# NEW RESULTS ON THE SKUTTERUDITE $Ce_yFe_{4-x}Co_xSb_{12}$*

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We report on sample preparation, annealing effects, electron microprobe analysis in the series $Ce_yFe_{4-x}Co_xX_{12}$ which shows that a phase separation occurs for substituted samples annealed at 650° C. The valence state of Ce in homogeneous single phase samples has been studied using X-ray absorption spectroscopy (XAS). Ce ions are trivalent in the series.

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## 1. Introduction

One of the most interesting ideas in the area of thermoelectric materials is to search for a solid that conducts heat like a glass but keeps good electrical properties found in crystals [1]. The idea is to check for semiconducting materials having a crystalline structure with large cages in which one weakly bound atom can be inserted and rattles independently of other atoms. In insulating materials, such localised rattlers can strongly reduce the thermal conductivity. Semiconducting or semimetallic compounds with such property can be found, for instance, in materials derived from skutterudite $CoAs_3$ [2]. After the synthesis of $LaFe_4P_{12}$ [3], the first ternary filled skutterudite, many isotypes with the formula $RM_4X_{12}$ have been discovered with R being a large electropositive metal (Ba, Ca, Sr, La to Sm, U, Th, ...); M a *d*-metal; X=P, As, Sb ... Interestingly, in $R_yM_4X_{12}$, electrical conductivity can be adjusted from insulating to metallic through semiconducting (generally better for the figure of merit ZT) by varying the filling factor $y$

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and/or playing on the valence state of the R- or M-element. When going from $CoAs_3$ to $CeFe_4Sb_{12}$, keeping the valence electron count constant implies that Ce would be tetravalent (so, the semiconducting behaviour can be maintained) or at least in a non trivalent state. In fact, $CeFe_4Sb_{12}$ has been successively classified as a normal trivalent material [4], or a heavy fermion system [5], or an intermediate valence material at low temperature from magnetic susceptibility results [6,7], or a trivalent Ce compound with strong hybridisation effects at low temperature [8], or a moderate heavy fermion system [9]. $L_3$ absorption edge (XAS) spectra seem to show 2 peaks [10]. In view of these contradictory results and the known tendency of white lines at the $L_3$ edge to broaden with local composition changes ( [11]) we decided to re-examine this question.

## 2. Experimental and results

All the compounds (for $x = 0, 1, 2, 3$ and 4) were prepared by standard arc melting on a water cooled copper hearth under Ar pressure. The skutterudite phase does not form during this process but is obtained after annealing of the materials, see details in [12]. As the peritectic temperature of $CoSb_3$ is 873°C [13] and that of $Ln_yFe_{4-x}Co_xSb_{12}$ (Ln= La, Ce, Th) is in between 750 and 850°C for $x = 1$ [8] we choose to anneal at lower temperatures: 650°C and 700°C. X ray diffraction (XRD), Rietveld analysis, Electron Probe MicroAnalysis (EPMA) analysis and XAS experiments (at the French synchrotron of LURE) are also described in [12]. The deconvolution of the XAS spectra has been made using the sum of two terms, an arc tangent and a Lorentzian, for each valence state [14]. A deconvolution with two Lorentzians for one valence state, assumed to account for the splitting of the final $5d$ state by crystal field effects [10] has also been performed.

All $Ce_yFe_{4-x}Co_xSb_{12}$ samples annealed at 650°C and containing both Fe and Co show two skutterudite phases in the XRD pattern — with slightly different lattice parameter values, see Fig. 1), whereas those with full Fe or Co contents are single phase. On the contrary, after annealing $Ce_{0.5}Fe_2Co_2Sb_{12}$ at 700°C the samples show only one skutterudite phase, independently of the annealing time (1 or 10 days). In figure 1, are reported on the left $y$ axis and on the right $y$ axis, the final compositions deduced from EPMA and the lattice parameters (dotted lines are guides for eyes). As shown in this figure, the final compositions of Fe- and Co- containing samples annealed at 650°C also reveal two slightly different local compositions, whereas those annealed at 700°C are single phase in agreement with XRD results. We, of course, measure the valence properties by XAS only on single phase materials.

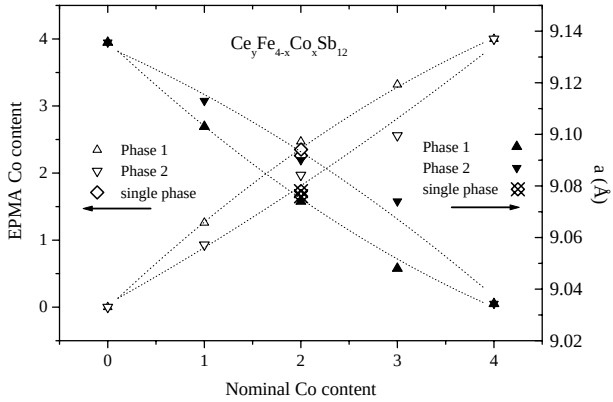


Fig. 1. EPMA compositions and lattice parameter in $CeFe_{4-x}Co_xSb_{12}$.

In the bottom part of figure 2 are shown twice the experimental absorption edges — at 300 K — of Ce in $CeFe_2Co_2Sb_{12}$ *versus* energy. The top spectrum (vertically shifted by +2 a.u.) shows the deconvolution into one arc tangent and one Lorentzian and their total. The bottom part of the figure shows the same spectrum with two Lorentzian contributions separated by 2.5 eV. In the top part of figure 2 is shown the intensity $I_0$ of the beam before the absorption process *versus* energy. Both fits with 1 or 2 Lorentzians involve comparable values of the half width of the Lorentzians (around 3 eV) which are consistent with the $2p$ hole lifetime in rare earth and give a similar good fit. The small shoulder on the right side of the main

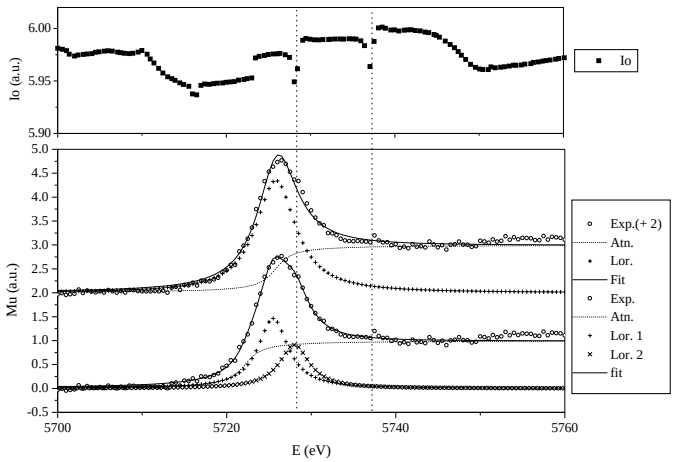


Fig. 2. $I_0$ (top curve) and $L_3$ absorption edge experimental spectra and deconvolution in $Ce_{0.5}Fe_2Co_2Sb_{12}$.

peak (at around 5728 eV) could have been taken as due to the effect of the splitting of the 5*d* band, however, at the same energy, the intensity of the beam shows the well known phenomena of a glitch (a characteristic of the used monochromator, here the Si 311 of the station D21 of LURE, as in [10] which occurs at a fixed energy — see the left vertical dotted line through the two curves). A second glitch at a slightly higher energy is indicated by the right vertical dotted line and gives also a shoulder of the same magnitude in the experimental curve. We consequently do not believe that the peak deconvolution needs two Lorentzian contributions.

In conclusion, the Ce is trivalent in this compound, as it is in the single phase $Ce_yM_4Sb_{12}$ (M = Fe, Co annealed at 650°C) and there is no clear effect of the splitting of the 5*d*-final state (in *eg*–*t*2*g* subbands). This agrees with our conception that in the skutterudites the Ce atom is weakly bound to the other atoms and thus crystal field effects are weak.

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