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Magnetic circular x-ray dichroism in Ce intermetallic compounds

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Magnetic circular x-ray dichroism (MCXD) studies at $L_{2,3}$ absorption edges in intermediate-valence (IV) compounds $CeFe_2$, $Ce(Fe_{0.8}Co_{0.2})_2$, $CeCo_5$, Ce_2Co_{17}, and trivalent $4f^1$ systems ($CeRu_2Ge_2$, Ce_3Al_{11}, CePd, $CeFe_2H_{3.8}$) at the Ce $L_{2,3}$ edges are presented. The comparison with reference compounds (La, Lu, Hf, Gd) confirms the existence, in such IV systems, of an ordered 5*d* magnetic moment on the Ce site antiferromagnetically coupled with the 3*d* Fe (Co) moment. Moreover, this study suggests, provided the 4*f* orbital moment is almost quenched, the existence of a simple proportionality between the MCXD intensity and the magnetic moment of the probed atom. For instance the MCXD method leads to a Ce 5*d* magnetic moment in $CeFe_2$ of about $0.35\mu_B$ antiferromagnetically coupled with the 3*d* Fe moment, in good agreement with band-structure calculations. The MCXD applications in $Ce(Fe,Co)_2$ and $CeFe_2H_x$ permit us to define precisely the electronic structure of Ce in such compounds. Particularly we will show that MCXD experiments at the $L_{2,3}$ absorption edges of Ce are able to yield valuable information on the degree of hybridization of the 4*f* electrons in the ground state. Indeed, systematic comparison between the MCXD signals of IV and normal trivalent Ce compounds reveals the extreme sensitivity of the $L_{2,3}$ MCXD experiments to the degree of localization of the 4*f* electrons.

I. INTRODUCTION

X-ray-absorption measurements at the $L_{2,3}$ edges have been widely performed on many rare-earth compounds. As such experiments involve $2p \rightarrow 5d$ transitions, in the presence of a core hole, it has been a matter of controversy whether these spectroscopic experiments can give, in the presence of final-state effects, information on the rare-earth ground state. However, the photoemission model, developed by Gunnarsson and Schönhammer,[1] based on an Anderson impurity model and modified by Kotani and co-workers[2] and by Malterre[3] shows that, provided the different Coulomb interactions (U_{fd}, U_{fc}) between the photoelectron and the system are taken into account, the $L_{2,3}$ absorption edges give a relevant representation of the electronic configuration in the ground state and yield, especially for Ce compounds, the 4*f* occupation number n_f.[3,4]

Due to the strong hybridization between the 4*f* and the conduction electrons, cerium is an exceptional case among the lanthanide series leading to exotic physical properties, which are also observed in Ce intermetallic compounds. In a large number of systems, the $L_{2,3}$ absorption edges of Ce exhibit a characteristic double-peak structure. The high-energy shoulder contribution ($\Delta E = 7-10$ eV), more or less pronounced, which reflects the degree of hybridization in the initial state, can be taken as a measure of the ground-state Kondo temperature of the system and then permits one to distinguish the different electronic states of cerium. The recent possibility of magnetic circular dichroism studies at the $L_{2,3}$ edges offers the opportunity of an interface between x-ray absorption and magnetism, especially in highly correlated Ce systems.

Magnetic circular x-ray dichroism (MCXD) studies at the $L_{2,3}$ edges of rare-earth (*R*) elements and *K* edge of transition metals (*M*) have illustrated the power of this method to give directly the magnetic response of a selected orbital of a chosen atomic species in the material. MCXD is defined as the measurement of the dependence of the x-ray-absorption cross section as a function of light polarization (right or left). In the case of 5*d* *M* $L_{2,3}$ absorption edges ($2p \rightarrow 5d$ transitions), it is admitted that MCXD experiments give the difference, as a function of the energy, of the spin-up and spin-down occupation in the empty 5*d* states of the probed atom and thus the 5*d* moment. In the case of *R* $L_{2,3}$ it is not so clear because, in addition to the net spin polarization of the 5*d* final states, the MCXD may be sensitive to the exchange coupling with the incomplete 4*f* shells responsible for the lo-

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calized magnetism.[5,6] The present debate concerns the existence of a simple proportionality between the dichroic response and the total magnetic moment of the absorbing atom. Only a few dichroic studies have been devoted to this problem. Thus recently, MCXD has been successfully used for the determination of the moment and the magnetic interactions in artificial structures as Nd-Fe (Ref. 7) or Co-Pt (Ref. 8) and as a measure of d moments for $5d$ impurities in Fe (Ref. 9).

The main purpose of this paper is to demonstrate in the case of highly correlated cerium compounds that a quantitative description of the MCXD signal can be obtained from the MCXD analysis. Consequently, it is possible to enlighten the exciting debate on the nature of the electronic structure of Ce in intermediate-valence (IV) systems (with $3d$ M partners), especially the magnetic contribution of the conduction electrons. We present a detailed MCXD study of Ce in $CeFe_2$, $Ce(Fe_{0.8}Co_{0.2})_2$, $CeCo_5$, and Ce_2Co_{17} at the Ce $L_{2,3}$, Fe K, and Co K edges and in a series of reference compounds (Ce, La, Lu, Hf, Gd), i.e., in compounds where the $4f^n$ localized character is undisputed.

Among the R intermetallic compounds $CeFe_2$ stands out as an archetype of the IV system with exotic physical properties. Firstly, there is a strong anomaly in the lattice parameter in comparison with the expected smooth decrease through the RFe_2 series, leading to a lattice constant for $CeFe_2$ as small as that for $HoFe_2$. Secondly, the magnetic properties present characteristic features: The Curie temperature ($T_c = 230$ K) is depressed by a factor of nearly 3 as compared to $LuFe_2$ ($T_c = 610$ K). The magnetic moment is also anomalously low ($M_s = 2.6\mu_B$/f.u.) with respect to $LuFe_2$ ($M_s = 2.9\mu_B$/f.u.).[10] It is generally admitted that the decreased ferromagnetic parameters, for $CeFe_2$ relative to $LuFe_2$, are essentially due to a charge transfer from Ce $5d$ to Fe $3d$ bands. Recently it was shown that hydrogen absorption in $CeFe_2$ leads, with increasing H concentration, to a variation of the Ce valence up to a nearly localized $4f^1$ state for $CeFe_2H_{3.8}$.[11] This system gives the opportunity of a MCXD study of Ce in the $CeFe_2$ structure in a nearly trivalent state. Moreover, magnetic and neutron-diffraction studies have shown that the substitution of small amounts (only a few %) of Fe by Co, Al, Si, or Ru reveals a second magnetic transition with an abrupt loss of ferromagnetism at T_N, lower than the bulk ordering temperature T_c. In particular, with Co substitution an antiferromagnetic phase appears for $T < 80$ K. These studies suggest that the ferromagnetic alignment of the Fe moment is close to an instability in $CeFe_2$,[12] which must be taken into account in the understanding of the peculiar electronic properties of this Ce compound.

It is generally admitted that in IV compounds the hybridization between the $4f$ states of Ce and the M $3d$ states leads to a nearly quenched $4f$ orbital moment and consequently to an antiparallel interaction between the Ce $4f,5d$ moment and M $3d$ moment. This is well confirmed by band-structure calculations in $CeFe_2$,[13] which yield a strongly reduced value of the $4f$ orbital moment resulting from a $4f$ band formation. The calculated total spin moment, $M_s = 2.16\mu_B$/f.u. is composed of antiferromagnetic coupled moments of $M_s^{\mathrm{Fe}} = 1.43\mu_B$ and $M_s^{\mathrm{Ce}} = -0.7\mu_B$, the latter moment being due to two parallel components of, respectively, $4f$ ($-0.4\mu_B$) and $5d$ ($-0.3\mu_B$) characters. Taking into account the orbital contribution ($M_l^{\mathrm{Ce}} = 0.15\mu_B$) the total magnetic moment is $2.41\mu_B$/f.u. Similar calculations in the case of $LuFe_2$ lead to a $5d$ moment ($0.27\mu_B$), almost of spin character, on the Lu site antiparallel to the $3d$ moment ($1.69\mu_B$/at Fe), with a total moment $M_s = 2.85\mu_B$/f.u.[14] Powder neutron-diffraction measurements on $CeFe_2$ evidence the existence of an ordered Ce moment coupled antiferromagnetically to the iron sublattice moment with $M_{\mathrm{Ce}}/M_{\mathrm{Fe}} = -0.3$ and a full moment on Ce about $-0.45\mu_B$, supposing $M_{\mathrm{Fe}} = 1.4\mu_B$.[15] There is of course no measured decomposition of the Ce moment. Notice that the moment calculations predict a magnetic moment on Ce ($4f + 5d$) of $-0.57\mu_B$, including the orbital contribution, which is not very far from the value extracted from neutron-diffraction analysis. Finally, neutron-diffraction measurements on $LuFe_2$ were unable to resolve a magnetic moment on the Lu sites.[16]

The physical properties of $CeCo_5$ are very similar to those of $CeFe_2$. Band-structure calculations performed on $CeCo_5$ and $LaCo_5$ (Ref. 17) lead to a magnetic moment on Ce of about $-0.4\mu_B$ ($-0.2\mu_B$ of $4f$ and $-0.2\mu_B$ of $5d$ character) and $-0.2\mu_B$ on La with only a $5d$ character. The experimental magnetic moments are $7.3\mu_B$/f.u. for $LaCo_5$ and $6.8\mu_B$/f.u. for $CeCo_5$. The lower moment value for the Ce compound witnesses a larger antiferromagnetic component.

In this study we demonstrate that the MCXD technique, in the case of R $L_{2,3}$ edges, allows us to give information on both the origin and the magnitude of the magnetic moment responsible for the dichroic effect, provided there is no localized $4f$ electron in the ground state.[5] Indeed, we establish the existence of a linear relationship between the $L_{2,3}$ edge dichroic intensity and the magnetic moment of $5d$ character in these R intermetallic compounds. As a general result, MCXD experiments on Co/Pd multilayers[18] suggest that when both spin and orbital Co $3d$ components contribute to the magnetic moment, there is no simple correlation between the MCXD signal and the magnetic moment.

II. EXPERIMENTAL DETAILS

MCXD spectra were recorded at LURE, using a position-sensitive detector in transmission mode, at 0.3 mrad below the orbit plane (i.e., for about 80% right circularly polarized light). The procedure of data collection and the experimental setup are described elsewhere.[7,19] Special attention was devoted to the preparation of the oxygen sensitive sample, in particular for the $CeFe_2$ system. The high quality of the preparations was probed by the absence of the typical x-ray absorption near-edge structures of CeO_2 in the Ce $L_{3,2}$ edges. All compounds under study were preliminary checked by magnetic measurements: The Curie temperatures and the saturated magnetic moments were obtained using a vibrating sample magnetometer. The compounds present ferromagnetic or ferrimagnetic phases and are thus suitable for MCXD studies. The external magnetic field used in these MCXD experiments is 0.5 T, strong enough to saturate the magnetic moment in most cases. The MCXD amplitudes are compared with the magnetization measured in the *same* magnetic field, on the *same* powder samples.

For a quantitative interpretation, the MCXD spectra are presented by the relation $[\mu^-(B_+)-\mu^-(B_-)]/A$ as a function of the energy, where $\mu^-(B_+)[\mu^-(B_-)]$ is the absorption coefficient with right-circularly polarized x rays and the magnetic field parallel [antiparallel] to the photon wave vector. In order to take into account the number of probed atoms, the MCXD signal is divided by the height A of the absorption jump. The origin of the energy scale is chosen as the inflection point in the upraise of the absorption and taken as the Fermi-level position.

III. RESULTS AND DISCUSSION

In Sec. III A we present the MCXD study of intermetallic R where the $4f$ localized state is well established and we compare the observed dichroic signal to the theoretical predictions of Erskine and Stern[20] and Brouder and Hikam.[6] Section III B concerns the MCXD study of Ce intermetallic compounds characterized by a Ce IV ground state. This analysis is centered on the well-documented ferromagnetic cubic Laves phase $CeFe_2$. The possibility to obtain, from the sign of the MCXD signals at the M K and at the R $L_{2,3}$ edges, information about the sign of the $5d$ polarization and about the magnetic interaction between the two sublattices of the systems under study is presented in Sec. III C. In Sec. III D we consider the possibility of extracting from the amplitude of the dichroic signal, the magnetic moment probed by MCXD studies. The discussion about the existence of $4f$ state contribution in the Ce IV compounds is presented in Sec. III E. Finally in Sec. III F we apply the results of the MCXD analysis to two particular cases, namely the valence change indiced by hydrogen in $CeFe_2$ and the ferromagnetic instabilities in systems such as $Ce(Fe,Co)_2$.

A. MCXD study in *R* intermetallics

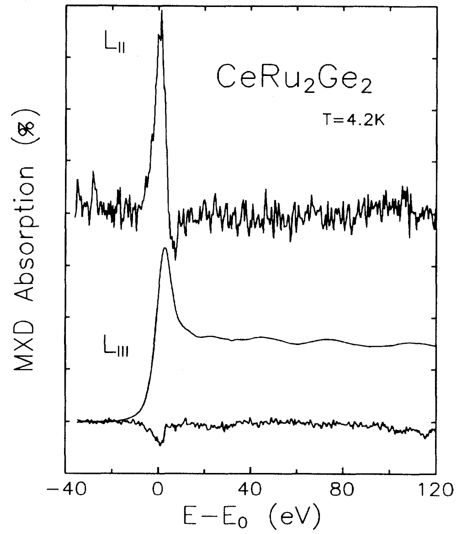

FIG. 1. MCXD spectra at the $L_{2,3}$ absorption edges in $CeRu_2Ge_2$ at $T=4.2$ K. Normalized absorption unit $=1\%$.

MCXD spectra are presented in Fig. 1 for the L_2 and L_3 edges of Ce in the ferromagnetic compound $CeRu_2Ge_2$, at $T=4.2$ K. The MCXD signal is essentially positive (negative) at the L_2 (L_3) edge. It appears clearly that the amplitude of the effect is very different according to the edge, with a ratio between the MCXD at L_2 and L_3 edges of about -8 (also observed in Ce_3Al_{11}) very far from the branching ratio (-2) expected by theoretical approaches based on the simple Erskine-Stern model, which supposes no spin orbit in the $5d$ final state. In principle, such disagreement with this simple model may be explained by the occurrence of a $5d$ orbital contribution.[20] However, it is hardly consistent with the variation of the MCXD branching ratio on the whole RFe_2 series.[5] The MCXD amplitudes and magnetic parameters are given in Table I. This compound is characterized by a ferromagnetic state for $T<7.9$ K (Ref. 21) and, as demonstrated by the white line character of the $L_{2,3}$ absorption edge (the L_3 spectrum is shown in Fig. 1), by a well localized $4f$ orbital. Since in this system the only contribution to the magnetic ordered moment comes from Ce atoms, the MCXD observed must be taken as a MCXD archetype for a pure trivalent Ce system with a sign corresponding to a Ce moment **M** in the magnetic-field direction.

In the Erskine-Stern approach, but also in the multiple-scattering theory of MCXD,[6] it can be shown that right-circularly polarized light induces preferential

TABLE I. $A(L_3)$, $A(L_2)$: MCXD amplitudes. $W(L_3)$, $W(L_2)$: energy widths at half height of the MCXD structures, at the Ce $L_{2,3}$ edges ($T=4.2$ K) compared to the magnetic parameters: magnetization at 0.5 T and Curie temperature in some well localized $4f$ Ce compounds.

Compounds	T_c (K)	M (μ_B/at Ce)	$A(L_3)$ (%)	$A(L_2)$ (%)	$W(L_3)$ (eV)	$W(L_2)$ (eV)
$CeRu_2Ge_2$	7.9	0.9	−0.5	4	4	6
Ce_3Al_{11}	7	0.3	−0.25	2	4	6
CePd	6.5	0.7	−0.15		5	

transitions towards unoccupied spin-up states (i.e., along $+Oz$) at the L_2 edge and spin-down states (i.e., along $-Oz$) at the L_3 edge. Thus a negative (positive) sign of the MCXD signal at the L_2 (L_3) means that the $5d$ unoccupied states are mainly of spin-down character. Consequently, the occupied states must be of spin-up character, i.e., the $5d$ magnetic moment is aligned along $-Oz$ when the magnitude field $\mathbf{B}$ ($\mathbf{M}$) is along $+Oz$. As it is generally admitted that the $4f$ and $5d$ spins in R are parallel,[22] then the MCXD signs observed in $CeRu_2Ge_2$, at the L_3 (negative) and at the L_2 (positive) edges, are not consistent with a $4f$ moment parallel to $+Oz$. The study of other trivalent Ce compounds, such as CePd and Ce_3Al_{11}, with T_c about 7 K, confirms all these characteristic features (Table I). Obviously, as expected, the amplitude of the MCXD effect cannot be taken as a measure of the total magnetic moment ($4f$, spin and orbital moments, and $5d$ contributions); indeed, the intensity of the MCXD, in $CeRu_2Ge_2$ and Ce_3Al_{11} for example, is not simply related to the bulk moment (see Table I). Moreover, the fact that the experiments are performed at $T=4.2$ K, near the Curie temperature of the compounds ($T_c<8$ K), can obscure the relationship between the MCXD intensity and the $5d$ magnetic moment. Nevertheless, the important point is that the strong resonance between the L_2 and L_3 MCXD intensities cannot be explained if we suppose only a spin contribution to the $4f$ moment. In absence of $5d$ moment calculation it is premature to draw conclusions concerning the relation between the total magnetic moment and the dichroic response. Similar conclusions can be drawn from our results on ferromagnetic intermetallic compounds with light R, such as Pr_2Co_{17}, Nd_2Co_{17}, or Nd_2Fe_{17}.[23]

B. MCXD study in $CeFe_2$

As described in the introduction, $CeFe_2$ exhibits relatively low magnetic parameters, compared to the other RFe_2. The nature of these anomalous properties has been the subject of a flurry of experimental and theoretical activity and the interest for $CeFe_2$ has been renewed by the first observation of a MCXD response at the Ce $L_{2,3}$ edges.[19]

The $L_{2,3}$ edges of Ce in $CeFe_2$ (Fig. 2) exhibit the well-known double-peak characteristic of the IV state of Ce in intermetallic compounds. It is generally accepted that due to a strong hybridization between the $4f$ states and the conduction band, the ground state, made of an admixture of $|4f^1\rangle$ and $|4f^0\rangle$ states, can be represented by $|\Psi_i\rangle=\alpha|4f^1\rangle+\beta|4f^0\rangle$. Then the double structure at the Ce $L_{2,3}$ edges reflects the two possible screening mechanisms of the $2p$ core hole: Either the core hole is (well) screened by a $4f$ electron in the final state yielding the low-energy structure, or it is (poorly) screened by the $5d$ electron explaining the higher (6–10 eV) energy structure.[24] It is admitted that the ground state of Ce IV compounds can be defined by the fractional $4f$ occupation number n_f obtained from the relative intensity of the two contributions $4f^1$ and $4f^0$, $n_f=\alpha^2/(\alpha^2+\beta^2)$. This phenomenological procedure,[24] which does not include the possible $4f^2$ final states, overestimates the valence $(4-n_f)$ deduced from elaborate many-body model of photoemission. Although the physical meaning of the fitting procedure is questionable, the extracted n_f gives, nevertheless, the $4f$ occupation in the ground state.[3] When applied to the $L_{2,3}$ edges of $CeFe_2$ the fitting procedure leads to a valence $v=3.29$, with an energy width at half height about 13 and 14 eV, respectively, for the two contributions ($\Delta=6$ eV), in agreement with previous results.[25]

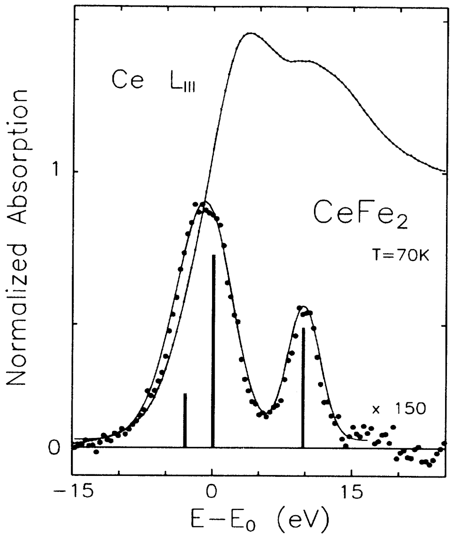

FIG. 2. Normalized Ce L_3 (···) and MCXD spectra (●●●), ×150, in $CeFe_2$ at 70 K. Continuous line: fit with three components (vertical bars).

The presence of a MCXD signal both at the L_2 and L_3 edges confirms the existence of an ordered magnetic moment on the Ce sites. Due to the selection rules ($5d$ final states) the dichroic signals have essentially a $5d$ origin. Quadrupolar transitions, i.e., transitions from $2p$ to $4f$ states, are in principle always possible.[26] However, in the systems under study, essentially Ce compounds, such contributions can be safely ignored. The very close agreement of the thermal variation of the bulk magnetic moment with that of the MCXD intensity shown in Fig. 3 demonstrates the ability of MCXD spectroscopy to measure ground-state properties.

The MCXD signal presents a characteristic shape that has been taken, in a first analysis, as a replica of the absorption edge. Indeed, the amplitude ratio of the two lines of the MCXD is identical to the valence deduced from the total absorption cross section ($v=3.3$).[19] Moreover, as already observed for the two components of the $L_{2,3}$ edges, i.e., the valence,[25] we have observed that the ratio of the two MCXD lines is nearly temperature independent.

Nevertheless, the quantitative analysis (see Table II) shows that the energy widths are much smaller than those observed in the absorption edges and that the high-energy magnetic contribution is about twice as small as the low-energy one, 4 and 7 eV, respectively. This en-

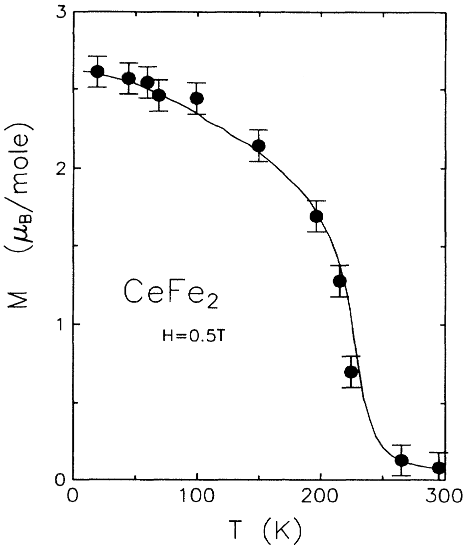

FIG. 3. Thermal variation of the magnetic moment (——) and MCXD intensity (●) in $H=0.5$ T. The dichroic effect is normalized to the magnetic moment at $T=20$ K.

ergy width difference, which has been already observed in the $L_{2,3}$ edges of IV compounds characterized by high Kondo temperatures,[27] can be explained by different exchange or screening mechanisms in the two channels of the $5d$ states, due to the absence of $4f$ electron in the "$4f^0$" final state. The high-energy structure peaks exactly at the energy of the absorption peak (Fig. 2) corresponding to the $4f^0$ contribution ($E=9.6$ eV), whereas the low-energy MCXD contribution appears at $E=0$, as generally observed in $4f^n$ localized systems (see Fig. 4). The energy splitting (11 eV) of the two MCXD maxima is larger than that observed in the standard $L_{2,3}$ spectra (6–8 eV). These two different behaviors of MCXD and absorption structures (width and splitting) mean that the MCXD analysis must be revised.

Due to the different energy widths in the MCXD lines, we must consider the integrated intensity ratio of the magnetic dichroic structures in order to compare them with the valence extracted from the $L_{2,3}$ edges. Thus the MCXD integrated intensity ratio is about 0.24 instead of 0.3 corresponding to the Ce valence $v=3.3$. This means that additional effects are present in the low-energy MCXD signal. The different structure splittings observed in the edges and in the MCXD spectra can be also explained by an extra contribution to the absorption edge. It is well known that $4f^2$ final states, in the special case of large $4f$ hybridization, contribute to x-ray photoemission spectroscopy (XPS) lines[28] and also to the $L_{2,3}$ absorption process.[29] The $4f^2$ contribution to the Ce $3d$ XPS core-level spectra in CeFe$_2$ is unknown but we know that it is around 20% in CeCo$_5$. Thus, if the $4f^2$ channel is at the origin of the unusual width of the low-energy MCXD channel, we should observe an intense $4f^2$ signature ($>30\%$) in the $3d$ XPS core-level spectra of CeFe$_2$. Such XPS experiments, including also the XPS study of CeCo$_5$, are now under progress. These states peak at an energy about 3 eV lower than $4f^1$ states and are clearly observed in photoemission spectroscopy. Due to the small energy splitting these $4f^1$ and $4f^2$ states are hybridized, and the $4f^1$-$4f^2$ mixture produces a single magnetic structure. As shown in Fig. 2 the Ce MCXD spectra can be fitted by three components lying at -3, 0, and 9.6

TABLE II. Parameters of the MCXD study of CeFe$_2$, LuFe$_2$, HfFe$_2$, GdFe$_2$, CeCo$_5$, and LaCo$_5$. ΔE_{edge}: energy splitting of the two lines in the $L_{2,3}$ edges. ΔE_{MCXD}: energy splitting of the two contributions in the MCXD signal. A_1 (A_2): amplitudes of the low- (high-) energy MCXD structures. W_1 (W_2): widths at half height of low- (high-) energy MCXD lines. μ_{5d}^{cal}: $5d$ contributions from band-structure calculations at $T=0$ (Refs. 13, 14, and 33). μ_{5d}^{exp}: $5d$ moment extracted from MCXD experiments. The incertitudes on the energy widths are estimated to ±1 eV.

Compounds		ΔE_{edge} (eV)	ΔE_{MCXD} (eV)	A_1 (%)	A_2 (%)	W_1 (eV)	W_2 (eV)	$-\mu_{5d}^{\text{exp}}$ (μ_B)	$-\mu_{5d}^{\text{cal}}$ (μ_B)
CeFe$_2$	L_2	6	11	-1.15	-0.70	7	4	0.35	0.3
(20 K)	L_3	6	11	0.6	0.35	7	3		
LuFe$_2$	L_2			-1.20		7			
(300 K)	L_3			0.60		6.5		0.2	0.3
HfFe$_2$	L_2			-2.35		8		0.4	
(300 K)	L_3			1.10		6.5			
GdFe$_2$	L_2			-6.3		6		1.3	0.6
(300 K)	L_3			3.60		5			
CeCo$_5$	L_3	7	10	0.40	0.30	~5	~4	0.25	0.2
(300 K)									
LaCo$_5$	L_3			0.40		~5		0.2	0.2
(300 K)									

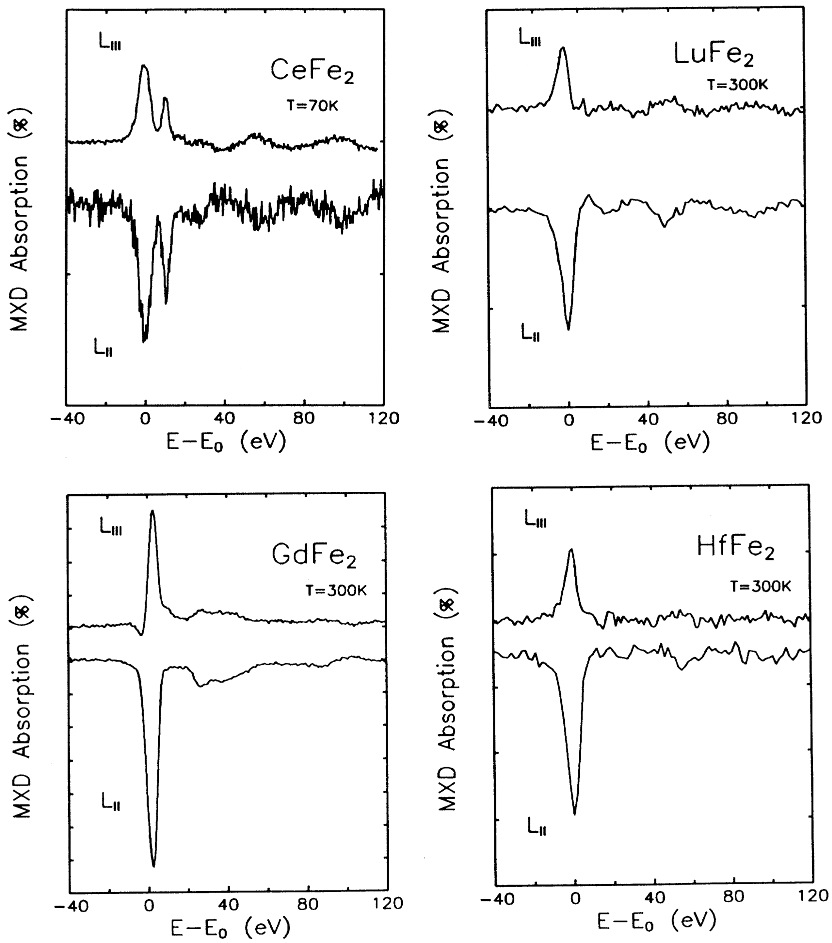

FIG. 4. MCXD normalized signals in CeFe$_2$ (70 K), LuFe$_2$ (300 K), GdFe$_2$ (300 K), and HfFe$_2$ (300 K) at the L_2 and L_3 absorption edges. Normalized absorption unit $=1\%$.

eV, respectively. The MCXD results, summarized in Table II, suggest that all these features are general trends for highly correlated Ce systems.

C. The sign of MCXD signals

Figure 4 shows that, for the presented $R\mathrm{Fe}_2$ compounds, the sign of the MCXD signal *is positive (negative) at the L_3 (L_2) edge and the MCXD branching ratio is about* -2. That means that, in these cases, the 5*d* magnetic moment is almost of spin character. In CeFe$_2$ the 3*d* magnetic moment of Fe is along $+Oz$, i.e., the spin S_{3d} is along $-Oz$, the antiferromagnetic interaction between S_{3d} and S_{5d} leads to a Ce 5*d* moment along $-Oz$. Then, in the framework of this interpretation a positive (negative) MCXD signal at the L_3 (L_2) edge yields as expected an antiferromagnetic coupling between 5*d* and 3*d* moments.[22] In order to be consistent with the results of neutron-diffraction experiments performed on CeFe$_2$, which show that the magnetic moments of Fe and Ce are antiferromagnetically coupled[15] (with $M_{\mathrm{Fe}} > M_{\mathrm{Ce}}$), we deduced directly from Fig. 5 that the orbital angular moment L_z^{4f} of cerium has to be very small in order to ensure that $L_z^{4f} \leq 2(S_z^{5d}+S_z^{4f})$. As shown in Fig. 6 and in Table II, similar conclusions are derived from the dichroic study at the R L_3 edge in CeCo$_5$, but also in Ce$_2$Fe$_{17}$ and Ce$_2$Co$_{17}$.[30]

When applied to the case of R compounds, with 4*f* localized electrons, this simple model, which gives a wrong sign for the direction of the magnetic moment, as shown previously for CeRu$_2$Ge$_2$, cannot be used and this is reflected by the departure of the $L_{2,3}$ MCXD ratio from the -2 value.[5] However, in GdFe$_2$, LuFe$_2$, and HfFe$_2$ systems (see Table II and Fig. 4) the ratio of the intensities of the two MCXD signals is not far from -2. Consequently, for these compounds the dichroic signal indicates that the 5*d* moment, as expected, is antiparallel to the 3*d* moment of Fe. Nevertheless, although the ratio -2 is also observed in Gd metal and compounds as GdFe$_2$ with a pure S state ($L_z^{4f}=0$), the dichroic signal leads to the wrong sign for the 5*d* moment, which we suppose, is again due to the presence of the open 4*f* shell in Gd.

By comparison with the corresponding metal, we have tested that *in all Ce-M intermetallic compounds,* the MCXD at the *M K* edge yields a magnetic moment of *M* in the direction of the external magnetic field, that is in the direction of the macroscopic moment. As shown in

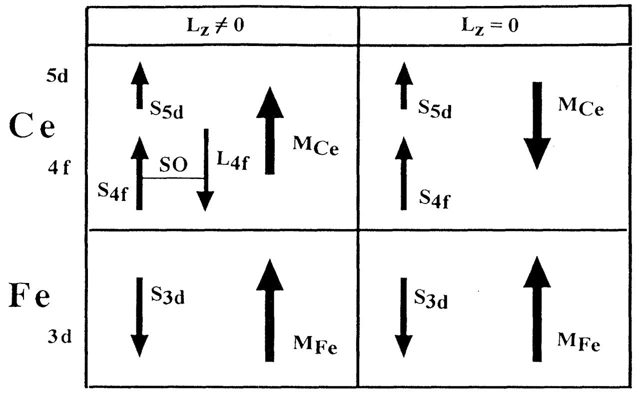

FIG. 5. Interactions between magnetic moments deduced from the hybridization and exchange interactions in the Ce-Fe system, in two cases: (a) $L_z \neq 0$ and (b) $L_z = 0$. S.O. denotes the spin-orbit coupling.

Fig. 7, the MCXD at the Fe K edge in $CeFe_2$ presents the same sign, but the signal is too small and noisy to permit a study of its shape. The opposite sign of the Fe dichroic signal in $GdFe_2$ confirms the ferrimagnetic state of this compound.

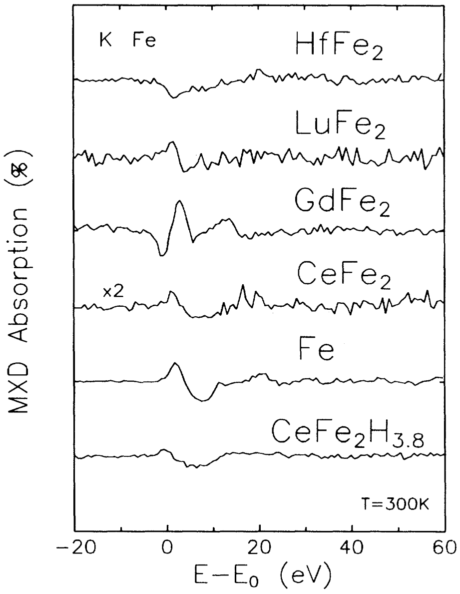

FIG. 7. MCXD normalized spectra at the Fe K edge in Fe, $CeFe_2$, $GdFe_2$, $LuFe_2$, $HfFe_2$, and $CeFe_2H_{3.8}$ at $T = 300$ K except for $CeFe_2$: $T = 70$ K. Normalized absorption unit $= 1\%$.

D. Relationship between MCXD intensities and magnetic moments

1. $L_{2,3}$ edge MCXD study

Since the MCXD calculations in the framework of the single-particle relativistic band-structure model are only available for Gd metal,[31] it is premature to get information on the $4f$ spin and orbital moment in the case where there is no simple relationship between magnetic dichroism at the L_2 and L_3 edges. However, in the presence of a full or empty $4f$ shell, as Hf, Lu, or La, leading to a zero angular moment contribution, we can assume that the MCXD spectrum intensities reflect the sole $5d$ magnetic moment. For $LuFe_2$ (Ref. 14) and $CeFe_2$ (Ref. 13), we take benefit of the self-consistent energy-band calculations and of the determination of the sign of the interaction between the R $5d$ and Fe $3d$. The magnetic-moment calculation indicates a $5d$ contribution of about $0.3\mu_B$, almost of spin character, on the R sites both in $LuFe_2$ and in $CeFe_2$. In the presence of a double MCXD contribution, as observed in Ce IV compounds, $4f^0$ and $4f^1$ channels contribute to the mean magnetic moment with weights α^2 and β^2, therefore the integrated intensities of the two lines must be taken into account. It has been demonstrated that the $L_{2,3}$ MCXD signal in Ce compounds is exclusively of $5d$ origin and therefore the M_{3d}^{Ce} moment in $CeFe_2$ can be evaluated from that of $LuFe_2$. The normalization takes into account the fact that the calculated reference value is given at $T = 0$ and that the room temperature R sublattice magnetization is about 70% of the $T = 0$ value.[32] The value obtained, $M_{5d}^{\mathrm{Ce}} = -0.35\mu_B$, is in good agreement with that deduced from band-structure calculations ($-0.3\mu_B$), the difference with the moment obtained from the neutron-diffraction analysis ($-0.45\mu_B$) (Ref. 15) can be explained by the $4f$ moment contribution.

In the case of $HfFe_2$ (Fig. 4) the MCXD amplitude is twice that of $LuFe_2$. The difference between the magnetic moment of $LuFe_2$ ($2.9\mu_B$/f.u.) and $HfFe_2$ ($2.4\mu_B$/f.u.) can be explained if we suppose that the Fe atoms bear

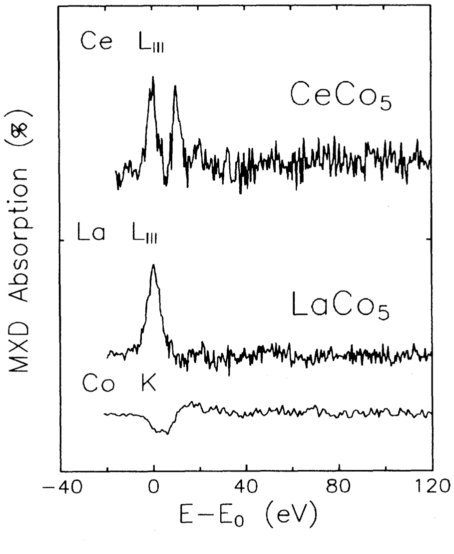

FIG. 6. MCXD normalized spectra at the La L_3, Co K edge in $LaCo_5$ and Ce L_3 edge in $CeCo_5$, at 300 K. Normalized absorption unit $= 1\%$.

about $1.6\mu_B$ and that the Lu and Hf atoms contribute, as deduced from MCXD analysis, with $-0.2\mu_B$ and $-0.4\mu_B$, respectively. The increase of the $5d$ moment with the $5d$ electron number backs up the validity of the proportionality between the dichroic intensity and the local $5d$ moment, provided the spin densities of states are quite similar. Such a phenomenon was already observed in the $5d$ Fe system[9] for the beginning of the $5d$ M row.

As shown in Fig. 4 and in Table II, for $GdFe_2$ the MCXD signal is 6 times larger than in $LuFe_2$, while the ratio of the $5d$ calculated moments is only two ($-0.65\mu_B$ and $-0.3\mu_B$, respectively).[33] Even in an $L_z^{4f}=0$ state we cannot reproduce the correct sign of the magnetic moment and there is no longer a simple relationship between the $L_{2,3}$ MCXD intensities and the magnitude of the $5d$ moment; once again the influence the $4f$ electrons on the MCXD signals is strongly suggested.

The analysis of the RCo$_5$ system leads to the same conclusions. As shown in Fig. 6 and Table II, the MCXD derived $5d$ moment corresponds to the calculated $5d$ moment ($-0.2\mu_B$) in $LaCo_5$,[17] while in $CeCo_5$ the moment estimated from MCXD ($-0.25\mu_B$) is in agreement with the calculated value ($-0.2\mu_B$). The lack of result on La or Lu MCXD and band-structure calculation, does not allow us to conclude for the case of R_2Co_{17}. However, it has been proposed for Ce_2Co_{17},[34] based on the results of $5d$ impurities diluted in iron,[9] a value of $-0.3\mu_B$ on the Ce site, while our normalization leads to a moment of about $-0.35\mu_B$.

2. *K-edge MCXD study*

Due to the absence of spin orbit in the initial state and because spin-orbit coupling interacts directly with the photoelectron the mechanism of the K-edge dichroism is more sophisticated than that of R $L_{2,3}$ edges and consequently the relationship between the dichroic signal and the magnetic properties is not so clear.[6] Nevertheless, in order to take advantage of the MCXD studies at the Fe K edge, in some RFe$_2$ compounds, we have compared the dichroic signals to the hyperfine field extracted from Mössbauer experiments on Fe sites, since this intrinsic field is, in principle, proportional to the $3d$ local moment. The Mössbauer results are summarized in Table III for $CeFe_2$, $GdFe_2$, $LuFe_2$, and $HfFe_2$ (Ref. 35) in addition to the Fe K MCXD amplitudes (Fig. 7). It appears that there is a rough correlation between the two parameters for $CeFe_2$, $LuFe_2$, and $HfFe_2$. In defiance of different T/T_c values and noisy signals, for $GdFe_2$ and MCXD amplitude is much larger that of $HfFe_2$, while the hyperfine fields, and therefore the $3d$ moments, are very similar ($1.6\mu_B$/at Fe). This result illustrates that the Fe K-edge magnetic dichroism is not only due to a pure contribution of the $3d$ states, via the polarized $4p$ states. As shown in Table III the Fe K-edge magnetic dichroism seems to be correlated to the ferromagnetic order temperature and thus the influence of the $5d$-$3d$ exchange interaction is a pertinent parameter in the description of the K-edge MCXD. An exhaustive study of the Fe K-edge dichroism in RFe series will be proposed in a forthcoming paper. Recently a study of several $3d$-$3d$ and $3d$-$4f$ systems at the K edge of the $3d$ element[36] demonstrates that there is no proportionality between the calculated p or d local moment on Fe and the MCXD signal.

TABLE III. Fe K MCXD absolute peak-to-peak amplitude A (±0.02), Curie temperatures T_c hyperfine field H_0 and magnetization M_s (4.2 K).

Compounds	A (%)	T_c (K)	H_0 (kOe)	M_s (4.2 K) (μ_B/f.u.)
$CeFe_2$	0.1	230	156	2.6
$LuFe_2$	0.2	610	208	2.9
$GdFe_2$	0.37	785	225	3.8
$HfFe_2$	0.18	585	202	2.3
$CeFe_2H_{3.8}$	0.13	360		4.2

E. The $4f$ state contribution in Ce IV compounds

We have seen that in IV Ce compounds MCXD experiments are able to determine not only the sign of the interaction between the $5d$ and $3d$ moment in R-M systems but also the magnitude of the $5d$ moment. This is done by normalizing the amplitude of the MCXD lines to the absolute value obtained, for example, from band-structure calculations of La or Lu reference compounds. The presence of a weak $4f$ magnetic moment in IV cerium systems, predicted, by band-structure calculations to be of about $-0.42\mu_B$ of spin character and $0.15\mu_B$ of orbital character in $CeFe_2$, has been recently experimentally confirmed by MCXD measurements at the Ce $M_{4,5}$ edges.[37] However, considering the value of the $5d$ magnetic moment, $-0.35\mu_B$, obtained from the $L_{2,3}$ MCXD analysis and the total Ce moment, $-0.45\mu_B$, extracted from neutron-diffraction analysis, the maximum value for the $4f$ contribution should be only in the $0.1\mu_B$ range. This study supports a bandlike description of the $4f$ states in strongly hybridized Ce compounds. This idea is supported by the $L_{2,3}$ edge study, as described in Sec. III C.

The observation of a positive (negative) sign for the low-energy structure at the Ce L_3 (L_2) MCXD signal seems, in fact, to rule out the contribution of localized $4f$ electron to the spectrum and consequently the dichroism absorption cross section does not involve any $4f$ localized state in the final states of the $L_{2,3}$ absorption process. This is of prime importance in order to have a thorough knowledge of the absorption process in the $L_{2,3}$ edges of Ce IV systems.

F. MCXD applications

1. *The $CeFe_2H_x$ system*

Like pressure, alloying or temperature, hydrogen absorption can localize the $3d$ Fe band and/or of the $4f$ states of Ce in IV compounds. In the case of the $CeFe_2H_x$ system previous x-ray-absorption spectroscopy results have indeed shown that the valence state of Ce changes with the increase of the hydrogen content from 3.3 to 3.0 when x reaches 3.7.[38] The localization of $4f$

states of cerium induces an increase of the Curie temperature (360 K) and of the saturated magnetic moment ($4.2\mu_B$/f.u.). The presence of a white line in the L_3 absorption edge [Fig. 8(a)] confirms the decrease of the $4f$-$5d$ hybridization for $CeFe_2H_{3.8}$. Figure 8(b) shows that the MCXD spectra are also affected. By hydrogenation both at the L_2 and the L_3 edges, very small effects replace the characteristic dichroic shape of the IV system. The change of sign of the MCXD signal at the Ce L_2 edge, with respect to $CeFe_2$, is undeniable and consequently the localization of the Ce $4f$ electrons is probably important. However, this localization does not reach the high degree observed in $CeRu_2Ge_2$, since the ratio of the MCXD at the L_2 for these two compounds is about 40. The MCXD signals detected at the $L_{2,3}$ edges seem to be the result of the compensation of two contributions, one of pure $5d$ origin and one other due to the presence of a localized $4f^1$ state. This latter contribution would act as a negative signal, which at the L_3 edge corresponds to a moment in the magnetic field direction (if we take as a reference the dichroism observed in $CeRu_2Ge_2$) and then to a ferromagnetic component in agreement with the M_{Ce}-M_{Fe} interactions expected for light R intermetallic compounds. This leads to a nearly zero magnetic dichroic effect at the L_3 edge and a relatively small signal at the L_2 edge. This supports the idea that, in this Ce hydrogenated system, the increase of the total magnetic moment (2.6–$4.2\mu_B$/f.u.) with hydrogenation probably comes from a huge enhancement of the Fe $3d$ magnetic moment rather than from a complete Ce $4f^1$ localization. This is supported by Mössbauer spectroscopy studies.[11]

The observation in $CeFe_2H_{3.8}$ of a MCXD different

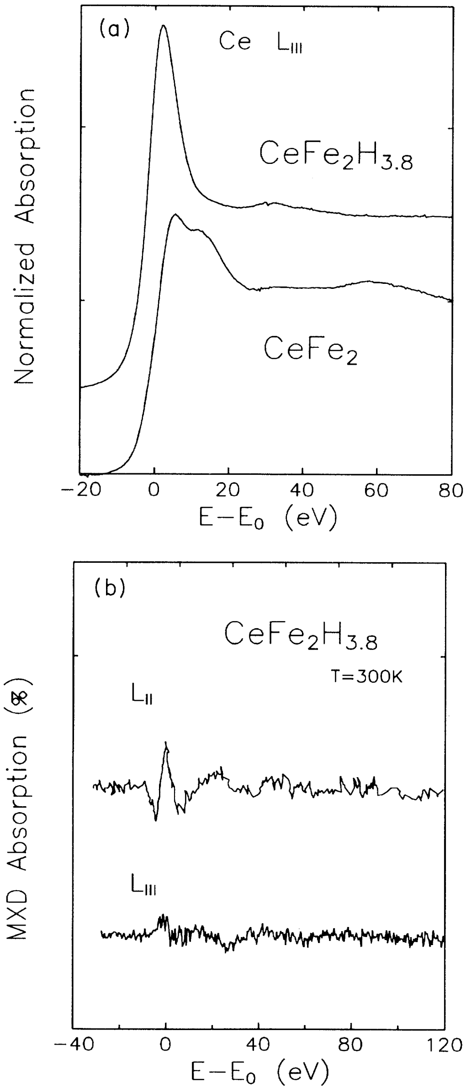

FIG. 8. Ce L_3 edges in $CeFe_2$ and in $CeFe_2H_{3.8}$ (a). MCXD spectra at the Ce $L_{2,3}$ in $CeFe_2H_{3.8}$ at $T=300$ K (b). Normalized absorption unit $=1\%$.

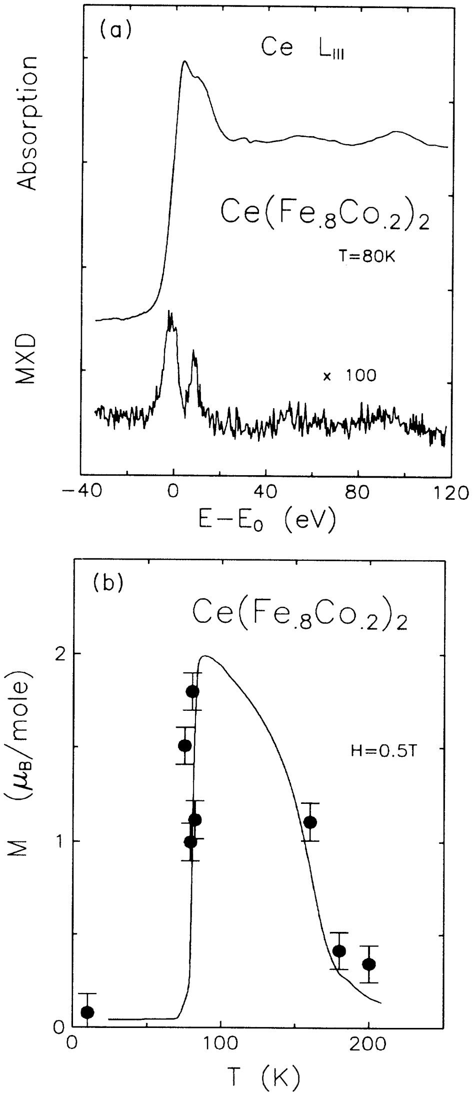

FIG. 9. Ce L_3 and MCXD in $Ce(Fe_{0.8}Co_{0.2})_2$ at $T=80$ K (a). Magnetic phase diagram obtained in $H=0.5$ (b). Magnetic moment (——), MCXD intensity (●).

from that found for Ce IV compounds proves that $4f$ orbitals contribute to MCXD and therefore that $4f^1$ states are magnetically ordered.

Note that the proposed enhancement of the magnetic moment on the Fe sites corresponds to a significant increase of the Fe K dichroism (see Table III) and then confirms the dichroic analysis made for the Fe K edge in RFe$_2$.

2. *The Ce(Co,Fe)$_2$ system*

The last application proposed concerns the ferromagnetic instabilities observed by substitution of small amounts of M=Al, Si, Co, Ru on the Fe sites in Ce(Fe$_{1-x}M_x$)$_2$.[39-41] Figure 9(a) illustrates the Ce L_3 edge and the corresponding MCXD at $T=80$ K in the pseudoternary compound Ce(Fe$_{0.8}$Co$_{0.2}$)$_2$. The first important point is the observation of a MCXD signal (sign, shape, and amplitude) identical to that presented by pure CeFe$_2$. Consequently the Co substitution in CeFe$_2$ does not influence the Ce magnetic moment. In agreement with magnetic experiments,[12] the strong effects of substitution observed on the magnetic phase diagram of this system do not seem to come from the electronic structure of Ce but rather from instabilities of the magnetic structure of Fe. Such instabilities have been already observed in pure CeFe$_2$.[15] The existence of magnetic moment on Ce sites in this compound is in contradiction with the interpretation of the neutron-diffraction measurements[15] which proposed a zero Ce moment whatever the temperature. Nevertheless, the use of a nonrelevant $4f$ electron-type factor in the neutron-diffraction analysis could explain this discrepancy. Another important point concerns the thermal variation of the Ce L_3 MCXD spectrum which matches very well the magnetization obtained in the same external magnetic field [Fig. 9(b)]. In particular the MCXD is nearly zero for $T<80$ K when the antiferromagnetic phase becomes stable. In this regime the magnetic moment on Ce is not zero but the MCXD signal is not observed, since the bulk moment vanishes. This study on Ce(Fe$_{0.8}$Co$_{0.2}$)$_2$ confirms experimentally *the importance of the Fe magnetic instabilities in the understanding of the electronic properties of CeFe$_2$* and illustrates the pertinence of the MCXD method to resolve some particular magnetic phase diagram and then to complete with neutron-diffraction measurements.

IV. CONCLUSION

MCXD experiments performed at the $L_{2,3}$ edges of R elements appear to be a powerful tool for the local magnetic properties of R atoms in any R intermetallic compound. The main conclusions of our paper can be summarized as follows.

(i) When the $4f$ shells are completely filled or empty (case of Lu and La compounds) or *when the $4f$ electrons are strongly hybridized* with the conduction electrons (case of IV Ce compounds), MCXD studies at the $L_{2,3}$ edges yield directly both the magnitude and the direction of the $5d$ moments that are essentially of spin character. The values deduced from such experiments well agree with the prediction of spin-resolved band-structure calculations. The situation is thus completely equivalent to that encountered when $5d$ impurities are diluted in $3d$ transition matrix elements.

(ii) When there are localized $4f$ electrons in the ground state, the situation becomes much more complex. The huge resonance effects observed between the MCXD at the L_2 and L_3 edges can reflect either the existence of an orbital contribution to the $5d$ moments or the influence of the $4f$ electrons themselves due, for instance, to exchange coupling between the $4f$ and the $5d$ electrons. The experiments we performed on Gd-Fe systems seem to privilege the last hypothesis.

The concluding point is that MCXD at the $L_{2,3}$ edges appears to be a fingerprint of the degree of localization of $4f$ electrons and this opens new and exciting possibilities in the study of the strongly correlated systems. The $4f$ and $5d$ magnetism can be independently investigated by performing MCXD both at the $M_{4,5}$ and $L_{2,3}$ edges of any R element, taking benefit from the high selectivity of the absorbing process. In this context, such experiments are quite unique for the study of magnetism, particularly when the orbital and spin contributions can be separated.

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