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Ce Valence State Probed by XAFS Study in $\text{Ce}_2\text{Fe}_{17-x}\text{Ga}_x\text{M}_y$ Compounds (M = Light Interstitial Element)

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Abstract. In the $\text{Ce}_2\text{Fe}_{17}$ alloy, cerium is known to be in an intermediate valence state. The sensitivity of cerium electronic state to its environment has been probed by XAFS experiment on the XAS3 station of the DCI Synchrotron radiation facility at LURE. We have studied the influence of interstitial element insertion on one hand and/or iron substitution by Ga on the other hand on the Ce L₃ absorption edge. The results of XAFS are discussed in the light of neutron diffraction experiments that yield the interstitial element location and the substitution scheme in the local environment. This study shows that the large macroscopic magnetic change induces a significant evolution of the Ce L₃ absorption edge. A partial relocalization of the 4f states is observed.

1. INTRODUCTION

Many investigations on the magnetic properties of iron-based compounds with the $\text{Th}_2\text{Zn}_{17}$ structure have been performed, since these compounds are of particular interest for applications as permanent magnet materials. Spectacular changes and improvements of their magnetic properties with respect to the ordering temperature can be achieved either by partial substitution of the iron atoms or upon interstitial insertion of light elements such as H, C or N [1,2]. Information on charge transfer is often of value in understanding the physical properties of compounds. In this paper we focus on the cerium-containing compounds for which many of their physical properties can be related to the electronic state of cerium.

The $\text{Ce}_2\text{Fe}_{17-x}\text{Ga}_x\text{H}_y$ system is thus a good probe to i) study the effect of Fe/Ga substitution and of hydrogen insertion on the degree of localization of the 4f states of cerium; ii) make a correlation between the electronic state of cerium and the changes of the magnetic properties. In this study we have used the L₃ XAS technique which has already been successfully employed to investigate even small valence variations in the cerium-containing compounds.

2. EXPERIMENTAL DETAILS

Information and details on the samples preparation can be found in reference [2]. The XAS experiments were performed at the DCI synchrotron radiation storage ring at LURE (Orsay), on the EXAFS 3 experimental station. 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. The energy of the Ce L₃ edge was calibrated against that of the Cr K edge.

A calibrated amount of powder sample was mixed with cellulose in order to optimize the edge jump. All absorption spectra were normalized to the edge jump. The determination of the valence has been performed using a deconvolution technique from the L₃ 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 Röhler [3,4].

3. RESULTS AND DISCUSSION

We present the XAS spectra of selected compounds in the $\text{Ce}_2\text{Fe}_{17-x}\text{Ga}_x\text{H}_y$ system in figures 1 and 2.

The spectrum of the $\text{Ce}_2\text{Fe}_{16}\text{Ga}$ compound is characterized by a clear splitting of the white line that can be associated to the 4f¹ and 4f⁰ channels, this shows that cerium is in an intermediate valence state. The fits to the spectra yield the following valence values $v=3.26$ for $\text{Ce}_2\text{Fe}_{16}\text{Ga}$ and $v=3.22$ for $\text{Ce}_2\text{Fe}_{15}\text{Ga}_2$. It is then clear that the progressive substitution of iron by gallium leads to a substantial relocalization of the 4f states of cerium. It is also interesting to note that hydrogenation of these compounds yields an almost similar effect. The as fit valence values are $v=3.16$ for $\text{Ce}_2\text{Fe}_{16}\text{GaH}_5$ and $v=3.15$ for $\text{Ce}_2\text{Fe}_{15}\text{Ga}_2\text{H}_{3.7}$. This shows that the combined effect of Ga and H is efficient to induce a strong relocalization of the 4f states of cerium.

We now remind the salient features of Ga to Fe substitution and of hydrogen insertion in $\text{Ce}_2\text{Fe}_{17}$. Neutron diffraction has shown [5] that in each case, gallium as well as hydrogen take part in the coordination of cerium even increasing the coordination number of cerium in the case of hydrogen insertion.

The effects on the magnetic ordering temperature are also much similar. For instance, the Curie temperature increases from 238K for $\text{Ce}_2\text{Fe}_{17}$ to 406K for $\text{Ce}_2\text{Fe}_{15}\text{Ga}_2$; however no increase of the dumbbell distance is observed upon Ga

substitution. Another interesting feature is the slight increase of the overall Fe moments that has been detected by neutron diffraction in the gallium-substituted compounds and in the hydrides.

Figure 1 : XANES signal recorded at the Ce L₃ edge in CeFe₁₅Ga₂ along with model decomposition in 4f¹ and 4f⁰ contributions.

This study has shown that gallium substitution or hydrogen insertion in Ce₂Fe₁₇ have similar effects on the electronic state of cerium, they lead to a significant relocation of the 4f states of cerium; furthermore their effects are additive. This collection of experimental results together with those from previous investigations [6] shows that the changes of the magnetic properties that are observed cannot be interpreted in a straightforward manner. No strongly localized 4f magnetic moment (i.e. no α to γ transition) has been detected in cerium. These preliminary data suggest that presumably the 3d (Fe)-5d (Ce) hybridization must be considered in order to account for the changes that are observed upon gallium substitution or hydrogen insertion in this system.

Figure 2 : XANES signal recorded at the Ce L₃ edge in CeFe₁₆GaH₅

4 CONCLUSION

This investigation by means of XAS at the Ce L₃ edge has shown that in the Ce₂Fe_{17-x}Ga_xH_y system, cerium remains in an intermediate valence state. Analysis of the preliminary data indicates that the changes of the magnetic properties that are observed upon gallium substitution or hydrogen insertion cannot be directly connected with an α - γ transition of the electronic state of cerium. More subtle and indirect effects have to be considered to account for these changes.

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