Linear magnetic dichroism in fluorescence spectra

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Abstract

We discuss possible linear magnetic dichroism effects in fluorescence radiation following photoionization by linearly polarized light in the inner shell of oriented and/or aligned atoms. A general expression for the fluorescence dichroism is presented and analysed for particular kinematical conditions. Simple dynamical predictions are made for a particular case of LSJ-coupling. © 1999 Elsevier Science B.V. All rights reserved.

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Circular magnetic dichroism (CMD) in X-ray fluorescence is known since the beginning of the 90s [1]; it has been observed in transition metals and their compounds [2–7], lanthanides and their compounds [8–11], and even in complex bioinorganic systems [12]. These observations demonstrated the feasibility of the magnetic dichroism study by means of fluorescence spectroscopy. Theoretical analysis of different aspects of CMD in fluorescence can be found in papers [1,3,13,14]. In contrast, as far as we know, the linear magnetic dichroism (LMD) in fluorescence has never been discussed and measured, although its existence follows, for example, from a general theoretical approach to the resonant Raman scattering [15]. A possible reason for the fact that the dichroic effects in fluorescence are studied less than in photoabsorption or in photoelectron emission, is the low fluorescence yield and the necessity of a very high flux of primary photons. On the other side, the advantage of the fluorescence spectroscopy in comparison with the photoelectron spectroscopy is that it can be used not only for studying the magnetic properties of surface layers or thin films, but also the magnetism of buried layers produced, for example, by ion-beam synthesis [16]. Besides, this detection mode is not influenced by the presence of the external magnetic field which is especially advantageous in the near threshold regions. New possibilities are created for the fluorescence spectroscopy due to the development of intense, energy-tunable sources of synchrotron radiation (SR) allowing to increase substantially the flux of the primary photons. The beams of SR are generally better suited for measurements with linear polarized ionizing light, therefore a dis-
cussion of dichroic effects with linear polarized light seems timely and useful for planning experiments with the new generation of SR sources.

In this Letter we consider the main features of the LMD in the fluorescence radiation following atomic photoionization. The feasibility of such experiments is supported by recent angle-resolved photoelectron studies of linear dichroism with free polarized atoms [17–22]. Our aim is to present the general expression for the fluorescence dichroism and to analyse it for some particular kinematical conditions which are most likely in future experiments. We discuss also an example of dynamical restrictions imposed on the dichroism pattern. The theoretical analysis of LMD in fluorescence spectra from atoms can serve as a basis for the analysis of this phenomenon also in solids, as it was the case in X-ray fluorescence spectroscopy studies of CMD [14].

We consider photoionization of polarized atoms

\[ \gamma(p_1,p_2,p_3) + A(\alpha_0 J_0) \rightarrow A^{+}(\alpha J_J) + e \rightarrow A^{+}(\alpha J_J) + \gamma, \]  

(1)

where \( p_1,p_2,p_3 \) are the Stokes parameters describing the photon beam, \( J_0, J_J, J_J \) are the total angular momenta of the atomic states, \( \alpha_0, \alpha, \alpha_J \) denote all other quantum numbers which are necessary to characterize the states. The photoionization of the atomic state \( \alpha_0 J_0 \) produces the ionic state \( \alpha J_J \) which decays to the state \( \alpha J_J \) by photon emission. We assume that the lifetime of the intermediate state is sufficiently long so the two-step picture of the fluorescence process is valid. We assume also that cascade transitions do not influence the population of the radiatively decaying state. Although this is a rather severe restriction, still there are many transitions which fulfill this requirement.

Suppose that the fluorescence is registered at a certain angle \( \theta, \phi \) in the laboratory frame by a polarization insensitive detector. Using the standard approach [23,24] based on the density matrix and statistical tensor formalism [25], the angular distribution of fluorescence can be cast into the form (details of derivation of this and the following expressions will be published elsewhere):

\[ I(\theta, \phi; n_a) = N \sum_{k_{\alpha}k_{\beta}} \bar{p}_{k_{\alpha},0}(\alpha_0 J_0) B^{l_{1}}_{k_{\alpha}k_{\beta}} F_{k_{\alpha}k_{\beta}}, \]  

(2)

where \( N \) is a positive normalization factor not relevant for the following analysis and the geometrical factor is

\[ F_{k_{\alpha}k_{\beta}} = 4\pi \sum_{q_{\alpha}} \{ Y_{k_{\alpha}}(\hat{\theta}, \phi) \otimes Y_{l_{1}}(\theta, \phi) \}_{k_{\alpha}q_{\alpha}, \rho_{q_{\alpha}}q_{\alpha}} \times (p_1, p_2, p_3). \]  

(3)

Here \( \rho_{q_{\alpha}}(p_1, p_2, p_3) \) are statistical tensors describing the polarization state of the incoming photon in the laboratory frame [25]; the unit vector \( n_a(\theta, \phi) \) characterizes the direction of polarization axis of the target atom in the laboratory frame; \( \bar{p}_{k_{\alpha},0}(\alpha_0 J_0) \) are statistical tensors describing the polarization state of the target atom in the atomic frame (the frame with \( \hat{z} \)-axis aligned with the axis of atomic polarization); and \( \{ Y_{k_{\alpha}}(\hat{\theta}, \phi) \otimes Y_{l_{1}}(\theta, \phi) \}_{k_{\alpha}q_{\alpha}} \) are bipolar harmonics [26].

Naturally, due to symmetry reasons Eqs. (2) and (3) for the angular distribution of fluorescence has the same form as for the angular distribution of photoelectrons [see Eqs. (12), (14) in [24]]. The difference is only in the dynamical factors \( B^{l}_{k_{\alpha}k_{\beta}} \), which will be discussed later, and in the fact that due to the dipole selection rules for the photon emission the summation over \( k \) in Eq. (2) is limited by \( k = 0,2 \). (The summation over \( k_0 \) is limited by the conditions \( k_0 \leq 2, k_0 \leq 2 J_0 \), respectively.) Since the geometrical factor in Eq. (2) is exactly the same as for photoelectron emission all geometrical properties of the dichroism in fluorescence emission are the same as for photoemission. In particular, there should exist a variety of dichroic effects in fluorescence which have their counterparts in photoemission, and the geometrical analysis of these effects, given e.g. in [27], is applicable also for fluorescence.

A magnetic dichroism is connected with the change of the polarization direction of initial atom i.e. with the variation of the angles \( \theta, \phi, \varphi_a \). Therefore, only terms with \( k_0 \neq 0 \) in the sum (2) contribute to the magnetic dichroism.

If the target is oriented (statistical tensors \( \bar{p}_{k_{\alpha},0} \) with odd ranks \( k_0 \) are present), the magnetic dichroism effects are studied by reversing the orientation direction. For linearly polarized ionizing light the difference in fluorescence intensity for opposite target orientations gives the LMD effect in the angular distribution of radiation. Its counterpart
in photoelectron emission is well known and has been observed in photoemission from solids [28,29] as well as from free oriented atoms [21]. If the target is aligned (i.e. only even rank tensors \( P_{\alpha} \) occur) then for linearly polarized light the dichroic effect in fluorescence can be studied for two mutually perpendicular directions of the alignment. We suggest to call this effect linear alignment dichroism (LAD) [30]. Its counterpart in photoelectron emission is also known [27] and has been observed in free atoms [19–21] and solids [31].

A general expression for the linear magnetic dichroism in the angular distribution (LMDAD) of fluorescence radiation for arbitrary geometry of experiment follows from Eqs. (2) and (3) (we choose the \( z \)-axis along the ionizing light propagation and the \( x \)-axis along its polarization; a contribution from higher order state multipoles with \( k_\alpha > 2 \) can be neglected in most cases in atomic studies [30]):

\[
I(\theta, \phi; n_\alpha) - I(\theta, \phi; - n_\alpha) = i \sqrt{\frac{15}{2}} \tilde{\rho}_{10} B_{122}^{(1)} \sin \theta \sin \phi \cos \cos \sin 2\theta.
\]

(4)

With the limitation \( k_\alpha \leq 2 \) only one dynamical coefficient \( B_{122}^{(1)} \) determines the dichroism. Eq. (4) is equivalent to Eq. (19) in [27] for photoemission. A general expression for the linear alignment dichroism in the angular distribution (LADAD) is more complicated and will not be shown here.

Having in mind experiments with atoms polarized by laser optical pumping we concentrate on a possible experimental arrangement shown in Fig. 1. The scheme with counterpropagating SR and laser beams is used, for example, in experiments [20–22]. For this geometry Eq. (4) yields for the LMDAD (target atoms are oriented along the \( z \)-axis by circularly polarized laser radiation)

\[
I(\theta, \phi; n_\alpha) - I(\theta, \phi; - n_\alpha) = -i \sqrt{\frac{15}{2}} \tilde{\rho}_{10} B_{122}^{(1)} \sin \theta \sin 2\phi
\]

(5)

(the direction \( n_\alpha = (\pi, \phi_\alpha) \) corresponds to the atom orientation by the right circularly polarized laser radiation). The maximal LMDAD is expected for the observation in the plane perpendicular to the beam at the angles \( \phi = (2n + 1)\pi/4 \). The formula for the LADAD (target atoms are aligned by linearly polarized laser radiation) in the geometry of Fig. 1 takes the form

\[
I_\parallel - I_\perp = I(\theta, \phi; n_\alpha) - I(\theta, \phi; n_\perp)
\]

\[
= i \sqrt{\frac{15}{2}} \tilde{\rho}_{10} B_{122}^{(1)} \sin 2\theta \cos \phi - \sqrt{\frac{15}{2}} \tilde{\rho}_{20} B_{202}^{(1)}
\]

\[
+ \sqrt{\frac{15}{2}} \tilde{\rho}_{20} B_{202}^{(1)} \sin 2\phi \cos 2\phi
\]

\[
- \frac{5\sqrt{3}}{4\sqrt{7}} \tilde{\rho}_{20} B_{222}^{(1)}
\]

\[
\times (1 + \cos 2\theta - 2 \cos 2\phi \sin^2 \theta).
\]

(6)

Here \( n_\alpha \) and \( n_\perp \) are unit vectors along the \( x \)- and \( y \)-axis, respectively. In this case four different dynamical parameters \( B_{k_\alpha kk}^{(1)} \) determine the dichroism.

Choosing the position for the fluorescence detector one can measure individual spectral distributions for the dynamical parameters \( B_{k_\alpha kk}^{(1)} \). In the angle integrated experiments \( (k = 0) \) the LMD in fluorescence vanishes in full similarity with the case of photoelectrons, while the LAD will be still determined by the term with \( B_{k_\alpha kk}^{(1)} \) [see Eq. (6); all other terms vanish at integration over the emission angles]. We note that in this case the dichroism in the fluorescence yield is proportional to the dichroism in photoabsorption. In the angular resolved experiments this is not true due to the anisotropy of the fluorescence radiation (see below).

Until now we discussed pure kinematical properties of the LMD in the fluorescence spectra. Being sometimes complicated they are important for the analysis of experiments but virtually reflect only the symmetry properties of the experiment and the general conservation laws of angular momentum and parity. The information about the electronic properties of the studied system, which is the ultimate goal
of such experiments, is contained in the dynamical coefficients $B_{i,j,k}^{11}$. Below we present their general expression in terms of matrix elements of photoionization and fluorescence decay and discuss one simple example where the atomic system can be described in the LSJ coupling scheme.

The coefficients $B_{i,j,k}^{11}$ can be presented in a product form corresponding to the two-step ansatz:

$$B_{i,j,k}^{11} = C_{i,j,k} A_i (J_i, J_f).$$

(7)

The factor $A_i (J_i, J_f)$ describes the emitted radiation and contains the reduced dipole amplitude for the radiation decay of the photoion, $D_{a_i J_i, a_f J_f} = \langle \alpha_f J_f || D || \alpha_i J_i \rangle$:

$$A_i (J_i, J_f) = (-1)^{J_i + J_f + 1} \left\{ \begin{array}{ccc} J_i & 1 & J_f \\ 1 & J_i & k \end{array} \right\} \times \left( \sqrt{2} \delta_{i0} + \delta_{i2} \right) D_{a_i J_i, a_f J_f}^2.$$

(8)

Here we use the standard notations for the 6j-symbols. The ratio

$$\alpha_i^2 = A_i (J_i, J_f) / A_0 (J_i, J_f)$$

(9)

is the intrinsic anisotropy coefficient for radiation, introduced in [32] and tabulated in [23]. Its value determines the relative importance of the anisotropic terms with $k = 2$ in Eq. (2) with respect to the isotropic part described by terms with $k = 0$. When $\alpha_i^2$ is zero or negligible the fluorescence intensity can be used for measuring the dichroism in photoabsorption without any corrections.

The factor $C_{i,j,k}$ in Eq. (7) describes the photoionization and contains the reduced photoionization amplitudes $D_{i,j} = \langle \alpha_f J_f || D || \alpha_i J_i \rangle$. $I_j$, $J_i$ and $J_f$ being the orbital and total angular momenta of the photoelectron and the total angular momentum of the system, respectively:

$$C_{i,j,k} (J_0, J_f) = \sqrt{3} \sum_{j j'} (-1)^{j + j' + j + k + k'},$$

$$\times \left\{ J J J j J J' j' k k \right\} \left\{ J_0 1 J f \right\} \left\{ J_0 1 J' f \right\} D_{i,j} D_{i',j'}.$$

(10)

Here we used the standard notations for the 9j-symbols and $J \equiv \sqrt{2} J + 1$.

To this point our analysis was very general basing on the dipole approximation for the interaction of the atom with the radiation field and on the two-step model for the process (1). Therefore, the results are applicable to any kind of the photoion fluorescence. To proceed further a particular atomic model is needed, including information on its shell structure, intershell couplings, and particular radiation decay transition. For illustration we consider subvalence-shell excitations in not very heavy atoms, when the inter-electron Coulomb interaction is much stronger than the spin-orbit interaction and the LSJ-coupling approximation is valid. The corresponding fluorescence radiation lies in the VUV/UV region. A case of deep inner shell excitation leading to the X-ray emission is described by other coupling schemes and will be discussed elsewhere.

Now we show that to a large extent spectral distributions of LMDAD and LAD can be predicted without further assumptions. Reducing the matrix element of the radiation decay $D_{a_i J_i, a_f J_f}$ [see Eq. (10) from [30]] and using Eqs. (7) and (8) we arrive at the dynamical coefficients $B_{i,j,k}^{11}$ in the form

$$B_{i,j,k}^{11} = \sqrt{3/2} \delta_{S J} \hat{S}_J^{-2} C_{i,j,k} (J_0, J_f) \times X_i (J_f) \left| D_{k, S J} \right|^2.$$

(11)

where $D_{k, S J} = \langle L_f S_f || D || L_i S_J \rangle$ is the LS-coupled reduced matrix element. The dependence on the total angular momentum $J_f$ of the final ionic state in Eq. (11) is determined only by a factor

$$X_i (J_f) = (-1)^{I_j + I_f + 1} \left\{ J_0 1 J_f \right\} \left\{ J_0 1 J_f \right\} \left( \sqrt{2} \delta_{i0} + \delta_{i2} \right).$$

(12)

Therefore, for fixed $k$ the relative strength of the fine structure components of the fluorescence signal across the final ion multiplet $L_i S_J$ within our approximations is fully determined and depends only on the quantum numbers of the initial and final multiplets. All kinds of dichroism contain a superposition of the two spectral distributions, corresponding to $k = 0$ and $k = 2$; each of the two can be easily evaluated up to a factor. Since the fine-structure components are arranged in a regular (ascending or descending) way on the energy axis due to the Landé
Fig. 2. Schematic LAD (a) and LMDAD (b) fluorescence spectra for a transition $^1P_i \rightarrow ^3P_j$ (see text).

interval rule, one can predict the shape of the dichroism spectrum in the case when only dynamical coefficients $B^1_{j^1k^1}$ with a single value of $k$ contribute. For example, this is the case for the LMDAD which depends only on one coefficient $B^{121}_{121}$ [see Eq. (4)]. Another example is the angle-integrated LAD, which is determined by $B^{202}_{202}$.

For illustration, in Fig. 2 we show the LAD and LMDAD spectra for the fluorescence transition $^3P_i \rightarrow ^3P_j$. The bars, proportional to the $X(J_i)$ from Eq. (12) and positioned on the energy axis according to the Landé interval rule, represent the relative strength of the dichroic effect. The curves are obtained by assuming a Gaussian instrumental function to simulate a possible experimental spectrum. Note, that the above spectral distributions were obtained under very general assumptions: the results will not depend on a possible contribution from higher rank tensors $\tilde{B}_{j^2k^2}$ with $k > 2$ and on a particular model for photoionization. The spectral patterns of the dichroism are sensitive to the multiplet quantum numbers and therefore can be used also as additional spectroscopic information even when the multiplets are not well resolved.

Magnetic dichroism measurements of fluorescence spectra allowing to distinguish different coefficients $B^{111}_{j^1k^1l^1}$, can serve as a useful additional method to perform the so-called 'complete' experiment, when the photoionization amplitudes are extracted from experimentally observed quantities. Note that the factors $B^{111}_{j^1k^1l^1}$ [Eqs. (7) and (10)] include only bilinear combinations of photoionization dipole amplitudes diagonal with respect to $l$ and $j$, which correspond to the trace over quantum numbers of the unobserved photoelectron. Therefore, the measurements of fluorescence radiation are better suited for getting partial photoionization cross sections.

In conclusion, we predict linear magnetic dichroism effects of different kinds (LMDAD, LADAD, and LAD) in the photoion fluorescence. Simple expressions for the magnetic dichroism are presented for the geometry which is used in the majority of experiments on photoemission. This phenomenon can be studied both with solid and gaseous oriented or aligned targets in various ranges of fluorescence wavelength. Using the general formalism we have formulated the condition under which the LMD in fluorescence can be used for monitoring the magnetic dichroism in photoabsorption and therefore may be applied for studying the magnetic properties of solids. The spectral pattern of the LMDAD and LAD across the final ion multiplet is predicted in the case when the fluorescence can be described in the LSJ-coupling approximation.

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References
