Effects of spin-dependent spectral weight on magnetic circular x-ray dichroism: Applications to $R(\mathrm{Ni}_x\mathrm{Co}_{1-x})_5$ intermetallic compounds

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This systematic study of $R(\mathrm{Ni}_x\mathrm{Co}_{1-x})_5$ compounds (R=La, Gd, and Tb) has allowed us to investigate the combined effects of the 3*d*-5*d* hybridization and 4*f*-5*d* exchange on the rare-earth $L_{2,3}$-edge magnetic circular x-ray dichroism (MCXD) signal. In La compounds, where the 5*d* polarization results only from the magnetic transition metals via the hybridization of 5*d* and 3*d* bands, the MCXD signal scales with the 5*d* moment and can be explained by a one-particle model for the absorption process. When the 4*f*-5*d* exchange intervenes, like in the Gd and Tb compounds, its effects on the MCXD sign, amplitude, and the amplitude variations are very important. A description of the $L_{2,3}$-edge MCXD spectra taking into account the spin-dependence of the radial matrix elements explains qualitatively the results of this study.

I. INTRODUCTION

The rare-earth–transition-metal intermetallic compounds offer the interesting characteristic of combining the itinerant magnetism of transition metals (TM) with the localized and anisotropic magnetism of the rare earths (RE's). Among these materials, the $R\mathrm{Ni}_5$ and $R\mathrm{Co}_5$ compounds, which crystallize in the hexagonal CaCu_5-type structure, have been widely investigated.[1] The Curie temperatures of $R\mathrm{Co}_5$ compounds are very high and the Co moment is close to its maximum value. These compounds order ferrimagnetically with the spins on the TM and RE sites coupled antiparallel. In contrast, in the $R\mathrm{Ni}_5$ series the Ni ions do not carry a magnetic moment. Magnetism comes from the RE ions only and these compounds exhibit very low Curie temperatures. The magnetic properties of these compounds are understood in terms of crystalline electric field (CEF) interactions and RE-RE, RE-TM, and TM-TM exchange interactions.[2,3] The 5*d*-3*d* coupling plays an important role in RE-TM compounds, since it mediates the interactions between RE 4*f* and TM 3*d* spins.[4,5]

In general, the polarization of the 5*d* bands in RE-TM compounds is tuned (i) by the hybridization of the 3*d* and 5*d* bands, (ii) by the positive 4*f*-5*d* direct exchange. At the formation of the RE-TM alloys the screening of the nuclear potentials are modified by the transfer of 5*d* (or 4*d*) electrons to the unfilled 3*d* band. The two *d* bands draw closer and hybridize to form bonding and antibonding bands. Using the molecular orbital formalism Brooks *et al.*[5] showed that in the case of LuFe_2 the entire content of the 5*d* band is due to hybridization. Hybridization also originates the antiparallel polarization of the local 3*d* and 5*d* moments. When the RE is magnetic, the 4*f*-5*d* exchange splits the 5*d* band further and increases both the antiparallel 3*d* and 5*d* moments. Quite similar effects occur in the $R\mathrm{Co}_5$ and $R\mathrm{Ni}_5$ compounds. Earlier calculations of the electronic structure of the Y-Ni compounds show that a large hybridization exists between *d* bands of Y and Ni atoms.[6] This hybridization transfers 0.1–0.2 Ni 3*d* electrons to the Y 5*d* band. In $R\mathrm{Ni}_5$ compounds, the polarization of the RE 5*d* band is mainly due to the local 4*f*-5*d* positive exchange. Because of the 5*d*-3*d* hybridization, a net moment is then induced on Ni.

It is well known that with the use of circular polarized light of synchrotron sources, x-ray-absorption spectroscopy has become a unique probe of local magnetism. Magnetic circular x-ray dichroism (MCXD) measures the dependence of the absorption cross section on the helicity of the incident radiation. This phenomenon is governed by the selection rules for dipolar electric transitions ($\Delta 1=\pm 1$, $\Delta J=0,\pm 1$, and $\Delta m_j=\pm 1$ for left and right polarization). The tunability of synchrotron radiation and the selectivity of x-ray-absorption spectroscopy allow the unoccupied electronic levels of a selected symmetry to be probed independently for each atomic species. With the use of hard x rays the magnetic polarization of 4*p* bands of TM and 5*d* bands of RE can be studied. Although the 5*d* electronic states are not directly responsible for the magnetism of RE compounds, they are of great interest since they govern the magnetic order through the indirect exchange with the 3*d* bands.

The MCXD spectra are well understood for the case of 4*f* magnetism, where the atomic multiplets approach can be applied ($M_{4,5}$ edges of RE).[7] The interpretation is still a matter of discussion for $L_{2,3}$ edges of itinerant ferromagnetic materials Co, Ni, and Fe. Important progress has been achieved with the sum rules proposed for MCXD. It has been shown that the ground-state orbital and spin moments of the 3*d* band can be deduced from MCXD signal of the 2*p* core level split by a spin-orbit interaction.[8] Some discussion is still open to precise the limits of applicability of the second or "spin" sum rule.

The interpretation of the $L_{2,3}$-edge signals of rare-earth elements is far more complex than that of $3d$ metals, essentially because of the $4f$-$5d$ exchange which is at the origin of a spin-dependent spectral weight. The shape and the magnitude of the spectra strongly depend on the rare-earth atom and, for the same element, the profiles can be very different for L_2 and L_3 edges.[9] For heavy rare earths like Gd, Tb, or Dy, the L_2 (L_3) edge spectra have one main negative (positive) peak due to dipolar transitions to the $5d$ band. The weak feature below the edge observed at the L_3 edge has been attributed to quadrupolar transitions ($2p \rightarrow 4f$) but there is no definite experimental proof for this interpretation.[10]

Using a simple one-particle model, the dipolar part of the $L_{2,3}$-edge MCXD spectra (μ_c) has been related to the spin-dependent final-state density by the expression[11]

$$\mu_c/\mu_0=(\mu^+-\mu^-)/\mu_0=P_E\Delta\rho(E)/\rho \ , \tag{1}$$

where $P_E=(n^\uparrow-n^\downarrow)/(n^\uparrow+n^\downarrow)$ is the photoelectron polarization, where $n^\uparrow$ and $n^\downarrow$ are the probabilities to create a photoelectron of a given spin. $\Delta\rho(E)=\rho^\uparrow(E)-\rho^\downarrow(E)$ is the difference between the unoccupied $5d$ states with opposite spins. In this approach, the radial part of the matrix element is assumed to be energy and spin independent.

Extensive studies of RE $L_{2,3}$-edge MCXD spectra in RE-TM compounds have shown that this model is adequate only for $5d$ impurities in TM (Ref. 11) and for nonmagnetic rare-earth elements, when the $5d$ moment is induced by the hybridization with the $3d$ band of the TM.[9,11,12] The MCXD signal has been shown to be proportional to the $5d$ magnetic moment in Hf, Lu, La, and intermediate valence Ce compounds. As soon as the rare earth has an uncomplete $4f$ shell, the one-particle model fails to explain the sign and the magnitude of the MCXD signal. For example, the $5d$ moment deduced by scaling the MCXD signal of $GdFe_2$ to that of $LuFe_2$ is much larger than the one deduced by neutron measurements.[9] Furthermore the direction of the $5d$ polarization deduced from the sign of the Gd L_3-edge MCXD is wrong when Eq. (1) is used. The correct sign is obtained only for RE "without $4f$ electrons." To explain this discrepancy Wang *et al.*[13] argue that when the $4f$ shell bears a magnetic moment the spin dependence of the matrix elements of the dipolar transitions should be taken into account. The dichroic signal μ_c is better approximated by the expression

$$\begin{aligned}\mu_c/(\mu^++\mu^-)&=(\mu^+-\mu^-)/(\mu^++\mu^-)\\&=P_E(\rho\Delta M+M\Delta\rho)/M\rho \ ,\end{aligned} \tag{2}$$

where $\Delta M=M^\uparrow-M^\downarrow$ is the difference between the spin-dependent radial parts of the matrix elements. The work by Harmon and Freeman[14] has shown that the spin-up $5d$ radial functions are pulled in towards the core of the atom with respect to the spin-down $5d$ orbitals. The $2p$-$5d$ overlap is therefore spin dependent. This increases the magnitude of the radial part of the matrix element of spin-up electrons (with respect in this case to the quantization axis associated with the $4f$ spin) and causes $M^\uparrow$ to be larger than $M^\downarrow$. According to Lang *et al.*[15] the difference between $M^\uparrow$ and $M^\downarrow$ can be as large as 30% in rare-earth compounds. The larger transition probability to spin-up states explains the positive sign of the L_3-edge dichroic spectra obtained for Gd and Tb, in spite of the fact that the number of unoccupied $5d^\uparrow$ states is smaller than that of $5d^\downarrow$ states. In other words, the term $\rho\Delta M$ dominates with respect to $M\Delta\rho$.

Since the second term in Eq. (2) is negative, it also follows that the MCXD signal decreases when the $5d$ polarization increases. It has been found that the L-edge signal measured for amorphous $GdFe_2$ is larger than that measured for crystalline $GdFe_2$ in spite of the larger polarization of the $5d$ band in the crystalline phase.[15]

In this paper we present the results of magnetic circular x-ray dichroism measurements performed at the $L_{2,3}$ edges of the rare earths in $La(Ni_xCo_{1-x})_5$, $GdNi_5$, and $TbNi_5$ and in the ferrimagnetic solid solutions $Tb(Ni_xCo_{1-x})_5$. In the $La(Ni_xCo_{1-x})_5$ solutions, as in $LuFe_2$, the polarization of the $5d$ band comes exclusively from the hybridization with the $3d$ band. Most of the $3d$ moment is carried by Co and the La $5d$ polarization is expected to increase as the Co content increases. In $GdNi_5$ and $TbNi_5$ the $5d$ polarization is induced exclusively by the $4f$-$5d$ local exchange while in the $Tb(Ni_xCo_{1-x})_5$ solid solutions the two aspects are combined. In these solutions the $5d$ polarization is expected to increase when the number of Co neighbors increases.

II. SAMPLES AND EXPERIMENTAL DETAILS

Polycrystalline $GdNi_5$, $TbNi_5$, and solid solutions of $Tb(Ni_xCo_{1-x})_5$ ($x=0.2$, 0.4, and 0.6) and $La(Ni_xCo_{1-x})_5$ ($x=0.4$, 0.2, and 0) were prepared at the Laboratoire Louis Néel by rf melting of the pure elements in a water-cooled crucible under argon pressure. The samples were finely powdered and deposited uniformly on a kapton foil in a layer less than 10 μm thick. The magnetic measurements on the same powders were carried out using an extraction magnetometer in magnetic fields up to 10 T. The ordering and compensation temperatures are reported in Table I as well as the ratios between the magnetization

TABLE I. Curie and compensation temperatures for all the studied compounds. Column 3 gives the reduced temperatures for the different measurements. Column 4 gives, for the powdered samples, the ratio between the magnetization of 0.6 T and the spontaneous magnetization deduced from magnetization processes at the same temperatures as the MCXD experiments.

	T_C (K)	T_{comp} (K)	T_{mes}/T_C	M/M_s
$GdNi_5$	32		0.3	
$TbNi_5$	23		0.4	0.94
$Tb(Ni_{0.2}Co_{0.8})_5$	$\approx$1000	200	$\approx$0.01	0.98
$Tb(Ni_{0.4}Co_{0.6})_5$	650	270	$\approx$0.01	0.98
$Tb(Ni_{0.6}Co_{0.4})_5$	300		$\approx$0.03	$\approx$1
$LaCo_5$	800			0.94
$La(Ni_{0.2}Co_{0.8})_5$	668			0.86
$La(Ni_{0.4}Co_{0.6})_5$	521			0.98

under a magnetic field of 0.6 T at the temperature of the MCXD measurements and the spontaneous magnetization at the same temperature.

Except for $GdNi_5$, all the studied samples present a very strong magnetocrystalline anisotropy. In $TbNi_5$ and $Tb(Ni_xCo_{1-x})_5$ the easy magnetization direction is along the **a** axis of the hexagonal cell.[2,16,17] In $TbNi_5$ the anisotropy within the basal plane is negligible while for the Tb solid solutions some anisotropy is still present within the basal plane. In single-crystal measurements, the magnetization measured in a magnetic field applied within the basal plane perpendicular to the **a** axis reaches only 90% of the magnetization along the **a** axis.[16,17] The good agreement between the magnetization values determined for our powdered samples and those found for single crystals is an indication of the good homogeneity of our powders. For $GdNi_5$ where no anisotropy is present, the magnetization of monocrystalline[2] and powdered samples are equivalent. In the La solid solutions the anisotropy imposed by the cobalt atoms is uniaxial along the **c** axis.[18] Since measurements on single crystals are not reported in the literature, our magnetization measurements on powdered samples could not be quantitative.

The MCXD measurements were carried out at the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (Orsay) on the energy-dispersion spectrometer of the 1.85-GeV DCI storage ring. The energy-dispersive setup combines an x-ray optics made of a curved Si(111) monochromator with a position-sensitive detector able to work under very high-flux conditions. Right circularly polarized x rays were selected by positioning a 1-mm-wide slit 3 mrad below the orbit plane of the storage ring. The MCXD signals were obtained from the XAS spectra recorded in transmission mode in a magnetic field of 0.6 T, applied alternatively in the direction parallel and antiparallel to the photon propagation vector **k**. The magnetization is therefore alternatively parallel and antiparallel to the x-ray beam direction and this is equivalent to the helicity reversal.

The thermal evolution of the Tb L_3-edge signal in $TbNi_5$ and $Tb(Ni_{0.4}Co_{0.6})_5$ was observed down to 4.2 K using a He cryostat. For all the other compounds the low-temperature measurements were carried out down to 10 K using a commercial closed-cycle refrigerator.

The MCXD signals are presented in the figures as the difference $\mu(\mathbf{B})-\mu(-\mathbf{B})$. The spectra were normalized to the height of the absorption edge step. In all the figures the origin of the energy scale has been chosen as the inflection point of the absorption edge. In Table II (column 1) the experimental MCXD values are corrected to take into account the variation with energy of the circular polarization rate.

III. RESULTS AND DISCUSSION

A. The role of the 3*d*-5*d* hybridization: $La(Ni_xCo_{1-x})_5$ solid solutions

In RE-TM compounds the polarization of the RE 5*d* band is tuned by the 4*f*-5*d* exchange and by the 3*d*-5*d* hybridization. The two mechanisms have different effects on the MCXD signals at the RE $L_{2,3}$ edges. When only the 3*d*-5*d* hybridization plays a role, the MCXD signal can be related directly to the 5*d* polarization, as already seen for La, Lu, and Hf compounds.[9] When the rare earth has an incomplete 4*f* shell, the presence of spin-dependent radial matrix elements makes it difficult to correlate the MCXD signal to the 5*d* polarization.

TABLE II. Column 1 gives the amplitude of the MCXD signal at the rare-earth L_3 edges for the Tb and La solid solutions. In column 2 the MCXD signal has been corrected for the M/M_s ratio.

	L_3 (%)	L_{3cor} (%)
	$T=10$ K	
$TbNi_5$	2.4 ± 0.1	2.55
$Tb(Ni_{0.6}Co_{0.4})_5$	2.2 ± 0.1	2.2
$Tb(Ni_{0.4}Co_{0.6})_5$	2.1 ± 0.1	2.14
$Tb(Ni_{0.2}Co_{0.8})_5$	1.8 ± 0.1	1.84
	$T=300$ K	
$La(Ni_{0.4}Co_{0.6})_5$	0.16 ± 0.02	≈0.16
$La(Ni_{0.2}Co_{0.8})_5$	0.25 ± 0.02	0.29
$LaCo_5$	0.32 ± 0.02	0.34

In $La(Ni_xCo_{1-x})_5$ solid solutions the amplitudes of the La $L_{2,3}$-edge MCXD signals are expected to vary according to the polarization of the 5*d* band. The La L_3-edge MCXD spectra measured at 300 K for $La(Ni_xCo_{1-x})_5$ with $x=0$, 0.2, and 0.4 are shown in Fig. 1. The signals consist of a weak single-peaked structure centered at the absorption edge, associated with $2p\rightarrow5d$ dipolar transitions. The sign of the spectra is positive in agreement with the previous results on other La, Lu, or Hf compounds. The MCXD amplitudes are of the same order of magnitude of that measured for $LuFe_2$.[9]

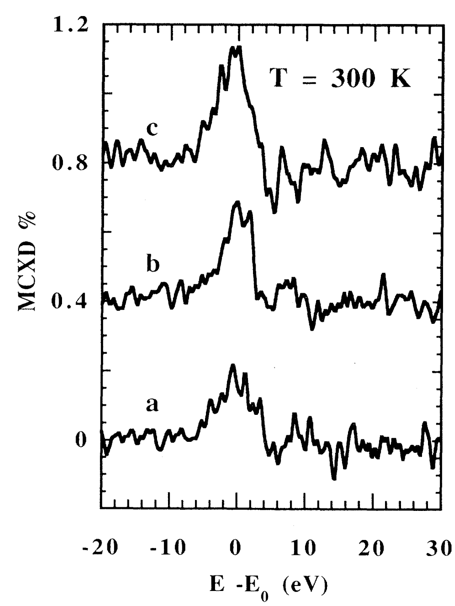

FIG. 1. MCXD spectra observed at the La L_3 edge in (a) $La(Ni_{0.4}Co_{0.6})_5$, (b) $La(Ni_{0.2}Co_{0.8})_5$, and (c) $LaCo_5$ at $T=300$ K. For clarity, the spectra have been offset by 0.4.

The MCXD amplitude decreases as Co content decreases, in agreement with the expected behavior of the 5d polarization. In Table II are reported the MCXD amplitudes corrected by the ratio M(0.6 T, 300 K)/M_S(300 K). A comparison between the three compounds shows that the MCXD amplitude is, within the experimental accuracy, proportional to the Co concentration (MCXD amplitude $\approx 0.06\%$ per Co atom). In earlier studies Brouha *et al.*[18] have shown that for high Co concentrations ($x \leq 0.4$) the $La(Ni_xCo_{1-x})_5$ magnetic behavior can be described in terms of a rigid band model. In this model the saturation moment per Co/Ni atom decreases by $1.1\mu_B$ replacing a Co by a Ni atom. Present results appear in good agreement with this description and therefore confirm experimentally that the La 5d band polarization is proportional to the 3d moment. It also shows that the MCXD signal can be directly correlated to the polarization $\Delta\rho$ of the La 5d band according to Eq. (2) since M is spin independent.

B. The role of the 4f-5d exchange: $GdNi_5$ and $TbNi_5$

In $GdNi_5$ and $TbNi_5$ the Stoner criterion is not satisfied for Ni and the polarization of the 5d band derives exclusively from the direct 4f-5d exchange. The MCXD signal at the Gd and Tb $L_{2,3}$ edges is related to the presence of a 5d moment ($\Delta\rho$) and to the presence of a spin-dependent spectral weight [ΔM in Eq. (2)].

The MCXD spectra of $GdNi_5$ and $TbNi_5$ recorded at the $L_{2,3}$ edges of Gd and Tb at 10 K are shown in Figs. 2 and 3. The L_3 (L_2) signal consists of strong positive (negative) peak due to dipolar transitions to the 5d states. The peak maxima are observed at around $E-E_0 \approx 1$ eV and the width at half maximum is 6 eV. The features at around 30 eV in the MCXD spectra reflect the arrangement of the magnetic atoms around the probed RE site

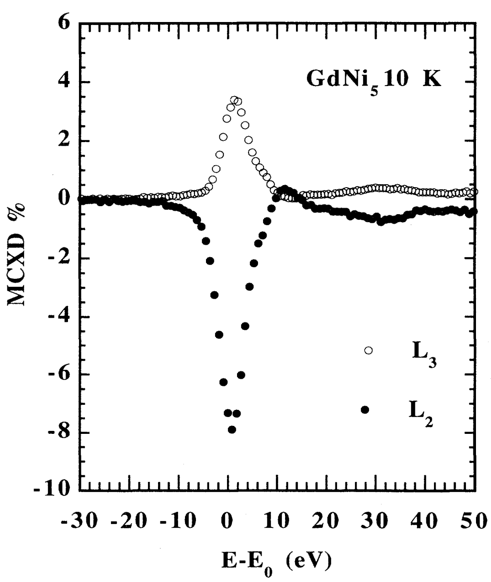

FIG. 2. MCXD signal at the $L_{2,3}$ edges of Gd in $GdNi_5$ measured at $T=10$ K.

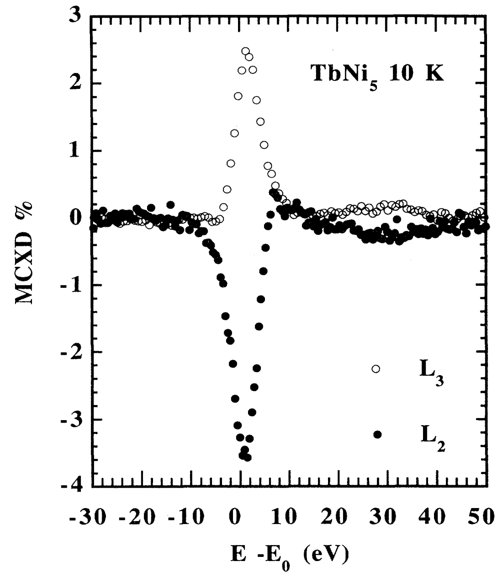

FIG. 3. MCXD signal measured at $T=10$ K at the $L_{2,3}$ edges of Tb in $TbNi_5$.

[it is the beginning of the so-called "magnetic" extended x-ray-absorption fine structure (EXAFS)].

The shape and the sign of the MCXD spectra are coherent with those previously found for other Gd and Tb intermetallics.[9,11,12] A peculiarity of $GdNi_5$ with respect to other Gd intermetallic compounds is the absence in the L_3-edge MCXD spectrum of the negative preedge structure, assigned in Ref. 13, to quadrupolar ($E2$) transitions to 4f states. The spectrum is however asymmetric, suggesting that a weak negative contribution may be overlapped on the low-energy side with the larger positive structure due to dipolar ($E1$) transitions. This point will be discussed in the next subsection.

In $GdNi_5$ and $TbNi_5$, the $L_{2,3}$-edge MCXD amplitudes have the same thermal variation as the bulk magnetization. In Fig. 4, we show the thermal evolution of the L_3-edge MCXD signal and the magnetization in $TbNi_5$. The MCXD signal is normalized to the magnetization at 10 K. Such a behavior is consistent with a 5p polarization driven only by the local 4f-5d exchange.

In order to compare the Gd and Tb signals it is necessary to take into account the effects of the magnetocrystalline anisotropy in $TbNi_5$. As the dipolar circular dichroism is proportional to the projection of the local magnetization on the photon momentum, in a powdered sample the correction can be roughly made multiplying the $TbNi_5$ amplitudes by $\frac{3}{2}$. We obtain that in $GdNi_5$ and $TbNi_5$ the $L_{2,3}$ MCXD signals have the same amplitudes $\approx 3.5\%$.

According to Eq. (2) the dichroic signal for dipolar transitions can be reduced to $\mu_c \approx \Delta M/M + \Delta\rho/\rho$. The first term measures the difference between radial matrix elements and can be of the order of 0.2–0.3 for Gd or Tb.[15] The second term is negative and can be of the order of $0.6/9 \approx 0.07$ (according to band-structure calculations,[5] the 5d moment of Gd and Tb in RFe_2 compounds

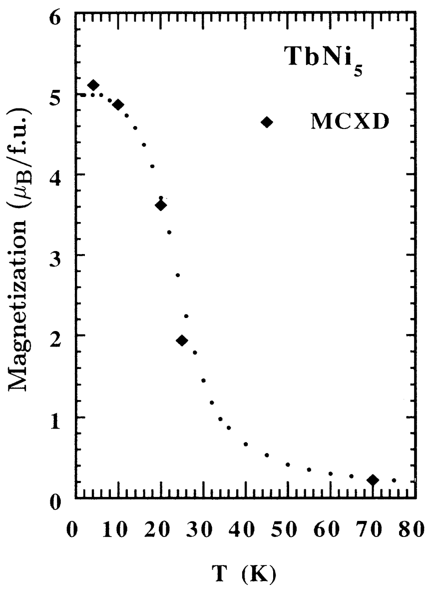

FIG. 4. The thermal variation of the Tb L_3-edge MCXD signal in $TbNi_5$ is compared with the macroscopic magnetization. The MCXD signal is normalized to the magnetization at 10 K.

is expected to be of the order of $0.5\mu_B$ and the number of holes in the 5*d* band of the order of 9). It is clear that the term induced by the spin dependence of M dominates the signal. In agreement with this estimation, a study of Gd-based compounds by Giorgetti *et al.*[9] and the present work show that the L_3-edge MCXD amplitude is of the same order of magnitude ($\approx 3\%$) for compounds as different as $GdFe_2$, Gd_2Fe_{17}, $GdFe_3$, $GdCo_2$, and $GdNi_5$.

The similar amplitudes of the MCXD signals in $GdNi_5$ and $TbNi_5$ can be explained using the same arguments. In the $R Fe_2$ series, Brooks *et al.*[5] calculate a 5*d* moment at the RE site decreasing from Gd to Yb. This may also be understood as a decrease of the local 4*f*-5*d* exchange interaction going from Gd to heavier rare earths. The same behavior is expected in the RNi_5 series. Then both $\rho\Delta M/M$ and $M\Delta\rho/\rho$ scale with the 4*f* filling and are expected to be larger in $GdNi_5$ with respect to $TbNi_5$. The two effects having opposite signs they apparently compensate to give similar MCXD amplitudes for the two compounds. All these results point out the delicate balance between the radial matrix $\Delta M/M$ and the polarization $\Delta\rho/\rho$ terms in the MCXD amplitude.

The L_2 to L_3 amplitude ratio, $R(L_2/L_3)$, is close to -2 in $GdNi_5$ but largely deviates from -2 for $TbNi_5$ [$R(L_2/L_3)\approx -1.4$]. The qualitative application of the first sum rule would indicate a larger 5*d* orbital moment for the Tb compound. We found $5\times10^{-4}\mu_B$ for $GdNi_5$ and about $1\times10^{-3}\mu_B$ for $TbNi_5$.

Despite the fact that Ni does not carry a magnetic moment, the significant MCXD signal measured at the Ni *K* edge on both $GdNi_5$ and $TbNi_5$ indicates that the 4*p* bands of Ni are polarized. The signals show a double-peaked structure similar in magnitude and shape to the Fe *K* edge observed in $GdFe_2$,[9,15] but opposite in sign. The double-peaked *K*-edge MCXD spectra of pure 3*d* metals are currently related to the weak ferromagnetic behavior of the 3*d* band with which the 4*p* band is hybridized. In the present case the polarization of the 4*p* band comes exclusively from the RE 5*d* band, since the 3*d* band does not carry a magnetic moment. The shape of Ni *K*-edge spectra is consistent with the weak ferromagnetic behavior of the 5*d* band and the sign with an antiparallel alignment between 4*p* and 5*d* moments.

C. The relative roles of 3*d*-5*d* hybridization and 4*f*-5*d* exchange: $Tb(Ni_xCo_{1-x})_5$ compounds

The MCXD signals of $Tb(Ni_xCo_{1-x})_5$ solid solutions are the most complex among the compounds examined in this work, since the polarization of the Tb 5*d* band is related to both 3*d*-5*d* hybridization and 4*f*-5*d* direct exchange.

The L_3-edge MCXD spectra measured at 10 K for $Tb(Ni_xCo_{1-x})_5$ solutions with $x=0.6$, 0.4, and 0.2 are presented in Fig. 5 and compared with that of $TbNi_5$ at the same temperature. All the spectra present a main positive peak, asymmetric on the low-energy side due to a weak negative structure, attributed to $2p\rightarrow 4f$ quadrupolar transitions. This structure becomes more well marked when the Co concentration increases.

For $Tb(Ni_xCo_{1-x})_5$ solutions, the observed main peak amplitudes are 1 order of magnitude larger than those observed in the $La(Ni_xCo_{1-x})_5$ solutions. Their evolution as a function of Co concentration is opposite in the two series of compounds. In Table II are reported the amplitudes observed at the L_3 edge in Tb and La solutions (column 1). In column 2, the amplitudes have been corrected with the ratio $M(T,0.6\ \mathrm{T})/M_S(T)$, where $M_S(T)$ is the spontaneous magnetic moment deduced from magnetization measurements. As the anisotropy is not very different in $TbNi_5$ and in the Tb solutions, the

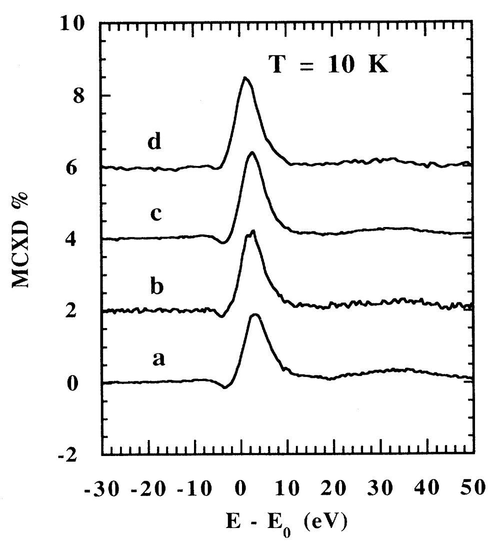

FIG. 5. MCXD spectra observed at the Tb L_3 edge in (a) $Tb(Ni_{0.2}Co_{0.8})_5$, (b) $Tb(Ni_{0.4}Co_{0.6})_5$, (c) $Tb(Ni_{0.6}Co_{0.4})_5$, and (d) $TbNi_5$ at $T=10$ K. The MCXD spectra have been offset by 2.

MCXD amplitudes could be directly compared. However, no direct comparison is possible between the amplitudes in La and Tb solutions. Table II points out the opposite evolutions with Co concentration. Going from $TbNi_5$ to Co-rich solutions, we expect a progressive increase of the 5*d* polarization. Experimentally, the L_3-edge signal is maximum for $TbNi_5$ (2.4%) and decreases down to 1.8% for $Tb(Ni_{0.2}Co_{0.8})_5$. This behavior can be explained according to Eq. (2). In Tb solutions $\Delta M/M$ dominates and should not change much with Co content. On the other hand, $\Delta\rho/\rho$ increases with Co content and since it is negative it leads to a global decrease of the MCXD signal.

In summary, the different behavior of the MCXD spectra for La and Tb solid solutions as a function of Co content is related to the 4*f*-5*d* exchange coupling which is responsible for a spin-dependent spectral weight. This interaction is responsible for the opposite signs of the *L*-edge MCXD spectra for magnetic and nonmagnetic RE (i.e., Tb vs La) and causes the amplitude of the spectra for magnetic RE to become larger for less polarized 5*d* bands.

For all the Tb compounds, a negative preedge feature, normally attributed to quadrupolar (E_2) transitions,[13] is clearly observed in all the MCXD spectra. The fact that this feature becomes more well marked as the Co concentration increases may be interpreted in terms of the decrease of the positive dipolar contribution to the MCXD signal. The unexpected absence of a preedge feature in the spectrum of $GdNi_5$ (note that all the Gd compounds studied so far present a negative preedge feature) may also be explained similarly, by the fact that the negative $E2$ contribution has collapsed into the much stronger $E1$ structure, leaving however an asymmetry at the low-energy side of the spectrum. According to Wang *et al.*,[13] the position of the E_2 peak relative to the Fermi level depends only on the rare earth and ranges almost linearly from −3.4 to −5.35 eV going from Gd to Tm. The larger separation between E_2 and E_1 in Tb compounds can explain the fact that the preedge feature becomes more pronounced in $TbNi_5$ with respect to $GdNi_5$. We attribute the difference in balance of quadrupolar and dipolar contributions in $GdNi_5$ and $GdFe_2$ spectra to the variation of $\Delta\rho/\rho$ due to the different 3*d*-5*d* hybridization in the two atomic environments.

Before concluding let us discuss the thermal variation of the Tb L_3-edge MCXD signal in $Tb(Ni_{0.4}Co_{0.6})_5$. The L_3-edge MCXD spectra are shown in Fig. 6. The amplitude of the signal decreases slowly as the temperature increases. It vanishes at about 270 K, the compensation temperature, and changes its sign for higher temperatures. Figure 7 shows that the MCXD signal decreases with temperature much more slowly than the net magnetization. This difference is related to the selectivity of MCXD which probes only the RE 5*d* band.

At low temperature the Tb moment exceeds that of the five Co atoms. The localized 4*f* moment follows a Boltzmann statistics and decreases with temperature faster than the 3*d* moment. At the compensation temperature, the magnetization of the Tb sublattice equals that of the TM sublattice. The net magnetization and therefore

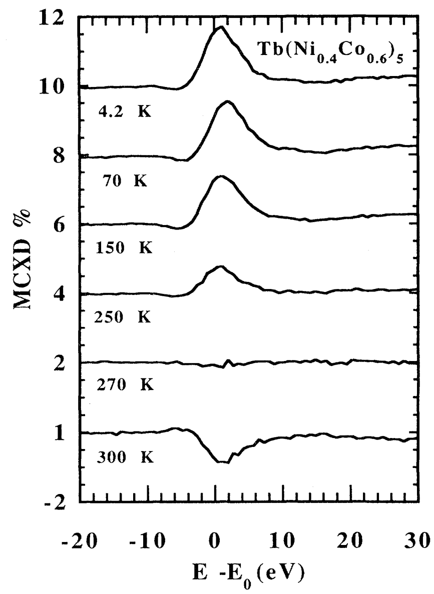

FIG. 6. Thermal evolution of the MCXD spectra in $Tb(Ni_{0.4}Co_{0.6})_5$ at the Tb L_3 edge. For clarity the spectra have been offset by 2.

the MCXD signal vanish. Beyond this temperature the magnetization of the TM sublattice becomes larger. In the presence of an external magnetic field **B**, the net magnetization, **M**, tends to align parallel to it. The Tb moments are therefore parallel to **B** for $T < T_{comp}$ and antiparallel for $T > T_{comp}$. This explains the opposite signs of the Tb L_3-edge MCXD signal on either sides of T_{comp}. The main difference between the thermal dependence of **M** and the MCXD spectra is the fact that the latter mainly reflects the temperature dependence of the 4*f* moment *via* the spin-dependent matrix elements. On the other hand, the net magnetization and its thermal evolution result from the contributions of both Tb and Co moments.

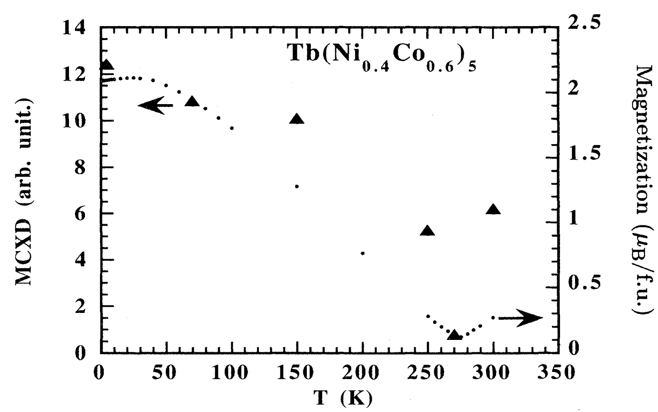

FIG. 7. Comparison between the thermal variation of the Tb L_3-edge MCXD amplitude and the bulk magnetization in $Tb(Ni_{0.4}Co_{0.6})_5$.

IV. CONCLUSIONS

This study of $R(\mathrm{Ni}_x\mathrm{Co}_{1-x})_5$ compounds (R =La, Gd, and Tb) has allowed us to investigate the effects of $3d$-$5d$ and $4f$-$5d$ exchanges on the RE $L_{2,3}$-edge MCXD spectra. In La compounds, where the $5p$ polarization is induced by the hybridization with the $3d$ band of magnetic TM, the signal can be explained using a one-particle model for the absorption process. When the $4f$-$5d$ exchange intervenes, like in the Gd or Tb compounds, its effects on the MCXD sign and amplitude are very important. The local $4f$-$5d$ exchange gives rise to the $5d$ polarization but also to the difference in the radial matrix elements for spin $\uparrow$ and spin $\downarrow$ transitions. A description of $L_{2,3}$-edge MCXD taking into account the spin dependence of the radial matrix elements appears to explain qualitatively our results and let suppose that the main contribution to the MCXD amplitude comes from the spin dependence of these radial matrix elements.

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