Field-Induced Magnetic Circular X-Ray Dichroism in Paramagnetic Solids: A New Magneto-Optical Effect

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(Received 8 July 2002; published 21 February 2003)

It is demonstrated that for paramagnetic solids an external magnetic field—in analogy to the magneto-optical Kerr effect in the visible regime of light—gives rise to a magnetic circular dichroism in x-ray absorption (MCXD). A detailed description of this new field-induced magneto-optical phenomenon is given. In particular it is shown that the resulting dichroic spectra may be used to deduce the spin and orbital susceptibility in a component resolved way by making use of a modified form of the MCXD sum rules.

DOI: 10.1103/PhysRevLett.90.077404 PACS numbers: 78.20.Ls, 71.15.Mb, 75.10.Lp, 78.70.Dm

Most properties of a spontaneously magnetized solid have their counterpart for a solid with its magnetization induced by an external magnetic field and that is otherwise paramagnetic. For example, the Knight shift observed in NMR corresponds to the magnetic hyperfine field that may be measured using Mössbauer spectroscopy. The magnetic form factor deduced from neutron scattering experiments is used to probe the spatial distribution of the magnetization of magnetically ordered solids. In analogy to this, the induced magnetic form factor reflects the magnetization induced by an external magnetic field in a solid that is normally paramagnetic [1]. Finally, the magneto-optical Kerr effect shows up not only for ferromagnets but can also be induced by an external magnetic field [2]. From this example it is obvious that any magneto-optical phenomenon observed for a spontaneously magnetized material should have its field-induced counterpart. This should apply, in particular, for the magnetic circular dichroism in x-ray absorption (MCXD) that is nowadays a widely used tool to probe spin and orbital magnetic moments in an element-resolved way on the basis of the MCXD sum rules [3–6].

In this Letter it is demonstrated that the MCXD indeed also occurs in paramagnetic solids in the presence of an external magnetic field. The reason for this is that time reversal symmetry is broken due to the magnetic field, as it is in magnetic solids due to the spontaneous magnetization. Because of this analogy the above mentioned sum rules could be adopted to the case of a field-induced MCXD. In particular it is shown that these rules allow in this situation to deduce from the corresponding dichroic spectra the spin and orbital susceptibilities of the absorbing atoms.

In addition to a formal description of the field-induced MCXD, results of corresponding calculations for various transition metals will be presented that are based on density functional theory. These calculations demonstrate the various aspects of the field-induced MCXD as well as its attractive and promising application to multicomponent systems.

A convenient starting point to investigate the source of a possible field-induced MCXD is the standard expression for the x-ray absorption coefficient [7]:

$$\mu_\lambda(\omega) \propto \sum_i \langle \Phi_i | X^\dagger_{\vec{q}\lambda} G^0(E) X_{\vec{q}\lambda} | \Phi_i \rangle \Theta(E - E_F). \qquad (1)$$

Here absorption of radiation with frequency ω and polarization λ is considered giving rise to transitions from the core states i with energy E_i to final states above the Fermi energy E_F that are represented by the Greens function $G^0(E)$ with the energy $E = E_i + \hbar\omega$. The corresponding relativistic electron-photon interaction operator $X_{\vec{q}\lambda} = e\vec{\alpha} \cdot \vec{A}_{\vec{q}\lambda}(\vec{r})$, with $\vec{\alpha}$ the vector of standard 4×4 Dirac matrices [8] and $\vec{A}_{\vec{q}\lambda}$ the vector potential representing the radiation field, is dealt with using the dipole approximation [7].

Considering $\mu_\lambda(\omega)$ for a paramagnetic solid in the absence of a magnetic field there will in general be no difference in the absorption of left and right circularly polarized radiation, i.e., there will be no MCXD (see Refs. [7,9]). In the presence of a magnetic field, however, time reversal symmetry is broken and a MCXD will occur. This situation can be accounted for by inserting in Eq. (1) the corresponding Greens function G^B that represents the final states in the presence of a magnetic field. Viewing the Hamiltonian $\mathcal{H}_B$ describing the coupling of the electronic system to the magnetic field as a perturbation, G^B is obtained up to first order in B from

$$G^B = G^0 + G^0 \mathcal{H}_B G^0 \qquad (2)$$

$$= G^0 + \delta G^B. \qquad (3)$$

The Hamiltonian $\mathcal{H}_B$ may be split into two parts representing separately the coupling of the field to the spin and orbital degrees of freedom of the electrons. Ignoring spin-orbit coupling, the conventional Pauli spin [10] and the orbital [11] susceptibilities can be straightforwardly deduced from Eqs. (2) and (3) setting up $\mathcal{H}_B$ within the framework of spin density theory. Obviously, δG^B leads to a corresponding correction to the absorption coefficient $\delta\mu_\lambda$

$$\delta\mu_\lambda(\omega) \propto \sum_i \langle \Phi_i | X^\dagger_{\vec{q}\lambda}\, \delta G^B(E)\, X_{\vec{q}\lambda} | \Phi_i \rangle \Theta(E - E_F). \qquad (4)$$

For that reason one finally has a MCXD signal $\Delta\mu = \delta\mu_+ - \delta\mu_-$ with its leading contribution linear in the external magnetic field B.

For spontaneously magnetically ordered solids corresponding dichroic spectra are frequently used to deduce the spin and orbital magnetic moment of the absorbing atom. Because no specific assumption has been made on the source of the magnetic order in deriving the underlying sum rules, these can be applied also for the situation considered above. This way one gets, for example, for *p*-*d* transitions dominating by far at $L_{2,3}$ edges, the modified sum rules (see, e.g., Refs. [3–6])

$$\int (\Delta\mu_{L_3} - 2\Delta\mu_{L_2})dE = \frac{BN}{3N_h\mu_B}(\chi_{\text{spin}} + 7\chi_T), \qquad (5)$$

$$\int (\Delta\mu_{L_3} + \Delta\mu_{L_2})dE = \frac{BN}{2N_h\mu_B}\chi_{\text{orb}}, \qquad (6)$$

where we have replaced the ratio of the induced spin and orbital magnetic moments μ_{spin} and μ_{orb}, respectively, and the magnetic field B by the corresponding spin and orbital magnetic susceptibilities, χ_{spin} and χ_{orb}, respectively. Accordingly, the additional term χ_T stands for the ratio of the induced T_z term and B; i.e., it represents the field-induced spin magnetic dipole moment (see, e.g., Ref. [7]). Concerning the susceptibilities χ_{spin}, χ_{orb}, and χ_T one has to consider here only their d contributions, that for transition metals are dominating all other ones. Finally, N_h is the number of d-like holes.

If the spin-orbit coupling can be ignored for the final states, χ_{spin} can be identified with the exchange enhanced Pauli spin susceptibility. Spin-orbit coupling leads to an additional contribution, that in general will be rather small, and that is due to the coupling of the field to the orbital degrees of freedom of the electrons. For spontaneously magnetized transition metals μ_{orb} is exclusively due to spin-orbit coupling and accordingly normally much smaller than μ_{spin}. For the field-induced magnetization considered here there is however a strong Van Vleck contribution to χ_{orb} due to the coupling of the magnetic field to the orbital degree of freedom that is in general in the same order of magnitude as χ_{spin}. From Eqs. (5) and (6) it is obvious that the field-induced MCXD will be the more pronounced the higher the susceptibilities, χ_{spin} and χ_{orb}, and the higher the external magnetic field is. For a field of 10 T, for example, the induced spin magnetic moment of most transition metals lies between $0.0016\mu_B$ and $0.014\mu_B$ [12]. In view of previous MCXD experiments [13], the corresponding field-induced MCXD should be detectable. In fact an experiment done very recently by Wilhelm *et al.* [14] at the European Synchrotron Radiation Facility on Pd leads to results in full accordance with the theory presented here.

To study the implication of the presented consideration in more detail we have performed corresponding numerical studies for various transition metal systems. These have been made in a fully relativistic way by making use of the Korringa-Kohn-Rostoker band structure method that is based on multiple scattering theory [15]. Results for the absorption and MCXD spectra for the $M_{2,3}$ edge of Rh in fcc-Rh are shown in Fig. 1. The absorption spectra $\mu_{M_{2,3}}$ is quite typical for a transition metal and very similar, for example, to that of Rh in the alloy fcc-Co$_x$Rh$_{1-x}$ [16]. In this magnetic alloy system a magnetic moment is induced for the normally nonmagnetic Rh atoms due to hybridization of band states with the magnetic alloy partner Co. Accordingly, a magnetic circular dichroism could be observed. Because the ratio of the spin-orbit induced orbital moment μ_{orb} to the spin moment is rather small for Rh, the ratio of the MCXD signal at the M_2 and M_3 edges do not deviate very much from the ratio -1:1 for the ferromagnetic alloy. In contrast to this situation there is a pronounced deviation from this ideal ratio in the case of the field-induced MCXD (see Fig. 1). This finding can be explained on the basis of the modified MCXD sum rules, to be a direct

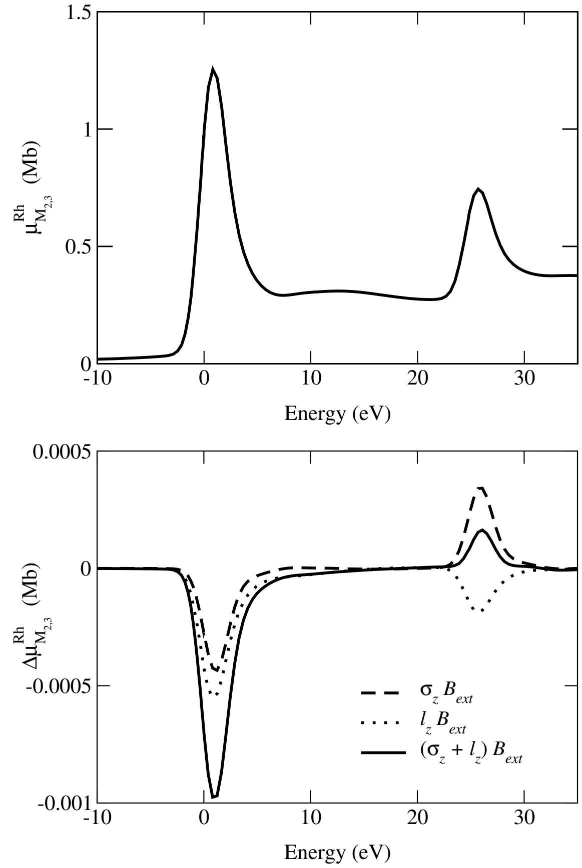

FIG. 1. Absorption coefficient $\mu_{M_{2,3}}$ and induced MCXD spectrum $\Delta\mu_{M_{2,3}}$ for the $M_{2,3}$ edges of Rh in fcc-Rh. An external field of 10 T was assumed for the calculation of $\Delta\mu_{M_{2,3}}$.

consequence of the large orbital Van Vleck susceptibility χ_{VV} in transition metals. For fcc-Rh, for example, one finds $\chi_{VV} = 63.5\ \mathrm{cm}^3/\mathrm{mol}$ that is comparable to the unenhanced Pauli spin susceptibility $\chi_{\mathrm{Pauli}} = 86.5\ \mathrm{cm}^3/\mathrm{mol}$ [17]. Allowing the external field to couple only to the spin of the electrons, i.e., to identity $\mathcal{H}_B$ with the Zeeman term $\mu_B \sigma_z B$, one finds a MCXD spectrum (dashed line in the lower panel of Fig. 1) $\Delta\mu_{M_{2,3}}$ that is very similar to that found for Rh in ferromagnetic $\mathrm{Co}_x\mathrm{Rh}_{1-x}$. However, if one considered only a coupling to the orbital degree of freedom via $\mu_B l_z B$ the situation completely changes and one gets an MCXD signal with a negative sign at the M_2 edge (dotted line in the lower panel of Fig. 1) in line with the sum rules in Eqs. (5) and (6). This explains why for the combined spectrum in Fig. 1 the ratio of the M_3- and M_2-edge peak heights is far away from $-1{:}+1$.

The modified sum rules not only give a qualitative explanation for the MCXD spectrum in Fig. 1, but also allow one to study in detail the origin of the field-induced MCXD. For this purpose we used the differential form of these rules that permits one to study the energy dependence of the various terms occurring in Eqs. (5) and (6) [18].

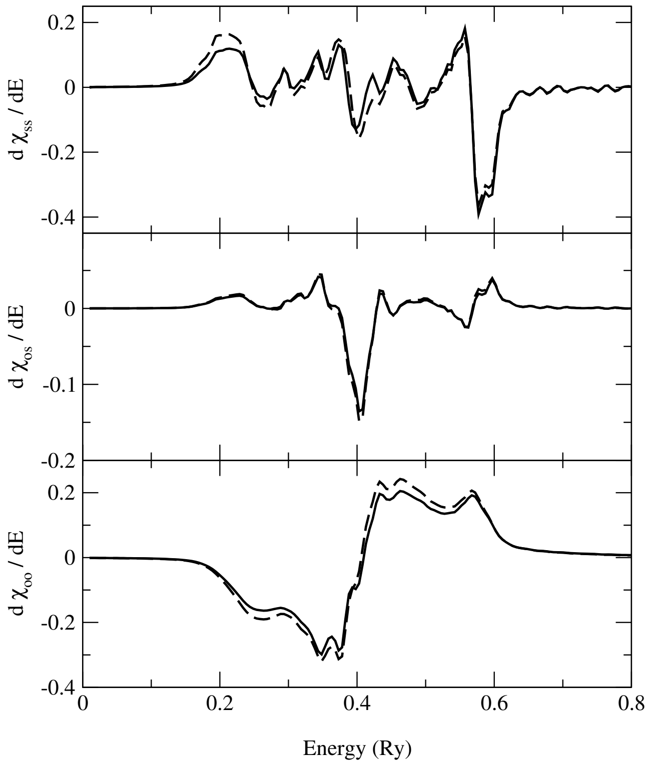

FIG. 2. Derivation of the partial susceptibilities χ_{ss}, χ_{os}, and χ_{oo} with respect to the energy for fcc-Pd as obtained from direct linear response calculations. The dashed lines give their spectroscopic counterparts $d\tilde{\chi}_{ss}/dE$, $d\tilde{\chi}_{os}/dE$, and $d\tilde{\chi}_{oo}/dE$, respectively, that have been obtained by application of the sum rules [Eqs. (5) and (6)] in their differential form.

Corresponding results are shown in Fig. 2 for fcc-Pd. Similar to Rh (see Fig. 1), one would see only spectral features in the white line regime above the Fermi energy E_F at 0.57 Ry, while the states below E_F would not contribute in a real x-ray absorption experiment. To demonstrate the reliability of the differential sum rules over a wide range of energy the Fermi energy was artificially moved to the bottom of the valence band. In addition, the MCXD caused by a coupling of the magnetic field to the spin and orbital degrees of freedom has been considered separately by setting up the Hamiltonian $\mathcal{H}_B$ in Eq. (3) accordingly. The top panel of Fig. 2 shows results for the energy derivative of the unenhanced Pauli spin susceptibility $d\chi_{ss}/dE$ of the d electrons of fcc-Pd calculated directly using linear response formalism [15]. This means that integrating the full curve in Fig. 2 (top panel) with respect to the energy up to E_F gives the unenhanced Pauli spin susceptibility χ_{ss} of the d electrons. Ignoring the influence of spin-orbit coupling this is proportional to the density of states at the Fermi energy $n(E_F)$. Using the differential form of the sum rule Eq. (5) and assuming a field that couples only to the spin, a spectroscopically determined counterpart $d\tilde{\chi}_{ss}/dE$ has been derived from the dichroic spectra at the $L_{2,3}$ edges. Based on the experience with the MCXD in spontaneously magnetized solids with cubic lattices the magnetic dipole moment term χ_T has been ignored here. As Fig. 2 shows $d\chi_{ss}/dE$ and $d\tilde{\chi}_{ss}/dE$ agree nearly perfectly. The small deviations to be seen are connected with the assumptions made when deriving the sum rules [3–6]. Among these assumptions, the most important one is the neglect of the energy dependency of the radial matrix elements entering the absorption coefficient μ_λ and in this way also $d\tilde{\chi}_{ss}/dE$. This finding holds also for the other partial susceptibilities χ_{os} and χ_{oo} considered in the middle and bottom panels of Fig. 2, respectively. Here χ_{oo} represents the induced orbital magnetic moment caused by the coupling of the field to the orbital degree of freedom of the electron; i.e., it corresponds to the Van Vleck susceptibility. Finally, χ_{os} represents the orbital magnetic moment induced by a coupling of the field to the spin of the electron due to the presence of spin-orbit coupling. If the exchange enhancement is ignored, as for the model calculations presented in Fig. 2, χ_{os} is identical to χ_{so} that gives the spin moment induced by a coupling of the field to the electron orbit. Obviously, the partial susceptibilities considered in Fig. 2 are connected to the spin and orbital susceptibilities entering the sum rules by

$$\chi_{\mathrm{spin}} = \chi_{ss} + \chi_{so} = \chi_{\mathrm{Pauli}} + \chi_{so}, \tag{7}$$

$$\chi_{\mathrm{orb}} = \chi_{oo} + \chi_{os} = \chi_{VV} + \chi_{os}. \tag{8}$$

Altogether, the results shown in Fig. 2 completely confirm the expectations based on the modified sum rules [Eqs. (5) and (6)], that, in particular, allow a separate determination of the spin and orbital susceptibilities. However, an additional decomposition, e.g., into Pauli and spin-orbit-induced spin susceptibility is obviously not possible.

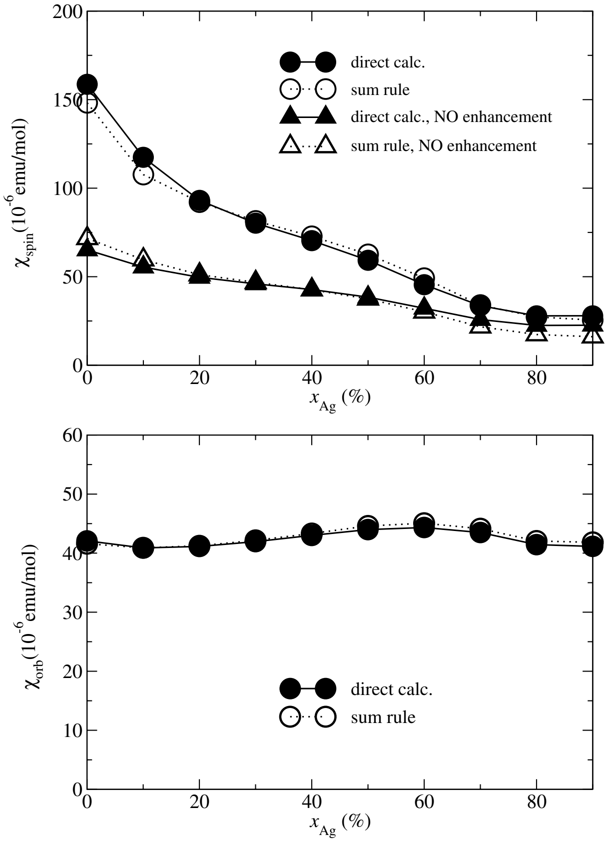

FIG. 3. Results of an application of the sum rules [Eqs. (5) and (6)] for Pt in $\mathrm{Ag}_x\mathrm{Pt}_{1-x}$. The upper and lower panels give the spin and orbital susceptibility, $\chi^{\rm Pt}_{\rm spin}$ and $\chi^{\rm Pt}_{\rm orb}$, respectively, as obtained from direct linear response calculations (full symbols) and the field-induced MCXD for the $M_{2,3}$ spectra (open symbols). The triangles in the upper panel represent results obtained ignoring the Stoner exchange enhancement of $\chi_{\rm spin}$.

To demonstrate the application of the integral form of the sum rules [Eqs. (5) and (6)] corresponding results will be presented for Pt in the alloy system $\mathrm{Ag}_x\mathrm{Pt}_{1-x}$. The total susceptibility of this alloy system is dominated by its Pt contribution and varies strongly with composition [19]. As Fig. 3 shows, the partial spin susceptibility of Pt decreases continuously with concentration if Ag is added to pure Pt. This decrease in $\chi^{\rm Pt}_{\rm spin}$ is less pronounced if the exchange enhancement is ignored. As one can see in Fig. 3 the variation of $\chi^{\rm Pt}_{\rm spin}$ is perfectly reproduced by its spectroscopic counterpart $\tilde{\chi}^{\rm Pt}_{\rm spin}$. This holds also for the orbital susceptibility $\chi^{\rm Pt}_{\rm orb}$ and its counterpart $\tilde{\chi}^{\rm Pt}_{\rm orb}$. In contrast to $\chi^{\rm Pt}_{\rm spin}$, the orbital susceptibility $\chi^{\rm Pt}_{\rm orb}$ hardly varies with concentration. This is due to the fact that $\chi^{\rm Pt}_{\rm spin}$ is primarily connected with the partial density of states at the Fermi level while $\chi^{\rm Pt}_{\rm orb}$ reflects the d-band filling.

The results presented demonstrate convincingly that the presence of an external magnetic field will give rise to MCXD even for normally paramagnetic solids. The emerging field-induced MCXD spectra can be analyzed by a modified form of the sum rules giving access to the spin and orbital susceptibility in a component resolved way. This is a rather unique feature of this new phenomenon not provided so far by any other experimental technique used to probe field-induced magnetism. This may be exploited, for example, to investigate multicomponent systems close to a ferromagnetic instability. Getting access to the spin and orbital parts of the susceptibility separately, will, in particular, allow one to study the influence of spin fluctuations and of enhancement effects due to electron-electron interaction in a more reliable and detailed way than it was possible before. Finally it should be mentioned that MCXD measurements on magnetic solids in the presence of an external field can be discussed as well on the basis of the considerations presented. In this case, the susceptibilities $\chi_{\rm spin}$ and $\chi_{\rm orb}$ stand for the corresponding high field susceptibilities of the system.

The authors would like to thank F. Wilhelm, J.-P. Kappler, and A. Rogalev for communicating their experimental results prior to publication. Financial support from the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged.

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