Core Hole Polarization in X-Ray Absorption Studied by Magnetic Circular Dichroism in $2p3p3p$ Resonant Photoemission

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We show that the possibilities of x-ray absorption spectroscopy are strongly increased when we detect the polarization of the core hole by the angle dependence of the resonant photoemission, where the polarization of the hole is transferred to the localized final state *LS* terms and the emitted photoelectron. In the geometry where the dichroism in the $2p$ absorption is forbidden, a circular dichroism of 9% is observed in the autoionization decay into a $3p^4$ state. The effect provides a way to separate the ground state spin magnetic moment from the magnetic dipole moment.

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Recently, much progress has been made in the area of magnetic surfaces, ultrathin films, and overlayers. Among the exciting new discoveries are perpendicular magnetic anisotropy, quantum-well states, oscillatory interlayer and exchange coupling, and giant magnetoresistance. These phenomena are of great scientific interest and of large technological importance in applications such as magnetic and magneto-optical recording and nanoscale magnetic structures. Knowledge of the orbital and spin parts of the magnetic moments is invaluable for the understanding of these effects which are due to the interplay between spin-orbit coupling, exchange interaction, hybridization, and crystal field at the surface and interface boundaries. One of the most successful methods, so far, to separate spin and orbital magnetic moments has been circular dichroism in x-ray absorption spectroscopy (XAS) [1], which utilizes the integrated signals of the spin-orbit split core level edges [2]. When in XAS a core electron is excited into a magnetic valence state, the dipole selection rules, together with the Pauli principle, give a difference in absorption probability for left and right circularly polarized light. We may say that XAS measures the monopole of the core hole, i.e., the amount of holes created.

Here we report on an important new result, namely, that it is possible to obtain the polarization, i.e., the higher-order multipoles, of the core hole in XAS by studying the angle dependence of the electrons emitted by the decay of the core hole. The polarization of the core hole created is due to the polarizations of the light and the valence shell. In the autoionization decay following the x-ray absorption the polarization of the core hole is transferred to the localized final state and the continuum electron [3]. The detection of the kinetic energy of the emitted electrons, which determines the final state *LS* term, together with their angular distribution allow us to determine the original core hole polarization. This information has always been there but was simply thrown away by detecting all electrons integrated over all angles. With the high photon flux from third-generation synchrotron radiation sources we should be able to obtain more of the detailed information contained in the decay processes.

We will treat the absorption and decay as a two-step process. The first step produces a core hole and an additional electron in the valence shell. The second step is the autoionization decay caused by the Coulomb interactions involving continuum states. The basic information can be extracted by neglecting the fine structure of the intermediate and final states. This is equivalent to integrating the photon energy over an absorption edge and integrating the final states over an *LS* term of the two hole system. We will present the coefficients determining the emission distribution of each type of core hole decaying to each of the final state *LS* terms. Measurements of the actual distribution, or rather the intensities, in only a few geometries determine which type of core hole has been present and from that the ground state moments can be assessed.

A deep core hole decays through a set of decay channels and each of these channels has different experimental possibilities to measure desired properties in the most direct way. In this Letter we will study the autoionization of a $3d$ transition metal $2p$ core hole via the $2p3p3p$ decay, i.e., $3d^n \rightarrow 2p^5 3d^{n+1} \rightarrow 3p^4 3d^{n+1}\varepsilon$, where ε is a continuum state. The intermediate state is characterized by the large spin-orbit coupling of the $2p$ hole dividing the absorption into two edges where j is a good quantum number. Since the $3d$ shell is merely a spectator in the decay, the final state $3p^4$ configuration can be treated in *LS* coupling. The $3p$ Coulomb interaction splits the *LS* term into two distinct peaks, where one is the ^3P state and other the overlapping ^1S and ^1D states [4], cf. Fig. 1. Our analysis will be in terms of the total intensities of the peaks with different spin. The decay to these states may be expected to depend on the spin of the core hole and consequently the emitted electrons will be spin polarized, but their orbital structure is also different. The ^3P state has the orbitals of the two holes aligned perpendicularly while the ^1S and ^1D have them antiparallel and parallel,

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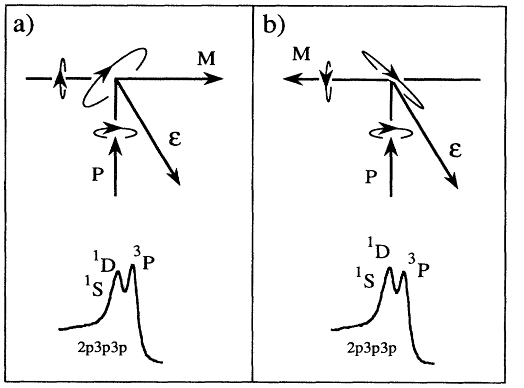

FIG. 1. (a) Geometry to illustrate the core hole polarization following XAS. **P** is the helicity vector of the incident circularly polarized light and **M** is the magnetization due to the valence hole spin. The orbit of the created core hole prefers to be parallel to the spin as well as to the orbital momentum of the light, so that the hole rotates in the bisecting plane. (b) Reversal of the magnetization direction changes the relative intensities of the ^3P and $^1S, ^1D$ peaks in the $2p3p3p$ resonant photoemission in the direction ε.

respectively. This may be expected to give different emission directions.

Figure 1 explains the origin of the orientation of the core hole as well as the angle-dependent emission when the valence shell spin is polarized. The $\Delta S = 0$ selection rule in the initial x-ray absorption causes an alignment of the core hole spin with the spin of the initial valence hole, which is opposite to the magnetization direction **M**. The light, which has circular polarization along **P**, aligns the core hole orbital moment. Classically, a particle orbits in a plane perpendicular to its orbital moment. While the light tries to align the orbital moment with **P**, the spin-orbit coupling in the $p_{3/2}$ hole prefers an orbital moment parallel to **M** and the hole has to rotate in a plane bisecting **P** and **M**. If we reverse **M** or **P** in the geometry with $\mathbf{P} \perp \mathbf{M}$, the absorption probability does not change, i.e., its dichroism is zero. Although this is not detected by XAS, such a reversal forces the hole to rotate in another plane [Fig. 1(b)].

From Fig. 1 we can also understand the angle dependence of the emission if we consider that the $2p3p3p$ decay is, in large part, due to a matrix element $R^0(2p, 3p; 3p, \varepsilon p)$ [4]. In this case the $3p$ electron that falls into the $2p$ hole must have the same orbital as the $2p$ hole itself. Likewise, the orbitals of the other created $3p$ hole and the emitted electron must be the same. This means that the two $3p$ holes have the same mutual spatial relationship as the $2p$ core hole and the emitted electron. So if the emission direction is perpendicular to the core hole orbit, the $3p^4$ final state will have its two holes mutually perpendicular which means that its state is ^3P. In the ^1S and ^1D states the moments of the two holes are antiparallel and parallel, respectively, which means they move in the same plane and the emission is in the plane of the core hole orbit. This explains already qualitatively the final state peak intensities shown in the lower part of Fig. 1.

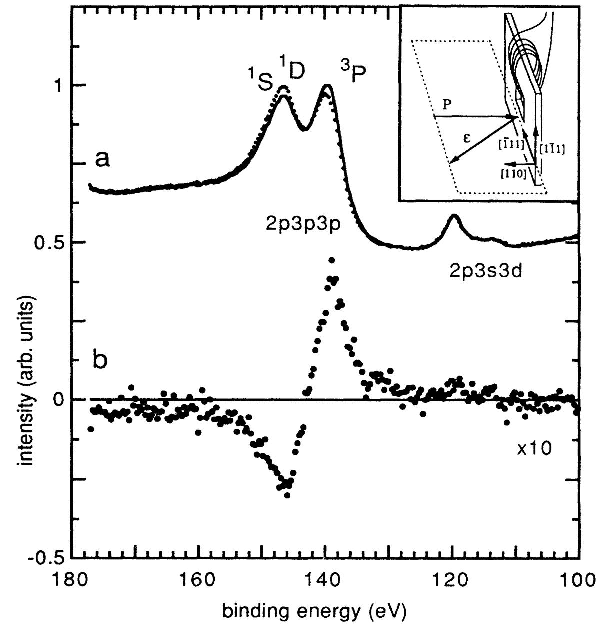

FIG. 2. (a) The $2p3p3p$ and $2p3s3d$ resonant photoemission spectra of nickel measured with circularly polarized light and magnetization direction (anti)parallel to the $[\bar{1}11]$ direction; (b) difference spectrum (10× enhanced). The experimental setup, which is similar to the one sketched in Fig. 1, is given in the inset.

Figure 2(a) shows the resonant photoemission spectra of nickel (110) at the $2p_{3/2}$ absorption edge measured in the geometry of Fig. 1. Circularly polarized x rays were used from beam line 1.1 of the Synchrotron Radiation Source at Daresbury. The Ni single-crystal picture frame was magnetized with a current pulse through a coil. The plane of measurement contained the [110] surface normal and the $[\bar{1}11]$ magnetization direction in the surface plane (see inset of Fig. 2). The x rays with a degree of circular polarization of 80% impinged on the sample at normal incidence while the photoelectrons were collected at an angle of 30° with the normal using a hemispherical multichannel analyzer with an acceptance angle of 5°. The magnetic dichroism in the ^3P state of nickel [Fig. 2(b)] has a magnitude of 0.090 ± 0.009 with respect to the background-corrected peak intensity with unpolarized light. For iron we measured a dichroism of similar shape with a magnitude of 0.071 ± 0.008 [5]. We found that the magnetic dichroism disappears when the magnetization direction is taken perpendicular to the plane of measurement or when linearly polarized light is used at normal incidence. This is expected since in both cases the orientation of the hole as viewed from the direction ε remains the same when **M** is reversed. We found a weak dichroism in resonance with the Ni $2p_{3/2}$ satellite at 3.7 eV above the absorption edge [1]. However, at other energies there was no detectable dichroism in the Auger decay. In the absorption step of the Auger process $3d^n \rightarrow 2p^5 3d^n \varepsilon \rightarrow 3p^4 3d^n \varepsilon\varepsilon$ the $3d^n$ is a spectator shell so that the spin alignment of the $3d$ holes is not transferred to the core hole. We also found no magnetic dichroism at the $2p_{1/2}$ absorption edge, which will be explained later.

The general expression for the angular-dependent emission intensity J_j^a for the transition from a core hole state with total angular momentum j to the LS terms of the two core hole state in an atom with cylindrical symmetry can be written as [6,7]

$$J_j^a(LS;\mathbf{P},\varepsilon,\mathbf{M}) = \frac{1}{4\pi}\sum_{rz}\left\{\sum_{xy}\langle \underline{w}^{xyz}\rangle C_j^{xyzar}\right\}U^{arz}(\mathbf{P},\varepsilon,\mathbf{M})B_j^r(LS). \quad (1)$$

For $a = 0$, we have the intensity for isotropic light, the sum of left, right, and Z polarized light. For circular dichroism we consider $a = 1$, the difference in intensities for right and left circularly polarized light with the helicity vector along $\mathbf{P}$. The value $a = 2$ denotes linear dichroism and will not be discussed here.

Equation (1) shows that J_j^a depends on the properties of the ground state which are expressed in terms of the moments of its empty levels $\langle \underline{w}^{xyz}\rangle$ with $\mathbf{M}$ as the quantization axis, where xyz is a systematic way to denote the kind of moments involved [8]. This systematics is needed in order to derive general formulas. For example, for a d shell $\underline{w}^{000}$ is the number of holes, $\underline{w}^{110} = -\sum l_i \cdot s_i$ is the spin-orbit coupling, $\underline{w}^{101} = \frac{1}{2}L_z$ is the orbital magnetic moment, $\underline{w}^{011} = 2S_z$ is the spin magnetic moment, and $\underline{w}^{211} = \frac{7}{2}T_z$ is the magnetic dipole moment. The $\underline{w}^{z0z}$ with z even describe the shape (the 2^z pole) of the charge distribution and the $\underline{w}^{x1z}$ describe spin-orbit correlations. In this Letter we will concentrate on magnetic moments that have odd z. The moments with $x + y + z$ odd describe axial couplings between spin and orbit, such as $\underline{w}^{111} = l \times s$. We will neglect such moments.

The coefficient C_j^{xyzar} is the probability to create a core hole with multipole moment r in a collinear geometry using a polarized light given a moment $\langle \underline{w}^{xyz}\rangle$ equal to unity. Its value is determined purely by angular momentum coupling. The coefficient $B_j^r(LS)$ gives the probability that a core hole with moment r decays into the state LS. It contains the radial integrals of the Coulomb matrix elements $R^k(2p,3p;3p,\varepsilon)$ that cause the decay with $k = 0,2$ to an εp continuum and $k = 2$ to an εf continuum. The three-vector function $U^{arz}(\mathbf{P},\varepsilon,\mathbf{M})$ gives the angle dependence of the total process. Viewed as a function of ε for fixed $\mathbf{P}$ and $\mathbf{M}$ it gives the angular distribution of the emitted electrons. The quantities relevant to us are given in Tables I and II.

TABLE I. The moments $\langle \underline{w}^{xyz}\rangle$, coefficients C_j^{xyzar}, and angle-dependent functions U^{arz} for $r = 0,2$ with isotropic ($a = 0$) and circularly polarized light ($a = 1$) for $p \rightarrow d$ XAS. $\underline{w}^{000}$ is the number of holes, $\underline{w}^{110} = -\sum l_i \cdot s_i$, $\underline{w}^{101} = \frac{1}{2}L_z$, $\underline{w}^{011} = 2S_z$, $\underline{w}^{211} = \frac{7}{2}T_z$, and $\underline{w}^{xy3}$ are the magnetic octupole moments.

a	r	$\underline{w}^{xyz}$	$C_{3/2}$	$C_{1/2}$	U^{arz}
0	0	$\underline{w}^{000}$	2	1	$U^{000} = 1$
0	0	$\underline{w}^{110}$	1	-1	
1	0	$\underline{w}^{101}$	2	1	$U^{101} = \mathbf{P} \cdot \mathbf{M}$
1	0	$\underline{w}^{011}$	$\frac{1}{3}$	$-\frac{1}{3}$	
1	0	$\underline{w}^{211}$	$\frac{2}{3}$	$-\frac{2}{3}$	
1	2	$\underline{w}^{101}$	$\frac{2}{5}$	0	$U^{121} = -\frac{1}{2}\mathbf{P} \cdot \mathbf{M} + \frac{3}{2}(\mathbf{P} \cdot \varepsilon)(\varepsilon \cdot \mathbf{M})$
1	2	$\underline{w}^{011}$	$\frac{2}{3}$	0	
1	2	$\underline{w}^{211}$	$\frac{2}{15}$	0	
1	2	$\underline{w}^{303}$	$\frac{3}{5}$	0	$U^{123} = -\frac{1}{2}\mathbf{P} \cdot \mathbf{M} - (\mathbf{P} \cdot \varepsilon)(\varepsilon \cdot \mathbf{M}) + \frac{5}{2}(\mathbf{P} \cdot \mathbf{M})(\varepsilon \cdot \mathbf{M})^2$
1	2	$\underline{w}^{213}$	$\frac{6}{5}$	0	
1	2	$\underline{w}^{413}$	0	0	

From the symmetry properties of C, B, and U we can find out what combinations of values for a, r, x, y, and z are allowed and then find the geometries that restrict the number of combinations further. First, the core hole moment r is even and is restricted to $0, \ldots, 2j$. So for $j = \frac{3}{2}$, only the monopole ($r = 0$) and quadrupole ($r = 2$) of the core hole can be observed. For $j = \frac{1}{2}$, r can only be 0. The second parity condition $x + y + r + a$ is even, i.e., $x + y + a$ is even. Because we suppose that $x + y + z$ is also even, we obtain that $z + a$ is even. This gives an extension of the rule in XAS where $z = a$. Here we have $z = |a - r|, \ldots, a + r$, which gives up to three values. To measure the odd z we need an odd a, i.e., $a = 1$, which means circularly polarized light. The possible values of z are then 1 for $r = 0$ and 1 and 3 for $r = 2$. Instead of measuring the $a = 1$ terms by subtracting the signals with right and left circularly polarized light we can, as well, subtract the signals obtained for mutually reversed magnetic directions. This changes the sign of all moments $\langle \underline{w}^{xyz}\rangle$ with odd z, which has the advantage that even when we do not know the direction of the magnetic moment the signal measures its component in the known direction of the applied field.

TABLE II. Relative values of $B_{3/2}^r(LS)$.

r	^3P	^1D	^1S
0	100	83.8	20.7
2	50	-30.3	-20.7

Table I gives the coefficients C for $a = 1$ and $r = 0$ and 2 and for comparison with isotropic light also the terms for $a = 0$ with $z = 0$. For $r = 0$, we measure XAS and using the table we indeed obtain the sum rules for the circular dichroism ($a = 2$) in XAS: The sum over the $j = \frac{3}{2}$ and $j = \frac{1}{2}$ intensity is proportional to $\underline{w}^{101}$; the $j = \frac{3}{2}$ intensity minus twice the $j = \frac{1}{2}$ intensity is $\underline{w}^{011} + 2\underline{w}^{211}$.

Inspecting the functions U in Table I we see that for $\mathbf{P} \cdot \mathbf{M} = 0$ we obtain only signals with $r = 2$. In this case there is only a $j = \frac{3}{2}$ signal, which explains our observation that at the $j = \frac{1}{2}$ resonance the signals for the two magnetization directions (or light polarizations) are the same. Moreover, when $\mathbf{P} \cdot \mathbf{M} = 0$, the angular distributions for $z = 1$ and 3 are equal. So measuring in three geometries is necessary to separate them from each other and from $r = 0$. We can also choose two geometries where $U^{123} = 0$ and determine $r = 0, z = 1$ and $r = 2, z = 1$. This brings us to an important result: For $r = 2, z = 1$, we measure $\frac{2}{5}\underline{w}^{101} + \frac{2}{3}\underline{w}^{011} + \frac{2}{15}\underline{w}^{211}$. Comparing this to the signal in XAS in the $j = \frac{3}{2}$ edge we see that relative to $\underline{w}^{011}$ the coefficients of $\underline{w}^{101}$ and $\underline{w}^{211}$ are both 10 times smaller. This means that the $r = 2$ signal measures the valence band spin rather purely which is an advantage over XAS where up to 10% or maybe 30% of the signal may be assignable to $\underline{w}^{211}$, depending on the symmetry of the magnetic site [9]. In addition, using the angular distribution, the $z = 3$ signal can give us the magnetic octupole moments $\frac{3}{5}\underline{w}^{303} + \frac{6}{5}\underline{w}^{213}$.

Neglecting linear dichroism ($a = 2$) the signal in the ${}^3P$ decay of the $j = \frac{3}{2}$ edge with right or left circularly polarized light is $\frac{1}{3}J^0 \pm \frac{1}{2}J^1$. Correcting for a polarization of 80% we obtain from our Ni data that $J^1/J^0 = 0.038 \pm 0.004$. From Eq. (1) together with Tables I and II we find for the normal-incidence geometry that

$$\frac{J^1}{J^0} = \frac{\left(\frac{2}{5}\underline{w}^{101} + \frac{2}{3}\underline{w}^{011} + \frac{2}{15}\underline{w}^{211}\right)\frac{3}{8}\sqrt{3} - \left(\frac{3}{5}\underline{w}^{303} + \frac{6}{5}\underline{w}^{213}\right)\frac{1}{4}\sqrt{3}}{2(2\underline{w}^{000} + \underline{w}^{110})}\,. \tag{2}$$

XAS measurements of bulk Ni show that $\underline{w}^{110} = 0.16$, $\underline{w}^{101} = 0.043$, and $\underline{w}^{011} + 2\underline{w}^{211} = 0.86$ per hole [1,2,9]. If we further assume that $\underline{w}^{011} \approx 1$, $\underline{w}^{303} \approx 0$, and $\underline{w}^{213} \approx \underline{w}^{211}$, we obtain a theoretical value of $J^1/J^0 = 0.11$. For iron we obtain the experimental and theoretical values of 0.030 ± 0.003 and 0.09, respectively [5]. There does not seem to be a clear reason why the experimental values are about 3 times smaller than the theoretical ones. Systematic measurements should point the way to whether the surface values of the moments are indeed very different from the bulk ones or whether some neglected effect influences the decay rates such that it decreases the dichroism. It is possible that some of the signal is due to Auger transitions reducing the resonant part [10]. Also the scattering of the emitted electron in the solid can give a strong deviation from atomic theory [11].

Concluding, we showed that, by studying the angular distribution of the electrons emitted in the decay to localized final state LS terms, XAS can be extended to determine the polarization of the core hole. This opens up quite a large new area of experimental possibilities to separate spin and orbital moments. We studied the $2p3p3p$ decay following the $2p$ absorption in $3d$ transition metals. In general, all three holes involved may be in other levels, including the valence band; thus in rare earths one could have $2p3d3d$ with spin-orbit coupling in the final state holes, which gives a different behavior. In principle, the spin polarization of the emission can be detected. However, it seems that spin-dependent properties can already be measured in spin-integrated measurements because of the spin-orbit coupling in the intermediate core hole. The information contained in all decay processes to two-core hole final states is the same, viz. the moments of the core hole after absorption. Further, instead of intensities integrated over the absorption edge the intensity as a function of photon energy may be studied.

Advantages of the technique are the element specificity, common to all core hole techniques, and a larger variation in the experimental geometry than in XAS: For example, one can use circularly polarized light perpendicular to the magnetization direction. Further, the final core hole LS terms are split by Coulomb interactions in the order of 10 eV, so that a high energy resolution is not necessary. The method is just as surface sensitive as photoemission but the intensity is higher due to the resonance process.

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