

Multielectron excitations in rare-earth compounds revealed by magnetic circular x-ray dichroism

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This paper reports experimental evidence of multielectron excitations in magnetic circular x-ray dichroism (MCXD) spectra, measured at the $L_{I,II,III}$ edges of rare earths (RE) in several RE-transition-metal (Fe, Co) compounds. These multielectron features involve transitions from the $2p$ and $4d$ levels and exhibit a very strong magnetic enhancement compared to normal MCXD.

Since the electric-dipole operator, which causes x-ray absorption, is a one-electron operator, multiple-electron excitations (MEE) in x-ray-absorption processes epitomize the complicated many-body effects that occur in a core-excited atom. In particular, the shakeup and shakeoff satellites indicate the degree of relaxation of the ion in the presence of a core hole. This information about relaxation is essential when x-ray-absorption spectra (XAS) are calculated in the multiple-scattering as well as multiplet approaches. Because of this fundamental interest, many detailed studies were carried out on MEE in x-ray-absorption spectra of atoms (see Ref. 1 and references therein). In the molecular or solid state, MEE were observed also,²⁻⁹ but analysis of experimental data is difficult because multielectron satellites are very small (typically 1% of the edge jump) as compared to the structural features due to photoelectron scattering (x-ray-absorption fine structure).

Magnetic circular x-ray dichroism (MCXD) reflects the fact that the absorption cross section of magnetic samples is different for left- and right-circularly polarized x rays. Recently, it has been shown that MCXD at the L edges of rare earths is a promising tool to study local magnetic properties of ions in ferromagnetic and ferrimagnetic compounds.¹⁰⁻¹² The order of magnitude of MCXD is a few percent of the absorption edge jump.

A priori, since MEE and MCXD are so small, the observation of MEE structures in MCXD spectra seems to be unlikely. However, we show in this paper that magnetic circular x-ray dichroism can be used as a powerful technique to study MEE. MCXD spectra were measured at the L edges of rare earths in a fair sample of intermetallic compounds. In some of these spectra, MEE involving the

$4d$ shell is observed as a structure, lying on a flat background, that can be as large as the edge structure. The tremendous increase in sensitivity to multielectron processes is made clear by the fact that MCXD spectra exhibit MEE features for nearly all light rare earths, whereas they were known only for La and Ce in standard XAS of carefully chosen samples.

MCXD spectra were recorded at the $D11$ station at LURE, using a dispersive optics and a position-sensitive detector. The data collection is described in Ref. 12. All the compounds studied are ferromagnetic or ferrimagnetic and thus suitable for MCXD experiments.

MCXD was measured at the L_I edge of Nd in Nd_2Co_{17} , at the L_{II} edge of Eu in EuO and $EuPd_2$, and at the L_{II} and L_{III} edges of rare earths in $LaCo_5$, $CeFe_2$, $CeFe_2H_{3.8}$, $CeRu_2Ge_2$, Pr_2Co_{17} , Nd_2Fe_{17} , $SmFe_2$, $GdFe_2$, $GdFe_3$, Gd_6Fe_{23} , Gd_2Fe_{17} , pure Gd, TbFe₂, DyFe₂, HoFe₂, ErFe₂, TmFe₂, and LuFe₂. All the compounds characterized by a Curie temperature much greater than room temperature were measured at room temperature in a magnetic field of 1 T. The other compounds were measured at 4.2 K in a magnetic field of 0.6 T.

All the MCXD spectra plotted in this paper represent the quantity $\mu^- - \mu^+$, where μ^- (μ^+) is the absorption coefficient with right-circularly polarized (helicity $-\hbar$) x rays and the magnetic field antiparallel (parallel) to the photon wave vector. μ^+ and μ^- are normalized to zero before the edge and to 1 far beyond the edge. The energy origin (E_0) was taken at the inflection point of the white line. The rate of circular polarization was estimated to be 80% from measurement of the rate of linear polarization.

The existence of magnetic MEE at the L edges of Ce, Pr, Nd, Sm, and Gd in intermetallic compounds is clearly

demonstrated in Fig. 1. The main structure at the edge is the normal MCXD, which will be discussed in a forthcoming publication,¹³ and the MEE features lie between 110 and 160 eV above the edge. For La and Tb the presence of a MEE structure is dubious, for the other rare earths, no MEE signal could be detected at all. Compared to the main magnetic structure at the edge, the MEE signal varies between 10% (Gd) and 100% (Ce) at

the L_{III} edges [Fig. 1(a)] and is broadly constant (10%) at the L_{II} edges [Fig. 1(c)]. Therefore, the amplitude of the MEE structure is not proportional to the amplitude of the edge peak in these MCXD spectra. On an absolute scale, the magnetic MEE amounts from 0.1% to 0.5% of the edge jump [Figs. 1(b) and 1(d)].

To investigate the variation of magnetic MEE with crystallographic structure, MCXD was measured at the

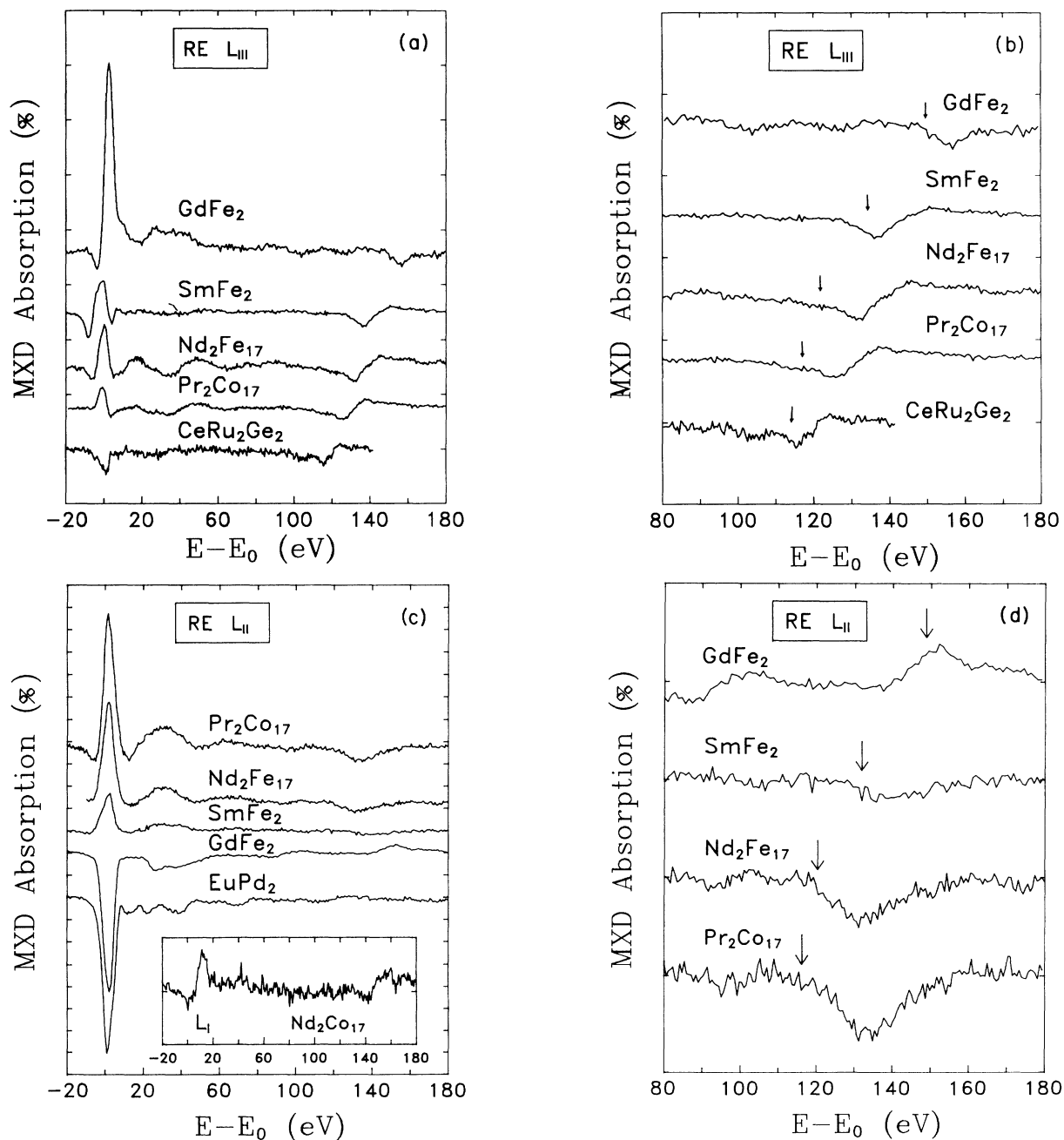


FIG. 1. One MCXD absorption unit equals 1% of the edge jump. (a) MCXD spectrum at the RE L_{III} edge in $GdFe_2$, $SmFe_2$, Nd_2Fe_{17} , Pr_2Co_{17} , and $CeRu_2Ge_2$ compounds. (b) Zoom in of the MEE energy range of (a). The vertical arrows mark the energy of the $(Z+1)4d$ core levels. (c) MCXD spectrum at the RE L_{II} edge in $GdFe_2$, $SmFe_2$, Nd_2Fe_{17} , Pr_2Co_{17} , and $EuPd_2$ compounds. Inset: $Nd L_I$ edge in Nd_2Co_{17} ($\times 2$). (d) Zoom in of the MEE energy range of (c). The vertical arrows mark the energy of the $(Z+1)4d$ core levels.

L_{III} edge of Gd in $GdFe_2$, $GdFe_3$, Gd_6Fe_{23} , Gd_2Fe_{17} , and pure Gd (Fig. 2). It is seen that the shape of the MEE feature is constant in this series, except for a change of sign in Gd_2Fe_{17} , due to the fact that the magnetic moment of the 17 iron atoms is now larger than the moment of the two gadolinium atoms. The MEE peak decreases with increasing iron concentration. Again, there is no clear connection between the amplitude of the main structure and that of the MEE peak in Fig. 2. Similar but weaker effects were observed at the L_{II} edge.

To study the dependence of magnetic MEE on the electronic structure of the rare earth, we measured MCXD of $EuPd_2$ and $GdFe_2$. These two compounds have the same crystallographic structure, the rare earths have the same electronic structure ($4f^7$), and the main structure of their MCXD spectra is identical [Fig. 1(c)]. However, the magnetic MEE are clearly different in $EuPd_2$ and $GdFe_2$, since no MEE peak is observed at the $4d$ binding energy of Eu [Fig. 1(c)].

The overall spectral shape of MEE is the same as the main structure of MCXD spectra at the L_{II} and L_{III} edges, although it is broader and in phase opposition with this main structure (except for $CeRu_2Ge_2$). MCXD is also observed at the L_I edge of Nd in Nd_2Co_{17} [inset of Fig. 1(c)], and there the MEE feature is in phase with the main structure at the edge.

Since a detailed interpretation of MCXD spectra is not yet available, a full understanding of their MEE structures is out of the question. However, a number of unambiguous conclusions can be drawn from our experimental results.

(i) $4d$ electrons are involved in the structures we attribute to MEE effects. This can be seen from Figs. 1(b)

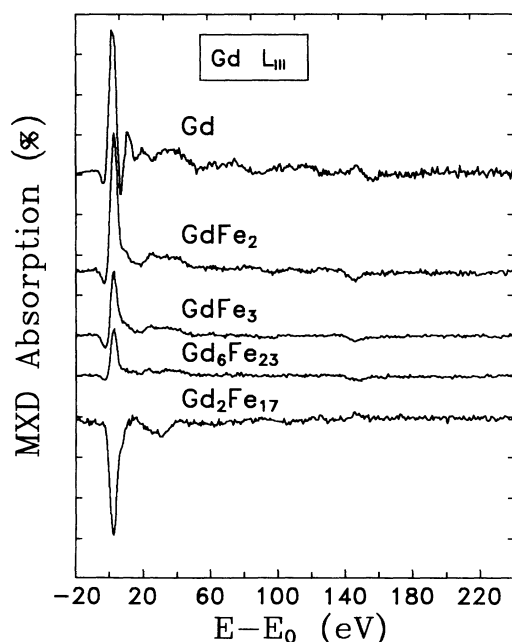


FIG. 2. MCXL spectrum at the Gd L_{III} edge in Gd, $GdFe_2$, $GdFe_3$, Gd_6Fe_{23} , and Gd_2Fe_{17} compounds. One MCXD absorption unit equals 1% of the edge jump.

and 1(d) where, for each rare earth, a vertical arrow marks the energy of the $M_{IV,V}$ edge of the $Z+1$ atom (the $Z+1$ nucleus mimics the $2p$ core hole). Moreover, these structures cannot be due to scattering effects, because they occur at energies where the contribution of photoelectron scattering is negligible.

(ii) The MEE structures are due to electric dipole transitions. Within our experimental accuracy, the influence of electric quadrupole transitions was ruled out by checking that, at the L_{II} edge of Sm in $SmFe_2$, the amplitude of the MEE signal is proportional to the cosine of the angle between the rare-earth magnetic moment and the x-ray wave vector.¹⁴

(iii) The magnetic contribution to the MEE peaks is very large. The amplitude of MEE structures observed in normal L -edge spectra of Ce usually represents 1% of the edge jump.⁵⁻⁷ For heavier rare earths, this amplitude is probably still smaller, since it was not observed yet. From the MCXD spectra of Fig. 1, the amplitude of the magnetic contribution to MEE peaks is broadly 0.3%. Therefore, $\approx 30\%$ of the MEE structure is of magnetic origin. Comparing this with the edge structure shows that the magnetic polarization of the MEE peak is enhanced by a factor of 10–25.

MEE structures in core hole spectra are usually considered to arise from a shakeup process. According to this model, the one-electron orbitals relax because of the presence of a core hole in the final state and, because of this relaxation, the final-state orbitals are no longer orthogonal to the initial-state orbitals. Within this framework, MEE features in L -edge spectra are described as follows.⁶ For a rare earth with initial state $2p^64d^{10}4f^n(5d6s)^3$, the normal configuration for the final state is $2p^54d^{10}4f^n(5d6s)^4$ at the edge and $2p^54d^{10}4f^n(5d6s)^3ed$ further. The MEE structures are then transitions towards the final state $2p^54d^94f^n(5d6s)^5$ corresponding to the monopole $4d \rightarrow 5d$ transition allowed by the nonorthogonality of initial-state $4d$ and final-state $5d$ orbitals. The shakeup picture explains that the magnetic MEE structures are at the same energy as the normal MEE for cerium. It can also help understanding further characteristics of the magnetic MEE. First, because of the presence of two open shells ($4d^94f^n$), there is a large number of multiplets in the final state, which makes the MEE structures very broad. This explains why, in standard spectra, MEE was only observed for La and Ce for which multiplet broadening is minimum. Second, the weakness of MEE effects in heavy rare earths is reasonable since the overlap between the $4d$ orbital in the initial state and the $5d$ orbital in the final state decreases for larger Z , due to the larger binding energy of the $4d$ shell. Third, the overall identity of spectral shape of the magnetic MEE and the main structure of MCXD can be understood since the one-electron transition is the same. Finally, the existence of MEE effects at the L_I edge [Fig. 1(c)] is also consistent with the shakeup interpretation.

However, as noticed in Ref. 1, the shakeup picture is not completely satisfactory. In the present case, it would be difficult to understand the large magnetic polarization of MEE structures with this model. On the other hand, the study of $4d \rightarrow 4f$ giant resonances has shown that ex-

citation spectra of rare earths involve strongly collective excitations due to the presence of localized $4f$ levels.¹⁵ In L -edge spectra, direct $4d \rightarrow 4f$ transitions are parity forbidden, but the importance of the magnetic contribution is a sign that the $4f$ shell is probably involved in a full explanation of MEE structures.

Clearly resolved multielectron structures were shown to exist in MCXD spectra of rare earths. These structures are much more clearly resolved than the MEE observed in normal spectra, mainly because the MEE signal lies on a flat background. Magnetic MEE features provide a tool to investigate the interplay between many-body effects and magnetism which is unique, since such magnetic effects cannot be observed in atoms or molecules. Although many aspects of MEE structures in MCXD are compatible with the standard shakeup approach, some fascinating

problems are left open, such as their strong magnetic enhancement. These many-body magnetic effects, together with other features observed in MCXD of rare-earth compounds,^{13,16} will probably lead to a better understanding of the magnetic terms of the many-body Hamiltonian, such as spin-other-orbit interaction, which are usually neglected.

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- ¹K. Zhang, E. A. Stern, J. J. Rehr, and F. Ellis, *Phys. Rev. B* **44**, 2030 (1991).
²H. W. Schnopper, *Phys. Rev.* **131**, 2558 (1963).
³E. A. Stern, *Phys. Rev. Lett.* **49**, 1353 (1982).
⁴A. Filippini, E. Bernieri, and S. Mobilio, *Phys. Rev. B* **38**, 3298 (1988).
⁵S. Benazeth, M. H. Tuilier, and M. Guittard, *Physica B* **158**, 39 (1989).
⁶J. Chaboy, J. Garcia, A. Marcelli, and M. F. Ruiz-Lopez, *Chem. Phys. Lett.* **174**, 389 (1990).
⁷V. Briois, Ph.D. thesis, Parix XI University, 1991 (unpublished).
⁸A. Singh, S. J. Gurman, and E. A. Davis, *J. Non-Cryst. Solids* **110**, 249 (1989).
⁹A. Bianconi, J. Garcia, M. Benfatto, A. Marcelli, C. R. Natoli, and M. F. Ruiz-López, *Phys. Rev. B* **43**, 6885 (1991).

- ¹⁰G. Schütz, R. Frahm, P. Mautner, R. Wienke, W. Wagner, W. Wilhelm, and P. Kienle, *Phys. Rev. Lett.* **62**, 2620 (1989).
¹¹G. Schütz and R. Wienke, *Hyperfine Interact.* **50**, 457 (1989).
¹²F. Baudelet, E. Dartyge, A. Fontaine, Ch. Brouder, G. Krill, J.-P. Kappler, and M. Picuch, *Phys. Rev. B* **43**, 5857 (1991).
¹³E. Dartyge, F. Baudelet, A. Fontaine, Ch. Giorgetti, S. Pizzini, J.-P. Kappler, G. Krill, and Ch. Brouder (unpublished).
¹⁴P. Carra and M. Altarelli, *Phys. Rev. Lett.* **64**, 1286 (1990).
¹⁵*Giant Resonances in Atoms, Molecules and Solids*, edited by J. P. Connerade, J. M. Esteva, and R. C. Karnatak, NATO Advanced Study Institutes Ser. B, Vol. 151 (Plenum, New York, 1987).
¹⁶F. Baudelet, Ch. Brouder, E. Dartyge, A. Fontaine, J.-P. Kappler, and G. Krill, in *Proceedings of the International Conference on Magnetism, Edinburgh, 1991*, edited by S. B. Palmer (North-Holland, Amsterdam, in press).