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Comparative investigation of CeNiSn₂ isotype compounds by X-ray absorption spectroscopy

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We present the comparative study of several CeM_{1-x}Sn₂ compounds where M stands for a transition metal element (Fe, Ni, Mn, Cu). All the reported samples are found to retain the CeNiSn₂ structure type with a deficiency in transition metal relative to the prototype concentration. Depending on the transition metal element used and or its concentration many different magnetic properties have been evidenced : antiferromagnetic order, ferromagnetic order... X-ray absorption spectroscopy has been performed on the L_{III} edge of Ce in order to probe the 4f electronic state of Ce. The spectra are discussed in terms of change in the Ce valence as result of M substitution and M-Ce bonding. The present results are compared to earlier reported neutron diffraction experiments.

Keywords: cerium electronic state; CeNiSn₂; magnetic order.

1. Introduction

The compounds CeM_{1-x}Sn₂ have attracted much attention among the last years. In particular, many studies were devoted to CeNiSn₂ phases (Skolozdra 1988, Francois, 1990, Schobinger-Papamentellos, 1997) which exhibits peculiar magnetic behaviour. Most of these compounds crystallises with the CeNiSi₂ (Bodak, 1970) structure type and forms a wide range of solid solutions depending on the different x value in CeM_{1-x}Sn₂ that is to say the M deficiency. Unlike the CeNiSi₂ type silicides which are reported to be stoichiometric compounds, recently discovered isostructural compounds germanides and stannides are off-stoichiometric phases characterized by large transition metal deficiency (Francois, 1990). An extensive investigation of the stability range and the crystal structure parameters of RM_{1-x}Ge₂ and RM_{1-x}Sn₂ phases can be found in reference (Francois, 1990). It was shown that simple geometric consideration can not explain the different homogeneity ranges observed for each transition metal alloyed. Other factors such as the electronic band structure may play a major role in stabilising this CeNiSi₂ structure type in narrow concentration range only.

In the case of the Ce containing compounds, the 4f electronic state are often markedly hybridized with the conduction electron 5d and 6s. Depending upon the surrounding atomic environment

and the strength of the Ce-neighbour band, one can expect a significant evolution of the Ce 4f electronic state. Such behaviour has been already observed in several intermetallic compounds (Isnard, 1997, Wohllenben, 1984). Here we intend to probe the evolution of the Ce electronic state upon the transition metal concentration in CeM_{1-x}Sn₂.

2. Magnetic features of the CeM_{1-x}Sn₂ compounds

It is to be reminded that in CeNi_{1-x}Sn₂ Ni atoms are known to be non magnetic, this is a general feature of the M elements in the CeM_{1-x}Sn₂ phases. The magnetic ordering of CeNi_{1-x}Sn₂ has been found to vary from ferromagnetism to antiferromagnetism for slight change of Ni concentration (Schobinger, 1998). Localized and ordered 4f magnetic moment are evidenced on the Ce atoms for high Ni concentration (Schobinger, 1998) but the kind of magnetic order depends upon the magnetic interactions between these moments. The Ni atoms and more generally the transition metal atoms concentration is found to be determinant on the magnetic properties of the CeNi_{1-x}Sn₂ compounds. The exchange interactions between the Ce localised moments are of RKKY type and consequently mediated by the conduction electron, density of which is expected to be strongly dependent on the transition metal concentration.

3. Experimental

The X-ray absorption spectroscopy experiments were performed at the DCI synchrotron radiation storage ring at LURE (Orsay), on the EXAFS 13 experimental station which uses a bending magnet. The monochromator consisted of two parallel Si crystals cut along the (311) plane. The rejection of harmonics was performed by adjusting the parallelism between the crystals. The detection used two ionization chambers filled with air. The energy scale was calibrated by reference to the Cr K absorption edge in Chromium metal foil.

A calibrated amount of powder sample was mixed with cellulosis in order to optimise the edge jump. All absorption spectra were normalised to the edge jump. The data collection was made using a step of 0.3 e.V. The determination of the valence has been performed using a deconvolution technique from the L_{III} spectra recorded at room temperature. The deconvolution process is based on a artan function which describes the transition from the 2p to the continuum states and a Lorentzian function that takes into account both the 5d density of unoccupied states and the finite lifetime of the 2p core hole. The equation which is used is taken from reference of Röhler (1985). The L₃ edge spectrum usually exhibit two white lines which are interpreted as 2p⁵4f¹ and 2p⁵4f⁰ final states, and the average valence is simply obtained from the relative intensities of the two edges. Each white line is decomposed into a artan and Lorentzian function. Although this simplified interpretation has been criticized, and although the ratio of the intensities of the two structures in the L₃ edge is not rigorously equal to the 4f occupation number, it has been demonstrated (Malterre, 1991) that this phenomenological approach provides information concerning the configuration mixing of the ground state and then keeps a physical meaning. The fit to the spectra have been made using the method described by Röhler (1985) where each line is built from two contributions: a Lorentzian function that describes

the transitions towards the localized 5d states and an arctan function that describes the transitions to the continuum states. It has been shown that the respective intensities of the two structures reflect the configuration mixing in the ground state. This technique is found to be very sensitive to slight changes in the Ce electronic configuration.

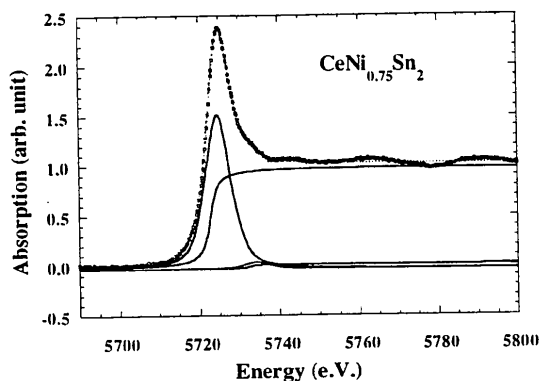


Figure 1

XANES signal recorded at the Ce L_{III} edge in CeNi_{0.75}Sn₂. The corresponding model decompositions into 4f₁ and 4f₀ contributions are also shown in the lower part of the figure.

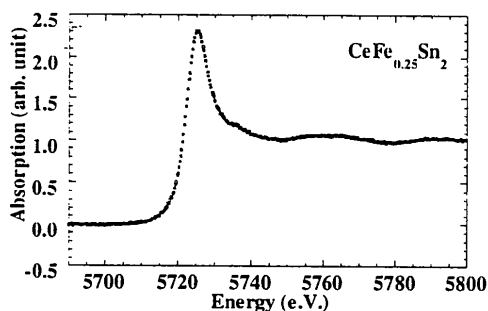


Figure 2

XANES signal recorded at the Ce L_{III} edge in CeFe_{0.25}Sn₂

4. X-ray absorption spectroscopy at the Ce L_{III} edge Results and discussions

As can be seen from figure 1, the Ce L_{III} X-ray absorption edge of CeNi_{0.75}Sn₂ exhibits a white line characterising a well localised Ce 4f electronic state. A similar absorption edge is obtained for CeFe_{0.25}Sn₂ figure 2 and CeMn_{0.35}Sn₂ indicating that the Ce state is very close from one compound to the other whatever the transition metal alloyed.

It is to be notice that the Ce absorption edge in the CeM_{1-x}Sn₂ phases is opposite to that observed for CeNi₂ or CeNi₂Si₂ which both exhibit mixed valent Ce electronic state (Wohlleben, 1984). The XANES measured in CeM_{1-x}Sn₂ is much more similar to that obtained by Wohlleben and Röhler for CeSn₃ (Wohlleben, 1984). The bonding between Ce and Sn may be at the origin of the localised 4f states in the CeM_{1-x}Sn₂ phases since Sn atoms are forming half of the Ce environment. The refined valence state

is 3.04, 3.07, and 3.05 for CeNi_{0.75}Sn₂, CeFe_{0.25}Sn₂ and CeMn_{0.35}Sn₂ respectively.

The Ce electronic state derived from XAS experiment on CeNi_{1-x}Sn₂ is consistent with the magnetic properties reported elsewhere (Skolozdra, 1988 and Schobinger, 1997) which are characteristic of trivalent state of Ce with magnetic moment of about 2μ_B per Ce atom.

The x-ray absorption spectroscopy results show that the CeM_{1-x}Sn₂ crystal structure favours a well localised 4f electronic state of Ce. The transition metal concentration determines the magnetic ordering (Schobinger, 1997) but our present investigation demonstrates that the Ce electronic state is mostly insensitive to the transition metal content.

The reason for this is probably related to the peculiar Ce atomic environment encountered in the crystal structure of the CeM_{1-x}Sn₂ compounds. In the CeNiSi₂ structure, Ce atoms have coordination number of 21, the Ni atoms being the closest near neighbours. Since 10 Sn atoms are forming half of the Ce environment, they are expected to be strongly bound to the Ce atoms and thus to play a major role in determining the Ce valence electronic state.

Six other Ce atoms are located at more than 4Å away from the Ce at the center of the polyhedron. In a pure stoichiometric CeNiSn₂ compound, 5 Ni atoms are expected to take part in the Ce environment. In the off-stoichiometric studied compounds, the transition metal deficiency leads to a reduction of the Ce coordination number of one to two atoms. In spite of this pronounced reduction, no significant effect is observed on the Ce L_{III} edge spectrum.

In the prototype compound CeNiSi₂ no anomaly was observed in the lattice parameter comparison with isostructural RNiSi₂ phases (where R is a rare-earth element)(Bodak, 1984). This is in favour of a Ce³⁺ electronic state. On the basis of magnetic measurements, Skolozdra et al. (Skolozdra, 1988) have proposed that the quantity of conduction electrons diminishes with rise of Ni content.

5. Conclusions

No significant influence of the nature of the transition metal and or its concentration has been observed on the 4f electronic state of cerium in the CeM_{1-x}Sn₂ compounds. All the studied compounds M = Ni, Fe, Mn exhibits a very localised 4f electronic state. On the contrary the type of magnetic ordering is determined by the transition metal concentration.

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