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The X-ray magnetic dichroism, the sum rule and spin fluctuations on the surface of manganite (LaPrCa)MnO_3

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ABSTRACT

The problem of determining the magnitude of the atomic magnetic moments in compounds with rare-earth and transition elements using the X-ray magnetic circular dichroism (XMCD) is investigated. The standard sum rules approach usually gives the moment values by several times smaller than their bulk values obtained from the direct magnetic measurements. We attribute this to the strong spin fluctuations in the surface layer which actually formed the soft XMCD signal. A method of determining the value of the local magnetic moments in the presence of strong fluctuations is proposed. The magnetic interactions in $La_{0.5}Pr_{0.2}Ca_{0.3}MnO_3$ are investigated by x-ray absorption spectroscopy, XMCD and bulk magnetization measurements. The proposed procedure is used to determine the values of atomic magnetic moments of transition and rare-earth elements as well as net magnetization on the surface and in the bulk from experimental Mn $L_{2,3}$ and Pr $M_{4,5}$ XMCD spectra.

1. Introduction

The X-ray magnetic circular dichroism (XMCD) is a very powerful tool to investigate the internal magnetic structure of complex compounds because XMCD gives a possibility to separate the element specific magnetic moments into their spin and orbital parts. Unfortunately, the shape of T $L_{2,3}$ and R $M_{4,5}$ XMCD lines (T stands for transition and R for rare earth elements) is often complex. (DyTb) Ni_2Mn**,** (LaPrCa)MnO_3, and (LaCa)(MnCr)O_3 are typical examples. As a result, the direct application of the sum rules gives very small values for the atomic magnetic moments as compared with the volume values obtained by magnetization measurements [1–3]. It is proven [4] that the sum rules for XMCD spectra that are used to separate spin and orbital contributions to the magnetic moment are formally correct for an arbitrary strength of electron-electron interactions. However, their practical application for strongly correlated systems can become complicated due to the spectral density weight spreading over a broad energy interval. In our opinion the reason for this discrepancy lies in the fact that (i) the total electron yield (TEY) method for measuring the radiation absorption gives information only on thin surface layer of about 10 nm thick and (ii) at the surface there are strong spin fluctuations which are absent deep inside the sample. The surface fluctuations are so strong that at temperature of 2 K the magnetic field of 7 T is not sufficient for saturation in the above mentioned compounds.

In this work we use a simple fluctuation theory for calculating the local spin density of states and the XMCD. The strong fluctuations of the electron spin density at the surface lead to spin-flip of a part of atomic magnetic moments and therefore the XMCD spectrum is described by the sum of the signals from the atoms whose magnetic moments are in opposite directions. We report a method for obtaining magnitudes of the local atomic moments on the surface and in the bulk. Using manganite $La_{0.5}Pr_{0.2}Ca_{0.3}MnO_3$ as an example we show how one can to decompose the experimental curve into two ones and then to calculate the magnitudes of fluctuating atomic magnetic moments using the standard sum rules. We can thereafter calculate the net magnetization at the surface and in the bulk of the sample.

2. The spin fluctuation approach

Using Stratonovich-Hubbard transformation one can write the exchange interaction in the electronic system as the interaction of the electron spin density with a fluctuating exchange field $H = v(n_+ - n_-)$ where n_s is the number of electrons in the atom with two spin projections $s = \pm$. The *d*-symmetry states and *f*-states are responsible for magnetism in transition metals and in rare earths, respectively. Let us consider the

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absorption spectrum of the circularly polarized X-rays near the L_3 edge of a transition element. We take the beam to be directed along the magnetization and normal to the sample surface. In the spin space the exchange field is expressed as a diagonal matrix $V = \begin{pmatrix} v & 0 \\ 0 & -v \end{pmatrix}$. The absorption of the right-polarized radiation by an atom can be written as $I_+(V, E) = w_1\rho_+(V, E) + w_2\rho_-(V, E)$, where ρ_s are unoccupied parts the local spin density of states (SDOS), and w_1 and w_2 are the corresponding transition rates for states with two spin projections. Here w_1 is not equal to w_2 because of the spin-orbit interactions in the $2p$ shell. In the case of the left-polarized radiation the expression for absorption is similar. The XMCD effect is proportional to the difference $D(V, E)$ between local spin density of unoccupied d-states in fluctuating exchange field V. Let $c(V)$ be probability that the exchange field is V. Then

$$D(V, E) = I_+(V, E) - I_-(V, E)$$
$$= (w_1 - w_2)c(V)(\rho_+(V, E) - \rho_-(V, E)). \tag{1}$$

To calculate the local SDOS $\rho_s(V, E)$ in a fluctuating field we use the saddle point approximation. Following [6] we assume that there are two saddle points at which exchange fields is equal to V_1 and V_2 (delivered minimums of free energy). The probability of the event $V = V_1$ is c_1 and the probability of $V = V_2$ is $c_2=1-c_1$, so that the average value of V is $\bar{V} = c_1V_1 + c_2V_2$. In the Stoner-Wohlfarth mean-field approximation the SDOS is $\rho_s(E) = \rho^0(E - s\bar{v})$ where $\rho^0(E)$ is the non-magnetic bare DOS; in other words, $\rho_s(E)$ are obtained by the shift of the energy in $\rho^0(E)$ to the mean field value.

Let us use the approximation of random fluctuations (independent of different atoms) [5–7]. The local spin density of states in the vicinity of an atom is given by

$$\rho_s(V, E) = \frac{1}{\pi}\mathrm{Im}G_s(V, E), \tag{2}$$

where $G_s(V, E)$ is the single-site Green's function. Taking into account multiple electron scattering at the local potential one can write $G_s(V, E)$ in the form

$$G(V, E) = \frac{g(E - \bar{V})}{1 - (V - \bar{V})g(E - \bar{V})}, \tag{3}$$

$$g(E - \bar{V}) = \int_{-\infty}^{\infty} \frac{\rho^0(E')}{E - \bar{V} - E' - i0}dE'. \tag{4}$$

Here $g(E - \bar{V})$ stands for the single-site Green's function in the mean field approximation whose imaginary part (divided by π) gives the density of states $\rho^0(E - s\bar{v})$.

The Eqs. (3) and (4) can be improved by replacing the mean field $\bar{V}$ by the energy dependent complex coherent potential $\Sigma(E)$[8–10]. However, such theory does not lead to qualitatively new results, so that the "virtual crystal" approximation (3, 4) is quite reasonable for our purposes.

Another limiting case is given by the long wavelength approximation or quasi-homogeneous fluctuations [11]. The exchange field of neighboring atoms can be regarded as nearly the same, and then the local DOS in the field V takes the simple form

$$\rho_s(V, E) = \rho^0(E - sv). \tag{5}$$

A more accurate consideration that takes into account the spatial correlations of spin fluctuations including the short-range magnetic order (SRMO) yields result lying between two limiting cases given by (2) and (5). This approach can be formulated as follows. Two XMCD spectra (1) at the atoms with magnetic moments along and opposite to the net magnetization are calculated by setting the two values for exchange field V. Their sum weighted with probabilities c_1 and c_2 gives the observed XMCD spectrum with electron spin density fluctuations.

Fig. 1a shows the spin density of states for the simple model in the long-wave approximation (5) (large SRMO), while Fig. 1b shows SDOS calculated in the single-site approximation (small SRMO). In the first case the exchange field simply shifts the DOS in the energy scale while in the second case the quasi-localized states are formed at certain energies. However, the effect of spin fluctuations on the form of the SDOS is qualitatively the same in both approaches.

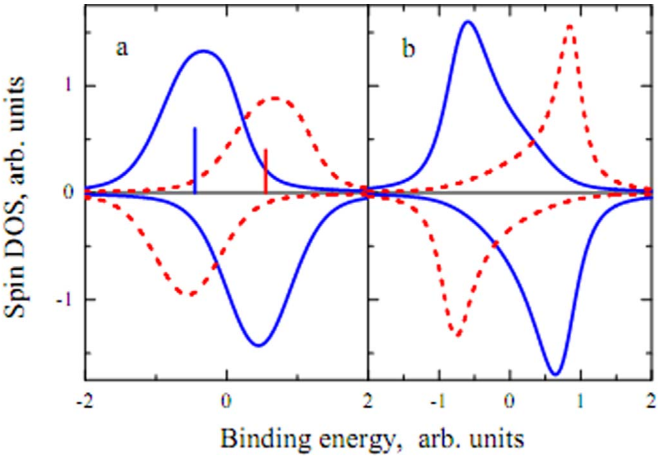

Fig. 1. Model spin DOS in quasi homogeneous fluctuating field (5) for v_1=− 0.45 (solid line) and v_2=0.55 (dashed line) multiplied by the probability field c_1=0.6, and c_2=0.4 (a) and in chaotic local field (2) of the same magnitude (b). The energy positions of the bars (a) show the values of the exchange field V, their heights define the probabilities c.

Fig. 2 shows the weighted difference of densities of states with opposite spin projections for the two values of the field v_1=− 0.45 and v_2=0.55 energy units and their sum which determines the form of the observed XMCD spectrum according to (1). The XMCD signal is an alternating function of photon energy in both asymptotic approximations. This is due to the fact that the less probable value of a random variable is farther from the center than its more probable value. As a result, peaks of the upper and lower SDOS curves in Fig. 1 have different positions, which lead to change in the sign of their difference in varying energy. The presence of the zigzag in the experimental L_3 or L_2 edge in XMCD spectrum of a transition element indicates that the spectrum is the sum of the signals from the atoms with different directions of the magnetic moments. The zigzag allows decomposing the original spectrum into two curves and ultimately calculating the fluctuating atomic magnetic moments.

3. Experimental results and analysis

The experiments were performed on $La_{0.5}Pr_{0.2}Ca_{0.3}MnO_3$ single crystals grown by the floating zone technique [12]. The XAS and XMCD

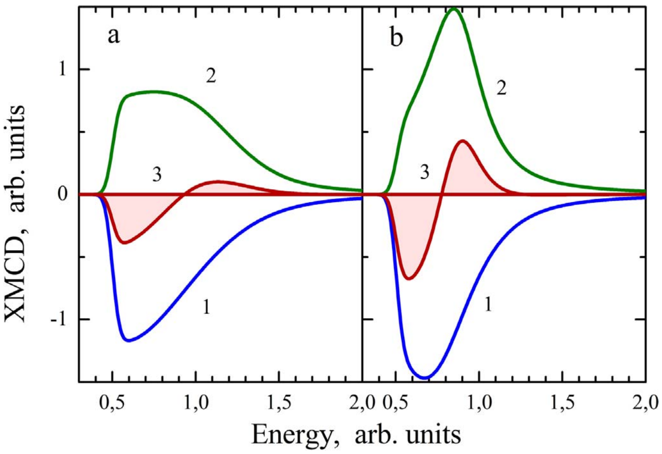

Fig. 2. The L_3 XMCD difference (1) (unoccupied spin-DOS) in the exchange field v_1 (curve 1), v_2 (curve 2) and their sum (curve 3) in the approximation of quasi homogeneous (large SRMO) electron spin density fluctuations (5) (a) and of single-site (small SRMO) fluctuations (2) (b).