physics, ul. Uniwersytecka 4, 40-007 Katowice, Poland*

[2]*Department of Chemistry, Christopher Ingold Laboratories, University College London, Gordon Street, London, WC1H 0AJ, United Kingdom*

[3]*The Davy-Faraday Research Laboratory, The Royal Institution of Great Britain, 21 Albermarle Street, London, W1S 4BS, United Kingdom*

[4]*Jagellonian University, Institute of Physics, ul. Reymonta 4, 31-007 Kraków, Poland*

[5]*M.V. Lomonosov Moscow State University, Vorobyevy Gory, 119899 Moscow, Russia*

[6]*Daresbury Laboratory, Warrington WA4 4AD, United Kingdom*

Keywords: chromium compounds, XAS, band structure, sulphur compound, spinel, XANES, $CuCr_{2-x}Sb_xS_4$

*) e-mail: pzajdel@us.edu.pl

The series of $CuCr_{2-x}Sb_xS_4$ spinels shows an unprecedented sensitivity in its physical properties with either an applied external magnetic field as well as temperature (crossover of magnetoresistance [1,2], see Fig. 1), which is also observed in the other family of spinels $Zn_{1-x}Cu_xCr_2Se_4$ [3].

It is accepted that in the spinels with general formula $A^{2+}B_2^{3+}X_4^{2-}$ one can induce a multivalent state in the B (*e.g.* Cr) cation by substituting in the A site a monovalent cation (*e.g.* Cu). This fact is beyond discussion in the case of oxide based spinels, however it is still discussed for other chalcogenide ions. *i.e.* S, Se, and Te [4-7].

The multivalence becomes crucial when one tries to explain the magnetic and electrical properties mainly by the competition between the double-exchange (acting between Cr^{4+} and Cr^{3+} ions) and super-exchange magnetic interactions as it was done for the selenide spinels [8]. One can influence the strength of the above interactions by substituting the A and B sites with cations with different formal valence, *e.g.* by mixing Cu^{1+} and Zn^{2+} on A site, or by substituting Cr^{3+} on B site with pentavalent elements (*e.g.* Sb).

The XANES studies on Cr K and Cu K edges have been carried out in order to establish the influence of antimony on both the effective charge of cations and the densities of states. The results are presented in Figures 2 and 3.
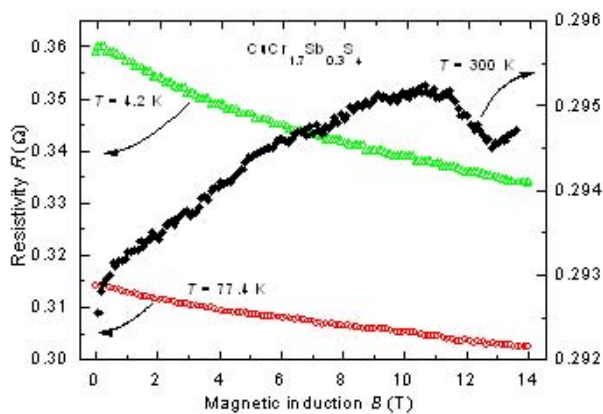

Figure 1. The crossover of magnetoresistivity in $CuCr_{1.7}Sb_{0.3}S_4$.
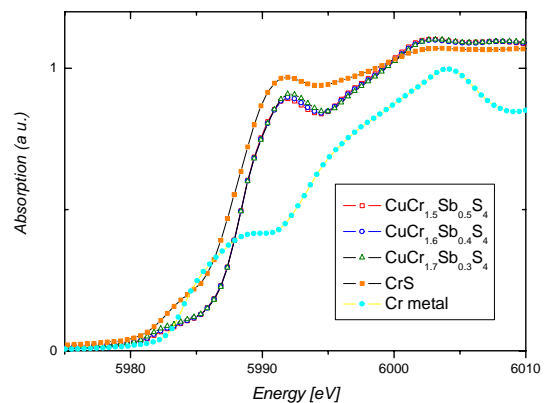

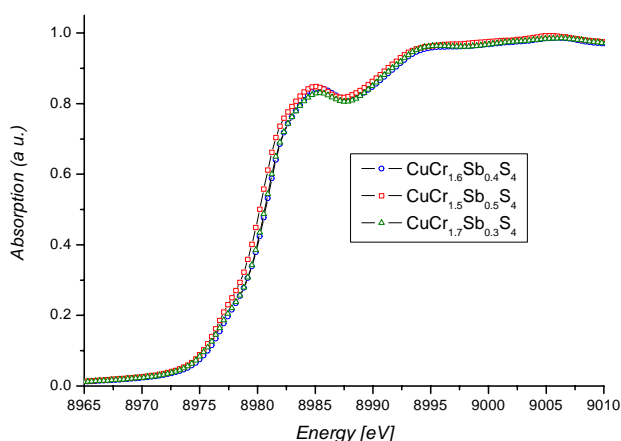Figure 2. Cr K edges with Cr metal and CrS as references.

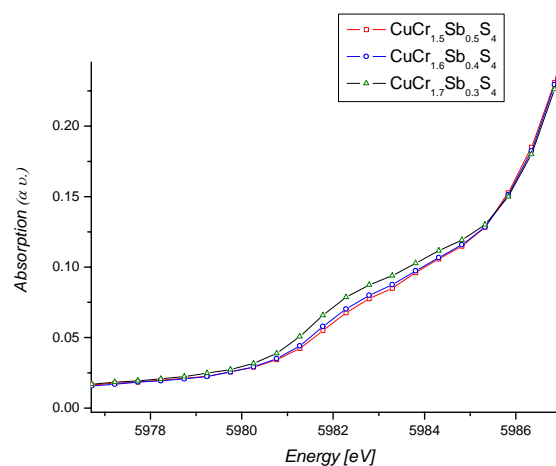Figure 3. Cu K edges with Cu-metal as reference.

Figure 4. The Cr K pre-edges change with increasing Sb content.

The lack of chemical shifts testifies to the fact that the increase of Sb content from 0.3 to 0.5 does not change the chromium valence [4] – as it was expected from the formal valence point of view. The same situation applies for the copper edge. This is in agreement with the previous studies [4-7], which indicated that the charge balance takes place on the anion *p*-type band.

The distinctive feature of Cr K edge is the decrease of the pre-edge structure with the increase of Sb content (Fig. 4), which was also observed for $(CuZn)Cr_2Se_4$ series [9].

This effect can be explained by the LAPW calculations, which show that the addition of antimony shifts the Cr *p*-like spin-up states below the Fermi level.

The present results confirm that in the case of sulphur spinels the substitution of the chromium with the antimony does not change both the chromium and copper effective charges. The agreement with the edge position for the pure compound [4, 5] and the changes in the S K edge [7] suggest that the properties of $CuCr_{2-x}Sb_xS_4$ are mainly influenced by the anion *p*-type (*p*-like in projected DOS) band. This effect suggests also that the magnetic properties would be affected stronger by the RKKY than the double exchange interactions.

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