ELSEVIER

Journal of Alloys and Compounds 262–263 (1997) 198–201

Journal of ALLOYS AND COMPOUNDS

# Ce valence state probed by XAFS study in $Ce_2Fe_{17-x}Ga_xH_y$ compounds

O. Isnard[a,*], S. Miraglia[a], C. Giorgetti[b], E. Dartyge[b], G. Krill[b], D. Fruchart[a]

[a] *Laboratoire de Cristallographie, Université J. Fourier, CNRS, BP 166, 38042 Grenoble Cedex, France*
[b] *L.U.R.E. Bat. 209 D, Université de Paris Sud, 91405 Orsay Cedex, France*

## Abstract

This system is a good probe for the study of the effect of Fe → Ga substitution and hydrogen insertion, on the degree of localization of the 4f states of cerium. We tried to correlate the electronic state of cerium with the changes in the magnetic properties. The studied compounds crystallize in the $Th_2Zn_{17}$ type of structure. Most of them are ferromagnetic with Curie temperatures near room temperature. Insertion of hydrogen or Fe → Ga substitution leads to spectacular changes in the ordering temperature. Both, hydrogen and gallium atoms take part in the cerium coordination leading to a change of the local environment of cerium. Measurements of X-ray absorption spectroscopy have been combined with magnetization measurements in order to probe the magnetic properties of the $Ce_2Fe_{17-x}Ga_xH_y$ system. X-ray absorption near edge spectroscopy XANES has been measured at the Ce $L_{2,3}$ edges. The Ce 5d magnetic moment has been estimated using polarized X-ray absorption spectroscopy. We discuss the effect of hydrogen on the rare earth 6s electronic states in the light of earlier Mössbauer spectroscopy. © 1997 Elsevier Science S.A.

## 1. Introduction

Many investigations on the magnetic properties of iron-based compounds with the $Th_2Zn_{17}$ structure have been performed, since these compounds are of particular interest for applications as permanent magnetic 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 $Ce_2Fe_{17-x}Ga_xH_y$ 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 $L_3$ X-ray Absorption Spectroscopy XAS technique which has already been successfully employed to investigate even small valence variations in the cerium-containing compounds. The use of polarized X-rays particularly the X-ray Magnetic Circular Dichroism (XMCD) technique allows us to probe orbital magnetism and we have used this technique at the Ce $L_{2,3}$ edges.

## 2. Experimental details

Stoichiometric amounts of the starting elements (3N purity) were melted in a HF furnace using the

---

[*] Corresponding author.

*PII* S0925-8388(97)00380-0

cold crucible technique. The resulting ingots were annealed for 2 weeks at 900°C in evacuated silica tubes. The single phase character of the samples was checked by means of X-ray powder diffraction. More information and details on the sample preparation can be found in reference [2]. We remind that under the thermodynamical conditions used in the spectroscopy experiment, the hydrogenated samples are stable. The Curie temperatures were determined in a laboratory made Faraday balance with an accuracy of 5 K. 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 done by adjusting the parallelism between the crystals. The detectors were two ionization chambers filled with air. The energy of the Ce $L_3$ edge was calibrated against that of the Cr K edge. A calibrated amount of powder sample was mixed with cellulosis in order to optimize the edge jump. All absorption spectra were normalized to the edge jump. The determination of the valence was performed using a deconvolution technique from the $L_3$ spectra recorded at room temperature. The deconvolution process is based on an arctang 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 used is taken from Röhler [3,4].

For the XMCD experiments, the spectra were recorded at the LURE-DCI synchrotron facility on the XAS 10 energy dispersive experimental station, using a position sensitive detector in transmission mode at 0.3 mrad below the orbit plane (i.e. for approximately 80% right circular polarized light). More details can be found in references [5]. The measured signals were normalized to the height of the unpolarized absorption jump.

## 3. Results and discussion

### 3.1. Crystallographic and bulk magnetic results

The $Ce_2Fe_{17}$ compound crystallizes in the $Th_2Zn_{17}$ type rhombohedral structure. X-ray powder diffraction has shown that this structure is retained after hydrogen insertion or Ga for Fe substitution. Neutron powder diffraction [2] has been used to locate hydrogen on one hand and the Fe to Ga substituted sites on the other hand [6]. It has been shown that hydrogen occupies octahedral sites (9e) up to three H atoms per formula unit, the remaining hydrogen atoms being accommodated in tetrahedral sites (18g) for $x > 3$. The Fe to Ga substitution leads to a preferential occupation for the 18h site which is the site having the most rare earth atoms ligands in the coordination shell. To summarize, either hydrogen insertion or Fe to Ga substitution lead to a strong modification of the rare earth coordination. 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. The lattice parameters as well as the bulk magnetic data are summarized in Table 1. It is seen that the unit cell volume increases both for the Fe to Ga substitution and even more significantly for H insertion.

It is to be underlined that a huge enhancement of the Curie temperature is induced either by Fe to Ga substitution or hydrogen insertion. This could either be due to a change of the Ce electronic state toward a γ-Ce like (magnetic) state or to a change occurring in the Fe sublattice. Here we intend to probe the possibility for magnetism on the Ce sublattice.

### 3.2. X-ray absorption experiments

We present the XAS spectra of selected compounds in the $Ce_2Fe_{16}Ga$, $Ce_2Fe_{16}GaH_5$ system in Figs. 1 and 2, respectively. The spectrum of the $Ce_2Fe_{16}Ga$ compound is characterized by a clear splitting of the white line that can be associated to the $4f^1$ and $4f^0$ channels, showing that cerium is in an intermediate valence state. The fits to the spectra yield the following valence values $v = 3.26$ for $Ce_2Fe_{16}Ga$ and $v = 3.22$ for $Ce_2Fe_{15}Ga_2$ (Table 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 previous work has evidenced that hydrogenation of these $Ce_2Fe_{17}$ [5] yields an almost similar effect. In the present study, we have tried to check whether the effect of Ga and H are additive. The as fit valence values are $v = 3.16$ for $Ce_2Fe_{16}GaH_5$ and $v = 3.15$ for $Ce_2Fe_{15}Ga_2H_{3.7}$. This shows that the combined effect of Ga and H is efficient in inducing a strong relocalization of the 4f states of cerium. In $Ce_2Fe_{15}Ga_2H_{3.7}$,

Table 1
Structural and magnetic parameters of $Ce_2Fe_{17-x}Ga_xH_y$ compounds

| Compound | a (Å) | c (Å) | V (Å$^3$) | $T_c$ (K) |
|---|---|---|---|---|
| $Ce_2Fe_{17}$ | 8.489 | 12.413 | 775 | 225$^a$ |
| $Ce_2Fe_{16}Ga$ | 8.529 | 12.479 | 786 | 359 |
| $Ce_2Fe_{15}Ga_2$ | 8.565 | 12.532 | 796 | 443 |
| $Ce_2Fe_{17}H_5$ | 8.657 | 12.568 | 816 | 444 |
| $Ce_2Fe_{16}GaH_5$ | 8.643 | 12.599 | 815 | 484 |
| $Ce_2Fe_{15}Ga_2H_{3.7}$ | 8.668 | 12.629 | 822 | 507 |

[a] Néel temperature.

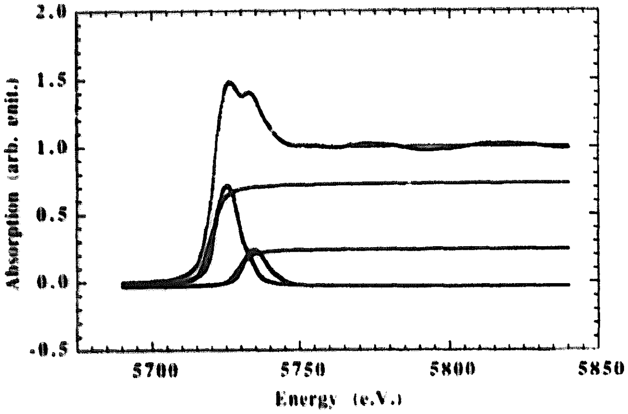

Fig. 1. Ce $L_{III}$ X-ray absorption edge spectra of $Ce_2Fe_{16}Ga$ along with the model decomposition into $4f^1$ and $4f^0$ contribution. The solid line refers to the fit, and the decomposition of the fit and the dots are the experimental data.

the Ce 4f electronic states are not completely localized and Ce is still in an intermediate valence state: no Ce $\alpha \rightarrow \gamma$ transition is observed Table 2.

### 3.3. X-ray Magnetic Circular Dichroism (XMCD) experiments

The detection of a dichroic signal at the Ce $L_{2,3}$ edges of cerium in these compounds is direct proof of the existence of a 5d moment carried by cerium atoms. Since cerium has been shown to be in an intermediate valence state, we propose that this 5d moment has the same origin as in the $Ce_2Fe_{17}H_x$ system that is a polarization by the 3d states of the neighbouring Fe atoms which have been modified by hydrogen insertion or Fe/Ga substitution. It has previously been demonstrated [5,7] that the orientation of the 5d magnetic moment can be derived from the sign of the observed XMCD signal. In the present study, the recorded XMCD spectra $L_{2,3}$ (Fig. 3) bear witness to a Ce 5d magnetic moment coupled antiparallel to the Fe 3d magnetic moment. This is precisely in agreement with the Campbell coupling scheme [8].

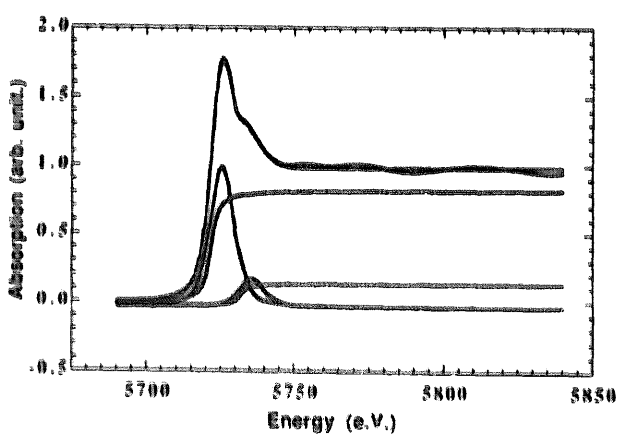

Fig. 2. Ce $L_{III}$ X-ray absorption edge spectra of $Ce_2Fe_{15}Ga_2H_5$ along with the model decomposition into $4f^1$ and $4f^0$ contribution. The solid line refers to the fit, and the decomposition of the fit and the dots are the experimental data.

Table 2
Ce valence state according to X-ray absorption spectroscopy

| Compound | Ce valency |
|---|---|
| $Ce_2Fe_{17}$ | 3.33 |
| $Ce_2Fe_{16}Ga$ | 3.26 |
| $Ce_2Fe_{15}Ga_2$ | 3.22 |
| $Ce_2Fe_{17}H_5$ | 3.26 |
| $Ce_2Fe_{16}GaH_5$ | 3.16 |
| $Ce_2Fe_{15}Ga_2H_{3.7}$ | 3.15 |

The present results show that the 5d magnetic moment carried by Ce is almost exclusively of spin origin (Fig. 3), its magnitude can be estimated to be approximately 0.35 $\mu$B scaled to the $CeFe_2$ signal for which calculation and experimental results are available [7]. It has been theoretically [9] shown that so-called 'sum rules' exist which enable us to extract the orbital magnetic contribution from the XMCD signal recorded at $L_2$ and $L_3$ edges. The application of the first sum rule leads to a small orbital contribution of the order or $10^{-2}$ $\mu_B$/ Ce atom for the 5d electronic states.

The observed XMCD spectrum recorded at the $L_{2,3}$ edges are typical of Ce mixed valence state, thus confirming the interpretation of the XAS experiment discussed above. The recorded XMCD signal is very similar to the signal measured for $Ce_2Fe_{17}N_3$ and $Ce_2Fe_{17}H_5$ exhibiting two main structures assigned to two different screening channels [7] of the core hole depending upon the localization of the 4f electrons.

We have successively probed the effect of Ga or H atom on the Ce 4f and 5d electronic states. No direct probe of the Ce 6s electronic state has been performed; nevertheless, information can be obtained from Gd Mössbauer spectroscopy on isostructural compounds. Previous study [10] has shown that insertion of hydrogen in the $R_2Fe_{17}$ structure induces a change of the electronic state of the rare-earth element. A charge transfer from the rare-earth 6s orbital onto the H atoms is evidenced by the rise of the isomer shift observed by Mössbauer spectroscopy on the rare-earth nuclei. This has been confirmed by $^{89}Y$ NMR analysis [11] of the rare-earth–iron hydrides. The relocalization of the 4f electronic state after H insertion in the Ce environment described above is probably related to the charge transfer that occurs between the Ce 6s orbitals and the neighbouring H atoms. In spite of the fact that no direct proof of this hypothesis can be given, it is reasonable to think that a decrease of the outer 5d–6s electrons leads to a reduction of the screening-effect played by these

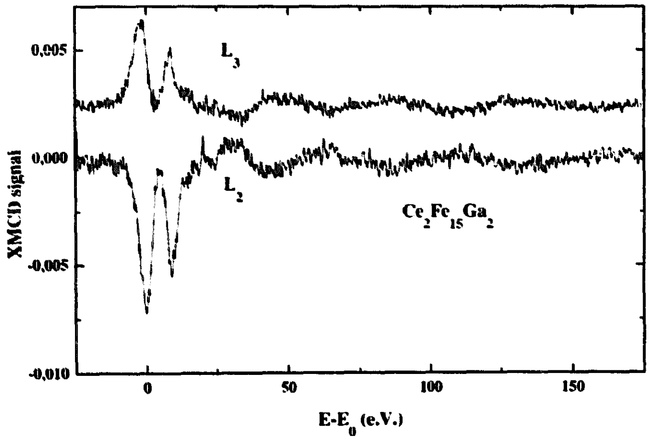

Fig. 3. Evidence of a Ce-5d magnetic moment from X-ray Magnetic Circular Dichroism signal recorded at the Ce $L_{II,III}$ edges at 10 K for $Ce_2Fe_{15}Ga_2$. The $L_3$ XMCD signal has been shifted vertically of 0.0025 for clarity of the figure.

shells. As a consequence this leads to inner 4f states more sensitive to their environment.

The increase of the cell that occurs upon Fe to Ga substitution as well as upon H insertion probably also plays a major role in the observed evolution of the 4f electronic state.

## 4. Conclusion

Fe to Ga substitution or hydrogen insertion in $Ce_2Fe_{17}$ have similar effects on the electronic state of cerium, they lead to a significant relocalization of the 4f states of cerium; furthermore their effects are additive. This collection of experimental results together with those from previous investigations [5] 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 $\alpha \rightarrow \gamma$ 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.

The magnetic moment carried by the Ce 5d states in these compounds is of spin origin, this Ce 5d moment is significant but is, however, much weaker than that expected for a Ce atom with purely 4f localized (magnetic) state. Generally 5d electrons of Ce in compounds are strongly delocalised, and only the strong influence of Fe ligands can induce some weak polarisation. The weakness of the Ce moment observed here shows that the spectacular change of the ordering temperatures in comparison with $Ce_2Fe_{17}$ can not be attributed to the Ce magnetism but is related to a change of the Fe sublattice. The most important change that occurs in the structure is an increase of the Fe–Fe interatomic distances upon Fe to Ga substitution or hydrogen insertion. This induces an overall increase of the magnetic exchange interaction which produces the observed raise by of the Curie temperature. Let us stress that H insertion is more efficient at expanding the cell than Fe to Ga substitution

## References

[1] J.M.D. Coey, H. Sun, J. Magn. Magn. Mater 87 (1990) L251.
[2] O. Isnard, S. Miraglia, J.L. Soubeyroux, D. Fruchart, A. Stergiou, J. Less Common Met. 102 (1990) 273–284.
[3] J. Röhler, J. Magn. Magn. Mater. 47 (1985) 175–180.
[4] J. Röhler, in: K.A. Gschneider, J.LR. Eyring, S. Hufner (Eds.), Handbook on the Physics and Chemistry of Rare Earths, vol. 10, Elsevier Science, 1987, pp. 453–544.
[5] O. Isnard, S. Miraglia, D. Fruchart, C. Giorgetti, S. Pizzini, E. Dartyge, G. Krill, J.P. Kappler, Phys. Rev. B 46 (1994) 15692–15701.
[6] H. Luo, Z. Hu, W.B. Yelon, S.R. Mishra, G.J. Long, O.A. Pringle, D.P. Middleton, K.H.J. Buschow, to be published in Journal of Appl. Phys.
[7] C. Giorgetti, S. Pizzini, E. Dartyge, A. Fontaine, F. Baudelet, C. Brouder, G. Krill, S. Miraglia, D. Fruchart, J.P. Kappler, Phys. Rev. B. 48 (1993) 12732.
[8] I.A. Campbell, J. Phys. F: Metal Phys. 2 (1972) L47.
[9] B.T. Thole, P. Carra, F. Sette, G. Van der Laan, Phys. Rev. Lett. 68 (1992) 1943.
[10] O. Isnard, P. Vuillet, A. Blaise, J.P. Sanchez, S. Miraglia, D. Fruchart, J. Magn. Magn. Mater. 131 (1994) 83.
[11] C. Kapusta, M. Rosenberg, J. Zukrowski, H. Figiel, T.H. Jacobs, K.H.J. Buschow, J. Less-Comm. Met. 171 (1991) 101.