PHYSICAL REVIEW B **82**, 214504 (2010)

Weak magnetism in insulating and superconducting cuprates

G. M. De Luca,[1,*] G. Ghiringhelli,[2] M. Moretti Sala,[2] S. Di Matteo,[3] M. W. Haverkort,[4] H. Berger,[5] V. Bisogni,[6] J. C. Cezar,[6] N. B. Brookes,[6] and M. Salluzzo[1]

[1]*CNR-SPIN, Complesso MonteSantangelo via Cinthia, 80126 Napoli, Italy*

[2]*CNR-SPIN, Politecnico di Milano, piazza Leonardo da Vinci 32, 20133 Milano, Italy*

[3]*Equipe de Physique des Surfaces et Interfaces, Institut de Physique de Rennes, UMR CNRS-UR1 6251, Université de Rennes 1, 35042 Rennes Cedex, France*

[4]*Max Planck Institute for Solid State Research, Heisenbergstraße 1, D-70569 Stuttgart, Germany*

[5]*Institut de Physique de la Matière Condensée, Ecole Polytechnique Féderale de Lausanne, 1015 Lausanne, Switzerland*

[6]*European Synchrotron Radiation Facility, 6 rue Jules Horowitz, BP 220, F-38043 Grenoble Cedex, France*

(Received 25 May 2010; revised manuscript received 20 September 2010; published 3 December 2010)

X-ray magnetic circular dichroism provides evidence of an out-of-plane spin moment in undoped and doped cuprates. In La_2CuO_4 this moment is related to the canting of the antiferromagnetically ordered Cu^{2+} spins caused by the Dzyaloshinskii-Moriya interaction within the CuO_2 planes. This canting gives rise to the well-known weak ferromagnetism in high magnetic fields. We find a similar behavior in doped compounds, both in the normal and in the superconducting state, but with a different temperature dependence typical of paramagnetic systems. This result suggests that, together with short-range in-plane antiferromagnetic correlations, the Dzyaloshinskii-Moriya interaction survives up to optimal doping and in the superconducting state.

DOI: 10.1103/PhysRevB.82.214504 PACS number(s): 74.25.Ha, 74.72.Gh, 75.25.−j, 78.70.Dm

I. INTRODUCTION

In pure metals and alloys, superconductivity and magnetism are mutually exclusive phenomena. Yet, this conventional wisdom is not generally true for several more complex materials: heavy fermions [e.g., URhGe (Ref. 1)], organic BEDT-TTF$_n$X$_m$ superconductors,[2] pnictides,[3] and layered cuprates[4] all show phase diagrams where magnetic and superconducting ground states are close to each other. In high-temperature superconductors, which are the subject of the present paper, undoped parent compounds are characterized by long-range three-dimensional (3D) antiferromagnetic (AF) order with strong AF exchange constants within the CuO_2 planes. These are modeled by a two-dimensional AF $S=1/2$ Heisenberg Hamiltonian on a square lattice of Cu^{2+} ions.[5] The spin-orbit coupling and the orthorhombic distortion of CuO_6 octahedra (specifically, the fact that in-plane oxygen atoms are no more at sites which are at a center of symmetry due to the exchange of two adjacent Cu ions) lead also to a Dzyaloshinskii-Moriya (DM) interaction that, in the specific case of La_2CuO_4, is responsible for a weak magnetic moment perpendicular to the CuO_2 planes. We underline that this effect is purely determined by in-plane distortions, as properly described in Ref. 6. In this case the interplane exchange interaction orientates the moments antiferromagnetically explaining the overall 3D-AF. However, by applying a high magnetic field perpendicular to the CuO_2 planes, the weak AF interplane exchange interaction is overcome and the out-of-plane magnetic moments give rise to weak ferromagnetism (WF).[7] Neutron-scattering experiments have demonstrated that the field-induced WF survives in $La_{2-x}Sr_xCuO_4$ for very low doping[8] but no data about this effect have been reported for larger doping up to the optimal one.

In this paper, we report the observation of a field-induced out-of-plane spin moment not only in undoped La_2CuO_4 but also in underdoped and optimally doped $La_{2-x}Sr_xCuO_4$ (LSCO) and $R_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ (R=Y and Nd). The data demonstrate the existence of magnetic correlations within the CuO_2 planes even in optimally doped compounds and both in the normal and superconducting state. This finding is based on extensive measurements of copper $L_{2,3}$ edge x-ray magnetic circular dichroism (XMCD) as a function of temperature, magnetic field and on the comparison to theoretical models.

II. EXPERIMENTAL DETAILS

Epitaxial (001) $Nd_{1.2}Ba_{1.8}Cu_3O_{7-\delta}$ (NdBCO) and $YBa_2Cu_3O_{7-\delta}$ (YBCO) films were deposited by high oxygen pressure diode sputtering. Concerning NdBCO films, we studied 100 nm and 4 nm thin samples characterized by T_c's of 64 K and 20 K and a doping (p_{pl}) of 0.10 and 0.06 holes per CuO_2 plane, respectively. The YBCO film studied was close to the optimal doping with T_c=90 K and p_{pl}=0.15. Underdoped (001) LSCO (T_c=21 K and p_{pl}=0.08) and the undoped La_2CuO_4 (LCO) (Néel temperature T_N close to room temperature[9]), on the other hand, were grown by pulsed laser deposition. The structural, morphological, and superconducting characterizations of these samples demonstrate their high structural quality and the absence of any secondary phase.[10–12] Optimally doped LSCO single crystals were prepared by traveling floating zone method. Data on a $Sr_2CuO_2Cl_2$ (SCOC) single crystal (T_N=251–310 K),[9,13] which is characterized by the absence of apical oxygen atoms replaced by Cl, are also presented for comparison.

The experiments were performed at the beam-line ID08 of the European Synchrotron Radiation Facility (Grenoble, France) using the high-resolution Dragon monochromator in an ultrahigh vacuum cryostat equipped with a superconducting high-field magnet. In the experimental setup, the mag-

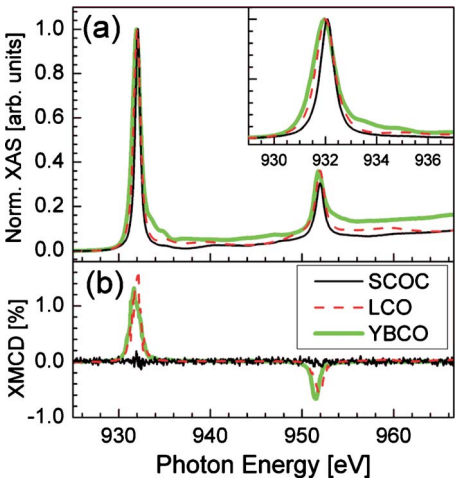

FIG. 1. (Color online) Total electron yield Cu $L_{2,3}$ edge (a) XAS and (b) XMCD spectra, measured at 4 T and 9 K, of YBCO [gray thick line (green, color online)], LCO [gray dashed line (red, color online)], and SCOC (black line) samples. The data are normalized to the L_3 peak. The inset in panel (a) shows an enlargement of the L_3 XAS region.

netic field and the photon beam are parallel to each other and lie in the horizontal plane of the laboratory frame. The sample surface, which is parallel to the CuO_2 superconducting layers, is mounted in the vertical plane. The x-ray absorption spectra (XAS) were measured simultaneously by total electron yield and fluorescence yield detection. The photon beam was normal to the sample surface and parallel to the c axis and to the external magnetic field. In the $L_{2,3}$-edge x-ray absorption process a $2p$ core electron is excited to the $3d$ empty states of Cu that are strongly spin polarized. The XMCD is obtained by the difference of XAS measured with the left and right circularly polarized light (μ_+ and μ_-, respectively) divided by the maximum at the L_3 of the sum spectrum

$$\mathrm{XMCD}(\hbar\omega) = \frac{\mu_+(\hbar\omega) - \mu_-(\hbar\omega)}{\mu_+(L_3) + \mu_-(L_3)}. \quad (1)$$

To minimize experimental uncertainties, each XMCD presented here is the average of up to eight spectra for each helicity, obtained by switching both the magnetic field direction and the light polarization.

III. EXPERIMENTAL RESULTS

The total electron yield Cu $L_{2,3}$-edges XAS and the corresponding XMCD spectra are shown in Fig. 1 for an optimally doped YBCO sample and for undoped LCO and SCOC samples, all at 9 K and 4 T. The XMCD spectra obtained from electron yield (more surface sensitive) and fluorescence yield (more bulk sensitive) give similar results. In all samples, except SCOC, a sizable dichroic signal is found, which disappears at zero magnetic field. The XMCD signal is 1.3% of the L_3 edge peak in YBCO and 1.5% in LCO with a field of 4 T. Since Cu $L_{2,3}$ XMCD is related to the value of the Cu^{2+} spin projected along the c axis (i.e., perpendicular to the CuO_2 planes) this is a clear indication that Cu spins are canted out of the CuO_2 planes in YBCO and LCO but not in SCOC. Notice that the origin of the dichroism cannot be explained through a purely paramagnetic canting of the spins induced by the field, which would require at least ten times higher magnetic fields to give the measured dichroic signal in the c direction.[14] Therefore, its origin should be searched for elsewhere.

Focusing on the two undoped samples, we point out that, although they are both antiferromagnetically ordered, the spin moments are slightly canted away from CuO_2 planes only in LCO. In SCOC, on the contrary, an intrinsic spin canting was never found by neutron diffraction due to the very small DM magnetic interaction among the Cu^{2+} spins within the CuO_2 planes.[9] This allows us to interpret our XMCD signal in undoped LCO as being due to well-known field-induced weak ferromagnetism in this compound, where a sufficiently large magnetic field parallel to the c axis aligns the net magnetic moment of canted spins in each plane along the field direction. Such an interpretation is in keeping with the absence of a dichroic signal in SCOC, where no intrinsic canting is present.

On the other hand, the similarities between the XMCD spectra measured on LCO and on doped superconducting cuprates suggest a more intriguing result, i.e., the possibility that the origin of the magnetic dichroism measured on the undoped LCO and on superconducting samples is the same.

In order to identify the origin of the experimentally observed magnetic dichroism, the XAS and the XMCD data have been compared with relativistic *ab initio* multiple-scattering calculation and with a single-ion approach. *Ab initio* multiple-scattering calculations were performed by means of the FDMNES code[15] that takes into account the full relativistic band structure of the investigated cuprates at the single-particle level. Such calculations are able to mimic some of the near-edge structural features, like the small bump around 940 eV in LSCO [Fig. 2(a)] and LCO, but they fail to reproduce the observed magnetic dichroism, which is modeled as a rigid shift of the spin-up and spin-down densities of states [Figs. 2(b) and 2(d)]. On the contrary, a much better agreement between the theory and experimental data is obtained by the single-ion method in a crystal field, based on the Cowan's atomic code.[16,17] This does not include Cu-O covalence effects but correctly takes into account the on-site Coulomb and exchange interactions and, therefore, all multiplet effects. In such a calculation, data are fitted by assuming a tetragonal crystal field and by adjusting the actual spin orientation as a parameter. The dichroic signal is therefore obtained from the out-of-plane component of the Cu^{2+}-ion spins in the $2p^63d^9$ configuration. The measured spectra, shown in Fig. 2, are well reproduced at the L_3 edge, whereas a small but non-negligible discrepancy is present at the L_2 edge, probably underlying some limitations of the purely atomic model. However, although this approach does not include solid-state effects, such as covalency, it represents the state-of-the-art modelization of L-edges spectroscopies, which are indeed better described than through band-structure calculations (see Fig. 2). For this reason, in the following we shall employ it for a quantitative analysis with some *caveat* that will be detailed in Sec. IV.

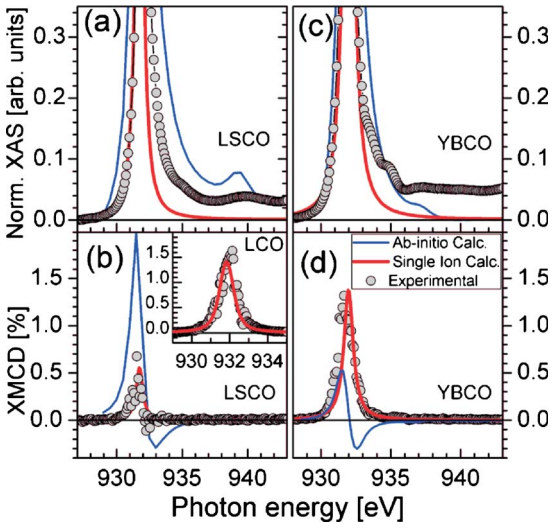

FIG. 2. (Color online) Comparison of *ab initio* (blue line) and single ion (red thick line) calculations with [panels (a) and (c)] XAS and [panels (b) and (d)] XMCD spectra at the L_3 edge. The experimental data (open circles) refer to [(a) and (b)] underdoped LSCO (T_c=21 K, p_{pl}=0.08) and [(c) and (d)] optimally doped YBCO samples. In the inset of panel (b) the comparison between experimental and theoretical XMCD of LCO is also shown.

IV. XMCD SUM RULES

X-ray magnetic circular dichroism is an extremely sensitive technique, commonly used to detect small magnetic moments in a variety of materials, including metals. Moreover, it gives direct access to the atomic magnetic moments with element selectivity through the use of sum rules applied to the experimental spectra.[18,19] However, in the case of cuprates, some precautions are needed in the applications of XMCD sum rules, as the average value of the so-called magnetic-dipole term $\langle T_z \rangle$ is not zero, as usually assumed and covalency effects may play a non-negligible role.

We rewrite the two sum rules for spin and orbital moments in a form suitable for our discussion. We define $I_{\mathrm{sum}}(L_j)=\int_{L_j}(\mu_+ + \mu_-)d\omega$ and $\Delta I(L_j)=\int_{L_j}(\mu_+ - \mu_-)d\omega$, the sum and difference of the spectra measured with left and right polarization integrated over a given spin-orbit split edge (L_3 or L_2). Then the expectation values of the z component of the atomic operators $\langle S_z \rangle$ (spin), $\langle L_z \rangle$ (orbital), and $\langle T_z \rangle$ are given by

$$2\langle S_z \rangle + \frac{7}{2}\langle T_z \rangle = \frac{\Delta I(L_3) - 2\Delta I(L_2)}{I_{\mathrm{sum}}(L_3) + I_{\mathrm{sum}}(L_2)} \times 2n_h, \tag{2}$$

$$\langle L_z \rangle = \frac{\Delta I(L_3) + \Delta I(L_2)}{I_{\mathrm{sum}}(L_3) + I_{\mathrm{sum}}(L_2)} \times \frac{4}{3}n_h, \tag{3}$$

where n_h is the number of holes in the $3d$ shell. For cuprates, we consider that the strong absorption peaks are mainly due to Cu^{2+} sites ($3d^9$), thus n_h=1. Moreover this hole is known to have x^2-y^2 symmetry.[20] In the absence of a spin-orbit interaction in the $3d$ states this would imply $\langle L_z \rangle$=0; however, the $3d$ spin-orbit interaction is not negligible in Cu and we should expect a non-negligible $\langle L_z \rangle$.[21] In fact, if we assume a perfect orientation of the atomic spin along the crystalline c axis (i.e., parallel to the quantization axis z) together with a x^2-y^2 ground state, atomic model calculations for Cu^{2+} give $\langle S_z \rangle$=−0.5, $\langle L_z \rangle$=−0.22, and $\frac{7}{2}\langle T_z \rangle$=−1,[16,17] in agreement with what Piamonteze *et al.* have found.[22]

The magnetic moments are related to the atomic operators through the relations: $m_{\mathrm{spin},z}=g\langle S_z \rangle \mu_B$ and $m_{\mathrm{orb},z}=\langle L_z \rangle \mu_B$. Since for a Cu^{2+} ion in tetrahedral environment $\frac{7}{2}\langle T_z \rangle = 2\langle S_z \rangle$,[23] we finally get a simple expression for the magnetic spin and orbital moments along the applied magnetic field direction (in our case the c axis)

$$m_{\mathrm{spin},z} \simeq \frac{\Delta I(L_3) - 2\Delta I(L_2)}{I_{\mathrm{sum}}(L_3) + I_{\mathrm{sum}}(L_2)} \times n_h \mu_B, \tag{4}$$

$$m_{\mathrm{orb},z} = \frac{\Delta I(L_3) + \Delta I(L_2)}{I_{\mathrm{sum}}(L_3) + I_{\mathrm{sum}}(L_2)} \times \frac{4}{3} n_h \mu_B, \tag{5}$$

where we have used the fact that $g \simeq 2$. By applying Eqs. (4) and (5) to the spectra of Fig. 1 we find that the XMCD signal has mainly a spin component and that the orbital moment is ~1/5 of the spin component, in good agreement with the ratio $m_{\mathrm{orb}}/m_{\mathrm{spin}}$=0.22 predicted by atomic calculations. For LCO and YBCO at 9 K we find, in particular, that $m_{\mathrm{spin},z}$ =0.022 μ_B and $m_{\mathrm{spin},z}$=0.019 μ_B, respectively.

If we compare the out-of-plane spin moment obtained using XMCD and the value reported in Ref. 6 for LCO samples, we find a value that is roughly ten times bigger. From this, we get a much greater value than obtained in Ref. 6 also for the canting angle of the Cu^{2+} spin (from 1.2° to 1.7°, instead of ~0.15°, depending on the assumptions made in the calculations[24,25]). Some comments are necessary about this discrepancy, though we cannot provide here a definitive explanation. As mentioned above, some care is needed when the effective spin moment is determined using the sum rules, since the degree of covalence in the Cu-O bond is not taken into account explicitly in our atomic model whereas in the case of cuprates it can play a non-negligible role.[26,27] In particular, the reduction in the number of holes at copper sites, due to weight transfer to oxygen atoms, can proportionally decrease the values obtained from Eqs. (4) and (5). However, we are not in condition to provide a reliable estimate for covalency corrections to the sum rules[28] and we must leave the discrepancy with the results of Ref. 6 as an open point for future investigations.

A central result of our work comes from the study of the temperature dependence of the out-of-plane spin moment. The effective out-of-plane spin moment at 4 T, determined using the sum rules, is shown as function of the temperature in Fig. 3. We can notice, in such a temperature dependence, striking differences between doped and undoped cuprates. In LCO the component of the spin moment along the c axis shows, from 9 to 280 K, the trend expected in the case of field-induced weak ferromagnetism in an antiferromagnetic system (see Ref. 6). The magnetic moment goes to zero above 250 K, i.e., close to the Néel temperature. On the contrary, as shown in Fig. 4(a), in the superconducting samples the c-axis spin moment increases as the inverse of the temperature, like in a paramagnet and independently of

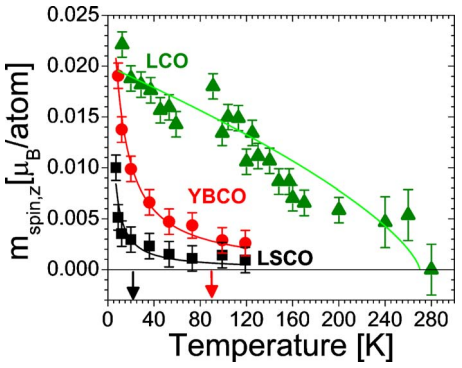

FIG. 3. (Color online) Temperature dependence, from 9 to 280 K, of the spin magnetic moment obtained from XAS and XMCD data at 4 T using the sum rules (samples cooled in zero field): LCO (green triangle), YBCO (red circle), and LSCO (black squares). The red and black arrows indicate the T_c of the optimally doped YBCO and underdoped LSCO samples, respectively.

the doping it goes to zero, within the experimental error, above 130 K. Moreover, the same spin moment measured at 9 K is linear as a function of the magnetic field with no remanent magnetic moment at zero field, as shown for YBCO and NdBCO in Fig. 4(b).

Therefore, the temperature and magnetic field dependence of the spin moment in the doped compounds is compatible with a system of spins characterized by a component of the magnetic moment perpendicular to the CuO_2 planes due to the DM interaction. These effective spin moments are aligned by the field and are progressively ordered by lowering the temperature. The idea is that the magnetic dichroism in this disordered spin state of the superconducting cuprates is determined by the competition between thermal disorder and the magnetic field, which gives rise to the observed magnetic and temperature behavior.

Quite interestingly, no change in the temperature dependence of the magnetic moments is observed at the critical temperature of the superconducting compounds (Fig. 3).

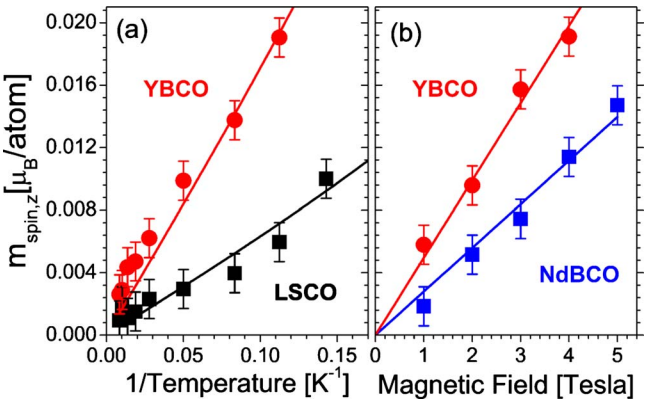

FIG. 4. (Color online) (a) Spin magnetic moment as function of the inverse of the temperature obtained from XAS and XMCD data at 4 T using the sum rules (samples cooled in zero field): YBCO (red circle) and LSCO (black squares). (b) Spin magnetic moment as function of the magnetic field for YBCO (red circles) and NdBCO (blue squares).

Moreover, the magnitude of the spin moment measured at 9 K is found to be independent of the way the samples are cooled below T_c, i.e., the same values and the same magnetic field dependence is observed in both zero-field-cooled and field-cooled conditions. These results exclude any correlation between the magnetic signal, due to the localized spin moments at the Cu^{2+} sites and the presence of vortices in the compounds, in contrast with Ref. 29 where a magnetic field-induced signal was attributed to orbital currents inside the vortices.

The different temperature dependence of the spin moments in undoped and doped compounds also underlines the differences between the magnetic correlations in the two cases. In undoped LCO a weak ferromagnetism develops because the canted Cu^{2+} spins posses a 3D-AF long-range order in zero field. The magnetic field just converts the overall antiferromagnetic ordering between adjacent CuO_2 planes along the c axis, to a weak ferromagnetic one. It is consequently understandable why, by increasing the temperature, the spin moment disappears at the Néel temperature. On the other hand, in doped compounds a magnetic component along the c axis survives but this component is not coupled with a long-range AF order of the Cu^{2+} spins that is, indeed, destroyed by doping.

V. DISCUSSION

The experimental results show an interesting coexistence of superconductivity and magnetic correlations within the CuO_2 planes. In particular, our data show that, even in superconducting and optimally doped cuprates, the DM interaction within the CuO_2 planes survives and gives rise to the out-of-plane spin canting.

A magnetic spin component in optimally doped cuprates was previously detected by XMCD only in $YBa_2Cu_3O_7$ (YBCO)/$La_{0.67}Ca_{0.33}MnO_3$ multilayers by Chakhalian *et al.*[30] The overall size of the XMCD signal and its shape are comparable to the ones measured here, therefore suggesting a common origin of our results and those of Ref. 30. Indeed, we believe that the spin moments found in the two cases have the same origin, i.e., a canting of the Cu spin out of the CuO_2 planes. The main difference between our data and those of Ref. 30 is in the temperature dependence of the spin moment. In the manganite/cuprate superlattices of Ref. 30 the temperature dependence is determined by the interaction of Cu^{2+} canted spins belonging to YBCO with the ferromagnetic manganite layer: Cu moments of YBCO show a typical ferromagnetic behavior up to the Curie temperature of the manganite. In our data only the external field acts on the Cu moments and we find different T dependences in LCO and in YBCO.

An additional important point to be answered is if there is any correlation between our data and the polarized inelastic neutron scattering[31] and Kerr effect experiments,[32] which found the presence of magnetic features in YBCO cuprates with different doping. First of all, the effect we observe cannot be attributed at all to the orbital currents proposed by Varma,[33] which cannot be probed by circular dichroism in absorption because their associated order parameter only

couples to linearly polarized x rays.[34] In Ref. 31 Fauqué *et al.* showed that their experimental results could be also explained by some form of ordered spin decoration of the CuO_2 plaquettes, which could agree with our results. However, from the temperature dependence of the spin magnetic moment we cannot establish a direct correlation between the field-induced spin component and the pseudogap temperature because the signal becomes too small to be measured above 130 K, which is well below the pseudogap temperature of the underdoped samples that have been analyzed. Similarly, the results of the Kerr effect experiment[32] and our results could probably have a similar origin, which is identified in our experiment to be related to the existence of an out-of-plane Cu^{2+} spin moments associated to the DM interaction even in optimally doped cuprates.

VI. CONCLUSIONS

In conclusion, in this paper we showed that the DM magnetic interaction within the CuO_2 planes, observed in underdoped cuprates, survives in both the normal and superconducting states of LSCO, YBCO, and NdBCO high-T_c superconductors. The magnetic coupling is revealed by the presence of a canting of the Cu^{2+} spins out of the CuO_2 planes, determined by x-ray magnetic circular dichroism measurements around the copper $L_{2,3}$ edge. The magnetic signal measured by XMCD does not show any anomaly at the superconducting critical temperature. Moreover, the data also demonstrate that, while in the undoped compound, the canted spins exhibit the well-known field-induced weak ferromagnetism, hole doping makes the canted spins of adjacent layers independent of one another. The results presented here should be considered for a complete understanding of the interplay between magnetism and superconductivity in cuprates.

ACKNOWLEDGMENTS

The authors are grateful to Antonio Barone, Lucio Braicovich, and Ruggero Vaglio for useful discussions.

*gdeluca@na.infn.it

[1] D. Aoki, A. Huxley, E. Ressouche, D. Braithwaite, J. Flouquet, J.-P. Brison, E. Lhotel, and C. Paulsen, Nature (London) **413**, 613 (2001).
[2] F. Kagawa, K. Miyagawa, and K. Kanoda, Nature (London) **436**, 534 (2005); R. H. McKenzie, Science **278**, 820 (1997).
[3] J. Zhao, Q. Huang, C. de la Cruz, S. Li, J. W. Lynn, Y. Chen, M. A. Green, G. F. Chen, G. Li, Z. Li, J. L. Luo, N. L. Wang, and P. Dai, Nature Mater. **7**, 953 (2008).
[4] M. A. Kastner, R. J. Birgeneau, G. Shirane, and Y. Endoh, Rev. Mod. Phys. **70**, 897 (1998).
[5] S. Chakravarty, B. I. Halperin, and D. R. Nelson, Phys. Rev. Lett. **60**, 1057 (1988).
[6] T. Thio, T. R. Thurston, N. W. Preyer, P. J. Picone, M. A. Kastner, H. P. Jenssen, D. R. Gabbe, C. Y. Chen, R. J. Birgeneau, and A. Aharony, Phys. Rev. B **38**, 905 (1988).
[7] A. Gozar, B. S. Dennis, G. Blumberg, S. Komiya, and Y. Ando, Phys. Rev. Lett. **93**, 027001 (2004).
[8] M. Reehuis, C. Ulrich, K. Prokes, A. Gozar, G. Blumberg, S. Komiya, Y. Ando, P. Pattison, and B. Keimer, Phys. Rev. B **73**, 144513 (2006).
[9] D. Vaknin, S. K. Sinha, C. Stassis, L. L. Miller, and D. C. Johnston, Phys. Rev. B **41**, 1926 (1990).
[10] M. Salluzzo, G. M. de Luca, D. Marré, M. Putti, M. Tropeano, U. Scotti di Uccio, and R. Vaglio, Phys. Rev. B **72**, 134521 (2005).
[11] L. Braicovich, L. J. P. Ament, V. Bisogni, F. Forte, C. Aruta, G. Balestrino, N. B. Brookes, G. M. De Luca, P. G. Medaglia, F. Miletto Granozio, M. Radovic, M. Salluzzo, J. van den Brink, and G. Ghiringhelli, Phys. Rev. Lett. **102**, 167401 (2009).
[12] L. Braicovich, J. van den Brink, V. Bisogni, M. Moretti Sala, L. J. P. Ament, N. B. Brookes, G. M. De Luca, M. Salluzzo, T. Schmitt, V. N. Strocov, and G. Ghiringhelli, Phys. Rev. Lett. **104**, 077002 (2010).
[13] L. L. Miller, X. L. Wang, S. X. Wang, C. Stassis, D. C. Johnston, J. Faber, Jr., and C.-K. Loong, Phys. Rev. B **41**, 1921 (1990).
[14] Assuming a nearest-neighbor superexchange interaction $J \simeq 125$ meV the effective molecular magnetic field (NSJ) is on the order of 250 meV in cuprates. The effect of an external magnetic field is $(2S+L)B$ on the order of 0.06 meV/tesla. A canting due to B would be on the order of 0.01°/tesla.
[15] Y. Joly, Phys. Rev. B **63**, 125120 (2001).
[16] R. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Berkeley, 1981).
[17] M. W. Haverkort, Ph.D. thesis, University of Cologne, 2005.
[18] B. T. Thole, P. Carra, F. Sette, and G. van der Laan, Phys. Rev. Lett. **68**, 1943 (1992).
[19] P. Carra, B. T. Thole, M. Altarelli, and X. Wang, Phys. Rev. Lett. **70**, 694 (1993).
[20] C. T. Chen, Y. U. Idzerda, H. J. Lin, N. V. Smith, G. Meigs, E. Chaban, G. H. Ho, E. Pellegrin, and F. Sette, Phys. Rev. Lett. **75**, 152 (1995).
[21] G. Ghiringhelli, L. H. Tjeng, A. Tanaka, O. Tjernberg, T. Mizokawa, J. L. de Boer, and N. B. Brookes, Phys. Rev. B **66**, 075101 (2002).
[22] C. Piamonteze, P. Miedema, and F. M. F. de Groot, Phys. Rev. B **80**, 184410 (2009).
[23] This is an exception to usual assumptions in XMCD sum rules, where T_z is considered negligible with respect to the spin moment. Our calculation for the case of Cu^{2+} ion is in agreement with Piamonteze *et al.* (Ref. 22).
[24] The canting angle θ can be calculated following the prescriptions of Ref. 25 or, as in Ref. 6, with the equation: $\theta = m_{\mathrm{spin},z}/(g\mu_B S)$. In the latter case, one can use a value of S reduced from $\frac{1}{2}$ by a factor 0.63 for quantum renormalization (as in Ref. 6) or not. In the former case, one can directly fit the XMCD spectrum or use the formula (Ref. 25) $\sin\theta = 2\mathrm{XMCD}(L_3)$. In all cases the values obtained for the canting angle are contained in the range given in the text.
[25] G. Ghiringhelli, Ph.D. thesis, Université J. Fourier, 2001.

[26] A. C. Walters, T. G. Perring, J.-S. Caux, A. T. Savici, G. D. Gu, C.-C. Lee, W. Ku, and I. A. Zaliznyak, Nat. Phys. **5**, 867 (2009).
[27] R. E. Walstedt and S.-W. Cheong, Phys. Rev. B **64**, 014404 (2001).
[28] If we assume the correctness of the value of Ref. 6 and suppose that all the discrepancy is determined by a reduced value of n_h, we would get $n_h \sim 0.1$ with 0.9 of the hole weight transferred away from the $d_{x^2-y^2}$ orbital, which is not plausible, also in the light of the results of Refs. 26 and 27.
[29] B. Lake, K. Lefmann, N. B. Christensen, G. Aeppli, D. F. McMorrow, H. M. Ronnow, P. Vorderwisch, P. Smeibidl, N. Mangkorntong, T. Sasagawa, M. Nohara, and H. Takagi, Nature Mater. **4**, 658 (2005).
[30] J. Chakhalian, J. W. Freeland, G. Srajer, J. Strempfer, G. Khaliullin, J. C. Cezar, T. Charlton, R. Dalgtesh, C. Bernhard, G. Cristiani, H.-U. Habermeier, and B. Keimer, Nat. Phys. **2**, 244 (2006).
[31] B. Fauqué, Y. Sidis, V. Hinkov, S. Pailhès, C. T. Lin, X. Chaud, and P. Bourges, Phys. Rev. Lett. **96**, 197001 (2006).
[32] J. Xia, E. Schemm, G. Deutscher, S. A. Kivelson, D. A. Bonn, W. N. Hardy, R. Liang, W. Siemons, G. Koster, M. M. Fejer, and A. Kapitulnik, Phys. Rev. Lett. **100**, 127002 (2008).
[33] C. M. Varma, Phys. Rev. Lett. **83**, 3538 (1999).
[34] S. Di Matteo and C. M. Varma, Phys. Rev. B **67**, 134502 (2003).