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Investigation of the CeTX system by means of X-ray absorption spectroscopy: correlation with other data

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RTX compounds (R = rare earth metal, T = d metal and X = semi metal) are known to exhibit original magnetic or superconducting properties. We have studied CeTSi compounds with the CeFeSi structure-type and which have been previously characterized for their structural and magnetic properties. These compounds can be described as a pseudo layer stacking of R, T and Si sheets. An interesting feature in this series is the lack of magnetic moment at the transition metal site.

We present an X-ray absorption spectroscopy of the Ce L_{2,3} edge and discuss the evolution of the cerium electronic state in correlation with structural and physical data obtained from X-ray diffraction and magnetic measurements.

Keywords : Cerium electronic state, CeFeSi, cerium magnetic moment

1. Introduction

For some years the study of RTX compounds where X is a semi metal alloyed with two metallic elements R (rare earth) and T (transition metal) with different electronegativities has been developing and consequently interesting phenomena in the field of superconductivity and magnetism have been revealed such as itinerant magnetism, valence fluctuations or heavy fermion behaviour.

These are peculiar compounds with a more or less metallic behaviour but localized interactions of covalent type between the metallic and metalloidal species (Venturini 1989, Welter 1994). Another much interesting feature of these materials arises from the fact that they combine two species that may bear a magnetic moment thus allowing to better understand rare earth-transition metal interactions.

In this paper we have focussed on some CeTSi silicides where T is a 3d or noble metal since it is known that many properties of cerium-containing compounds can be related to the electronic state of cerium. In particular, the degree of localization of the 4f states of cerium which is very sensitive to temperature or pressure may be varied with alloy concentration or in the present study with metal or metalloidal substitution. A summary of the structural and magnetic properties of the studied CeTX silicides is given, then the electronic state of cerium has been studied using X-ray absorption spectroscopy at the cerium L₃ edge.

2. Experimental

The X-ray absorption spectroscopy experiments were performed at the DCI synchrotron radiation facility of the 1.85 GeV storage ring at LURE (Orsay), on the EXAFS13 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 made by adjusting the parallelism between the crystals. The detectors were two ionization chambers filled with air. In order to ensure a good accuracy in the energy scale, the energy of the cerium L₃ edge was calibrated against that of the Cr K edge. The sample was powdered down to a grain size of about 40µm; then a calibrated amount of powder sample was mixed with cellulosis in order to optimize the edge jump.

The fit to the spectra have been made using the method described by Röhler (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 towards the continuum states. Then the respective intensities of the two structures reflect the configuration mixing in the ground state.

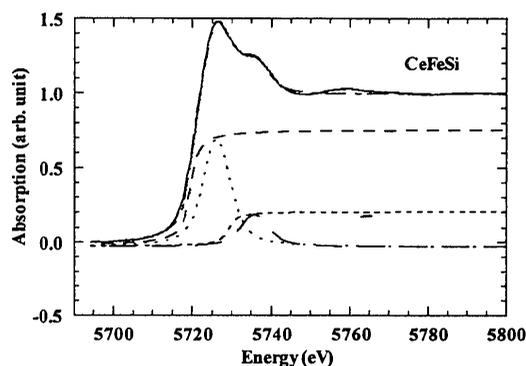


Figure 1

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

3. Structural and magnetic properties

The CeFeSi structure-type has been reported in 1970 (Bodak, 1970) and the crystal structure is tetragonal with space group P4/nmm. The susceptibility of CeFeSi is very weak (a few e.m.u./g) and independent of temperature; CeFeSi behaves then like a Pauli paramagnet. This behaviour suggests that Fe does not carry a magnetic moment in this structure as already observed in the RFe₂Si₂ and RFeSi₂ structure types. (Szytula, 1989). The lack of magnetic moment on transition metal is a general feature of the CeFeSi structure type. The rare earth μ_{eff} values deduced (for R above Nd) from the susceptibility measurements are in good agreement with those for free R ions corroborating, then, the lack of magnetism at the transition metal site. In the case of CeFeSi an additional confirmation of the lack of magnetic moment on Fe has been established by Mössbauer spectroscopy measurements carried out at room temperature and 4.2K respectively. The variation of the lattice parameters observed across the RFeSi series suggests that Ce is in an intermediate valence state and a similar behaviour has led to the same conclusions in the CeFe₂Si₂ and CeFeSi₂ compounds.

The Co analogou silicide CeCoSi is paramagnetic at room temperature and the variation of susceptibility as a function of

temperature is of Curie-Weiss type. Again, similar considerations based on the susceptibility measurements across the RCoSi series suggest that cobalt does not carry a magnetic moment in this structure type. In order to complete the systematic study of CeTX phases in which the transition metal does not carry a magnetic moment, we have extended our investigation to some silicides containing noble metals namely CeRuSi, CeOsSi. No magnetic ordering above 4.2K has been detected in these three compounds. They are paramagnetic at room temperature and the variation of their susceptibility as a function of temperature is of Curie-Weiss type. The μ_{eff} values for cerium that were extracted from the susceptibility measurements are gathered in table 1. To summarize, structural considerations as well as magnetic measurements suggest either intermediate valence or strongly localized states for cerium in these compounds.

4. X-ray absorption spectroscopy

X-ray absorption spectroscopy at the L₃ edge has been widely used to study cerium-containing materials. It is a bulk spectroscopy that does not require ultrahigh vacuum. In order to have some quantitative estimate of the cerium valence state we used a phenomenological approach which has been successfully applied in the case of metallic intermediate valence compounds. In this approach, the two white lines of the L₃ edge spectrum are usually interpreted as $2p^5 4f^1$ and $2p^5 4f^0$ final states, and the average valence is simply obtained from the relative intensities of the two edges. An example of the fit to the spectra is given in figures 1&2, and the cerium valence values derived from the fitting procedure are summarized in table 1.

The cerium valence values extracted from the fit to the spectra lie in a narrow range and indicate a partial delocalization of the cerium 4f electrons. It is also seen that the nature of the transition metal does not affect much the electronic state of cerium in this system where no strong intermediate valence state has been evidenced. The measured valence of 3.23 for CeFeSi is typical of an intermediate valence state of Ce and is consistent with the lack of localized magnetic moment evidenced by the magnetic measurements. According to the XAS experiments Co for Fe substitution leads to a relocation of the 4f electronic state in fair agreement with the appearance of a magnetic moment. In the CoOsSi compound a slight decrease of the magnetic moment with respect to that of CeCoSi is observed. Correspondingly, the XAS signal indicates a more delocalized character of the 4f state due to a stronger 4f-5d hybridization. The Ce magnetic moment reduction in CeOsSi may be accounted for by crystal electric field effects which are induced by a significant decrease of the lattice constants.

Sample	μ_{eff} (μ_B)	Valence
CeFeSi	-	3.23
CeCoSi	2.8	3.13
CeRuSi	2.56	3.14
CeOsSi	2.03	3.16

Table 1

Valence and magnetic moment of cerium in CeTSi compounds

5. Discussion

The method used to extract a valence state 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 that this phenomenological approach

provides information concerning the configuration mixing of the ground state and then keeps a physical meaning in the case of metallic intermediate valence compounds. Traditional one-electron methods of calculation of absorption spectra (band structure, multiple scattering approaches) fail to reproduce the L₃ edge spectra of intermediate valence systems. The interaction between the photoelectron and the remaining system must be taken into account explicitly (the photoelectron contributes to the screening of the core hole); such an interaction leads to the breakdown of the sudden approximation. Models to describe the L₃ edge of cerium-based IV compounds have been developed (Gunnarson, 1983) based on the Anderson impurity model. Jo and Kotani consider (Jo, 1985) that the photoelectron goes into the conduction band d and interacts with the core hole and the f states via Coulomb terms. Malterre has proposed a modified approach (Malterre 1991) in which the hybridization of the photoelectron with the conduction states is taken into account.

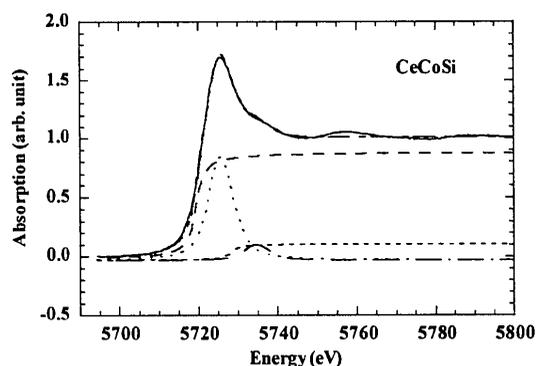


Figure 2

XANES signal recorded at the Ce L_{III} edge in CeCoSi. The corresponding model decompositions into $4f^1$ and $4f^0$ contributions are also shown in the lower part of the figure.

6. Conclusion

We have shown that the magnetism in this system is carried by cerium and is mainly of delocalized character; the study at the Ce L₃ edge evidences a partial delocalization of the 4f electrons. To summarize, considerations based on structural and magnetic measurements, in the CeTSi system, suggest that the cerium 4f states are sensitive to the nature of the transition metal participating to the coordination of cerium.

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