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ON THE DEVELOPING OF NET Ce MAGNETIC MOMENT UPON H_2 ABSORPTION IN $Ce_2Fe_{14}B$: AN XCMD INVESTIGATION.

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We present a combined X-ray Absorption Spectroscopy (XAS) and X-Ray Circular Magnetic Dichroism (XCMD) investigation performed at the Ce L-edges in the case of $Ce_2Fe_{14}B$ and its hydride derivatives. Both XAS and XCMD data do not show any modification of the mixed-valence electronic state of cerium upon hydriding. In fact, our results rule out the hypothesis of the presence of a pure Ce^{3+} configuration in the hydride derivative and the resulting induction of a localized 4f magnetic moment on the Ce sites upon hydriding.

Introduction.

Since the first works on the new $R_2Fe_{14}B$ (R=rare earth) magnetic materials published at the early eighties,[1,2] worldwide efforts have been devoted to investigate the intrinsic magnetic properties of rare-earth intermetallic compounds, to provide new alloys for application in the permanent magnets technology. The later discovery of the ability of these intermetallic alloys to absorb large quantities of hydrogen in a reversible way, giving as a result the rising of the Curie temperatures has attracted a great deal of attention in the experimental research of the interstitial substituted R-Fe intermetallics, whereby interstitial atoms such as hydrogen, nitrogen or carbon are introduced into the structure by a reaction of a powder of the intermetallic with an appropriate gas. So far many studies have been carried out to establish the effect of interstitial hydrogen on the magnetic behavior of intermetallic compounds but several questions remain unsolved as is the case of the dynamics of Ce valence in $Ce_2Fe_{14}B$ upon hydriding.

In 1987 Dalmas de Reotier et al.[3] reported a neutron diffraction investigation performed on $Ce_2Fe_{14}B$ and its hydride derivatives showing that in the parent compound, that presents anomalous cell volume, cerium is a priori non-magnetic (Ce^{4+}) at both 4f and 4g crystallographic sites. On the contrary, the analysis of the patterns recorded on the hydrides revealed that whereas Ce at the 4f site

shares a null magnetic moment, a 2.2 and 2.5 μ_B magnetic moment is developed on the Ce-4g site for deuterated and hydrided samples, respectively. However, these assignements have not been yet confirmed by the spectroscopic techniques applied to investigate the Ce valence. Neither XPS[4] nor XAS[5] experiments reported changes of the cerium mixed-valence state upon hydriding in the $Ce_2Fe_{14}BH$ system. Notwithstanding the clarity of the spectroscopic results based on these site selective techniques, the discussion about the electronic state of Ce in $Ce_2Fe_{14}BH_x$ compounds has been recently stimulated by a work of Capehart et al.[6] that addressed to, from analyses of XAS data, a decrease of the Ce valence in the hydride. These results were interpreted in terms of the 4f localization at the Ce site, supporting the neutron diffraction results. Although the decrease of the valence derived in Ref. [6] is quantitatively far from the expected value if an $\alpha-\gamma$ like transition should take place at one of the two Ce sites, such disagreement has been tentatively associated to the existence of different local electronic structure at the two Ce sites that can not be separated by standard XAS analysis. As a consequence, the expected valence change may be partially masked. This interpretation opens the question of the reliability of the results obtained from XAS data. In addition, if as discussed by Fruchart et al.[4], one considers the possibility that during the XPS experiments fast desorption takes place on the sample producing an hydrogen free surface layer on top of the hydride, which

easily exceeds the probing depth of XPS, also the XPS results on the $Ce_2Fe_{14}B$ hydride could be questioned. Actually, as a consequence, no unambiguous answer has been provided to date about the presence of a localized Ce magnetic moment in these materials after hydrogen absorption.

To clarify the controversy, we performed an X-ray Absorption Near Edge Structure (XANES) investigation at the Ce L_3-edge and in addition, the first X-Ray Circular Magnetic Dichroism (XCMD) experiments at the L_2-edge of Ce in $Ce_2Fe_{14}B$ and $Ce_2Fe_{14}BH_x$ compounds. The capability of the XANES spectroscopy to probe the electronic state of the cerium atoms and its change upon hydriding and the results obtained by XCMD which probe directly the localization of the Ce magnetic moment, will help us to provide a solution to the controversy described above.

Experimental.

Experiments were performed at the National Laboratory for High Energy Physics (KEK) at Tsukuba. Averaged polarized XANES at the Ce L_3-edge were made on beamline 7C at Photon Factory (PF). The PF storage ring was operated with a positron energy of 2.5 GeV and a stored current of about 300 mA. Rejection of higher harmonics at low energy was achieved by using a pair of quartz uncoated mirrors with the critical angle set at 4.7 mrad. This procedure guaranties the complete rejection of harmonics whose presence in the beam affects XAS data and, in particular, the intensity of the white-line features.

XCMD experiments were performed on the Accumulator Ring (AR) of TRISTAN at the beamline AR NE1.[7] Experiments were performed with the Accumulator Ring mainly working in the parasitic mode at 6.5 GeV with a maximum stored current of 30 mA. Left circular polarized x-ray radiation was used with a degree of polarization of more than 0.6 after monochromatization. Higher harmonics rejection at the energy of the L_2-edge of Ce was obtained by detuning the two crystals of the Si(111) fixed-exit-beam double crystal monochromator. [8] Sagittal focusing was also used yielding to a final energy resolution $\Delta E/E$ estimated to be about 2×10^{-4}. [9]

Samples were prepared by arc-melting the starting elements (purity 99.9 %) under purified Ar atmosphere. Both phase and structural analysis were performed on a standard x-ray diffractometer. The hydrogen absorption-desorption properties were established according to the standard methods.[10]

For these experiments fine powders of the material were homogeneously spread on an adhesive tape. Thickness and homogeneity of the samples were optimized to obtain the best signal to noise ratio using two layers of powdered material giving a total absorption jump, $\Delta\mu x$, of 0.4 . Both XAS and XCMD measurements

were carried out at room temperature in the transmission mode. X-rays incident on the sample and transmitted through it were monitored with two independent ionization chambers with N_2-Ar flowing gas mixture optimized for each energy range. XCMD spectra were recorded by reversing the sample magnetization for a fixed polarization of the incoming radiation. A magnetic field of 0.6 T was applied parallel to the plane of the sample at 45° to the incident beam and reversed twice for each energy value. Data were accumulated every 2 seconds in order to minimize any time-dependent drift while multiple scans acquisition were adopted (~14 acquisitions) to reduce the statistical uncertainty to about 2×10^{-4}.

Results and discussion.

XANES spectra were normalized according to standard procedures. The background contribution from lower energy absorption edges $\mu_{back}(E)$ was approximated according to the Victoreen rule and subtracted from the experimental spectrum $\mu(E)$. Then, spectra were normalized to the absorption coefficient at ~30 eV from the edge, $\mu_N(E) = (\mu(E) - \mu_{back}(E)) / \mu(30 \text{ eV})$, to eliminate thickness dependence. The energy origin, E_0, was defined to be at the inflection point of the absorption edge.

In the case of the XCMD spectra, an identical procedure was applied for parallel, μ^+, and antiparallel, μ^-, orientation of the photon spin and the magnetic field applied to the sample, i.e. to sample magnetization. Therefore, the dichroic signal is defined in the following as $\Delta\mu(E) = \mu_N^+(E) - \mu_N^-(E)$ and corresponds to the thickness-independent spin-dependent absorption coefficient.

Normalized XANES spectra at the Ce L_3-edge are displayed in Fig. 1 for the case of $Ce_2Fe_{14}B$ and its hydride derivative. In both cases, the threshold resonance presents a characteristic double-peak profile that is typical of all mixed valence Ce-based materials.[11] The presence of the two structures at the $L_{2,3}$ edges reflects the mixing of the $4f^0$ and $4f^1$ configurations in the ground state throughout the superposition of the atomic-like $2p \rightarrow 5d$ transition (white-line) for each electronic configuration. Indeed, due to the screening of the 4f electron, the white line corresponding to the $4f^1$ configuration is shifted to lower energy respect to that of the $4f^0$ one.[12] The resolution of both electronic states is made possible because the time scale of the absorption process is about three orders of magnitude smaller than the valence fluctuation time.[13] Consequently, neglecting final state effects, the fractional occupation of the 4f configurations in the ground state can be determined by measuring the weight of the two white-lines in the absorption spectra. In this sense, estimates of cerium valence can be obtained by standard deconvolution methods, described elsewhere.[14-16]
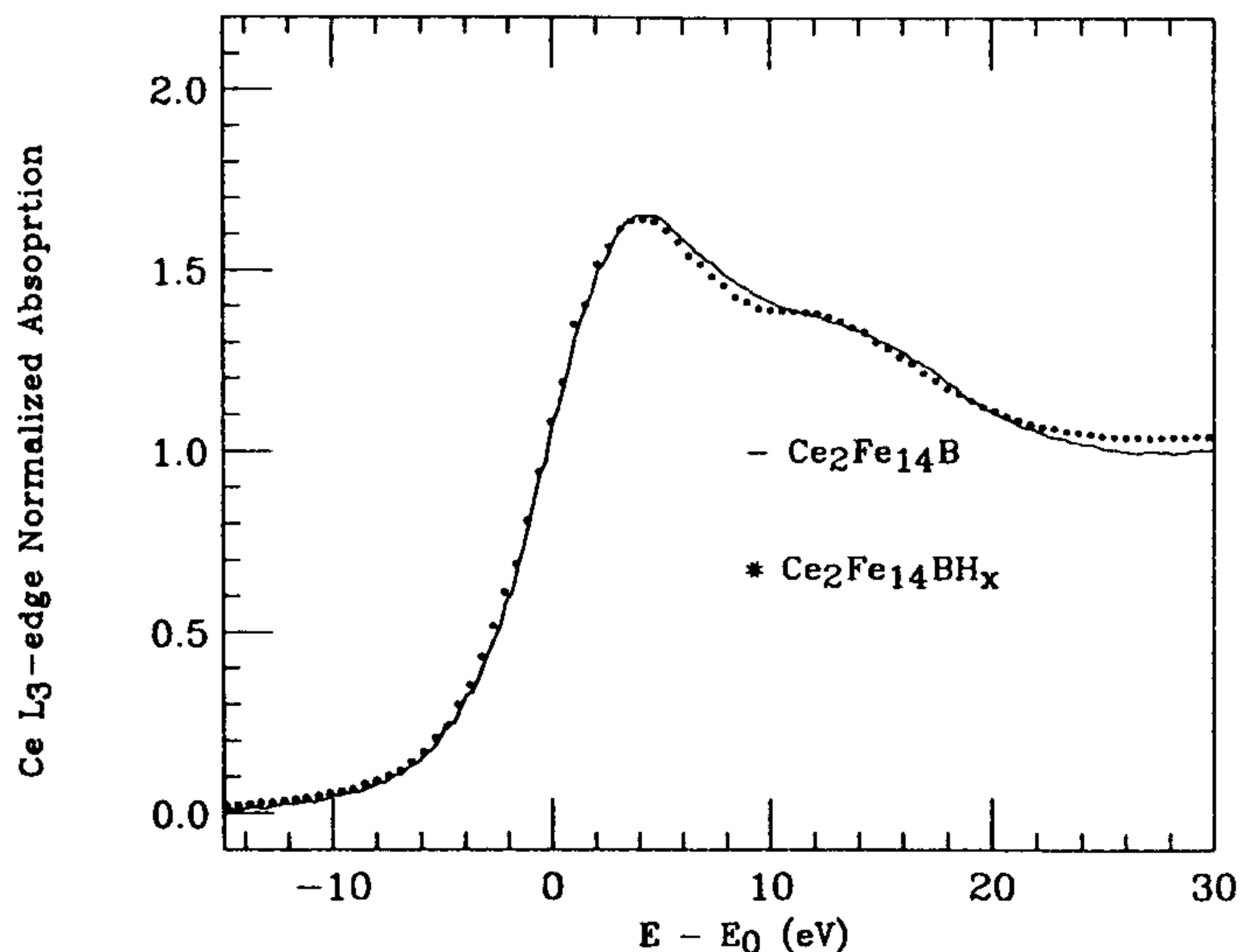
Fig. 1 Comparison between the experimental XANES spectra at the cerium L_3-edge in $Ce_2Fe_{14}B$ (join) and $Ce_2Fe_{14}BH_x$ (dots) systems.

Fig. 3 Normalized XCMD signals recorded at the cerium L_2-edge in the case of $Ce_2Fe_{14}B$ (join) and its hydride derivative (dots).

In the case of $Ce_2Fe_{14}B$ and $Ce_2Fe_{14}BH_x$, reported in Fig. 1, no marked differences between the two XANES spectra at the Ce L_3-edge are observed. Indeed a valence of about 3.22 is determined for the two compounds. Within the signal to noise ratio, the present experimental spectra are identical to those previously reported in Refs. [5] and [6], in such a way that also a qualitative direct comparison of the absorption spectra does not support the modification of the Ce-valence state upon hydriding in these materials. Moreover, if a full $\alpha-\gamma$ like transition takes place on the 4g site,[3] an increase of the $4f^1$ component to the expense of the $4f^0$ should be expected contrary to the observed experimental behavior. To better clarify this point we present in Fig. 2 the comparison of the Ce L_3-edge XANES spectra in the $CeFe_2$ and $CeFe_2H_x$ compounds.[17] Here the loss of the $4f^0$
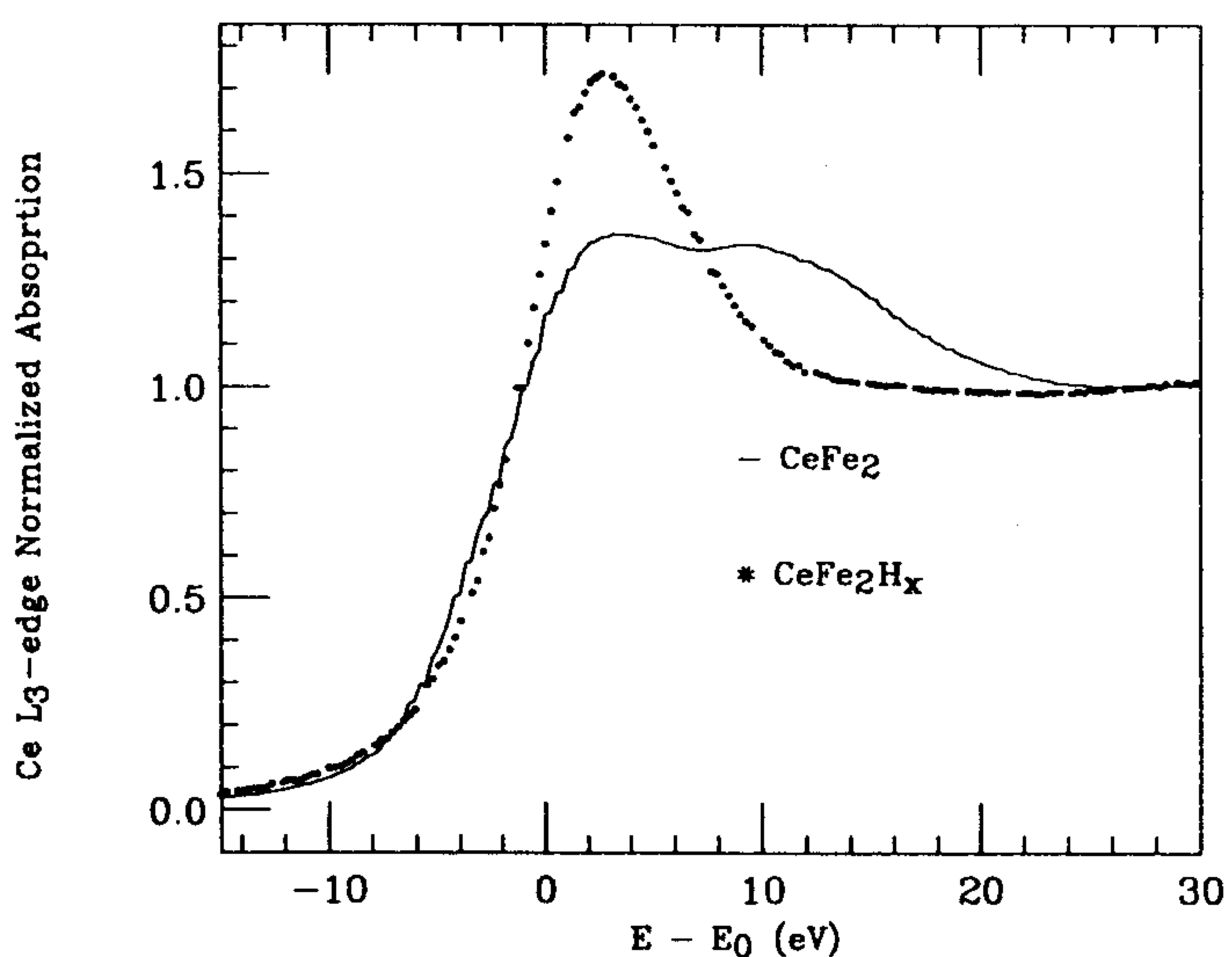

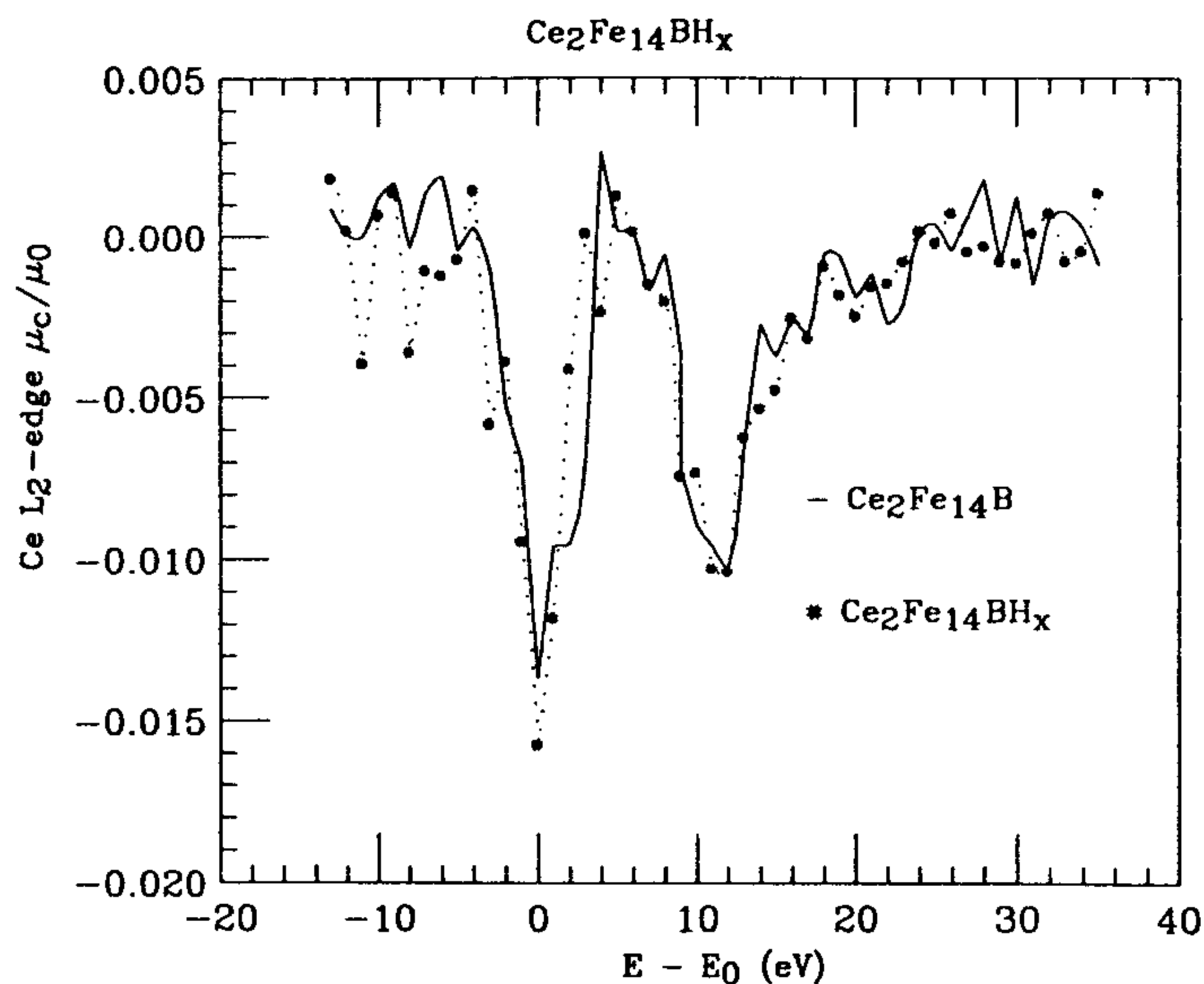Fig. 2 Comparison between the experimental XANES spectra at the cerium L_3-edge in $CeFe_2$ (join) and $CeFe_2H_x$ (dots) compounds.

contribution in the hydride, that is interpreted as the evidence of the localization of the 4f electron and the promotion of localized magnetic moment at the Ce site, is clearly detected.

Contrary to the case of the $CeFe_2$ hydride, the presence of two non-equivalent Ce sites (4f and 4g) in $Ce_2Fe_{14}B$ may support an averaged effect in such a way that the typical double-peaked profile has to be partially retained. However, if the $\alpha-\gamma$ like transition occurs only at one crystallographic site, a sharp modification of the relative weight of the two configurations should be observed. Indeed, according to this hypothesis, a mean value of 3.11 is expected for the Ce valence. Such a change should be easily detected contrary to the present experimental results. Indeed, a similar but larger change, from 3.33 to 3.22, was previously determined by XAS to occur in the Ce_2Fe_{17} and $Ce_2Fe_{17}H_x$ compounds.[5] In this last case also neutron diffraction work has been performed. [18] However, no indication about the existence of a localized magnetic moment at the Ce site in $Ce_2Fe_{17}H_x$ has been provided to date.

Although XAS data can only provide an indirect insight to the magnetic state of cerium, the presence of localized Ce 4f magnetic moment in these materials can be directly probed by using X-Ray Circular Magnetic Dichroism (XCMD). This technique yields the spin-dependent absorption cross section on a given atomic specie in a material with a net magnetization. To detect any variation of the Ce magnetic configuration upon hydrogenation, we have performed XCMD measurements at the Ce L_2-edge in $Ce_2Fe_{14}B$ and $Ce_2Fe_{14}BH_x$ systems. The XCMD signal at the Ce L_2-edge probes directly the empty d-states above the Fermi level projected on the cerium site, i.e. mainly Ce(5d) empty states, by exciting 2p core electrons,

and can be written as:[19]

$$\Delta\sigma_{L_2} = \frac{\sigma^+(B) - \sigma^-(B)}{\sigma^+(B) + \sigma^-(B)} = \frac{\sigma_{2,1/2}^{\downarrow} - \sigma_{2,1/2}^{\uparrow}}{2\left(\sigma_{2,1/2}^{\downarrow} + \sigma_{2,1/2}^{\uparrow}\right)} \quad [1]$$

where according to the definition given above for the dichroic signal, $\sigma^{\uparrow(\downarrow)}$ holds for the reduced transition probability towards spins parallel (antiparallel) to sample magnetization.

Comparison of the XCMD spectra at the Ce L_2-edge in the case of $Ce_2Fe_{14}B$ and $Ce_2Fe_{14}BH_x$ is shown in Fig. 3. Also the XCMD spectra of these intermetallics are characterized by a double-peak structure due to the configurational mixing in the ground state and similar to the case of polarized averaged XAS spectra (see Fig. 1). Within the signal to noise ratio no remarkable differences between the XCMD spectrum of $Ce_2Fe_{14}B$ and its hydride derivative are found. The observed XMCD behaviour is extremely important because confirms the lack of any significant increase on the magnetic moment of cerium. It is important to underline here that while in the XAS case both $4f^1$ and $4f^0$ contributions are always added with the same sign to the spectra determining the two positive features at the $L_{2,3}$-edges, the sign of the XCMD signal is different for mixed-valence and Ce^{3+}

systems, i.e. $\alpha-$ and $\gamma-$like cerium.[20] According to Eq. [1], because the different spin-polarization of the unoccupied 5d states in $Ce_2Fe_{14}B$ and upon the development of a localized magnetic moment upon hydriding, a change of sign of the dichroic signal is expected[21] and recently shown in the case of $CeFe_2$ and $CeFe_2H_x$ compounds.[20] Therefore, also if an $\alpha-\gamma$ like transition takes place at only one Ce site in these systems upon hydrogen uptake, a large change of the XCMD should be expected. On the contrary, this effect is clearly not observed in our experiments supporting the interpretation of the cerium valence evolution based on standard Ce L_3 XAS analyses given in Ref. [5].

As a conclusion, we report the experimental evidence of the no induction of localized 4f magnetic moment at the Ce sites upon hydrogenation of the $Ce_2Fe_{14}B$ system.

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