

## Observation of magnetic circular dichroism in resonant inelastic x-ray scattering at the $L_3$ edge of gadolinium metal

M. H. Krisch, F. Sette, U. Bergmann, C. Masciovecchio, R. Verbeni, and J. Goulon  
*European Synchrotron Radiation Facility, Boîte Postale 220, F-38043 Grenoble Cedex, France*

W. Caliebe and C. C. Kao  
*National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York 11973*

(Received 12 September 1996)

Magnetic circular dichroism is observed in inelastic x-ray scattering from  $d$  core electrons in magnetically aligned gadolinium at incident photon energies resonant with the Gd  $2p_{3/2}$  excitations. The dichroism is dominated by the magnetic interactions between the valence  $4f$  electrons and the final state  $d$  core hole. Unlike photoabsorption spectroscopy, but similar to core photoelectron spectroscopy, this method allows one to probe electron-correlation effects in the valence ground-state population. [S0163-1829(96)52642-1]

The measurement of dichroic effects in the x-ray region in ferromagnetic and ferrimagnetic materials has been largely motivated by the site and chemical selectivity of core spectroscopies. X-ray magnetic circular dichroism (XMCD) in core photoabsorption has been related to the spin-dependent band structure, and to the exchange, spin-orbit and magnetic correlation effects among valence electrons.<sup>1,2</sup> Circular dichroism has also been observed in the  $L\alpha$ -valence emission lines of ferromagnetic transition metals.<sup>3,4</sup> This technique can give information on the spin-dependent occupied density of states (DOS), and therefore is complementary to absorption XMCD, which probes the spin-dependent unoccupied DOS. Unfortunately, however, in most cases a simple one-electron picture does not hold, and the spectra reflect the complicated multiplet structure between initial, intermediate, and final states, weighted by the selection rules arising from the transition operators.<sup>5</sup> It is therefore believed that the interpretation of the spectra always requires relevant calculations, further complicated by the fact that in photoabsorption and valence emission spectroscopies, the number of valence electrons is different in the ground and final states. A different approach is based on the excitation of a core electron into a free electron state in the continuum, without modifying the number of valence electrons. Under these circumstances, one can study the multiplet structure arising from the interaction between the valence electrons and a core incomplete shell. The associated circular dichroism, determined by the dominant magnetic character of these multiplets, will give information on the magnetic properties of the different electronic configurations. These dichroism studies can be performed by core x-ray photoelectron spectroscopy (XPS) excited with circular polarized light in magnetically aligned samples, as was shown for the iron  $2p$  core level,<sup>6</sup> other  $3d$  transition metals and related oxides,<sup>7-9</sup> and the rare earths.<sup>10</sup>

In this paper we show that resonant inelastic x-ray scattering (RIXS) excited with circular polarized x rays can provide an alternative method to the dichroism in XPS data. We studied magnetically aligned gadolinium metal as a prototypical example, and investigated excitations which are characterized by intermediate states with a hole in the Gd  $2p_{3/2}$  core level, and final states with a hole either in the  $3d_{5/2,3/2}$

shell ( $L\alpha_{1,2}$  emission), or in the  $4d_{5/2,3/2}$  shell ( $L\beta_{2,15}$  emission) and an electron in the continuum. We show that the dominant magnetic character of the multiplet features constituting the  $L\alpha_{1,2}$  and  $L\beta_{2,15}$  emission lines is derived directly from the circular dichroism of these features, without requiring a specific multiplet calculation. Our results, which are different for the  $L\alpha_{1,2}$  and  $L\beta_{2,15}$  lines, due to the different relative strengths of exchange and spin-orbit interactions, compare well with similar limit cases measured in XPS (Refs. 6 and 11) and RIXS with linear polarized x-rays.<sup>12,13</sup> Finally, tuning the incident photon energy from values well above the  $L_3$  edge to values resonant with the gadolinium  $2p_{3/2}$ - $4f$  and  $2p_{3/2}$ - $5d$  transitions, we relate the modification of the circular dichroism spectra to the changes in the ground state configuration of the  $4f$  and  $5d$  orbitals. These modifications can be directly associated with the dichroism obtained in photoabsorption measurements.

The experiment was performed on beamline BL21-ID16 at the European Synchrotron Radiation Facility using a helical undulator consisting of two magnetic arrays, each one producing a horizontal or a vertical periodic magnetic field.<sup>14</sup> The polarization was chosen changing the relative phase between the two arrays, and inverted by a shift of half the magnetic period. The calculated circular polarization rate was 98% in the utilized energy range. The x rays were monochromatized by a cryogenically cooled silicon (111) double crystal to  $\approx 1$  eV bandwidth. The beam was sized to 0.3 mm horizontally and 2 mm vertically, and the photon flux on the sample was typically  $5 \times 10^{10}$  photon/s. The scattered radiation was analyzed at  $90^\circ$  scattering angle in the horizontal plane by a Rowland circle crystal spectrometer with a radius of 1 m. The overall experimental resolution was 1.5 eV. The sample was a gadolinium metal foil 25  $\mu\text{m}$  thick, kept in vacuum at 0  $^\circ\text{C}$ , and magnetized by a field of  $\approx 0.3$  T along its surface. The typical recording time for one spectrum was  $\approx 40$  min and up to ten spectra were added together. Measurements with a nonmagnetized sample and opposite photon helicities, and with the sample above the Curie temperature and opposite magnetic fields, were also made to exclude artifacts responsible for spurious intensity differences.

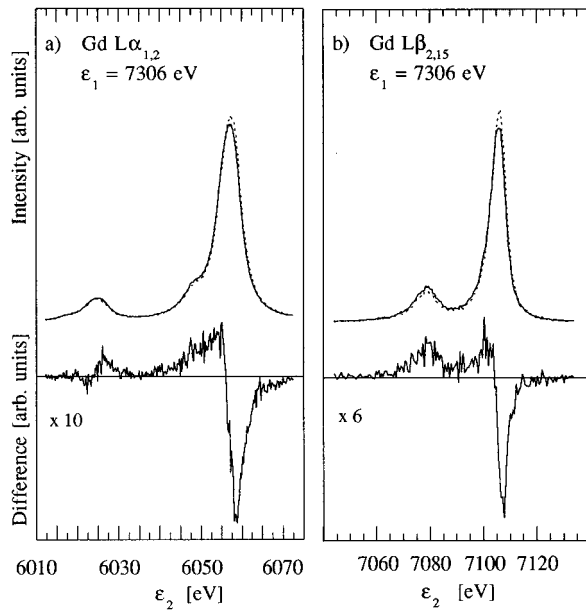


FIG. 1. Resonant inelastic x-ray scattering spectra of Gd metal for opposite circular polarization at the indicated photon energy  $\epsilon_1$ . The spectra were normalized to the incident photon beam intensity, and taken with antiparallel (solid line) and parallel (dashed line) orientations between photon helicity and sample magnetization. The corresponding dichroic signals, obtained from the difference of the two top spectra (antiparallel minus parallel orientations), are displayed in the bottom panel after multiplication by the indicated factor: (a)  $L\alpha_1$  and  $L\alpha_2$  emission lines and (b)  $L\beta_{2,15}$  emission line.

The top of Figs. 1(a) and 1(b) shows resonant inelastic scattering spectra taken with opposite photon helicities ( $I^+$  and  $I^-$ ) at the excitation energy  $\epsilon_1 = 7306$  eV, a value well above the  $L_3$  absorption edge located at 7243 eV. The  $L\alpha_{1,2}$  spectra are displayed in Fig. 1(a), and the  $L\beta_{2,15}$  spectra in Fig. 1(b), as a function of the scattered photon energy  $\epsilon_2$ . The spectra are normalized to the incident intensity and corrected for self-absorption effects. The corresponding dichroism spectra, obtained from the difference between the top spectra, are displayed in the bottom of Figs. 1(a) and 1(b), and show modulations of  $\Delta I/I = 2(I^+ - I^-)/(I^+ + I^-)$  up to  $\approx 15\%$ .  $\Delta I/I$  goes up to 25% when corrected for the geometrical factor  $1/\cos\theta$  ( $\theta = 30^\circ$  is the angle between the incident photons and magnetic field directions), the incomplete photon polarization, and the depolarization induced by the two Bragg reflections in the monochromator.

The emission spectra are characterized by two main multiplet families, which are known to have a very different origin. In the case of the  $L\alpha_{1,2}$  emission spectrum, the average separation between the two main features is  $\approx 32$  eV, and corresponds to the spin-orbit splitting of the  $3d$  level, while the fine structure in each line arises from the magnetic and electrostatic interactions between the incomplete  $4f$  and  $3d_{5/2}$  ( $L\alpha_1$  at 6057 eV) or  $3d_{3/2}$  ( $L\alpha_2$  at 6025 eV) shells. On the contrary, the two main features in the  $L\beta_{2,15}$  emission spectrum are not due to the spin-orbit interaction in the  $4d$  shell, which is less than 0.2 eV. They are rather caused by magnetic and electrostatic interactions between the  $4d$  and  $4f$  electrons, much stronger here because both shells have

the same principal quantum number,  $n = 4$ . In particular, the two lines of Fig. 1(b), separated by  $\approx 27$  eV, are due to configurations with the spin of the  $4d$  electrons either mostly parallel (line at 7106 eV) or antiparallel (line at 7079 eV) to the spin of the  $4f$  electrons. Consequently, the ejected photoelectron has dominantly spin-up character for the line at 7079 eV and spin-down character for the line at 7106 eV.

This qualitative analysis of the emission spectra of Fig. 1 is consistent with atomic calculations in similar systems.<sup>12,13</sup> This kind of calculations typically requires the knowledge of the occupation of the valence shell in the ground and excited states, and the local symmetry and chemical environment of the considered atom. This information, however, is not always available. On the contrary, the determination of the circular dichroism, as is shown in the following, can give directly the dominant magnetic character of each multiplets family, thus providing an experimental method independent of detailed calculations.

In the case of the  $L\alpha_{1,2}$  emission lines, where the spin-orbit interaction dominates over the electrostatic and magnetic interactions between the  $3d$  and the  $4f$  electrons, we observe a derivative-like dichroic signal for both lines. A negative dichroic feature at the high energy side of the  $L\alpha_1$  line is followed by a positive feature at the low energy side, and this sequence is inverted at the  $L\alpha_2$  emission line. The shape of the dichroism signal of both emission lines indicates the presence of two dominant multiplet families with magnetic moments of opposite sign, which are separated by an exchange energy of  $\approx 8$  eV, readily estimated from the two features in the derivative-like spectrum. The  $(-+)(+-)$  signature of the dichroism is due to the reversed level ordering of the  $3d_{5/2}$  and  $3d_{3/2}$  Zeeman split  $m_j$  levels.<sup>11</sup> Since spin and orbital momentum couple parallel (antiparallel) for the  $3d_{5/2}$  ( $3d_{3/2}$ ) levels, we can further conclude that the main line of both emission lines has mainly spin-down character while the low energy satellite has predominantly spin-up character. This straightforward analysis is in agreement with analogous conclusions obtained from  $2p$  XPS data in iron<sup>6,11</sup> and in other transition metals,<sup>7,9</sup> where also the spin-orbit interaction in the core-level dominates over the electrostatic and magnetic interactions between core and valence electrons.

In the case of the  $L\beta_{2,15}$  emission line, the electrostatic and magnetic interactions between the  $4d$  and  $4f$  electrons by far dominate the spin-orbit interaction. There, we observe a positive dichroism around 7078 eV, associated with the satellite line in the emission spectrum, and a derivative-like dichroism of dominant negative character around 7105 eV, associated with the main line. This dichroism spectrum, therefore, shows that the satellite line is completely polarized with a magnetic moment antiparallel to the  $4f$  shell (photoelectron of spin-up character), while the main line is due to states with both negative and positive magnetic moments. The stronger negative dichroism indicates multiplets with a magnetic moment parallel to the  $4f$  moment (spin-down photoelectron), while the weaker positive dichroism indicates multiplets with a magnetic moment antiparallel to the  $4f$  moment (spin-up photoelectron). These findings are in agreement with experimental data and calculations on similar systems such as  $\text{Mn}^{2+}$ , where both  $K\beta_{1,3}$  emission<sup>12</sup> and  $3p$  XPS (Ref. 15) are dominated by the magnetic interac-

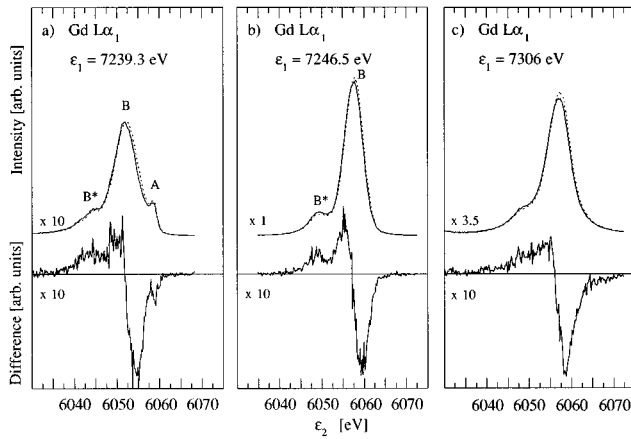


FIG. 2. Normalized and self-absorption corrected resonant inelastic x-ray scattering spectra of the Gd metal  $L\alpha_1$  emission line, taken at the indicated incident photon energies. The solid (dashed) line corresponds to antiparallel (parallel) orientation between photon helicity and sample magnetization. The spectra are multiplied by the indicated scaling factor, due to the different Gd  $L_3$ -absorption coefficient at the considered incident photon energies. The dichroic signals are obtained taking the difference between the two spectra of opposite helicities and multiplying them by a factor of 10.

tions between the  $3p$  and the  $3d$  electrons. Moreover, recent ligand field multiplet calculations of the  $L\beta_{2,15}$  and the  $L\alpha_{1,2}$  emission lines in Gd are in very good agreement with our experimental results and assignments.<sup>16</sup>

We consider now the modifications of the dichroism in the RIXS spectra when the incident photon energy is tuned from the continuum to values resonant with excitations into bound and magnetically polarized states, and, whether it is possible to relate the observed changes to the dichroism in photoabsorption. More specifically, by tuning the incident photon energy to 7239.3 and 7246.5 eV, the intermediate state is characterized by the excitation of the  $2p_{3/2}$  core electron into either the Gd  $4f$  or  $5d$  bands.<sup>17</sup> In the case of the  $L\alpha_1$  line, the emission for both photon helicities and the dichroism spectra are shown in Figs. 2(a) and 2(b) for the two bound states at these two incident photon energies, and, for comparison, in Fig. 2(c) for the state in the continuum with  $\epsilon_1 = 7306$  eV. The spectra were corrected for self-absorption effects and multiplied by a scaling factor arising from the different photoabsorption cross section of Gd at the considered incident photon energies. The spectral features in Fig 2(a) are shifted towards lower scattering energies due to the resonant Raman effect.<sup>17</sup> In agreement with Ref. 17, the structure, labeled A in Fig. 2(a) is due to the increased population of the  $4f$  band. The associated dichroism is negative,

consistent with the spin-down character of the empty  $4f$  states and with the analogous negative feature observed in absorption XMCD.<sup>18</sup> The spectrum taken at 7246.5 eV, corresponding to a transition of the excited photoelectron into the empty states of the  $5d$  bands, shows final state multiplets families, labeled  $B$  and  $B^*$ , which are qualitatively similar to those of the spectrum displayed in Fig. 2(c). The dichroism in Fig. 2(b), however, shows an increased intensity of the positive lobe when compared to the dichroism spectrum of Fig. 2(c). This behavior cannot be related simply to the density of states as for the  $4f$  bands, because also the  $5d$  bands should have empty states with a dominant spin-down character, and therefore the negative feature should become more intense with respect to the positive one. These observations agree with XMCD in photoabsorption,<sup>18</sup> which also shows for the  $5d$  bands a feature of opposite sign to the quadrupolar dichroism of the  $4f$  states. This behavior is still not well understood, and it was proposed to arise from differences in the  $5d$  radial wave function, which are calculated to be more localized for electrons with spin parallel to that of the  $4f$  electrons.<sup>19,20</sup> The results of the present experiment not only confirm the XMCD data, but also show that the positive feature in the photoabsorption dichroism, in spite of its sign, really arises from the  $5d$  bands with its majority spin character.

In conclusion, we have shown that the dichroism arising from RIXS excited with circular polarized radiation gives signals with an extremely high signal-to-background even when photoabsorption XMCD gives a negligible effect, as in the case of excitations well above or below the absorption threshold. The information contained in these data is basically equivalent to the dichroism in XPS, and therefore RIXS can be an alternative to this method whenever surface sensitive techniques cannot be applied. We showed, using gadolinium as an example that, independently from a specific theoretical model, it is possible to determine the magnetic character of each multiplet structure in the almost ideal situation where the number of valence electrons is the same in the ground and excited states. Tuning the incident photon energy to specific excitations near threshold, it is possible to determine the dichroism of a given final state configuration. Therefore one can get information similar to photoabsorption XMCD from the comparison with data taken above threshold, as well as indications on the contributions of specific multiplet configurations to the integral dichroism measured in photoabsorption.

We acknowledge B. Gorges and J.-F. Ribois for technical assistance, and J. Chavanne and P. Elleaume for the construction of the helical undulator, and help in its commissioning. We also acknowledge F. M. F. deGroot for useful discussions.

<sup>1</sup>G. Schütz, W. Wagner, W. Wilhelm, P. Kienle, R. Zeller, R. Frahm, and G. Materlik, Phys. Rev. Lett. **58**, 737 (1987).

<sup>2</sup>C.T. Chen, F. Sette, Y. Ma, and S. Modesti, Phys. Rev. B **42**, 7262 (1990).

<sup>3</sup>C.F. Hague, J.-M. Mariot, P. Strange, P.J. Durham, and B.L. Gyroffly, Phys. Rev. B **48**, 3560 (1993).

<sup>4</sup>L.-C. Duda, J. Stöhr, D.C. Mancini, A. Nilsson, N. Wassdahl, J. Nordgren, and M.G. Samant, Phys. Rev. B **50**, 16 758 (1994).

<sup>5</sup>P. Carra, M. Fabrizio, and B.T. Thole, Phys. Rev. Lett. **74**, 3700 (1995).

<sup>6</sup>L. Baumgarten, C.M. Schneider, H. Petersen, F. Schäfers, and J. Kirschner, Phys. Rev. Lett. **65**, 492 (1990).

- <sup>7</sup>G. van der Laan, Phys. Rev. Lett. **66**, 2527 (1991).
- <sup>8</sup>B.T. Thole and G. van der Laan, Phys. Rev. Lett. **67**, 3306 (1991).
- <sup>9</sup>B.T. Thole and G. van der Laan, Phys. Rev. B **44**, 12 424 (1991).
- <sup>10</sup>K. Starke, E. Navas, L. Baumgarten, and G. Kaindl, Phys. Rev. B **48**, 1329 (1993).
- <sup>11</sup>G. van der Laan, J. Magn. Magn. Mater. **148**, 53 (1995).
- <sup>12</sup>G. Peng, F.M.F. deGroot, K. Hämäläinen, J.A. Moore, X. Wang, M.M. Grush, J.B. Hastings, D.P. Siddons, W.H. Armstrong, O.C. Mullins, and S.P. Cramer, J. Am. Chem. Soc. **116**, 2914 (1994).
- <sup>13</sup>F.M.F. deGroot, A. Fontaine, C.C. Kao, and M. Krisch, J. Phys. Condens. Matter **6**, 6875 (1994).
- <sup>14</sup>P. Elleaume, J. Synchrotron Rad. **1**, 19 (1994).
- <sup>15</sup>B. Hermsmeier, C.S. Fadley, M.O. Krause, J. Jimenez-Mier, P. Gerard, and S.T. Manson, Phys. Rev. Lett. **61**, 2592 (1988).
- <sup>16</sup>F.M.F. deGroot *et al.* (unpublished).
- <sup>17</sup>M.H. Krisch, C.C. Kao, F. Sette, W.A. Caliebe, K. Hämäläinen, and J.B. Hastings, Phys. Rev. Lett. **74**, 4931 (1995).
- <sup>18</sup>G. Schütz, M. Knülle, R. Wienke, W. Wilhelm, W. Wagner, P. Kienle, and R. Frahm, Z. Phys. B **73**, 67 (1988).
- <sup>19</sup>B.N. Harmon and A.J. Freeman, Phys. Rev. B **10**, 1979 (1974).
- <sup>20</sup>X. Wang, T.C. Leung, B.N. Harmon, and P. Carra, Phys. Rev. B **47**, 9087 (1993).