Electronic structure and x-ray magnetic circular dichroism of YBa$_2$Cu$_3$O$_7$/La$_{1-x}$Ca$_x$MnO$_3$ superlattices from first-principles calculations

Xiaoping Yang, A. N. Yaresko, V. N. Antonov, and O. K. Andersen

Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, D-70569 Stuttgart, Germany
Institute of Metal Physics, 36 Vernadsky Street, 03142 Kiev, Ukraine

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The origin of x-ray magnetic circular dichroism (XMCD) at the Cu $L_{2,3}$ edge in YBa$_2$Cu$_3$O$_7$/La$_{1-x}$Ca$_x$MnO$_3$ superlattices is revealed by performing first-principle electronic structure calculation using fully-relativistic spin-polarized linear muffin-tin orbital and projected augmented plane wave methods. We show that the XMCD spectra at the Cu $L_{2,3}$ edges are proportional to the difference of the densities of Cu $d_{\uparrow\uparrow}d_{\downarrow\downarrow}$ and $d_{\uparrow\downarrow}d_{\downarrow\uparrow}$ states. Although the Cu $d_{\uparrow\uparrow}$ states lie well below the Fermi level, a small number of $d_{\uparrow\downarrow}d_{\downarrow\uparrow}$ holes is created by the Cu $d_{\uparrow\downarrow}d_{\downarrow\uparrow}$-$\text{O}_{\text{i}}$ $p_{e}$-$\text{Mn}d_{3z^2-r^2}$ hybridization across the interface. Even this tiny number of holes is sufficient to produce appreciable Cu $L_{2,3}$ XMCD.

The robustness of this conclusion is verified by studying the influence of doping, atomic relaxation, correlation effects, and antiferromagnetic order in a CuO$_2$ plane on the XMCD spectra.

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I. INTRODUCTION

Artificially grown heterostructures and superlattices of alternating superconducting (SC) and ferromagnetic (FM) materials have become an important tool for exploring the interplay between superconductivity and ferromagnetism. Various interaction phenomena that may occur, like proximity effects, coupling phenomena, charge transfer etc., are directly influenced by the structure and especially by the physical and/or chemical disorder of the interfaces that separate them. The combination of ferromagnetic and superconducting materials could end up in devices like a spin-controlled transistor with a high gain current and short switching times.

In the last years much attention has been paid to oxide based FM/SC superlattices (SL), combining a high-$T_c$ superconductor YBa$_2$Cu$_3$O$_7$ (YBCO) with a La$_{2/3}$Ca$_{1/3}$MnO$_3$ (LCMO) manganite which exhibits colossal magnetoresistance. Both YBCO and LCMO have oxide perovskite structure with very similar in-plane lattice parameters, which allows the growth of superlattices with sharp interfaces, thus strongly reducing extrinsic "structural" effects which otherwise could obscure the FM/SC interplay. Using scanning transmission electron microscopy and high spatial resolution electron energy loss spectroscopy, Varela et al. showed in Ref. 2 that individual layers of the YBa$_2$Cu$_3$O$_7$/La$_{1-x}$Ca$_x$MnO$_3$ superlattices are flat over long lateral distances. The interfaces are coherent, free of defects, exhibiting no roughness, and are located at the BaO plane of the superconductor. Concerning chemical disorder, EELS measurements show the absence of measurable chemical interdiffusion within experimental error bars.

The work on the perovskite oxide FM/SC superlattices is motivated by the appealing properties of the cuprate high-$T_c$ superconductors (HTSC) whose high SC critical temperatures make them potentially useful for technological applications. Further, since HTSC are believed to be susceptible to a variety of competing instabilities, there is a high potential for SC/FM quantum states in multilayer structures. It has been suggested by Si in Ref. 12 that electron injection from hole-doped rare earth manganites into high-temperature superconductors can yield information on spin-charge separation in high-$T_c$ superconductors. The spin-polarization, in addition to the ferromagnetic ordering nature, is one particular property of hole-doped rare earth $R_{1-x}A_x$MnO$_3$ manganite, where $R$ is a trivalent rare-earth ion and $A$ is a divalent alkaline-earth ion. In the case of $La_{2/3}Ca_{1/3}$MnO$_3$ a nearly full spin polarization of the transport electrons can be found.

Magnetization measurements of epitaxially grown bilayers of LCMO and YBCO show a coexistence of ferromagnetism and superconductivity in these bilayer samples at low temperatures. Both magnetization measurements which are used to determine $T_c$ and magneto-optical measurements for the $j_c$ evaluation of the superconducting film show up a critical thickness for the YBCO film of about $d=30$ nm, below which the superconductivity is strongly affected by the magnetic film. Sefrioui et al. in Ref. 8 studied the interplay between magnetism and superconductivity in high-quality YBCO/LCMO superlattices. They found evidences for the YBCO superconductivity depression in the presence of the LCMO layers. Due to its short coherence length, superconductivity survives in the YBCO down to a much smaller thickness in the presence of the magnetic layer than in low $T_c$ superconductors. For a fixed thickness of the superconducting layer, superconductivity is depressed over a thickness interval of the magnetic layer in the 100 nm range.

Holden et al. in Ref. 4 reported ellipsometry measurements of the far-infrared dielectric properties of SL composed of thin layers of YBCO and LCMO. The optical
data provide clear evidence that the free-carrier response is strongly suppressed in these SL as compared to the one in the pure YBCO and LCMO films. The suppression occurs in the normal as well as in the SC state and involves a quite large length scale.

This research is in its early stage, and relatively little is known about the nature of magnetism at the interface, the spatial distribution of the magnetization throughout the layers, and the interplay of FM and SC order parameters in general.

X-ray magnetic circular dichroism (XMCD) spectra at Mn and Cu $L_{2,3}$ edges in YBCO/LCMO SL were measured by Chakhalian et al. in Ref. 10. It was shown that magnetic dichroism is clearly present at both Mn and Cu edges, although the Cu XMCD signal is small compared to that of Mn (27%) and does not exceed 1.4%. The measurements suggest the presence of an uncompensated induced magnetic moment in a YBCO layer close to the YBCO/LCMO interface. As manganite layers undergo a ferromagnetic transition at around 180 K, the large dichroism at the Mn $L_{2,3}$ edge is expected. However, the presence of the net ferromagnetic magnetization on Cu is quite surprising. Authors investigated also the temperature dependence of the dichroic signals at both the Mn and Cu $L_{2,3}$ edges. At temperatures above 170 K, the dichroism on Mn disappears, consistent with the ferromagnet-paramagnet transition. Similar behavior was also found for Cu, except that already above 150 K its XMCD signal decreases below the detection limit. From the similar temperature dependences of the XMCD spectra authors concluded that the magnetic moment on Cu is induced by strong interactions between Cu spins and the ferromagnetic moment of Mn across the interface.

Later, x-ray absorption spectra (XAS) and x-ray linear dichroism (XLD) at Mn and Cu $L_{2,3}$ edges were recorded in the total electron yield (TEY) and fluorescence-yield (FY) modes from the same sample of YBCO/LCMO SL. In contrast to strong Cu $L_{2,3}$ XLD detected in the bulk sensitive FY mode, only a very weak XLD signal was measured in the TEY mode, which is supposed to probe interfacial Cu ions. This led authors to the conclusion that the electronic states of Cu ions at the YBCO/LCMO interface are strongly reconstructed, with the number of holes in the Cu $d_{3z^2-1}$ states being close to the number of Cu $d_{x^2-y^2}$ holes. A mechanism for such orbital reconstruction was proposed.

In the present study, we focus our attention on the electronic band structure of YBa$_2$Cu$_3$O$_7$/La$_{1-x}$Ca$_x$MnO$_3$ superlattices and their XMCD and XAS spectra. We show that the magnetic circular dichroism at the Cu $L_{2,3}$ edges appears due to the hybridization between completely filled Cu $d_{3z^2-1}$ states and unoccupied Mn $d_{3z^2-1}$ states split by the on-site exchange interaction. The number of Cu $d_{3z^2-1}$ holes created by the hybridization is much smaller than the number of holes in the Cu $d_{x^2-y^2}$ states. Nevertheless, even this tiny number of $d_{3z^2-1}$ holes is sufficient to produce appreciable Cu $L_{2,3}$ XMCD.

The robustness of the results is verified by studying the influence of doping, atomic relaxation and correlation effects on the electronic structure and XMCD spectra of YBCO/LCMO SL.

The paper is organized as follows. The details of the calculations are described in Sec. III. A structural model of YBCO/LCMO superlattices considered in this study is presented in Sec. III. Section IV is devoted to the electronic structure and XMCD spectra of the YBCO/LCMO SL calculated using the local spin-density approximation (LSDA) and the LSDA+$U$ method. Finally, the results are summarized in Sec. V.

II. COMPUTATIONAL DETAILS

The electronic structure and XMCD spectra of YBCO/LCMO SL were investigated by means of ab initio calculations based on the spin-polarized density functional theory. The energy band structure, densities of states (DOS), and magnetic moments were calculated within the local spin-density approximation (LSDA) using the projected augmented plane wave (PAW) method\cite{pa1,pa2,pa3,pa4} and the linear muffin-tin orbital (LMTO) method.\cite{lmto1,lmto2} The cutoff energy of the plane-wave expansion was 500 eV and the spacing between $k$ points was 0.03 Å$^{-1}$.

XMCD calculations were performed using the spin-polarized fully relativistic LMTO method (see Refs. 19,20 for details). To investigate the effect of electronic correlations on the XMCD spectra the rotationally invariant LSDA+$U$ method\cite{lmto3,lmto4} with the double-counting term approximated by the atomic limit\cite{lmto5} was used. The screened on-site Coulomb repulsion $U$ was considered as an adjustable parameter. We used $U=3$ to 5 eV for the Mn $d$ states and $U=7.5$ eV for the Cu $d$ states. For the exchange integral $J$ the value of 1.0 eV estimated from constrained LSDA calculations was used.

The finite lifetime of a core hole was accounted for by folding the XMCD spectra with a Lorentzian. The instrumental resolution was accounted for by a Gaussian of 0.5 eV.

III. STRUCTURAL MODEL

The crystal structure of YBCO/LCMO SL was approximated by a tetragonal ($P4/mnm$) unit cell consisting of one YBCO and up to 3 LMO unit cells stacked along the $c$ direction. The interface is formed by a BaO plane from the YBCO side and a MnO$_2$ plane of LMO, which replaces a CuO plane of YBCO. The unit cell consisting of one YBCO and one LMO layer is shown in Fig. 1. For the in-plane lattice constants $a=b=3.94$ Å the experimental value for pseudo-cubic LMO is used. Thus,
the orthorhombic distortion of bulk YBCO is neglected and the YBCO layer is slightly expanded in the $ab$ plane. The $c$ constant of 15.61 Å is taken to be equal to the sum of the lattice constants of bulk YBCO ($c_{YBCO}$=11.67 Å) and pseudo-cubic LMO ($c_{LMO}$=3.94 Å).

Interfacial ions are subject to forces different from those in the bulk and, thus, can change their positions. The mere transfer of charge at an interface can lead to "electronic reconstruction". Since the exact atomic structure at the YBCO/LCMO interface is not known, atomic positions were optimized using the PAW method. During the optimization the $a$ and $c$ lattice constants were fixed to the above mentioned values. As can be expected, the most sensitive to the optimization are the positions of the atoms which are close to the YBCO/LCMO interface. An oxygen ion denoted as $O_{Ba}$, which sits in the BaO plane between the nearest Cu and Mn ions, moves in the course of the optimization towards Mn. As a result, the Cu–O$_{Ba}$ distance increases from 2.29 Å in bulk YBCO to 2.37 Å in the superlattice and, thus, becomes even larger as compared to the separation of 1.98 Å between Cu and O$_{Cu}$ ions within the CuO$_2$ plane. The Mn–O$_{Ba}$ distance decreases from 1.97 Å to 1.82 Å. The optimized separation between Cu and Mn ions is slightly (4.18 Å vs. 4.15 Å) larger than between Cu ions residing in CuO$_2$ and CuO planes in bulk YBCO. The structure optimization leads also to weak buckling of MnO$_2$ planes. Nevertheless, the Mn–O$_{Mn}$ distance (1.98 Å) remains practically the same as the Mn–O$_{La}$ one (1.97 Å). As the LaO plane is a mirror plane, the positions of O$_{La}$ ions do not change during the optimization. Thus, the interfacial Mn ion is surrounded by a slightly distorted O$_{6}$ octahedron formed by O$_{Ba}$, O$_{La}$, and 4×O$_{Mn}$ ions.

Atomic positions were also optimized for 1×YBCO/2×LMO SL with $c$=19.55 Å ($c_{YBCO}$+2$c_{LMO}$) containing 2 LMO unit cells. In this case, the Cu–O$_{Ba}$ and Mn–O$_{Ba}$ distances of 2.48 Å and 1.80 Å were obtained, which gives the separation of 4.28 Å between Cu and Mn ions at the interface. As the $c$ lattice constant was fixed, the expansion at the interface occurs at the expense of some decrease of the distances between CuO$_2$ planes and between the “bulk” and “interfacial” MnO$_2$ planes.

Under the assumption that O $p$ states are completely filled and $s$ and $d$ states of Ba, Y, and La are empty, Mn and Cu $d$ states in the SL shown in Fig. 1 are filled with 24 electrons. Taking into account that the unit cell contains 2 Cu and 2 Mn ions and assuming that some charge $\delta$ may be transferred across the interface, the occupations of the $d$ shells are Cu $d^{9+\delta}$ and Mn $d^{3+\delta}$. Hence, the occupation of Mn $d$ states in this model SL corresponds to La$_{1-x}$Ca$_x$MnO$_3$ with $x \sim 1$. With each LMO layer, consisting of one MnO$_2$ and one LaO plane, added to a model unit cell, the number of electrons which fill the $d$ states of transition metal ions increases by 4, while the number of Mn ions only by 1. Consequently, the average occupation of Mn $d$ states increases with the increase of the LMO layer thickness. This should be taken into account when comparing the results calculated for different model YBCO/LMO SL.

IV. RESULTS AND DISCUSSION

A. XMCD spectra

The x-ray magnetic circular dichroism in the YBCO/LCMO SL has been measured at the Mn and Cu $L_{2,3}$ edges by Chakhalian et al. (Ref. 10). The measurements were carried out at 30 K in an applied field of 500 Oe on a superlattice of alternating 100 Å-thick, $c$-axis-oriented YBa$_2$Cu$_3$O$_7$ and La$_{2/3}$Ca$_{1/3}$MnO$_3$ layers. A circularly polarized x-ray beam was shined at a small angle to the film surface, so that the x-ray propagation direction was almost parallel to the LCMO magnetization oriented in the $ab$ plane.

Figure 3 shows XMCD spectra at the Mn and Cu $L_{2,3}$ edges calculated within LSDA for the 1×YBCO/1×LMO SL together with the experimental spectra from Ref. 10. The corresponding normalized theoretical x-ray absorb-
FIG. 2: (Color online) The theoretical and experimental (Ref. 10) XMCD spectra of the YBCO/LCMO superlattice at the Mn and Cu $L_{2,3}$ edges. The experimental Cu $L_{2,3}$ XMCD spectrum is multiplied by a factor of 2. The insets show theoretical XAS spectra averaged over two circular polarizations (solid line). The Cu $L_{2,3}$ XAS calculated with the x-ray polarization along the $c$ axis is plotted by dashed line. All the spectra are plotted relative to the corresponding $L_3$ absorption edge marked by vertical dashed lines.

The measured XMCD signal, whereas inner CuO$_2$ planes are XMCD-inert. With the increase of the YBCO layer thickness in the model unit cell, the XAS intensity would increase proportionally to the number of CuO planes, but not the dichroism. Since the calculated XMCD spectra were normalized by the intensity of the corresponding x-ray absorption spectra, the normalized XMCD signal would tend to decrease with the increase of the YBCO layer thickness, which would improve the agreement between the calculations and the experiment.

Our calculations for the 1×YBCO/1×LMO SL result in strong linear dichroism at the Cu $L_{2,3}$ edges. The XAS spectrum calculated for the x-ray polarization $\varepsilon$ parallel to the $c$ axis is compared to the spectrum averaged over two circular polarizations, which in this geometry corresponds to the averaging over $\varepsilon || b$ and $\varepsilon || c$ polarizations, in the inset to the lower panel of Fig. 2. A prominent peak at ~1 eV in the averaged spectrum is strongly suppressed when $\varepsilon$ becomes parallel to $c$. The strong XLD at the Cu $L_{2,3}$ edges is at variance with the interface-sensitive TEY measurements, which showed a very weak polarization dependence of Cu $L_{2,3}$ XAS.

In the case of Mn, the experimental $L_{2,3}$ XMCD spectrum shows two additional positive peaks at the energies around 4 eV and 10 eV which are absent in the theoretical spectrum. The cause of such a disagreement is yet unclear. One of possible reasons may be many-body effects, e.g., the interaction of the partially filled Mn $3d$ states with $4s$ core hole, which is not taken into account in the theoretical calculations. The Mn $L_{2,3}$ XMCD spectrum may change if the magnetization in interfacial MnO$_2$ planes is reversed relative to the rest of the LCMO layer or it may be strongly influenced by possible orbital ordering in LCMO. These questions need further theoretical consideration.

In the following we focus on the origin of the magnetic circular dichroism at the Cu $L_{2,3}$ edges, but first we turn our attention to the electronic band structure of YBCO/LMO superlattices.

B. Energy band structure

Symmetry-resolved densities of Cu $d$, Mn $d$, and O $p$ states calculated within LSDA for the model 1×YBCO/1×LMO SL (Fig. 1) assuming ferromagnetic ordering of Mn magnetic moments are presented in Fig. 3. Mn $d$ states are split by the octahedral component of the ligand field into rather narrow $d_{xy}$ and $d_{xz,yz}$ ("$t_{2g}$") states and much wider $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ ("$e_g$") ones. The latter are strongly hybridized with, respectively, O$_{3\text{Mn}}$ $p_{x,y}$ and O$_{Ba}$ and O$_{La}$ $p_z$ states. The $d_{3z^2-1}$ states, or more precisely their antibonding combinations with O $p$ states, are shifted to higher energies due to the shortening of the Mn–O$_{Ba}$ bond at the interface. Because of the small thickness of a LMO layer, they are narrower than the $d_{x^2-y^2}$ states.

The on-site Hund’s coupling splits the Mn $t_{2g}$ states...
into almost completely occupied majority- and unoccupied minority-spin states. The $t_{2g}$ states provide the dominant contribution (2.21$\mu_B$) to the magnetization $M_{\text{Mn}}=2.75\mu_B$ inside a Mn sphere. The rest comes from the Mn $d_{x^2-y^2}$ (0.32$\mu_B$) and $d_{3z^2-1}$ (0.21$\mu_B$) states which are also split by the on-site exchange interaction. While the minority-spin $e_g$ states are empty, the bottom of the majority-spin $d_{3z^2-1}$ and, especially, $d_{x^2-y^2}$ states is partially filled.

Figure 3 shows that, as it is usual for cuprates, all Cu $d$ states, except for $d_{x^2-y^2}$ ones, lie well below the Fermi level ($\varepsilon_F$). The $d_{x^2-y^2}$ states, interacting strongly in the $ab$ plane due to d-p type bonds with O Cu $p_{x,y}$ states, form 3 eV–wide bands in the range from $-1$ to 2 eV, as can be seen in Fig. 3 which shows the contributions of the $d_{3z^2-1}$ and $d_{x^2-y^2}$ states of Cu and Mn to the bands calculated for the 1×YBCO/1×LMO SL. The bands originating from Cu and Mn $d_{x^2-y^2}$ states have similar dispersions. The Cu $d_{x^2-y^2}$ bands for both spin directions are nearly degenerate and cross $\varepsilon_F$. The majority-spin Mn bands also cross $\varepsilon_F$, whereas the minority-spin ones lie 2 eV higher and are completely empty. Mn $d_{3z^2-1}$-derived bands are split into bonding and antibonding ones by strong interaction between the $d_{3z^2-1}$ orbitals of Mn ions from two MnO$_2$ planes via O Ba $p_z$ states. The bonding majority-spin Mn $d_{3z^2-1}$ bands are found just above $\varepsilon_F$.

Finally, Cu $d_{3z^2-1}$ bands for both spin directions lie about 2 eV below $\varepsilon_F$ and hybridize strongly with O p bands. Owing to the hybridization of the Cu $d_{3z^2-1}$ states with the spin-split Mn $d_{3z^2-1}$ states, which is mediated by O Ba $p_z$ orbitals, the densities of the majority- and minority-spin Cu $d_{3z^2-1}$, as well as O Ba $p_z$, states are remarkably different (see Fig. 3), with the differences being mostly restricted to the occupied bands. However, due to the Cu $d_{3z^2-1}$–O Ba $p_z$–Mn $d_{3z^2-1}$ hybridization, the Cu $d_{3z^2-1}$ states contribute also to the unoccupied Mn $d_{3z^2-1}$-derived bands. Because of the large (2.37 Å) Cu–O Ba separation and a large energy difference between the Cu and Mn $d_{3z^2-1}$ states, this contribution is quite small and can hardly be seen in Fig. 3. It is, however, important for understanding the origin of Cu $L_{2,3}$ XMCD spectra presented in Fig. 4.

It is well documented that LSDA fails to produce a local Cu magnetic moment in HTSC cuprates. In the model 1×YBCO/1×LMO SL, a tiny Cu moment $M_{\text{Cu}}=-0.002\mu_B$, i.e., directed oppositely to the Mn moment, is induced by the proximity of a ferromagnetic MnO$_2$ plane. The dominant contribution of $-0.014\mu_B$ to $M_{\text{Cu}}$ is provided by the $d_{3z^2-1}$ states. It is, however, partially compensated by the magnetization of opposite sign (0.012$\mu_B$) induced in the $d_{x^2-y^2}$ channel. The contributions of the $d_{x^2}$ (0.003$\mu_B$) and $d_{x^2-y^2}$ ($-0.003\mu_B$) states are even smaller and cancel each other. Such a small difference in the occupations of the majority- and minority-spin Cu $d$ states produces negligibly small exchange splitting of the $d$ shell. The $d_{3z^2-1}$ states become spin-polarized as a result of their hybridization with the spin-split unoccupied Mn $d_{3z^2-1}$ states. The majority-spin Mn $d_{3z^2-1}$ bands disperse just above $\varepsilon_F$, about 3 eV higher than the center of Cu $d_{3z^2-1}$ states, while the minority-spin bands are shifted by the on-site exchange splitting $\Delta_{\text{ex}} \sim 2$ eV to higher energies (Fig. 3). Because of this energy difference, the Cu $d_{3z^2-1}$–O Ba $p_z$–Mn $d_{3z^2-1}$ hybridization creates a larger number of holes in the majority- than in the minority-spin O Ba $p_z$ and Cu $d_{3z^2-1}$ states, as illustrated schematically in Fig. 4. Consequently, the sign of the corresponding contributions to Cu and O Ba magnetizations is opposite to the magnetization of Mn. The negative O Ba $p_z$ spin-polarization is, however, over-compensated by the positive one, induced by the hybridization of $p_{x,y}$ orbitals with Mn $d_{x^2-y^2}$ states: as the majority-spin $d_{x^2-y^2}$ states are completely filled, only minority-spin $p_{x,y}$ holes are created and the calculated total O Ba spin moment of 0.13$\mu_B$ is parallel to $M_{\text{Mn}}$.

The sparial distribution of the spin-density (SD) calculated for the 1×YBCO/1×LMO SL is presented in Fig. 4. Large positive iso-surfaces surrounding Mn ions (right panel of Fig. 4) depict the spin-density of the completely spin-polarized Mn $t_{2g}$ states. The Mn $d_{x^2-y^2}$–O Ba $p_{x,y}$ hybridization is responsible for the positive SD surface around O Ba. The left panel of Fig. 4 shows clearly that negative SD surfaces surrounding O Ba and Cu ions appear due to the polarization of O Ba $p_z$ and Cu $d_{3z^2-1}$ states, respectively, which, as it is explained above, is caused by their interaction with the spin-split unoccupied Mn $d_{3z^2-1}$ states.

Test calculations in which O Ba was shifted along the line connecting Mn and Cu ions, while all other atomic positions were kept fixed, showed that the calculated Cu
moment is very sensitive to the position of the interfacial O_{Ba} ion. The variation of the Mn–O_{Ba} and Cu–O_{Ba} distances has a twofold effect: first, the increase of the Mn–O_{Ba} separation weakens the Mn d_{3z^2−1−O_{Ba}} p_z hybridization, which leads to a downward shift of

the mostly unoccupied d_{3z^2−1} bands relative to d_{x^2−y^2} ones. The majority-spin d_{3z^2−1} states become more populated, which provides the dominant contribution to the increase of the Mn spin moment from 2.75\mu_B, when the optimized O_{Ba} position is used (d_{Mn−O_{Ba}}=1.82 \text{ Å}), to 3.01\mu_B, when O_{Ba} is equidistant to the Mn and Cu sites (d_{Mn−O_{Ba}}=2.09 \text{ Å}). It should be noted, that in spite of the increase of the Mn–O_{Ba} distance, the negative spin-polarization of the p_z states increases as O_{Ba} moves away from Mn. This can be explained by the decrease of the energy separation between the majority-spin Mn d_{3z^2−1} and O_{Ba} p_z states as a result of the downward shift of the former and an upward energy shift of the latter. Second, strengthening of the Cu d_{3z^2−1−O_{Ba}} p_z hybridization due to the decrease of the Cu–O_{Ba} distance increases the Cu d_{3z^2−1} weight in the Mn d_{3z^2−1}-derived bands and, consequently, the spin-polarization of the Cu d_{3z^2−1} states. As O_{Ba} is shifted from the optimized position (d_{Cu−O_{Ba}}=2.37 \text{ Å}) to the middle of the Cu–Mn line (d_{Cu−O_{Ba}}=2.09 \text{ Å}), M_{Cu} increases from −0.002 to −0.036\mu_B.

C. Origin of XMCD at Cu L_{2,3} edges

The calculated Cu L_2 and L_3 XMCD spectra and the spin-polarization of Cu d_{3z^2−1} and d_{x^2−y^2} states, i.e., the difference of the densities of corresponding majority- and minority-spin states, are plotted together in lower and
upper panels of Fig. 4 In order to make the similarities more clear, the spectra are plotted without the life-time and instrumental broadening and are aligned to the corresponding absorption edges which are shifted to zero energy. Figure 7 shows unambiguously that the energy dependence of the calculated XMCD signal at the Cu L₂ and L₃ edges is determined by the spin-polarization of the Cu d₃z²−1 states.

Qualitative understanding of the Cu L₂,3 XMCD absorption spectra is provided by the analysis of the matrix elements for 2p₁/₂,3/₂ → 3d₃/₂,5/₂ transitions. XMCD at the L₂,3 edges is mostly determined by the strength of the spin-orbit coupling of the initial 2p core states and spin-polarization of the final 3d states while the exchange splitting of the former as well as the SO coupling of the latter are usually of minor importance. Squared angular matrix elements for the absorption of a photon with left (p=+1) or right (p=−1) circular polarization, Ω₂, by exciting an electron from the SO-split p₁/₂,3/₂ core levels to spin- and crystal-field split d states are collected in Tables I and III. The matrix elements were calculated in the dipole approximation neglecting the SO splitting of the d states and assuming that x-rays propagate along the spin quantization axis which is parallel to z.

| f       | m_j | Ω₂⁺ | m_j | Ω₂⁻ | Ω₂⁺ + Ω₂⁻ | Ω₂⁺ − Ω₂⁻ |
|---------|-----|-----|-----|-----|------------|------------|
| d₁yz   | −1/2| 3   | −1/2| 3   | 6          | 0          |
| d₁xz   | −1/2| 3   | −1/2| 3   | 6          | 0          |
| d₁xy   | 1/2 | 12  |     |     | 12         | 12         |
| d₁3z²−1| 1/2 | 4   |     |     | −4         | −4         |
| d₁x²−y²| 1/2 | 12  |     |     | 12         | 12         |
| d₂yz   | 1/2 | 3   | 1/2 | 3   | 6          | 0          |
| d₂xz   | 1/2 | 3   | 1/2 | 3   | 6          | 0          |
| d₂xy   | −1/2| 12  | 12  | 12  | −12        | −12        |
| d₂3z²−1| −1/2| 4   | 4   | 4   | 4          | 4          |
| d₂x²−y²| −1/2| 12  | 12  | 12  | −12        | −12        |
TABLE II: Squared angular matrix elements $\Omega^2_{ij}$ for dipole allowed transitions at the $L_3$ edge. The notations are the same as in Table I.

| $p = +1$ | $p = -1$ |
|----------|----------|
| $m_j$ | $\Omega^2_{ij}$ | $m_j$ | $\Omega^2_{ij}$ | $\Omega^2_{ij} + \Omega^2_{ij}$ | $\Omega^2_{ij} - \Omega^2_{ij}$ |
| $d_{yz}$ | $-1/2$ | $6$ | $-1/2$ | $6$ | $12$ | $0$ |
| $d_{zx}$ | $-1/2$ | $6$ | $-1/2$ | $6$ | $12$ | $0$ |
| $d_{xy}$ | $1/2$ | $6$ | $-3/2$ | $18$ | $24$ | $-12$ |
| $d_{13z-1}$ | $-3/2$ | $1/2$ | $6$ | $2$ | $8$ | $4$ |
| $d_{yz-3z}$ | $1/2$ | $6$ | $-3/2$ | $18$ | $24$ | $-12$ |

| $d_{yz}$ | $1/2$ | $6$ | $1/2$ | $6$ | $12$ | $0$ |
| $d_{zx}$ | $1/2$ | $6$ | $1/2$ | $6$ | $12$ | $0$ |
| $d_{xy}$ | $3/2$ | $18$ | $-1/2$ | $6$ | $24$ | $12$ |
| $d_{13z-1}$ | $1/2$ | $2$ | $3/2$ | $6$ | $8$ | $-4$ |
| $d_{yz-3z}$ | $3/2$ | $18$ | $-1/2$ | $6$ | $24$ | $12$ |

By comparing Tables I and II we can conclude that neglecting the radial matrix elements and different lifetimes of $2p_{1/2}$ and $2p_{3/2}$ core holes, the unpolarized XAS intensity, proportional to $\Omega^2_{ij} + \Omega^2_{ji}$, is twice as high at the $L_3$ edge as at the $L_2$ one. The corresponding XMCD signals, $\Omega^2_{ij} - \Omega^2_{ji}$, are, however, of the same magnitude, with the sign of the dichroism at the $L_2$ edge being opposite to the $L_3$ one. This can be clearly seen in the lower panel of Fig. 7 where the unbroadened $L_2$ and $L_3$ XMCD spectra are plotted. The almost twofold difference in the intensities of the $L_2$ and $L_3$ XMCD spectra presented in Fig. 2 appears because of the large difference in the inverse life times of $2p_{1/2}$ ($\Gamma_{L_2}=1.04$ eV) and $2p_{3/2}$ ($\Gamma_{L_3}=0.61$ eV) core holes.

The dependence of the matrix elements on the symmetry of the final $3d$ state can be summarized as follows: the dominant contributions to the $x$-ray absorption and to the dichroism, i.e., the difference of the absorption probabilities for left and right polarized photons, $\Omega^2_{ij} - \Omega^2_{ji}$, come from the transitions to $d_{xy}$ and $d_{z^2-y^2}$ states. The transitions to $d_{3z^2-1}$ states are weaker and their contribution to the dichroism is of the opposite sign. Finally, the probabilities to excite a core $2p$ electron to a $d_{xz}$ or $d_{yz}$ state with either left or right polarized photons are equal so that these transitions do not contribute to the XMCD spectra.

It should be emphasized that the contributions to the dichroism from transitions to final states with different spin projections have opposite signs. Consequently, if majority- and minority-spin $d$ states with particular orbital character are degenerate their contributions to XMCD spectra cancel each other. This is exactly what happens to the Cu $d_{x^2-y^2}$ contribution to the XMCD spectra calculated for the $1\times YBCO/1\times LMO$ SL: although the density of the unoccupied Cu $d_{x^2-y^2}$ states is much higher than of the $d_{3z^2-1}$ ones (see Fig. 3 and, consequently, transitions to the final states of the $d_{x^2-y^2}$ character control the $x$-ray absorption at the $L_2$ and $L_3$ edges, the majority- and minority-spin $d_{x^2-y^2}$ bands are degenerate and their contribution to the dichroism is very weak.

In contrast to $d_{x^2-y^2}$, the unoccupied Cu $d_{3z^2-1}$ states, which, as explained in Sec. IVB follow the dispersion of the spin-split Mn $d_{3z^2-1}$ bands, are strongly polarized due to the Cu $d_{3z^2-1}$–O$_{Ba}$ $p_z$–Mn $d_{3z^2-1}$ hybridization. As the minority-spin Mn bands are shifted to the energies above 2 eV by the strong exchange interaction within the Mn $d$ shell (see Fig. 4), only the majority spin Cu $d_{13z-1}$ holes are created in the energy range up to 2 eV above $\varepsilon_F$. Although the number of the $d_{13z-1}$ holes is very small, it is sufficient to produce the appreciable XMCD signal at Cu $L_{2,3}$ edges.

According to Tables I and II the matrix elements for the transitions to the final states of the $d_{3z^2-1}$ character are small. It should be noted, however, that they were derived for the light propagation and magnetization directions parallel to $z$, i.e., to the tetragonal $c$ axis, whereas the XMCD spectra shown in Fig. 2 were calculated for the experimental geometry in which circularly polarized x-rays propagate along the direction of the Mn magnetization which is parallel to the $a$ axis. The dependence of the XMCD spectra on the light propagation direction can be estimated by expanding the Cu $d_{3z^2-1}$ orbital in terms of cubic harmonics defined in the rotated frame with $z^\prime||a$:

$$d_{z^2} = -\frac{1}{2}d_{z^2} + \frac{\sqrt{3}}{2}d_{x^2-y^2}.$$

Because of the appearance of the $d_{x^2-y^2}$ contribution in the expansion of the corresponding wave functions, the Cu $L_{2,3}$ XMCD spectra calculated in the $z^\prime||a$ geometry should change sign and become more intense compared to the $z||c$ spectra. This strong orientational dependence of the Cu XMCD spectra was verified by performing calculations for the $1\times YBCO/1\times LMO$ SL with $M_{\text{Cu}}||c$. Indeed, due to the weakness of the matrix elements for the transitions to the $d_{3z^2-1}$-like final states, the magnitude of the Cu $L_{2,3}$ XMCD spectra calculated in this geometry is smaller and their signs are opposite compared to the spectra shown in Fig. 2 which were obtained with the light propagation and $M_{\text{Mn}}$ directions parallel to $a$.

D. Robustness of calculated Cu $L_{2,3}$ XMCD

The proposed explanation for the strong XMCD at the Cu $L_{2,3}$ edges and robustness of the calculated spectra have been confirmed by a number of additional calculations. As explained in Sec. IVB the Cu magnetization induced by the proximity to the LMO layer is sensitive to the position of O$_{Ba}$. This is also true for the XMCD spectra. The increase of the Cu $d_{3z^2-1}$–O$_{Ba}$ $p_z$ hybridization strength with the decrease of the Cu–O$_{Ba}$ distance leads to the growth of the Cu $d_{3z^2-1}$ weight in the Mn $d_{13z-1}$–derived bands. Because of the increased number
of Cu $d_{3z^2-r^2}$ holes the calculated Cu $L_{2,3}$ XMCD spectra become more intense as O$_{Ba}$ shifts from Mn toward Cu.

As was mentioned above the number of electrons occupying Cu ($d^{10.5}$) and Mn ($d^{5.5}$) 3$d$ shells in the model $1\times$YBCO/$1\times$LMO SL corresponds to the composition of the La$_{1-x}$Ca$_x$MnO$_3$ layer with $x \sim 1$. By using the virtual crystal approximation we performed also LSDA calculations with the increased number of valence electrons corresponding to Ca doping of $x=2/3$ and $1/3$. The added electrons fill mainly Cu $d_{3z^2-r^2}$ and majority-spin Mn $d_{d-2-y^2}$ bands crossing the Fermi level. Due to the increase of the Fermi energy, the Mn $d_{3z^2-1}$-derived bands moves closer to $\varepsilon_F$ but their occupation does not change. As a consequence, the change of the electron count has only a very weak effect on the Cu XMCD spectra.

Finally, the effect of the increase of the LMO layer thickness on the Cu $L_{2,3}$ XMCD spectra was studied by performing LSDA calculations for $1\times$YBCO/$n\times$LMO ($n=2$, $3$) superlattices with FM alignment of Mn magnetic moments. A LMO layer in these SL consists of 2 and 3 unit cells of pseudo-cubic LaMnO$_3$, respectively, i.e., $3\times$MnO$_2$+2×LaO and $4\times$MnO$_2$+3×LaO planes. The distance between the MnO$_2$ planes was fixed to $c_{LMO}=3.94$ Å. For ions at the interface the positions obtained from the structure optimization for the $1\times$YBCO/$1\times$LMO SL were used. In contrast to the latter, in which both MnO$_2$ planes are at the interface with the YBCO layer, the thicker superlattices have additionally one ($n=2$) or two ($n=3$) “bulk” MnO$_2$ plane(s). Mn ions in these bulk MnO$_2$ planes are surrounded by an undistorted O$_8$ octahedron, with all the Mn–O distances of 1.97 Å being equal to that in pseudo-cubic LaMnO$_3$.

Assuming that the Cu valency does not depend on the LMO layer thickness, the effective Mn $d$ electron count in these SL increases compared to the SL with $n=1$ and corresponds to Ca content of $x=2/3$ for $n=2$ and $x=1/2$ for $n=3$. In order to separate the effects of the LMO layer thickness and that of the varying occupation of the Mn 3$d$ shell, XMCD calculations for all three SL were performed for the same effective Mn $d$ occupation corresponding to $x=2/3$.

The magnetic moment of $\sim3.2\mu_B$ calculated for the bulk Mn ions is higher than for the interfacial ones and close to the LSDA value obtained for pseudo-cubic La$_{1-x}$Ca$_x$MnO$_3$ with the same $x=2/3$. The moment of the interfacial Mn ions and the magnetization induced on Cu remain nearly constant independently of $n$. As a consequence, the Cu $L_{2,3}$ XMCD spectra calculated for the SL with $n=1$, $2$, and $3$ are nearly identical, which shows that they are not sensitive to the LMO layer thickness.

**E. Effect of electronic correlations**

The influence of electronic correlations on the Cu $L_{2,3}$ XMCD spectra calculated for the $1\times$YBCO/$1\times$LMO SL was investigated using the rotationally invariant LSDA+$U$ method. In order to understand the LSDA+$U$ results it is worth recalling that the expression for the additional orbital dependent LSDA+$U$ potential $V_i$ acting on $i$-th localized orbital becomes particularly simple if non-spherical contributions to the screened Coulomb $U$ and exchange $J$ integrals are neglected:

$$V_i = (U - J)(\frac{1}{2} - n_i),$$

where $n_i$ is the occupation of the $i$-th orbital. Thus, the occupied (unoccupied) states are shifted downwards (upwards) by $\sim (U - J)/2$.

When $U$ is applied only to the Mn $d$ states its main effect is to increase the splitting between the occupied majority- ($n_\uparrow \sim 0.9$) and unoccupied minority-spin ($n_\downarrow \sim 0.1$) Mn “$t_{2g}$” states. This causes some increase of $M_{Mn}$ from the LSDA value of 2.8$\mu_B$ to 3.0$\mu_B$ for $U=3$ eV and 3.3$\mu_B$ for $U=5$ eV. The minority-spin $d_{3z^2-1}$ and $d_{d-2-y^2}$ states with $n_\downarrow \sim 0.2$ are also shifted to higher energies. The occupation numbers of the majority-spin Mn $d_{3z^2-1}$ and $d_{d-2-y^2}$ states are close to 0.5 because of their strong hybridization with O $p$ states and partial filling of the corresponding bands (see Fig. 4). As a consequence the majority-spin Mn $d_{3z^2-1}$- and $d_{d-2-y^2}$-derived bands are almost unaffected by $U$. Hence, the Cu $L_{2,3}$ XMCD spectra, which are mostly determined by the Cu $d_{3z^2-1}$-Mn $d_{3z^2-1}$ hybridization, show weak dependence on $U$ applied to the Mn $d$ states.

LSDA+$U$ calculations with $U=7.5$ eV acting within the Cu $3d$ shell were performed for an $\sqrt{2a} \times \sqrt{2a} \times c$ unit cell of the $1\times$YBCO/$1\times$LMO SL. In this enlarged cell two Cu sites in each CuO$_2$ plane become inequivalent which enables calculations with antiferromagnetic (AFM) ordering of Cu moments. The calculations were performed for a collinear magnetic arrangement with both Cu and Mn magnetic moments parallel to the tetragonal $a$ axis.

LSDA calculations for the double cell converge to the same magnetic solution which was obtained for the single cell and is characterized by FM ordering of Mn moments and a tiny FM moment induced across the interface on Cu ions. However, when $U=7.5$ eV is applied to the Cu $d$ states and AFM ordering within a CuO$_2$ plane is allowed, Cu ions acquire a spin moment of $\sim0.4\mu_B$. The moment appears due to splitting of the partially occupied majority- and minority-spin Cu $d_{d-2-y^2}$ states by the on-site Coulomb repulsion. The other Cu $d$ states, including $d_{3z^2-1}$ ones, which are completely filled already in LSDA calculations, are shifted $\sim 3$ eV downwards to the bottom of O $p$ bands.

Because of the proximity to FM MnO$_2$ planes the Cu moments which are parallel (0.44$\mu_B$) and antiparallel (0.45$\mu_B$) to $M_{Mn}$ are slightly different, with the difference being comparable to the LSDA moment induced in the Cu $d_{3z^2-1}$ channel by the Cu $d_{3z^2-1}$-O$_{Ba}$ $p_z$-$Mn\ d_{3z^2-1}$ hybridization as discussed in Sec. [VIII]. Although the hybridization causes a small ($\sim 0.01\mu_B$) difference in the moments of two inequivalent Mn ions which have Cu
neighbors with either parallel or antiparallel magnetization, the calculated $M_{	ext{Mn}}$ of 2.75$\mu$B and 2.76$\mu$B are very close to the LSDA value.

Figure 8 shows that the spin-polarization of the Cu $d_{x^2-y^2}$ states affects strongly the $L_{2,3}$ XMCD spectra calculated for Cu ions with the moment parallel ($\text{Cu}_p$) and antiparallel ($\text{Cu}_a$) to $M_{\text{Mn}}$. As the majority- and minority-spin Cu $d_{x^2-y^2}$ states are split by the on-site Coulomb repulsion, transitions to the $d_{x^2-y^2}$ final states give a substantial contribution to the dichroism. In the geometry with the x-ray propagation and magnetization directions parallel to the c axis the contribution of the $d_{x^2-y^2}$ states would be the dominant one and the $\text{Cu}_p$ and $\text{Cu}_a$ XMCD spectra would be of the same shape but opposite signs. Since the calculations were performed with $M_{\text{Cu}_i}/a$ the matrix elements for the transitions to the $d_{x^2-y^2}$ states are strongly reduced and their contribution is comparable to the $d_{z^2}$ one, which is induced by the hybridization with FM ordered Mn and, thus, is of the same sign for both Cu ions. As a result, the shapes of the $\text{Cu}_p$ and $\text{Cu}_a$ $L_3$ XMCD spectra are different (Fig. 8), whereas the $L_2$ spectra are of the same sign although the $\text{Cu}_p$ and $\text{Cu}_a$ moments are antiparallel. Nevertheless, when the individual $\text{Cu}_p$ and $\text{Cu}_a$ spectra are averaged, the net Cu XMCD spectrum becomes similar to the LSDA spectrum calculated for the single 1$\times$YBCO/1$\times$LMO cell, which is also shown in Fig. 8 for comparison sake. The magnitude of the averaged spectrum is two times smaller, which may be explained by a decrease in the weight of the Cu $d_{z^2}$ states in the minority-spin Mn $d_{z^2}$ bands caused by the downward shift in the LSDA+$U$ calculations. Hence, even in the presence of the sizable Cu moment the dichroic signal at the Cu $L_{2,3}$ edges is still governed by the spin-polarization of the Cu $d_{z^2}$ states induced by the Cu $d_{z^2}$-$\text{Mn} d_{3z^2-1}$ hybridization via the $p$ states of interfacial O$_{\text{Ba}}$ ions.

Note, that if the AFM aligned Cu $d_{x^2-y^2}$ moments were oriented perpendicular to the Mn magnetization and, consequently, to the x-ray propagation direction they would not contribute to the dichroism, which also in this case would be determined by the transitions to the Cu $d_{3z^2-1}$ states.

\section{V. Conclusions}

We studied the electronic structure, XAS and XMCD spectra of YBCO/LMO superlattices by means of the \textit{ab initio} PAW and fully-relativistic spin-polarized LMTO methods.

Our results contradict to the orbital reconstruction model, proposed in Ref. \textsuperscript{10} in order to explain weak XLD at the Cu $L_{2,3}$ edges measured in the TEY mode. In all the calculations performed in the present work the number of Cu $d_{3z^2-1}$ holes is significantly smaller than the number of $d_{x^2-y^2}$ ones. The large difference in the number of $d_{3z^2-1}$ and $d_{x^2-y^2}$ holes causes strong linear dichroism of the calculated Cu $L_{2,3}$ XAS.

On the other hand, the LSDA calculations reproduce very well the experimental Cu $L_{2,3}$ XMCD spectra of Ref. \textsuperscript{10}. We have shown that the theoretical XMCD spectra are proportional to the difference of the densities of unoccupied majority- and minority-spin Cu $d_{3z^2-1}$ states. Although the Cu $d_{3z^2-1}$-derived bands lie $\approx 2$ eV below the Fermi level, a small number of $d_{3z^2-1}$ holes is created because of the Cu $d_{3z^2-1}$-$\text{O} _{\text{Ba}}$ $p_{z}$-$\text{Mn} d_{3z^2-1}$ hybridization, which induces a small Cu magnetic moment opposite to the moment of Mn ions. However, this tiny number of $d_{3z^2-1}$ holes is sufficient to produce substantial XMCD at the Cu $L_{2,3}$ edges.

The calculated Cu $L_{2,3}$ XMCD spectra are very robust: they are not sensitive to Ca doping of the La$_{1-x}$Ca$_x$MnO$_3$ layer simulated using the virtual crystal approximation, nor to the LMO layer thickness. Remarkably, the shape of the XMCD spectra obtained from LSDA+$U$ calculations does not change much even when $U=7.5$ eV is applied to the Cu $d$ states and AFM order with the Cu moment of 0.4$\mu$B is induced in the CuO$_2$ plane.

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