Dichroic X-Ray Fluorescence

P. Strange,(1) P. J. Durham,(2) and B. L. Gyorffy(3)
(1)*Physics Department, Keele University, Keele, Staffordshire ST5 5BG, United Kingdom*
and Neutron Divison, Rutherford Laboratory, Chilton, Oxon OX11 0QX, United Kingdom
(2)*Daresbury Laboratory, Daresbury, Warrington, Cheshire WA4 4AD, United Kingdom*
(3)*Physics Department, Bristol University, Tyndall Avenue, Bristol BS8 1TL, United Kingdom*
(Received 29 July 1991)

We point out that dichroism in x-ray-emission spectra can be studied in fluorescence experiments without resolving the chirality of the emitted radiation, provided the incident photons are circularly polarized. We argue that such experiments would be unique probes of metallic magnetism. The effect is demonstrated in iron using a first-principles calculation based on a fully relativistic multiple-scattering theory.

PACS numbers: 78.70.En, 75.10.Lp, 75.25.+z, 78.70.Ck

Currently, the availability of tunable, intense x-ray sources generates considerable interest in using x rays to study magnetic phenomena in condensed matter [1]. The two most promising effects are magnetic-resonance scattering [2,3] and circular dichroism [4-7]. In this Letter we discuss a novel example of the latter with a close connection to the former.

The experimental discovery by Schütz *et al.* [4] that left- and right-handedly polarized photons are absorbed at different rates near absorption edges has led to considerable efforts to study this phenomenon in magnetic transition [4-7] and rare-earth [8,9] metals. Noting that this probe yields potentially very useful information about magnetism in the empty part of the conduction band, it is easy to see that the complementary information relating to the filled part of the band structure, from the analogous dichroism in the emission spectra, would be of interest. In what follows we propose an experimental scheme for exploring this hitherto unexamined feature of the x-ray spectra of solids.

Evidently, the filling of an appropriately prepared core hole by an electron from a spin-polarized conduction band will be accompanied by the emission of a photon with a characteristic state of polarization. However, detecting the polarization of emitted photons in the x-ray range of frequencies is fraught with considerable experimental difficulties. To avoid these we propose to investigate the x-ray-fluorescence process in which the incident photons are circularly polarized, but only the frequency of the emitted photons is detected. As we shall show, presently, the emission dichroism can be said to be measured by the intensity anisotropy:

$$A(\mathbf{q}_{\text{in}},\omega_{\text{in}};\mathbf{q}_{\text{out}},\omega_{\text{out}})=\frac{I^{+}(\mathbf{q}_{\text{in}},\omega_{\text{in}};\mathbf{q}_{\text{out}},\omega_{\text{out}})-I^{-}(\mathbf{q}_{\text{in}},\omega_{\text{in}};\mathbf{q}_{\text{out}},\omega_{\text{out}})}{I^{+}(\mathbf{q}_{\text{in}},\omega_{\text{in}};\mathbf{q}_{\text{out}},\omega_{\text{out}})+I^{-}(\mathbf{q}_{\text{in}},\omega_{\text{in}};\mathbf{q}_{\text{out}},\omega_{\text{out}})}, \tag{1}$$

where $\mathbf{q}_{\text{in}}$, ω_{in}, $\mathbf{q}_{\text{out}}$, and ω_{out} are the wave vectors and frequencies of the incident and outgoing photons, respectively, and the + and − refer to the state of circular polarization of the former.

The above application apart, x-ray fluorescence is of general interest because it is the limiting case of Raman scattering of photons by electrons [10-12] and hence is closely related to the magnetic resonance (anomalous) scattering of photons [2,3]. Hopefully, it will be clear that the theory we shall present below has direct bearing on this more general subject as well as on the circular dichroism in x-ray emission.

In short, we wish to study the inelastic process depicted in Fig. 1(a), in which an incident photon, described by the wave vector $\mathbf{q}_{\text{in}}$, frequency ω_{in}, and polarization index λ $(=\pm)$, scatters to become an outgoing photon corresponding to $\mathbf{q}_{\text{out}}$, ω_{out}, and λ' with an electron-hole pair left behind in the conduction band. It may be helpful to note that the scattering rate corresponds to the Keldysh diagram shown in Fig. 1(b). For orientation we also show the diagram for one of the contributions to the elastic anomalous scattering amplitude $f^{\pm}(\mathbf{q}_{\text{in}},\mathbf{q}_{\text{out}};\omega)$ in Fig. 1(c). This is the process which governs the phenomena studied by Kao *et al.* [13]. These two diagrams make explicit the relationships we have referred to above between the Raman and anomalous scattering processes. In the limit where $\hbar\omega_{\text{in}}-E_f$ and $\hbar\omega_{\text{out}}-E_f$ are greater than the core-hole and final-state-hole inverse lifetimes, Γ_c and Γ_f, respectively, and $\hbar\omega_{\text{in}}>E_f-E_c>\hbar\omega_{\text{out}}$, Fig. 1(b) describes ordinary fluorescence. The corresponding formula works out to be

$$\begin{aligned}I^{\lambda}(\mathbf{q}_{\text{in}},\omega_{\text{in}};\mathbf{q}_{\text{out}},\omega_{\text{out}})=&\frac{1}{\Gamma_f^2\Gamma_i^2}\sum_{\Lambda\Lambda'}n_{\Lambda}(E_c+\hbar\omega_{\text{in}})n_{\Lambda'}(E_c+\hbar\omega_{\text{out}})\\&\times|M^{\lambda}_{\Lambda_c\Lambda}(\mathbf{q}_{\text{in}},E_c+\hbar\omega_{\text{in}})|^2\sum_{\lambda'}|M^{\lambda'}_{\Lambda_c\Lambda'}(\mathbf{q}_{\text{out}},E_c+\hbar\omega_{\text{out}})|^2.\end{aligned} \tag{2}$$

Here Λ_c, Λ, and Λ' represent the quantum numbers of the core state, the state to which the initial electron is excited, and the state of the final conduction-band hole, respectively. $n_\Lambda(E)$ is the Λ-projected density of states,

$$n_\Lambda(E) = -\frac{1}{\pi}\int_\Omega d^3r\,\psi^*_\Lambda(\mathbf{r})\,\mathrm{Im}G(\mathbf{r},\mathbf{r},E)\psi_\Lambda(\mathbf{r})\,, \tag{3}$$

where $G(\mathbf{r},\mathbf{r},E)$ is the relativistic spin-polarized Green function. The transition matrix element $M^\lambda_{\Lambda_1\Lambda_2}(\mathbf{q},E)$ is given by

$$M^\lambda_{\Lambda_1,\Lambda_2}(\mathbf{q},E_c+\hbar\omega) = \int d^3r\,\psi^*_{\Lambda_1}(E_c,\mathbf{r})\,\delta H^\lambda_{\mathbf{q},\omega}(\mathbf{r})\,\psi_{\Lambda_2}(E+\hbar\omega,\mathbf{r})\,. \tag{4}$$

δH is the electron photon interaction Hamiltonian. Since magnetic-resonance scattering and x-ray dichroism are due to the combined effect of spin-orbit coupling and the exchange interaction the most straightforward way to proceed is to use a fully relativistic theory [5]. Thus

$$\delta H^\lambda_{\mathbf{q}}(\mathbf{r}) = -e\boldsymbol{\alpha}\cdot\mathbf{A}(\mathbf{r}) = -e\boldsymbol{\alpha}\cdot\mathbf{a}_\lambda\exp[i(\mathbf{q}\cdot\mathbf{r}+\omega t)] + \mathrm{H.c.}\,, \tag{5}$$

where $\boldsymbol{\alpha}$ are the 4×4 Dirac $\boldsymbol{\alpha}$ matrices and right (left) circularly polarized x rays are described by $\mathbf{a}_\lambda = a_\lambda(1,i,0)$ ($\mathbf{a}_\lambda = a_\lambda(1,-i,0)$). Moreover, when Eq. (4) is substituted into (2), $\psi_c(\mathbf{r})$ is a four-component solution to the Dirac equation corresponding to the initial core state. $G(\mathbf{r},\mathbf{r}',E)$ is a 4×4 bispinor Dirac Green function describing the conduction band. To calculate the Green function we use the very efficient, spin-polarized, and relativistic multiple-scattering Korringa-Kohn-Rostoker (KKR) method of Strange *et al.* [14].

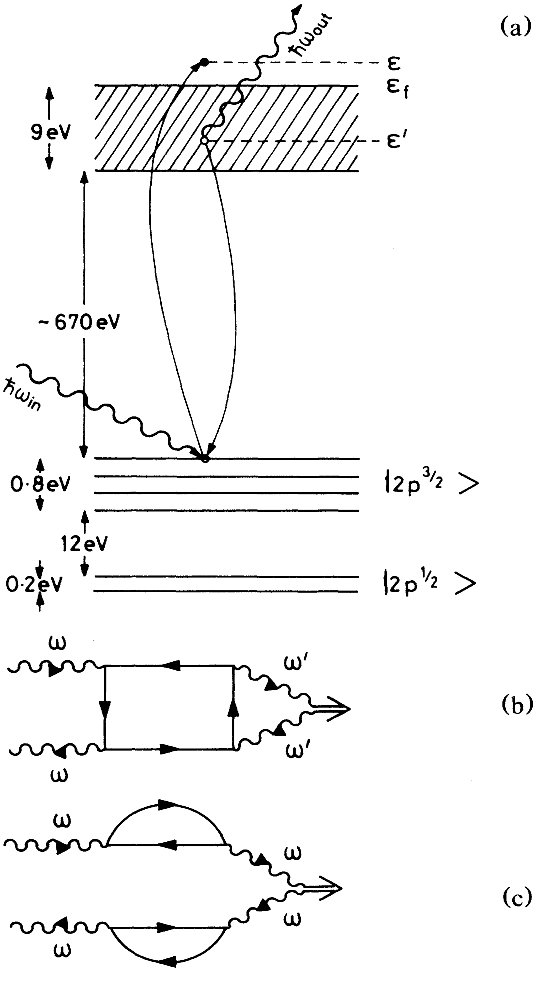

FIG. 1. (a) Schematic representation of the fluorescence process near the L edge of Fe. (b) The Keldysh diagram which yields the corresponding transition rate. (c) The Keldysh diagram for the elastic anomalous scattering amplitude.

Throughout this work we have worked with the (κ,m_j) quantum numbers. For interpretation of our results it is more convenient to consider the familiar (l,m,s) representation. The relation between the two representations is discussed in detail by Strange *et al.* [14]. Furthermore the core-level wave function $\psi_c(\mathbf{r})$ and energy E_c were calculated using the theory and codes of Ebert [15]. Finally, in all our calculations we have included quadrupole as well as dipole radiation effects by taking $e^{i\mathbf{q}\cdot\mathbf{r}} \approx 1 + i\mathbf{q}\cdot\mathbf{r}$ in Eq. (5).

Clearly Eq. (2) has a simple interpretation. The matrix elements represent the probability of transitions occurring and the density-of-states factors represent the number of states available for the transitions.

Our fully relativistic spin-polarized KKR calculation yields a band structure which is in good agreement with that of Fritsche, Noffke, and Eckhardt [16]. For the $2p$ core multiplet we find six states split into two groups separated by some 13 eV and intervals of roughly 0.2 eV between the levels in each group, as indicated in Fig. 1.

We study the case of normal incidence and normal emission of photons and add the rates of transitions originating from each of the four states in the upper group of $2p$ states with equal weight. Without spin polarization these would be a single fourfold-degenerate $2p^{3/2}$ state. Thus the core hole can be said to be created by an L_{III} absorption process.

The frequency of the incident photon ω_{in} is chosen to excite electrons into the empty part of the exchange-split d band within 1.3 to 2 eV of E_f. This ensures a highly polarized core hole which will lead to significant dichroism in the emission spectra.

The calculated L_{III} fluorescence spectrum of iron for right-handed circularly polarized incident photons, I^+, is displayed in Fig. 2 as a function of $E_f - \hbar\omega_{\mathrm{out}}$. As explained above this result is summed over the polarization

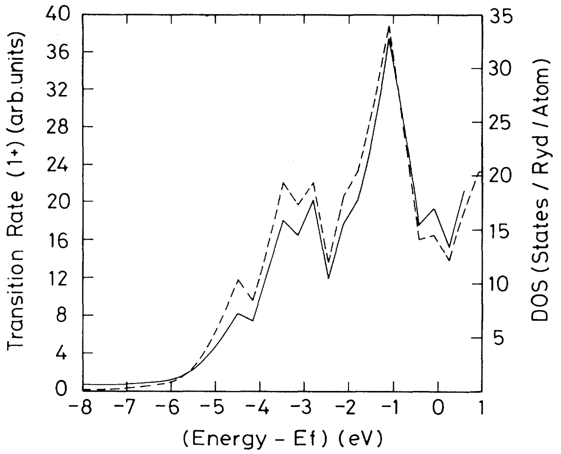

FIG. 2. The transition rate for the $L_{\rm III}$ fluorescence spectrum of Fe (solid line) and density of states (DOS) corresponding to the filled part of the conduction band (dashed line). The incident photons are right circularly polarized and the helicity of the emitted photons is summed over. Rigorously, the curves should be zero above $E-E_f=0$; however, we extend them a little higher so the probable effect of populating levels just above E_f can be seen.

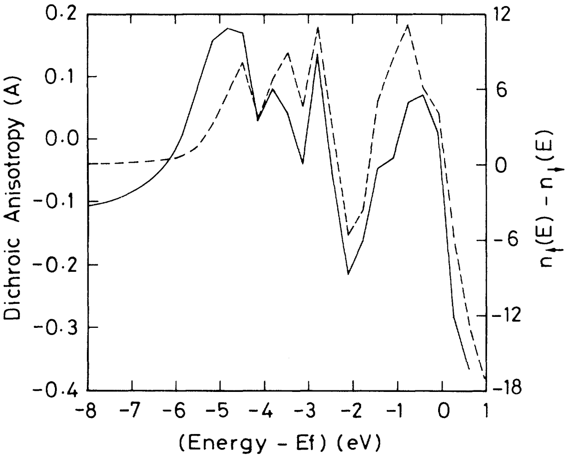

FIG. 3. The dichroic anisotropy of $L_{\rm III}$ x-ray fluorescence $A(\omega_{\rm in};\omega_{\rm out})$ (solid line) as defined in Eq. (1), and the energy-resolved spin polarization $n_\uparrow(E)-n_\downarrow(E)$ (dashed line) for Fe. Rigorously, the curves should be zero above $E-E_f=0$; however, we extend them a little higher so the probable effect of populating levels just above E_f can be seen.

of the outgoing photons. In Fig. 3 we show the intensity anisotropy $A(\mathbf{q}_{\rm in},\omega_{\rm in};\mathbf{q}_{\rm out},\omega_{\rm out})$ defined in Eq. (1). In agreement with standard dichroism experiments [4–7] we find that the L-edge dichrosim is an order of magnitude larger than that from the K edge. This is partly due to the high exchange-split d density of states around E_f and partly due to the fact that we do not excite all the $2p$ electrons, only those associated with $L_{\rm III}$ absorption.

To interpret the above results we show the density of states $n_\uparrow(E)+n_\downarrow(E)$ and the degree of spin polarization $n_\uparrow(E)-n_\downarrow(E)$ in the occupied part of the band in Figs. 2 and 3, respectively. Clearly I^+ measures the former (so does I^-) and A measures the latter.

These curves are the principal results of this Letter. On the basis of them, lifetime and instrumental broadening of a few eV notwithstanding, dichroism in the emission spectrum is observable in the proposed fluorescence experiments and it measures the spin magnetization energy by energy. In support of the above assertion we have tried a generic broadening of 1.8 eV, which gave a good account of the absorption dichroism in the experiments discussed previously [5], and found that all the prominent features of the spectra in Fig. 3 remained clearly visible.

It should be noted that the complementary information about the unoccupied band structure would be readily available if, in the above experiment, $\omega_{\rm in}$ was varied rather than $\omega_{\rm out}$.

Recall that in the theory of itinerant magnetism it appears to be important whether E_f is crossed by majority spin, minority spin, or both kinds of bands. For instance, in the Fe$_c$Ni$_{1-c}$ alloys the moment per site collapses when E_f enters the majority d band [17,18]. Evidently the above dichroic fluorescence (DF) experiments are ideally suited for studying how the spin polarization changes across the Fermi energy. Interestingly, it would facilitate the study of the Ni and Fe moment formation separately as we could tune the incident radiation to the Ni and Fe $L_{\rm II,III}$ edges alternately.

At the heart of our account of the dichroic fluorescence effect lies a description of the spin-polarized and spin-orbit-coupled $2p$ core levels. How accurate is this description? A particularly important point for our discussion is the extent to which self-consistent spin-polarized solutions of the effective one-electron Dirac equation can represent core-level excitations. The physical picture underlying these calculations is quite simple—the spin density, originating primarily from the $3d$ electrons, produces, according to density-functional theory, an effective spatially varying internal magnetic field which splits the core levels essentially as in the Zeeman effect. This picture does not include any exchange effects between the core hole and the conduction electrons which may be important in the excited state itself.

Hillebrecht, Jungblut, and Kisker [19] have reported spin-resolved photoemission results for the $3s$ levels of Fe, showing a clear exchange splitting of around 4.5 eV. This compares with a value of 2.3 eV derived from spin-polarized Dirac-equation calculations [15]. Spin-resolved photoemission from the $3p$ core levels in iron has also been reported [20]. On the other hand, Baumgarten *et al.* [21] have reported a dichroism in photoemission from the $2p$ core levels of Fe in which the shape and intensity of the core-level photoemission spectra excited by circularly polarized x rays depends on the relative orientation of photon spin and sample magnetization. These authors gave a qualitative explanation of their results using a simple "Zeeman-split" one-electron core-level structure of the kind we calculate here. They deduced an exchange splitting of 0.3 ± 0.2 eV and 0.5 ± 0.2 eV for the $2p^{1/2}$ and $2p^{3/2}$ components, respectively, values consistent with our calculated (ground-state) core-level eigenvalues [see Fig. 1(a)]. This suggests that exchange effects between the $2p$ hole and $3d$ electrons in the excited state are fairly small. Recently, quantitative calculations of the full $2p$ photoemission spectra appear to substantiate this view [22].

A second piece of evidence for our description of spin-polarized core levels relates to the spin density at the nucleus. Hyperfine field measurements are in qualitative agreement with spin-polarized relativistic density-functional calculations [15], as expected for ground-state properties, although quantitative discrepancies remain. We believe, therefore, that our core-level solutions of the local-density-approximation, spin-polarized Dirac equation constitute a useful basis from which to discuss more complex spectroscopies such as dichroic fluorescence.

Finally we wish to stress two points. First, it is trivially easy in the theory to evaluate Eq. (2) and not sum over the polarization of the outgoing photon. If this could also be achieved experimentally, even more detailed information about the electronic structure could be obtained. Second, we wish to stress that restricting interest to normal incidence and normal emission of photons is only a minor convenience both experimentally and theoretically. There is much useful information in the variation of DF with the direction of propagation of both kinds of photons, i.e., $\mathbf{q}_{\mathrm{in}}$ and $\mathbf{q}_{\mathrm{out}}$. We shall return to these in a future publication.

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