

Magnetic circular dichroism in angular distributions of core-level photoelectrons

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Magnetic circular dichroism in angle-resolved, core-level photoemission from surfaces is reinterpreted by comparing it to circular dichroism in angular distributions of photoelectrons in nonmagnetic systems. The analogy highly recommends the use of the terminology *magnetic* circular dichroism in angular distributions of photoelectrons for the former effect, since it emphasizes both the role of the photoelectron wave vector \mathbf{k} , and the use of an experimentally induced chirality. Two phenomena are predicted in experimental geometries that do not have spatial mirror symmetry: first, the dichroism that results from reversal of the light helicity is not equivalent to what results from reversal of the sample magnetization; second, a linear dichroism exists upon *reversal* of the sample magnetization. The latter effect, termed "magnetic linear dichroism in angular distributions," is a pure interference term, which disappears in an angle-integrated experiment, and may greatly simplify the study of magnetic-exchange effects at core levels.

I. INTRODUCTION

Over the last five years, there has been a remarkable growth in the use of circular dichroism to study molecules and crystal surfaces using synchrotron radiation. Originally, these experiments were performed in the gas or liquid phase, in analogy with classical analytical chemistry experiments, and it was the high brightness and linear polarization of the synchrotron light in the plane of the synchrotron that was exploited to study chiral molecules.¹ Since a magnetic field is an axial-vector field, and introduces a chirality of its own, applied magnetic fields allowed the study of nonchiral molecules using magnetic circular dichroism (MCD).² However, the technique became widely used for studies of magnetic surfaces only after the development of monochromators which operated in the soft x-ray region. These photon energies are matched to the absorption thresholds of core transitions in many magnetic solids, and allow the use of magnetic circular dichroism to characterize the magnetic properties of crystals, surfaces, and films. The first experiments were performed using linearly polarized radiation,³ but the further development of monochromators which operated above and below the synchrotron plane, and produce light with a large component of circular polarization, has made MCD a more straightforward magnetic probe.⁴

In a typical core-level MCD experiment, the absorption is monitored using the fluorescence yield, the secondary electron yield, or even the sample neutralization current. The absorption spectra are collected as a function of photon energy for either each light helicity (and constant magnetization) or for two reversed sample magnetizations (and constant light helicity). The difference in the two spectra is the MCD, and it is related to the existence and geometry of magnetization, and the interaction of spin-orbit coupling and exchange splitting in the conduction bands.⁵ This experiment is very practical, as

the large count rates in total absorption allow short data acquisition times (~ 10 min), information about magnetic orientation and/or domains is obtained by inspection of the data,⁶ and (due to sum rules⁷) the orbital and spin contributions of the magnetic moment may be determined simply. Related angle-integrated photoemission experiments, often termed partial-yield experiments, can be analyzed in a similar manner using sum rules.^{7a}

An alternative MCD experiment is MCD in angle-resolved (and energy-resolved) core-level photoemission.^{8,9} This method introduces the wave vector \mathbf{k} of the photoelectron as an experimental variable and allows access to a different set of information than absorption experiments. It is related to magnetic exchange effects involving core states, as opposed to valence states.^{10,11} The introduction of angular resolution invalidates both the sum rule and the simple geometric interpretation of the angular variation of the dichroism that is found for MCD in absorption. The characteristic shape of the dichroism curve is changed, a complicated dependence on the experimental¹² and crystalline geometry is introduced,¹³ and even the sign of the dichroism cannot be interpreted at a glance. Angular resolution also greatly reduces the count rates and increases the experimental times (~ 2 h). These complications bring with them the potential to recover more (and different) information, since it is not integrated away.

The purpose of the present paper is to develop a strong analogy between MCD in angle-resolved photoemission, and a related technique for studying nonmagnetic materials: circular dichroism in angular distributions of photoelectrons (CDAD). This latter technique can be traced to theoretical speculations 10–15 years ago,¹⁴ and has been reviewed by Schönhense.¹⁵ It depends on an *experimentally induced* chirality to study circular dichroism in solids or surfaces which are not in themselves chiral or magnetic, and does not require an applied magnetic field. CDAD has recently been observed in core-level photo-

emission from carbon.¹⁶ The analogy between the two techniques is so strong and productive, that it is useful to abandon the terminology MCD in angle-resolved photoemission, and to use instead *magnetic* circular dichroism in angular distributions of photoelectrons (MCDAD). This leaves the abbreviation MCD for absorption experiments, thus avoiding confusion and emphasizing the different information contained in absorption and angle-resolved photoemission experiments. By exploiting the analogy with CDAD, the present paper restates several results which have been observed experimentally, and predicts new magnetic effects, among them a new type of magnetic linear dichroism. This latter result may greatly simplify MCDAD and make it more widely accessible.

The remainder of this paper is divided into three sections. In Sec. II, CDAD is reviewed briefly in order to define notation and to present intermediate results which will be used in Sec. III to discuss MCDAD. The final section summarizes the results, and discusses experimental questions related to testing the predicted effects in MCDAD.

II. CIRCULAR DICHOISM IN ANGULAR DISTRIBUTION (CDAD)

Circular dichroism in angular distributions in photoemission is the change in the intensity of the angle- and energy-resolved photoelectron distribution when the circular helicity of the exciting radiation is reversed. It is assumed that spin-orbit coupling is not important in the system. CDAD may be denoted as $D^{\pm h}(\mathbf{k}, \mathbf{q}, \mathbf{n})$, where¹⁷

$$D^{\pm h}(\mathbf{k}, \mathbf{q}, \mathbf{n}) = |\langle \Psi_f(\mathbf{k}) | O^+(\mathbf{q}) | \Psi_i(\mathbf{n}) \rangle|^2 - |\langle \Psi_f(\mathbf{k}) | O^-(\mathbf{q}) | \Psi_i(\mathbf{n}) \rangle|^2. \quad (1)$$

In this expression $|\Psi_f(\mathbf{k})\rangle$ is the photoelectron state with wave vector \mathbf{k} , which is ultimately detected as a plane wave far from the sample under study, $O^h(\mathbf{q})$ is the dipole operator for the monochromatic light of wave vector \mathbf{q} and circular helicity $h = \pm$, which is incident on the sample, and $|\Psi_i(\mathbf{n})\rangle$ is the initial electron state oriented according to the vector \mathbf{n} . In the original formulations of CDAD, the initial states were orbitals of molecules which were oriented by adsorption onto a surface with normal vector \mathbf{n} .¹⁷ More recently, it has been shown that \mathbf{n} need not be formally associated with the initial state alone. For UV photoemission from a semi-infinite solid, both the initial and final states carry the electron wave vector \mathbf{k} , and it is symmetry relations of both states with respect to the surface normal \mathbf{n} which are important.¹⁸ It should be understood that an energy-conserving delta function and an index for possible degeneracy of the initial state has been omitted from Eq. (1). Since spin-orbit coupling is ignored, the degenerate states with spin $|\uparrow\rangle$ and $|\downarrow\rangle$ have the same spatial wave function, and the sum over spin states has been factored out of Eq. (1).

Various photoexcitation geometries are shown schematically in Fig. 1. The XYZ coordinate axis in this figure is attached to the dipole operator, such that Z is parallel to \mathbf{q} , and the YZ plane could represent the plane of the synchrotron. Most of the essential physics and

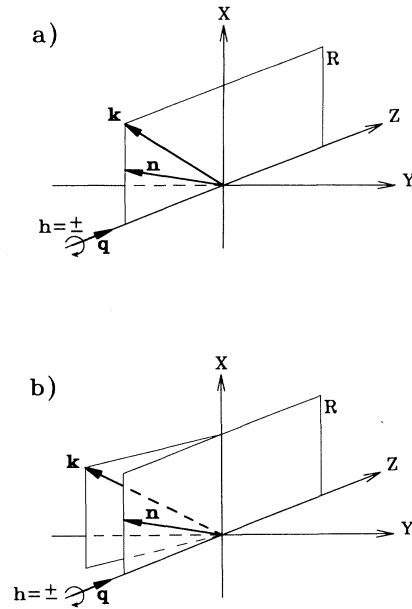


FIG. 1. Illustration of the CDAD geometry. The XYZ coordinate system of the dipole operator for circularly polarized light of helicity h , has the photon wave vector \mathbf{q} along the Z axis. The normal to the crystal surface \mathbf{n} is in the mirror symmetry plane R , which coincides with the XZ plane. The photoelectron wave vector \mathbf{k} is in the mirror symmetry plane in part (a), and outside the mirror symmetry plane in part (b).

qualitative behavior can be derived through a simple argument presented by Dubs, Dixit, and McKoy.¹⁷ If R is an operator corresponding to reflection in the XZ plane of Fig. 1 (i.e., containing \mathbf{q}), then

$$R^{-1}O^h(\mathbf{q})R = O^{-h}(\mathbf{q}). \quad (2)$$

The second matrix element in Eq. (1) may therefore be written as

$$\langle \Psi_f(\mathbf{k}) | O^-(\mathbf{q}) | \Psi_i(\mathbf{n}) \rangle = \langle \Psi_f(\mathbf{k}) | R^{-1}O^+(\mathbf{q})R | \Psi_i(\mathbf{n}) \rangle, \quad (3)$$

and it is necessary to consider the effect of the reflection operators on the wave functions. Figure 1(a) illustrates a situation where all three of \mathbf{k} (electron wave vector), \mathbf{q} (light wave vector), and \mathbf{n} (surface normal) are coplanar. When this plane is a mirror symmetry plane of the system (for example, for a polar molecule upright on a surface, or a crystalline mirror plane), then

$$R|\Psi_f(\mathbf{k})\rangle = \pm|\Psi_f(\mathbf{k})\rangle, \quad (4a)$$

$$R|\Psi_i(\mathbf{n})\rangle = \pm|\Psi_i(\mathbf{n})\rangle, \quad (4b)$$

and substitution into Eq. (1) shows that there is no circular dichroism.

The situation of Fig. 1(b) is much different. Here \mathbf{k} is not coplanar with \mathbf{q} and \mathbf{n} . The detected photoelectrons are not in states of definite parity, but have both symmetric (s) and antisymmetric (a) parts with respect to reflection in the mirror plane of the system:

$$|\Psi_f(\mathbf{k})\rangle = |\Psi_{fs}(\mathbf{k})\rangle + |\Psi_{fa}(\mathbf{k})\rangle, \quad (5a)$$

$$R|\Psi_f(\mathbf{k})\rangle = |\Psi_f(R^{-1}\mathbf{k})\rangle = |\Psi_{fs}(\mathbf{k})\rangle - |\Psi_{fa}(\mathbf{k})\rangle. \quad (5b)$$

Substitution of this result into Eqs. (3) and (1) yields a nonzero circular dichroism:

$$D^{\pm h}(\mathbf{k}, \mathbf{q}, \mathbf{n}) = 4 \operatorname{Re}[\langle \Psi_i(\mathbf{n}) | O^-(\mathbf{q}) | \Psi_{fs}(\mathbf{k}) \rangle \times \langle \Psi_{fa}(\mathbf{k}) | O^+(\mathbf{q}) | \Psi_i(\mathbf{n}) \rangle]. \quad (6)$$

This is purely an interference effect. It changes sign as \mathbf{k} moves through the mirror plane because the antisymmetric part of the photoelectron state changes sign. Equation (6) can be interpreted in terms of an experimentally induced chirality.¹⁵ The three vectors \mathbf{k} , \mathbf{q} , and \mathbf{n} can be used to define a three-dimensional coordinate system which has a definite handedness. Then the system has a type of chirality, even though the sample under the study does not, and circular dichroism can arise when it is probed by circularly polarized light of opposite helicities. When all three vectors are coplanar in a mirror symmetry plane, they cannot define a three-dimensional coordinate system, and there is no chirality, and no circular dichroism.

CDAD has been observed in a number of molecules adsorbed on crystalline surfaces,¹⁹ from the clean graphite surface,¹⁸ and from core levels of carbon.¹⁶ The dichroic intensity asymmetry A , which is the normalized dichroism, is given by

$$A^{\pm h} = [I(O^+) - I(O^-)] / [I(O^+) + I(O^-)], \quad (7)$$

where $I(O^h)$ is the angle-resolved photoemission intensity for light of helicity h . It is not uncommon to find a dichroic asymmetry of 40–60% in CDAD.

CDAD is a more general phenomenon than the argument based on experimentally induced chirality would predict. For example, suppose that the reflection plane in Fig. 1(a) is not a mirror symmetry plane of the system. Then, even though $R\mathbf{k} = \mathbf{k}$, Eq. (5) still holds (since symmetric and antisymmetric parts with respect to reflection in any plane can be defined). A comparable condition will, in general, hold for the initial state, so that CDAD can persist even in a coplanar geometry. This situation is discussed in detail by Chandra.²⁰

III. MAGNETIC CDAD

A. Inclusion of spin-orbit coupling

CDAD is a type of circular dichroism which exists even in the absence of spin-orbit coupling. A magnetically ordered solid, on the other hand, requires the presence of spin-orbit coupling to link the spin orientation to a specific crystalline direction of spontaneous magnetization. A discussion of magnetic CDAD should distinguish between circular dichroism which arises due to the magnetization and that which exists because of spin-orbit coupling in the absence of magnetization.

In the presence of spin-orbit coupling, the spin functions no longer factor out of Eq. (1), and they must be explicitly included. Thus the photoelectron states, for example, are $|\Psi_f^s(\mathbf{k})\rangle$, where $s = +(-)$ are states which

are primarily $|\uparrow\rangle(|\downarrow\rangle)$, but have an admixture of the opposite spin state due to the spin-orbit coupling. For the case of Fig. 1(a), where both \mathbf{k} and \mathbf{n} lie in a mirror symmetry plane, the situation is essentially unchanged. The action of the reflection operator gives

$$R|\Psi_f^s(\mathbf{k})\rangle = a|\Psi_f^{-s}(\mathbf{k})\rangle, \quad (8a)$$

$$R|\Psi_i^s(\mathbf{n})\rangle = a|\Psi_i^{-s}(\mathbf{n})\rangle, \quad (8b)$$

where a is ± 1 or $\pm i$, depending on the orientation of the axes.²¹ Substitution shows that CDAD disappears.

For an emission direction out of the mirror symmetry plane, as in Fig. 1(b), the situation is more complicated. Because of the lack of inversion symmetry in a semi-infinite system, there is no general relation between the spatial parts of the wave function multiplying the $|\uparrow\rangle$ and $|\downarrow\rangle$ portions of the states for $s = +$ and $-$. Thus, the diagonal matrix elements of the symmetric and antisymmetric parts of the spatial wave function, which get cancelled out in a sum over $|\Psi_f(\mathbf{k})|\uparrow\rangle$ and $|\Psi_f(\mathbf{k})|\downarrow\rangle$ when spin-orbit coupling is absent, do not cancel out in the sum over $|\Psi_f^+(\mathbf{k})\rangle$ and $|\Psi_f^-(\mathbf{k})\rangle$ in the presence of spin-orbit coupling. As a result, there are diagonal terms in the circular dichroism in addition to the interference terms which appear in Eq. (6). Because

$$R|\Psi_f^s(\mathbf{k})\rangle = a|\Psi_f^{-s}(\mathbf{k}')\rangle, \quad (9)$$

where $\mathbf{k}' = R\mathbf{k}$, still holds, the circular dichroism continues to change sign as \mathbf{k} passes through the mirror plane.

Although these effects of spin-orbit coupling have just been presented in the framework of CDAD, and although they alter the qualitative results seen in CDAD only by the addition of diagonal terms in the noncoplanar geometry, they are *not* included in the conventional understanding of the name CDAD. The acronym CDAD is restricted historically to the effects which persist in the absence of spin-orbit coupling.¹⁵ The effects noted above in the presence of spin-orbit coupling have been termed "surface transmission effects" instead. This distinction arose from consideration of the three-step model of photoemission, where photoexcitation in the bulk of the crystal, transport to the surface, and transmission into vacuum are considered separately. In this point of view, photoexcitation in the bulk creates *no* circular dichroism, since Eq. (8) holds even for \mathbf{k} outside a mirror symmetry plane *if* the system is infinite and therefore has inversion symmetry.²² The inversion symmetry is broken in the transmission step, and the circular dichroism is ascribed to spin-dependent transmission at the surface.²² It therefore depends only of the presence of spin-orbit coupling in the unbound photoelectron states. These interesting effects have been studied experimentally.²³ For the present purposes, it is only necessary to understand that they exist, that they have been historically excluded from CDAD, and that they should be excluded from a discussion of what would be conventionally understood as magnetic CDAD.

In order to focus on purely magnetic effects, it is necessary to choose photoelectron states with negligible spin-orbit coupling, such as might well approximate the conditions in 3d ferromagnets for energies well above the Fer-

mi level. It is then impossible for spin-dependent transmission to cause circular dichroism. If a spontaneous magnetization \mathbf{M} exists, it plays an important role as an orienting vector itself, and can lead to new types of angle-resolved circular dichroism which should be called MCDAD. \mathbf{M} defines the axis of spin quantization and, through spin-orbit coupling in the bound states, the natural polar axis of the spatial wave functions. For angle-resolved photoemission from core levels, a number of simplifications may be made. The core states are well localized, so it is not necessary to consider their dependence on \mathbf{k} . They take the form of atomiclike eigenfunctions of the total electronic angular momentum \mathbf{J} and its projection μ onto the quantization axis defined by \mathbf{M} .²⁴ The electron states can therefore be denoted

$$|\Psi_f(\mathbf{k}, \mathbf{M})\rangle, |\Psi_i^\mu(\mathbf{n}, \mathbf{M})\rangle. \quad (10)$$

Since Eq. (1) calculates the energy-resolved circular dichroism, the core states are overdefined. This is because the photoelectrons excited from each core sublevel μ emerge with a different kinetic energy, due to exchange splitting of the core sublevels¹⁰ (independent electron picture) or due to interaction of the core hole with the exchange-split valence bands¹¹ (interacting electron picture). In either formalism, only the initial states $|\Psi_i^\mu(\mathbf{n}, \mathbf{M})\rangle$ and $|\Psi_i^{-\mu}(\mathbf{n}, -\mathbf{M})\rangle$ produce photoelectrons of the same energy, and one index \mathbf{M} is sufficient to distinguish between them. Finally, assuming again that the photoelectrons are sufficiently above the Fermi energy, it is permissible to neglect the magnetic exchange splitting in the photoelectron states (but not in the bound states). Thus, for a simplified model appropriate to core-level photoemission, the MCDAD is given by

$$D^{\pm h}(\mathbf{k}, \mathbf{q}, \mathbf{n}, \mathbf{M}) = |\langle \Psi_f(\mathbf{k}) | O^+(\mathbf{q}) | \Psi_i(\mathbf{n}, \mathbf{M}) \rangle|^2 - |\langle \Psi_f(\mathbf{k}) | O^-(\mathbf{q}) | \Psi_i(\mathbf{n}, \mathbf{M}) \rangle|^2. \quad (11)$$

In what follows, the surface normal will always be in a mirror reflection plane, such that $\mathbf{n} \rightarrow \mathbf{n}$ under reflection, and it will therefore be dropped from the notation. In the vacuum ultraviolet (VUV) regime, where very few experiments have been reported,²⁵ Eq. (11) will not be adequate, since it would probably not be permissible to neglect the spin-orbit coupling and exchange splitting in the photoelectron state, or the electron wave vector in the initial state. The circular dichroism would then have contributions from both MCDAD and from spin-dependent surface transmission of photoelectrons, and it would be difficult to separate them (except, perhaps, for emission in a mirror plane).

B. Circular dichroism

The relevant geometry is illustrated in Fig. 2. It is essentially unchanged, except that now the axial vector \mathbf{M} also represents an important direction of orientation of the initial wave function. In Fig. 2(a) all the vectors \mathbf{q} (light wave vector), \mathbf{k} (photoelectron wave vector), \mathbf{n} (surface normal), and \mathbf{M} (magnetization), are coplanar and in a mirror symmetry plane. Thus,

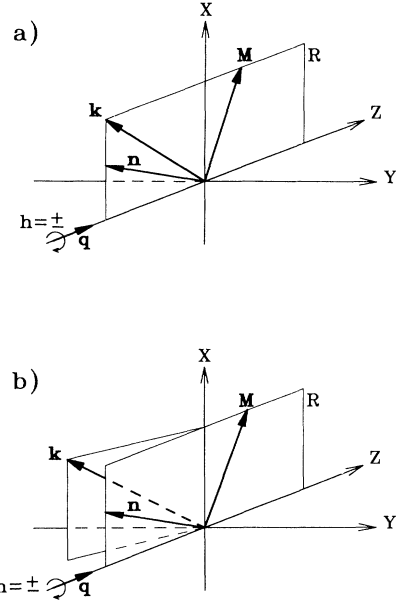


FIG. 2. Illustration of the MCDAD geometry. The XYZ coordinate system of the dipole operator for circularly polarized light of helicity h , has the photon wave vector \mathbf{q} along the Z axis. The normal to the crystal surface \mathbf{n} , and the sample magnetization \mathbf{M} , are in the mirror symmetry plane R , which coincides with the XZ plane. The photoelectron wave vector \mathbf{k} is in the mirror symmetry plane in part (a), and outside the mirror symmetry plane in part (b).

$$\begin{aligned} \langle \Psi_f(\mathbf{k}) | O^-(\mathbf{q}) | \Psi_i(\mathbf{M}) \rangle &= \langle \Psi_f(\mathbf{k}) | R^{-1} O^+(\mathbf{q}) R | \Psi_i(\mathbf{M}) \rangle \\ &= \langle \Psi_f(\mathbf{k}) | O^+(\mathbf{q}) | \Psi_i(-\mathbf{M}) \rangle, \end{aligned} \quad (12)$$

where the reflection properties of an axial vector have been used for \mathbf{M} . Substitution into Eq. (11) yields

$$D^{\pm h}(\mathbf{k}, \mathbf{q}, \mathbf{M}) = |\langle \Psi_f(\mathbf{k}) | O^+(\mathbf{q}) | \Psi_i(\mathbf{M}) \rangle|^2 - |\langle \Psi_f(\mathbf{k}) | O^+(\mathbf{q}) | \Psi_i(-\mathbf{M}) \rangle|^2. \quad (13)$$

Recalling that $|\Psi_i(\mathbf{M})\rangle$ and $|\Psi_i(-\mathbf{M})\rangle$ have opposite values of μ and correspond to a different combination of spherical harmonics, it is clear that MCDAD is nonzero in a mirror plane. The diagonal matrix elements which cancel in CDAD do not cancel in MCDAD. This is the same effect which has been previously studied experimentally^{8,9,12,13} and theoretically¹⁰⁻¹³ under the name of MCD in angle-resolved core-level photoemission. Equation (13) already contains many features which have been observed for MCDAD in a mirror symmetry plane. First, it is clear that in this geometry MCDAD may be measured equivalently by keeping a constant direction of magnetization and reversing the light helicity, or by keeping a constant light helicity and reversing the direction of magnetization. Next, for this geometry,

$$D^{\pm h}(\mathbf{k}, \mathbf{q}, \mathbf{M}) = -D^{\pm h}(\mathbf{k}, \mathbf{q}, -\mathbf{M}). \quad (14)$$

Hence, the circular dichroism measured at the energies corresponding to the initial sublevels μ (for $+\mathbf{M}$) and $-\mu$ (for $-\mathbf{M}$) are equal and opposite. If the core level of angular momentum \mathbf{J} is sufficiently well separated from other core levels by the spin-orbit coupling, the energy-resolved MCDAD will have the form of a plus/minus feature with equal²⁶ and opposite lobes.^{8,10,11} Finally, the explicit dependence on \mathbf{k} implies a dependence of the MCDAD on the emission direction¹² and, to the extent that $|\Psi_f(\mathbf{k})\rangle$ samples the semi-infinite crystal [as an inverse low-energy electron diffraction (LEED) state or, equivalently, as a result of photoelectron diffraction], a dependence on crystalline symmetry.¹³ These dependences will be different in detail than those observed in

conventional angle-resolved photoemission intensities. For this reason, it is usual to collect the “white line” spectrum [i.e., the sum of the matrix elements in Eq. (11)] as well as the MCDAD. Alternatively, it can be useful to normalize the circular dichroism, as in Eq. (7).

The noncoplanar geometry in Fig. 2(b) yields several new phenomena. Here \mathbf{q} , \mathbf{M} , and \mathbf{n} remain in the mirror symmetry plane, but \mathbf{k} is not. Now the photoelectron state can be divided into symmetric and antisymmetric parts with respect to reflection in the mirror plane, as in Eq. (5). Since $|\Psi_i(\mathbf{M})\rangle$ and $|\Psi_i(-\mathbf{M})\rangle$ are distinct states, the diagonal matrix elements do not cancel (as they do in CDAD), and the two interference terms are different. For MCDAD,

$$D^{\pm h}(\mathbf{k}, \mathbf{q}, \mathbf{M}) = |\langle \Psi_{fs}(\mathbf{k}) | O^+(\mathbf{q}) | \Psi_i(\mathbf{M}) \rangle|^2 - |\langle \Psi_{fs}(\mathbf{k}) | O^+(\mathbf{q}) | \Psi_i(-\mathbf{M}) \rangle|^2 \\ + |\langle \Psi_{fa}(\mathbf{k}) | O^+(\mathbf{q}) | \Psi_i(\mathbf{M}) \rangle|^2 - |\langle \Psi_{fa}(\mathbf{k}) | O^+(\mathbf{q}) | \Psi_i(-\mathbf{M}) \rangle|^2 \\ + 2 \operatorname{Re}[\langle \Psi_i(\mathbf{M}) | O^-(\mathbf{q}) | \Psi_{fs}(\mathbf{k}) \rangle \langle \Psi_{fa}(\mathbf{k}) | O^+(\mathbf{q}) | \Psi_i(\mathbf{M}) \rangle] \\ + 2 \operatorname{Re}[\langle \Psi_i(-\mathbf{M}) | O^-(\mathbf{q}) | \Psi_{fs}(\mathbf{k}) \rangle \langle \Psi_{fa}(\mathbf{k}) | O^+(\mathbf{q}) | \Psi_i(-\mathbf{M}) \rangle]. \quad (15)$$

Letting $\mathbf{M} \rightarrow -\mathbf{M}$ immediately yields

$$D^{\pm h}(\mathbf{k}, \mathbf{q}, \mathbf{M}) \neq \pm D^{\pm h}(\mathbf{k}, \mathbf{q}, -\mathbf{M}), \quad (16)$$

since the diagonal terms in Eq. (15) change sign, but the interference terms do not. It is not clear, *a priori*, what the relative size of the diagonal and interference terms is, but since Bansmann *et al.*¹⁶ observe strong interference terms in CDAD from core levels, they probably cannot be neglected. Therefore, in this geometry, the energy-resolved MCDAD will continue to consist of plus/minus features, but of *unequal* opposite lobes. More fundamentally, it is no longer an equivalent experiment to keep the light helicity constant and reverse the direction of magnetization. This is due to interference terms, and is a result unique to MCDAD that will not be observed in angle-integrated MCD.

In the noncoplanar geometry, it is necessary to introduce a new quantity which is not strictly MCDAD, but corresponds to the intensity change when the light helicity is held constant and the magnetization direction is reversed. This is

$$D^{\pm M}(\mathbf{k}, \mathbf{q}, \mathbf{n}, h) = |\langle \Psi_f(\mathbf{k}) | O^h(\mathbf{q}) | \Psi_i(\mathbf{n}, \mathbf{M}) \rangle|^2 \\ - |\langle \Psi_f(\mathbf{k}) | O^h(\mathbf{q}) | \Psi_i(\mathbf{n}, -\mathbf{M}) \rangle|^2, \quad (17)$$

where, in the following, the dependence on \mathbf{n} is again dropped. Since this quantity is equivalent to MCDAD in the coplanar geometry, it too will be referred to as MCDAD, with the qualification “under magnetization reversal” where ambiguity exists. It is clear from the definition itself that letting $\mathbf{M} \rightarrow -\mathbf{M}$ merely changes the sign of this dichroism, so the energy-resolved circular dichroism has equal and opposite plus/minus lobes. Expanding Eq. (17) shows that $D^{\pm M}(\mathbf{k}, \mathbf{q}, h = +)$ and $D^{\pm h}(\mathbf{k}, \mathbf{q}, \mathbf{M})$ differ only by the sign of the last interference term in Eq. (15). Letting $h \rightarrow -h$ in Eq. (17) and comparing the result to using Eq. (2) in Eq. (17) shows

that

$$D^{\pm M}(\mathbf{k}, \mathbf{q}, h) \neq \pm D^{\pm M}(\mathbf{k}, \mathbf{q}, -h). \quad (18)$$

Thus, the energy-resolved dichroism taken with negative helicity light continues to have plus/minus features which are equal and opposite, but of different size and opposite sign to those found for positive helicity light. These relations have important consequences in Sec. III C.

A final noncoplanar geometry of interest is illustrated in Fig. 3. Here \mathbf{k} , \mathbf{q} , and \mathbf{n} are coplanar in a mirror symmetry plane, but the magnetization is normal to this plane. Earlier studies¹² of iron $2p \rightarrow 3d$ photoemission in the coplanar geometry [Fig. 2(a)] found that, in this specific circumstance, MCDAD disappeared only when $(\mathbf{q} \cdot \mathbf{M}) = 0$ and $(\mathbf{q} \cdot \mathbf{k})(\mathbf{k} \cdot \mathbf{M}) = 0$ simultaneously.²⁷ This suggested that the circular dichroism will also disappear in the noncoplanar geometry of Fig. 3. Using Eq. (2) and

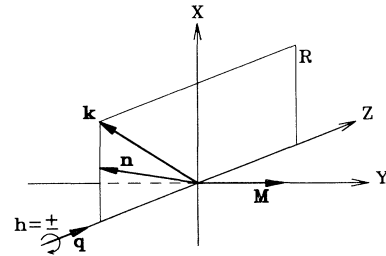


FIG. 3. Illustration of an alternate MCDAD geometry. The XYZ coordinate system of the dipole operator for circularly polarized light of helicity h , has the photon wave vector \mathbf{q} along the Z axis. The normal to the crystal surface \mathbf{n} , and the photoelectron wave vector \mathbf{k} , are in the mirror symmetry plane R , which coincides with the XZ plane. The sample magnetization \mathbf{M} , is normal to the mirror symmetry plane.

the reflection properties of an axial vector gives

$$\langle \Psi_f(\mathbf{k}) | O^-(\mathbf{q}) | \Psi_i(\mathbf{M}) \rangle = \langle \Psi_f(\mathbf{k}) | O^+(\mathbf{q}) | \Psi_i(\mathbf{M}) \rangle, \quad (19a)$$

$$D^{\pm h}(\mathbf{k}, \mathbf{q}, \mathbf{M}) = 0, \quad (19b)$$

confirming this suggestion.

C. Magnetic linear dichroism in angular distributions (MLDAD)

Magnetic linear dichroism (MLD) in absorption has been studied at absorption edges for a number of years, and was in fact the first magnetic dichroism in core-level photoexcitation to be observed experimentally.³ In these experiments, the dichroism appears as a change in the absorption spectrum as the linear polarization vector is first parallel and then perpendicular to the magnetization.⁵ This type of effect appears as well in an angle-resolved core-level photoemission experiment. In Fig. 4(a), the light is polarized linearly along either the X or Y axes, and \mathbf{k} , \mathbf{q} , \mathbf{n} , and \mathbf{M} are in a mirror symmetry plane. For these two particular directions of linear light polarization,

$$\begin{aligned} R^{-1} O^x(\mathbf{q}) R &= O^x(\mathbf{q}), \\ R^{-1} O^y(\mathbf{q}) R &= -O^y(\mathbf{q}), \end{aligned} \quad (20)$$

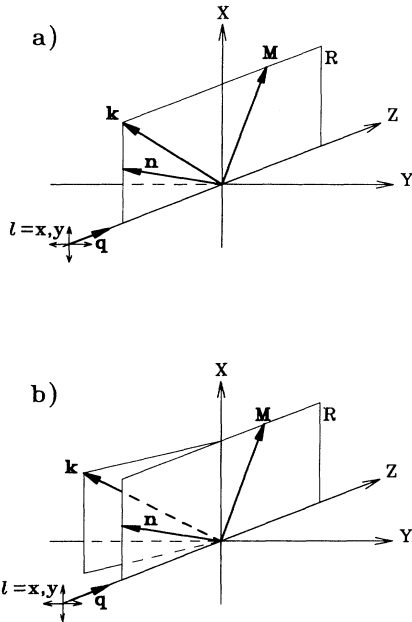


FIG. 4. Illustration of the MLDAD geometry. The XYZ coordinate system of the dipole operator for linearly polarized light has the photon wave vector \mathbf{q} along the Z axis. The normal to the crystal surface \mathbf{n} , and the sample magnetization \mathbf{M} , are in the mirror symmetry plane R , which coincides with the XZ plane. The photoelectron wave vector \mathbf{k} is in the mirror symmetry plane in part (a), and outside the mirror symmetry plane in part (b).

where O^l ($l = x$ or y) is the dipole operator for linearly polarized light. A linear dichroism upon changing from x - to y -polarized linear light can be defined as

$$L^{x,y}(\mathbf{k}, \mathbf{q}, \mathbf{n}, \mathbf{M}) = |\langle \Psi_f(\mathbf{k}) | O^x(\mathbf{q}) | \Psi_i(\mathbf{n}, \mathbf{M}) \rangle|^2 - |\langle \Psi_f(\mathbf{k}) | O^y(\mathbf{q}) | \Psi_i(\mathbf{n}, \mathbf{M}) \rangle|^2, \quad (21)$$

and is, in general, nonzero. Because of the nonzero diagonal matrix elements, it survives in an angle-integrated experiment. Use of Eq. (20) shows that

$$L^{x,y}(\mathbf{k}, \mathbf{q}, \mathbf{M}) = L^{x,y}(\mathbf{k}, \mathbf{q}, -\mathbf{M}), \quad (22)$$

indicating that the energy-resolved dichroism has the same sign for the μ and $-\mu$ core sublevels, and therefore is not a plus/minus feature, but rather a plus or minus feature within a core level of given \mathbf{J} (which is well separated from other core levels). It can be shown that similar effects result for a constant linear polarization and rotation of the magnetization by 90° . This type of linear dichroism in angle-resolved photoemission is an interesting effect which is not simply related to MCDAD, since it does not involve reversal of light helicity or sample magnetization. It is mentioned here to distinguish it from what follows.

An entirely new effect, which does not exist in angle-integrated experiments, is suggested by Eq. (18). The acronym MLDAD is proposed for the predicted dichroism in an angle-resolved photoemission experiment which results for constant linear polarization of light, and reversal of the magnetization $\mathbf{M} \rightarrow -\mathbf{M}$:

$$L^{\pm M}(\mathbf{k}, \mathbf{q}, \mathbf{n}, l) = |\langle \Psi_f(\mathbf{k}) | O^l(\mathbf{q}) | \Psi_i(\mathbf{n}, \mathbf{M}) \rangle|^2 - |\langle \Psi_f(\mathbf{k}) | O^l(\mathbf{q}) | \Psi_i(\mathbf{n}, -\mathbf{M}) \rangle|^2, \quad (23)$$

where $l = x$ or y . Use of Eq. (20) shows that this effect disappears in the coplanar geometry of Fig. 4(a). However, in Fig. 4(b), where the photoelectron wave vector is not in the mirror plane, it does not disappear. Expressing the photoelectron state as a symmetric and antisymmetric parts under reflection in the mirror plane yields

$$\begin{aligned} L^{\pm M}(\mathbf{k}, \mathbf{q}, l) &= 4 \operatorname{Re}[\langle \Psi_i(\mathbf{M}) | O^l(\mathbf{q}) | \Psi_{fs}(\mathbf{k}) \rangle \\ &\quad \times \langle \Psi_{fa}(\mathbf{k}) | O^l(\mathbf{q}) | \Psi_i(\mathbf{M}) \rangle]. \end{aligned} \quad (24)$$

This is a pure interference effect whose origin may be traced to the inequivalence of the circular dichroism resulting from the reversal of light helicity and that resulting from the reversal of magnetization. From its definition, it reverses sign upon letting $\mathbf{M} \rightarrow -\mathbf{M}$, and therefore the energy-resolved dichroism has the equal plus/minus lobes characteristic of MCDAD. It also changes sign upon \mathbf{k} passing through the mirror plane. Since it is an interference effect, detailed calculations are needed to estimate its magnitude, but, again, the observation of large interference effects in CDAD from core levels is encouraging.¹⁶ In fact, Eq. (24) bears a striking resemblance to Eq. (6) for CDAD for nonmagnetic materials in the same geometry. MLDAD will not, in general, be equal and opposite for polarization vectors along X and Y . Since unpolarized light is an incoherent superposition of these two linear polarizations, MLDAD

should exist even for unpolarized light.

It is appealing to try and understand MCDAD and MLDAD in terms of chirality arguments analogous to those used for CDAD. There appears to be a surfeit of chiral entities: the helicity of the light, the axial magnetization vector, and the “handedness” of the coordinate system established experimentally by the polar vectors \mathbf{k} , \mathbf{q} , and \mathbf{n} . The situation is clarified by distinguishing between the “natural” chirality of light helicity and magnetization, and the “artificial,” experimentally induced chirality. For MCDAD in a mirror symmetry plane, there is no experimentally induced chirality; only the two natural chiralities exist. Circular dichroism results when the senses of these two natural chiralities agree or disagree, and leads to nonzero diagonal matrix elements. These effects persist even in angle-integrated photoemission and in MCD in absorption, where the absence of \mathbf{k} ensure the absence of experimentally induced chirality. In CDAD, there is no magnetization, so it is the experimentally induced chirality which is probed by the helicity. This leads to interference terms. In MLDAD, there is no light helicity, so it is the experimentally induced chirality which is “probed” by the magnetization, and which again leads to interference terms. This concurs with the existence of MLDAD even for unpolarized light, and strengthens the analogy between CDAD and MLDAD. The intermediate case of MCDAD in a noncoplanar geometry is complicated by the simultaneous presence of three chiral entities. This results in Eq. (15), where there are diagonal terms (which can be traced to the interaction of the two natural chiralities), and two distinct interference terms (one term resulting from the interaction of the light helicity and the experimentally induced chirality, for each sense of magnetization).

This scheme is a very useful construct for qualitative understanding of these angle-resolved circular dichroism measurements. However, it must be recalled that they are sufficient, but not necessary, conditions. Just as CDAD exists in a coplanar geometry provided that the plane is not a mirror symmetry plane,²⁰ it is straightforward to show that MLDAD persists under the same circumstances.

IV. CONCLUSIONS AND DISCUSSION

The description of circular dichroism in angular distributions in photoemission (CDAD) has been extended to magnetic systems (MCDAD). In the simplified case of photoexcitation from localized core states to photoelectron states with negligible spin-orbit coupling and exchange splitting, MCDAD is seen to correspond to the experiments formerly called “MCD in angle-resolved core-level photoemission.” Since the photoelectron wave vector \mathbf{k} plays such an important role in this experiment, and because the CDAD formalism emphasizes this role, it is preferable to use the abbreviation MCD only for angle-integrated experiments (such as absorption experiments), and to adopt MCDAD for the angle-resolved magnetic circular dichroism experiments. For MCDAD

in a mirror symmetry plane, past experimental and theoretical results have been confirmed. When \mathbf{k} is outside the mirror symmetry plane, two new predictions are made. The first is that the dichroism upon reversal of the light helicity is not equivalent to that upon reversal of the magnetization direction. The second is that an intensity difference upon reversal of the magnetization exists even for linearly polarized or unpolarized light. The latter effect is termed MLDAD. It is a pure interference effect and will not occur in angle-integrated experiments.

In order to observe these effects, soft x-ray synchrotron experiments on a magnetic surface or film should be extended to a noncoplanar geometry, as in Fig. 4(b), where only \mathbf{k} is not in a crystalline mirror plane. The most useful experiment is to search for MLDAD, since the other predictions must exist to support MLDAD, and because the new effects in MCDAD involve comparisons of the absolute dichroism and are more sensitive to experimental artifacts. The experiment should measure the normalized dichroism, or dichroic asymmetry [compare Eq. (7)] upon magnetization reversal, since normalization will remove the effects of changes in the light intensity, and the effects of overall changes in the photoexcitation cross section with emission geometry. The difficulty will be to establish the condition of linearly polarized light. For this purpose, angle-resolved Auger electrons involving the same core state can be used. Angle-resolved Auger electron emission is, to a good approximation, an *angle-integrated* measure of the photoexcitation. Thus, the angle-resolved Auger electrons show essentially the same MCD as angle-integrated absorption.^{13,28} It will disappear when the light is linearly polarized, or when $\mathbf{q} \cdot \mathbf{M} = 0$. If the sample surface and magnetization vector are tipped, as in Fig. 4(b), then $\mathbf{q} \cdot \mathbf{M} \neq 0$. In a series of measurements of both MCDAD in photoemission and MCD in angle-resolved Auger electrons, taken as the monochromator slits are moved through the synchrotron plane, the Auger electrons will indicate when (if) the light is linearly polarized, and the MLDAD should then be present. Using the same electron optics, sample positions, and magnetization procedure for both sets of measurements (they could be interleaved) will guard against experimental artifacts.

The use of MLDAD to study ferromagnet surfaces and films could greatly ameliorate MCDAD experiments. Monochromators or insertion devices which provide high-intensity circularly polarized light would not be required. The high flux in the synchrotron plane would reduce measurement times, and, unlike conventional MLD in absorption, no sample manipulation would be required. The experiments would be simple, and complementary to conventional MCD, as they emphasize magnetic exchange effects at the core (or core hole) and phase information in the photoelectron state, whereas MCD emphasizes magnetic exchange information near the Fermi level.

Note added in proof. Recently, the experimental observation of a form of MLDAD was reported by Ch. Roth, F. U. Hillebrecht, H. B. Rose, and E. Kisker, in *Phys. Rev. Lett.* **70**, 3479 (1993). These authors investigated the geometry with \mathbf{k} , \mathbf{n} , and \mathbf{M} in a mirror plane and \mathbf{q}

out of it, rather than the geometry treated here. The situation is comparable, since there is still an experimentally induced chirality. MLDAD results from interference between matrix elements of the symmetric and antisymmetric parts of the dipole operator, rather than of the photoelectron state.

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- ¹P. A. Snyder and E. M. Rowe, *Nucl. Instrum. Methods* **172**, 345 (1980).
- ²P. A. Snyder, *Photochem. Photobiol.* **44**, 237 (1986).
- ³G. van der Laan, B. T. Thole, G. A. Sawatsky, J. B. Goedkoop, J. C. Fuggle, J. M. Esteve, R. Karantak, J. P. Remeika, and H. Dabkowska, *Phys. Rev. Lett.* **34**, 6529 (1986).
- ⁴G. Schütz, W. Wagner, W. Wilhelm, P. Kienle, R. Zeller, R. Frahm, and G. Materlik, *Phys. Rev. Lett.* **58**, 737 (1987); G. Schütz, M. Knülle, R. Wienke, W. Wilhelm, W. Wagner, P. Kienle, and R. Frahm, *Z. Phys. B* **73**, 67 (1988); C. T. Chen, F. Sette, Y. Ma, and S. Modesti, *Phys. Rev. B* **42**, 7262 (1990); N. V. Smith, C. T. Chen, F. Sette, and L. F. Mattheiss, *ibid.* **46**, 1023 (1992).
- ⁵B. T. Thole, G. van der Laan, and G. A. Sawatsky, *Phys. Rev. Lett.* **55**, 2085 (1985); P. Carra and M. Altarelli, *ibid.* **64**, 1286 (1990); C. Brouder and M. Hikam, *Phys. Rev. B* **43**, 3809 (1991).
- ⁶Microscopy of magnetic domains using MCD is under development: J. Stöhr, Y. Wu, B. D. Hermsmeier, M. G. Samant, G. R. Harp, S. Koranda, D. Dunham, and B. P. Tonner, *Nature* **259**, 658 (1993); C. M. Schneider, K. Meinel, K. Holldack, M. Grunze, H. P. Oepen, and J. Kirschner, *Mat. Res. Soc. Symp. Proc.* (to be published).
- ⁷B. T. Thole, P. Carra, F. Sette, and G. van der Laan, *Phys. Rev. Lett.* **68**, 1943 (1992); P. Carra, B. T. Thole, M. Altarelli, and X. Wang, *ibid.* **70**, 694 (1993); (a) B. T. Thole and G. van der Laan, *ibid.* **70**, 2499 (1993).
- ⁸L. Baumgarten, C. M. Schneider, H. Petersen, F. Schäfers, and J. Kirschner, *Phys. Rev. Lett.* **65**, 492 (1990).
- ⁹D. G. Waddill, J. G. Tobin, and D. P. Pappas, *Phys. Rev. B* **46**, 552 (1992).
- ¹⁰H. Ebert, L. Baumgarten, C. M. Schneider, and J. Kirschner, *Phys. Rev. B* **44**, 4406 (1991).
- ¹¹G. van der Laan, *J. Phys.* **3**, 1015 (1991); *Phys. Rev. Lett.* **66**, 2527 (1991).
- ¹²C. M. Schneider, D. Venus, and J. Kirschner, *Phys. Rev. B* **45**, 5041 (1992).
- ¹³D. Venus, L. Baumgarten, C. M. Schneider, C. Boeglin, and J. Kirschner, *J. Phys.* **5**, 1239 (1993).
- ¹⁴B. Ritchie, *Phys. Rev. A* **12**, 567 (1975); N. A. Cherepkov, *Chem. Phys. Lett.* **87**, 344 (1982).
- ¹⁵G. Schönhense, *Phys. Scr. T* **31**, 225 (1990).
- ¹⁶J. Bansmann, Ch. Ostertag, G. Schönhense, F. Fegel, C. Westphal, M. Getzlaff, F. Schäfers, and H. Petersen, *Phys. Rev. B* **46**, 13 496 (1992).
- ¹⁷R. Dubs, S. N. Dixit, and V. McKoy, *Phys. Rev. Lett.* **54**, 1249 (1985).
- ¹⁸G. Schönhense, C. Westphal, J. Bansmann, M. Getzlaff, J. Noffke, and L. Fritsche, *Surf. Sci.* **251/252**, 132 (1991); G. Schönhense, C. Westphal, J. Bansmann, and M. Getzlaff, *Europhys. Lett.* **17**, 727 (1992).
- ¹⁹C. Westphal, J. Bansmann, M. Getzlaff, and G. Schönhense, *Phys. Rev. Lett.* **63**, 151 (1989); C. Westphal, J. Bansmann, M. Getzlaff, G. Schönhense, N. A. Cherepkov, M. Braunstein, V. McKoy, and R. L. Dubs, *Surf. Sci.* **253**, 205 (1991).
- ²⁰N. Chandra, *Phys. Rev. A* **39**, 2256 (1989).
- ²¹C. J. Bradley and A. P. Cracknell, *The Mathematical Theory of Symmetry in Solids* (Clarendon, Oxford, 1972).
- ²²R. Feder, in *Polarized Electrons in Surface Physics*, edited by R. Feder (World Scientific, Singapore, 1985), Sec. 4.5.6.
- ²³H.-P. Oepen, K. Hünlich, and J. Kirschner, *Phys. Rev. Lett.* **56**, 496 (1986).
- ²⁴H. Ebert, *J. Phys.* **1**, 9111 (1991).
- ²⁵C. M. Schneider, M. S. Hammond, P. Schuster, A. Cebollada, R. Miranda, and J. Kirschner, *Phys. Rev. B* **44**, 12 016 (1991); J. Bansmann, C. Westphal, M. Getzlaff, F. Fegel, and G. Schönhense, *J. Magn. Magn. Mater.* **104-107**, 1691 (1992).
- ²⁶Strictly speaking, the plus/minus lobes will not be precisely equal in amplitude, since the core state is never an exact eigenfunction of \mathbf{J} . See Refs. 10 and 24. Experimentally, the plus/minus lobes are not equal in amplitude because of a background of secondary electrons.
- ²⁷This is different than angle-integrated MCD, where only $\mathbf{q} \cdot \mathbf{M} = 0$ is required.
- ²⁸C. M. Schneider and J. Kirschner (private communication).