

X-ray absorption spectroscopy study of the instability of ferromagnetism in CeFe_2 : Effects of Co and Al substitutions

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We present in this work an x-ray absorption spectroscopy (XAS) investigation performed at the L_3 -edge of Ce in the intermetallic compounds $\text{Ce}(\text{Fe}_{1-x}\text{Co}_x)_2$ and $\text{Ce}(\text{Fe}_{1-x}\text{Al}_x)_2$. The mixed-valence behavior of Ce is found to be preserved in both series upon Fe substitution. This result rules out the development of a localized $4f$ magnetic moment at Ce atoms driven by the Fe–Co and Fe–Al substitution at the origin of the anomalous magnetic behavior of this series.
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An innermost feature of the RCO_2 compounds, where R is not magnetic, is that unlike the corresponding RFe_2 compounds, they never show magnetic order. Substantial amount of research has been done on RCO_2 – RFe_2 systems to study the ways in which magnetic order sets in. Special interest has been focused on the enigmatic magnetic properties of the $\text{Ce}(\text{Fe}_{1-x}\text{Co}_x)_2$ series ranging from the superconductivity of CeCo_2 to the reduced magnetic moment and low Curie temperature of CeFe_2 .

CeFe_2 is a simple ferromagnet with a Curie temperature, T_c , of about 230 K. Its magnetization behavior and the magnetic hyperfine field follow approximately the molecular-field theory with a $J=1/2$ Brillouin function.^{1,2} The low value of the magnetic hyperfine field has been associated to both the reduced magnetic moment of the iron ions, $1.2 \mu_B$, as compared to $1.7 \mu_B$ in other RFe_2 compounds, and to the low T_c that ranges between 500 and 700 K in other RFe_2 compounds. Due to the reduced lattice parameter of CeFe_2 , these anomalies were earlier ascribed to the transfer of the Ce $4f$ electron to the conduction band, resulting in the increase of the Fe $3d$ -band occupancy.² However, the discovery that the substitution of Fe by a small amount of impurity destabilizes the ferromagnetism in CeFe_2 , yielding to a spin-canting or re-entrant spin-glass-like behavior for small Al substitutions,³ and to the total loss of ferromagnetism for 4% to 5% Al substitution,⁴ has stimulated studies on the instability of ferromagnetism in this compound.

The current framework for the understanding of the CeFe_2 magnetic properties considers both that its ferromagnetism is very close to some type of instability and the itinerancy of the Ce $4f$ electrons that could prevent the formation of $4f$ magnetic moments. In the light of the peculiar magnetic properties of $\text{Ce}(\text{Fe}_{1-x}\text{Co}_x)_2$, it would be particularly interesting to see how the Ce valence and the $4f$ – $5d$ – $3d$ hybridization behave between CeFe_2 and

CeCo_2 . To this end, we have performed a systematic x-ray absorption spectroscopy (XAS) on the L_3 -edge of Ce through the $\text{Ce}(\text{Fe}_{1-x}\text{Co}_x)_2$ and $\text{Ce}(\text{Fe}_{1-x}\text{Al}_x)_2$ series.

$\text{Ce}(\text{Fe}_{1-x}\text{Co}_x)_2$ samples with $x=(0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, \text{ and } 0.8)$ and $\text{Ce}(\text{Fe}_{1-x}\text{Al}_x)_2$ samples with $x=(0.01, 0.035 \text{ and } 0.05)$ were prepared by argon arc melting of at least nominal 99.9% purity, followed by annealing at 850 °C in an evacuated quartz tube for 1 week. CeCo_2 was prepared by a levitation technique using Ce and Co from a different source. Both phase and structural analysis were performed by using a standard x-ray diffractometer. X-ray analysis shows that all the samples have a single phase of C15 Laves structure and that the lattice parameter of the pseudobinary compounds obeys Vegard's law, in agreement with previous reports.⁵

X-ray absorption spectroscopy (XAS) experiments were carried out at the ESRF BM29 XAFS beamline. The storage ring was operated in 2/3 filling mode with typical currents between 150 and 200 mA at an electron beam energy of 6 GeV. XAS experiments were performed in the transmission mode on homogeneous thin layers of the powdered samples at the Ce L_3 -edge. Both magnetization and absorption experiments were carried out on the same polycrystalline samples.

The magnetization of the investigated $\text{Ce}(\text{Fe}_{1-x}\text{Co}_x)_2$ samples measured under an applied field of 10 kOe is shown in Fig. 1. The magnetization (M) vs temperature (T) behavior of CeFe_2 shows the transition from the high-temperature paramagnetic phase (PM) to the ferromagnetic one (FM) taking place at about 236 K. The temperature at which the PM–FM occurs diminishes as the Co content increases to be $T_c \sim 69$ K for $x=0.8$. In the case of CeCo_2 , the ferromagnetic character is lost through all the investigated temperature range (from room temperature to 4.2 K) and a superconducting transition is observed at $T \sim 0.82$ K.⁶ Moreover, for $\text{Ce}(\text{Fe}_{0.9}\text{Co}_{0.1})_2$ and $\text{Ce}(\text{Fe}_{0.8}\text{Co}_{0.2})_2$ the substitution of Fe by Co results in the appearance of a second transition at a temperature $T_S=72$ and 62 K, respectively, lower than the fer-

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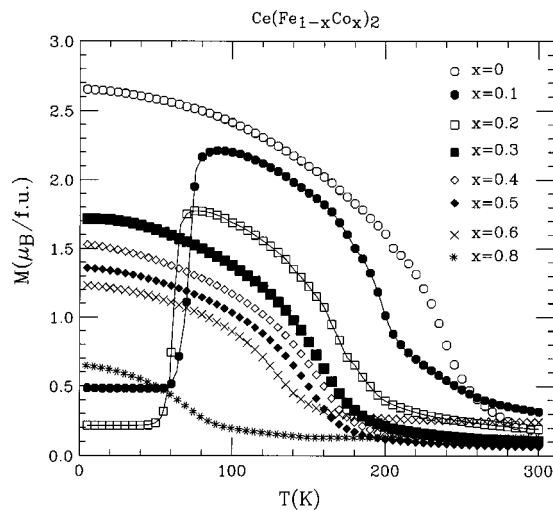


FIG. 1. Temperature dependence of magnetization for the $\text{Ce}(\text{Fe}_{1-x}\text{Co}_x)_2$ series measured under an external applied field of 10 kOe.

romagnetic ordering temperature. This second transition has been interpreted in terms of a magnetic behavior in which ferromagnetism gives way to a canted spin structure, via partial loss of ferromagnetism initially, and that as more iron is replaced this canted spin structure reaches a point where total loss of ferromagnetism is observed.⁷ One of the most striking features in the magnetic behavior of the $\text{Ce}(\text{Fe}_{1-x}\text{Co}_x)_2$ series is the evolution of the Curie temperature as a function of the cobalt content. While the lattice parameter shows a linear decrease as cobalt content (x) increases, T_c departs from a linear behavior between $x=0.2$ and 0.7 , showing a relative minimum for $x=0.3$ and a relative maximum at $x=0.4$. In principle, the complexity of the magnetic phase diagram has often been related to the special character of Ce in CeFe_2 for which electronic structure calculations have predicted an itinerant character given to the $4f$ electrons by f - d hybridization. Then, it would be particularly interesting to see how the Ce valence behaves between CeFe_2 and CeCo_2 .

To answer this open question, we have recorded the x-ray absorption spectra (XAS) at the Ce L_3 -edge through the whole $\text{Ce}(\text{Fe}_{1-x}\text{Co}_x)_2$ series. The results, compiled in Fig. 2, show that for all the investigated compounds the Ce L_3 -edge absorption exhibits the double-peak profile at the edge, characteristic of a mixed-valence character, i.e., reflecting the existence of both the $4f^1$ and $4f^0$ configurations in the initial state.⁸ This peculiar profile is made by the superposition of the atomic $2p \rightarrow 5d$ transition for each ground-state configuration. The white line corresponding to the $4f^{n+1}$ configuration is shifted to lower energy with respect to that of the $4f^n$ due to the screening of the additional $4f$ -electron.⁹ Hence, estimates of the Ce valence can be obtained through the deconvolution of absorption spectra according to standard methods.^{8,10} Upon increasing cobalt content, no significant changes are found on the intensity, width, and relative energy position of the two white lines. Our results indicate that the Ce mixed-valence behavior is retained in all the $\text{Ce}(\text{FeCo})_2$ systems, the Ce valence being about 3.3. In the case of the end members of the series, CeFe_2 and CeCo_2 , this value is in agreement with previous estimates.¹¹

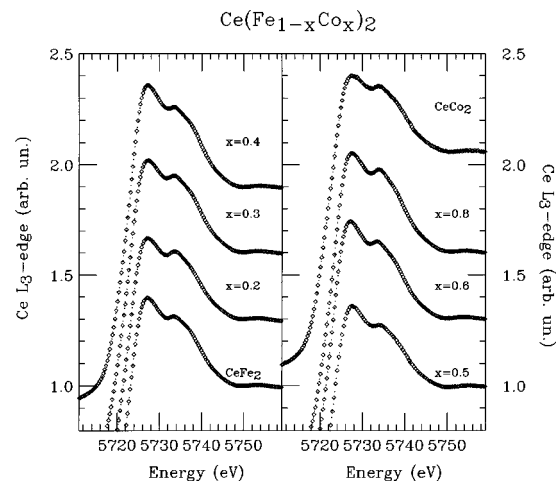


FIG. 2. Comparison between the experimental XAS spectra at the Ce L_3 -edge in the case of the $\text{Ce}(\text{Fe}_{1-x}\text{Co}_x)_2$ compounds.

The immediate conclusion that one can obtain from this analysis of Ce L_3 absorption is that the peculiar T_c vs cobalt content behavior seems to be independent of any modification of the cerium electronic state. On the contrary, it seems to be due to the modification of the density of states (DOS) as the contribution of Co states to the DOS becomes dominant. A further verification of this interpretation can be obtained by performing the same class of study in the $\text{Ce}(\text{Fe}_{1-x}\text{Al}_x)_2$ series in which Al substitution leads to the loss of ferromagnetism too, but at the same time, and contrary to the Fe-Co case, the crystal cell is expanded upon substitution. As in the case of the $\text{Ce}(\text{FeCo})_2$ systems, Ce L_3 spectra (reported in Fig. 3) show that the mixed-valence behavior is retained upon Al substitution, the Ce valence being about 3.3 too.

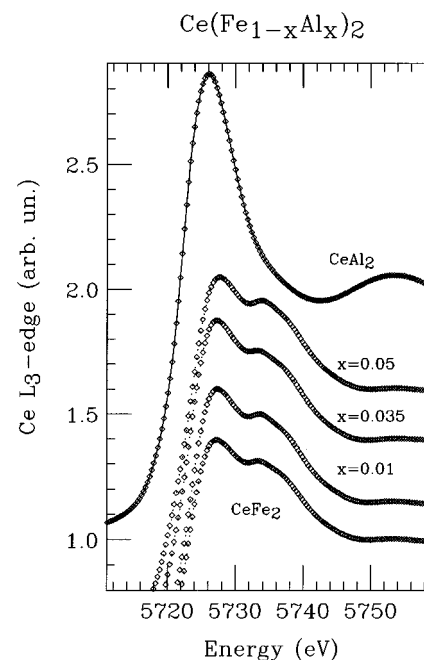


FIG. 3. Comparison between the experimental XAS spectra at the Ce L_3 -edge in the case of the $\text{Ce}(\text{Fe}_{1-x}\text{Al}_x)_2$ compounds.

The results of the present investigation are in agreement with electronic-structure calculations, showing direct details of the reduction of the $f-d$ hybridization induced by Co substitution. The electronic and structural modifications are not enough to determine the localization of the Ce $4f$ states and the subsequent turn up of a $4f$ magnetic moment at the Ce sites. Ce L_3 -edge XAS experiments suggest that the observed anomalous magnetic behavior in both $\text{Ce}(\text{Fe}_{1-x}\text{Co}_x)_2$ and $\text{Ce}(\text{Fe}_{1-x}\text{Al}_x)_2$ series is not due to the modification of cerium electronic state but is determined by the peculiarity of the DOS mainly determined by the transition metal $3d$ -states and its modification upon the substitution of Fe.

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