

Effect of the chemical pressure on bimagnons in antiferromagnetic insulators: CaCuO_2 and BaCuO_2 studied with Cu-L_3 resonant inelastic X-ray scattering

V. Bisogni^{1,a}, L.J.P. Ament², C. Aruta³, G. Balestrino⁴, N.B. Brookes¹, F. Forte⁵, G. Ghiringhelli^{6,7}, P.G. Medaglia⁴, J. van den Brink⁸, and L. Braicovich⁷

¹ European Synchrotron Radiation Facility, BP. 220, 38043 Grenoble Cedex, France

² Institute-Lorentz for Theoretical Physics, Universiteit Leiden, PO Box 9506, 2300 RA Leiden, The Netherlands

³ CNR-INFM Coherentia, Dipartimento di Scienze Fisiche, Università di Napoli “Federico II”, Complesso di Monte S. Angelo, via Cinthia, 80126 Napoli, Italy

⁴ CNR-INFM-Coherentia and Dipartimento di Ingegneria Meccanica, Università di Roma Tor Vergata, via del Politecnico 1, 00133 Roma, Italy

⁵ Dipartimento di Fisica “E.R. Caianiello,” Università di Salerno, 84081 Baronissi, Salerno, Italy and Laboratorio Regionale SuperMat, INFN-CNR, Baronissi (SA), Italy

⁶ INFN-CNR-Coherentia, Dip. di Fisica, Politecnico di Milano, p. Leonardo da Vinci 32, 20133 Milano, Italy

⁷ INFN-CNR-SOFT, Dip. di Fisica, Politecnico di Milano, p. Leonardo da Vinci 32, 20133 Milano, Italy

⁸ Institute for Molecules and Materials, Radboud Universiteit Nijmegen, PO Box 9010, 6500 GL Nijmegen, The Netherlands

Abstract. Substitution of Ca with Ba in CaCuO_2 increases the lattice parameter which in turn modifies all interactions between the constituent ions. Here we study the effect on the bimagnon propagating in the Cu-O planes as seen with Resonant Inelastic X-ray Scattering at the Cu-L_3 peak. The bimagnon energy is reduced by a factor of 0.67 ± 0.06 while its spectral weight decreases at least by a factor of 0.5. This scaling is understood from the dependence on superexchange, which is linear in the former case and quadratic in the second. Moreover the scaling of the bimagnon energy can be understood from the distance dependence of the transfer integrals.

1 Introduction

The antiferromagnetic cuprates are very important mainly because upon doping they change, in many cases, into high T_c superconductors. In this context the study of the magnetic excitations of these parent compounds is a crucial issue because this is the reference magnetic situation that, upon doping, is modified into a spin liquid. Recently a new experimental approach to the study of magnetic excitations in cuprates has been introduced. It has been demonstrated that magnetic excitations are seen with Resonant Inelastic X-ray Scattering (RIXS) both at the Cu K-edge [1] and at the Cu-L_3 peak [2]. The RIXS approach allows measurements vs. the

^a e-mail: vbisogni@esrf.fr

transferred momentum giving access to regions in the parameter space not explored till now. The experiments are cross fertilizing with theoretical work which is developing rapidly ([3–6]).

In RIXS from cuprates, as in traditional Raman scattering and in general in Infra-Red spectroscopy, one observes essentially the bimagnon [7] which is the simplest excitation conserving total spin. The bimagnon can be described as two coherent magnons propagating along appropriate directions in the Cu-O planes in order to conserve total momentum. Since these RIXS results ([1,2]), although very recent, are rather well established it is timely to proceed to second generation RIXS experiments taking advantage of the above results. This is the case of the present communication dealing with the following question: what happens to the bimagnon excitation in two systems having the same crystal structure but different lattice parameters? Here we address a prototypical case in which the variation of the lattice parameter is obtained by chemical substitution. For this reason this effect is referred to as chemical pressure. We present RIXS data at the Cu-L₃ peak comparing CaCuO₂ (CCO) and BaCuO₂ (BCO) where the substitution of Ca with Ba increases considerably the lattice parameters. We show that as a consequence there is a strong reduction of the bimagnon energy, while its spectral weight decreases even more. We discuss the results in connection with theory ([3,4]).

2 Experimental

The measurements were taken at Room Temperature at the ID8 beam-line of the ESRF (Grenoble) with the AXES spectrometer [8] and a dedicated monochromator before the sample [9] allowing a combined line-width of 400–440 meV at the Cu-L₃ absorption edge (930 eV). We use normal incidence on the sample surface and 110° scattering angle (70° backscattering). The incident light is linearly polarized in the scattering plane to minimize the elastic contribution. This greatly simplifies data analysis. The CCO thin films have been epitaxially grown by Pulsed Laser Deposition (PLD) on (110) NdGaO₃ substrate and BCO thin films on (100) SrTiO₃ substrate. The thicknesses were respectively 450 Å and 700 Å. Structural properties have been investigated by X-ray Diffraction showing very good crystallographic quality of the films that are relaxed at these thicknesses. The structure is particularly convenient for studying the effect of chemical substitution. The unit cell of the ideal stoichiometric substances is shown in Fig. 1(a). The square lattice Cu-O planes are separated by layers containing either Ca or Ba (in yellow in the figure). Our systematic X-ray analysis based on many growth experiments gives the following lattice parameters: CCO ($a = b = 3.84 \pm 0.01$ Å and $c = 3.18 \pm 0.01$ Å); BCO ($a = b = 3.96 \pm 0.01$ Å and $c = 4.03 \pm 0.01$ Å).

The real CCO samples correspond always to this situation. The BCO films grow with some self-doping due to some excess of oxygen which goes into the Ba planes. This introduces a tiny distortion and X-ray diffraction shows a very weak reflex indicating a doubling of the cell in the z direction [10]. This has negligible effect on the Cu-O planes we are interested in and the local coordination is always that of Fig. 1(a). In X-ray absorption at Cu-L₃, not reported here for space reasons, this self-doping contribution is much smaller than that seen in BCO grown with an oxygen excess in superconducting BCO-CCO multilayers ([11,12]). Thus in the RIXS measurements we see the spin excitations essentially free of a charge contribution.

In our setup we explore the Brillouin Zone (BZ) in the direction from (0,0) to (0, π). With normal incidence, the transferred momentum along the basal plane is 1.71 in CCO and 1.82 in BCO in units with zone boundary at π . Thus we are working at 0.55 of the zone extension in CCO and 0.58 in BCO. This tiny difference does not prevent the comparison of the data.

3 Results and discussion

In Fig. 1(b) on CCO we indicate the energy regions of interest to our purposes. The RIXS spectrum can roughly be divided in three regions: as it is well known [13] at high energy losses the tail in region C is due to charge transfer excitations while the peak B is due to dd -excitations. The new result, previously not seen because of insufficient resolution, is that the Mid-Infrared

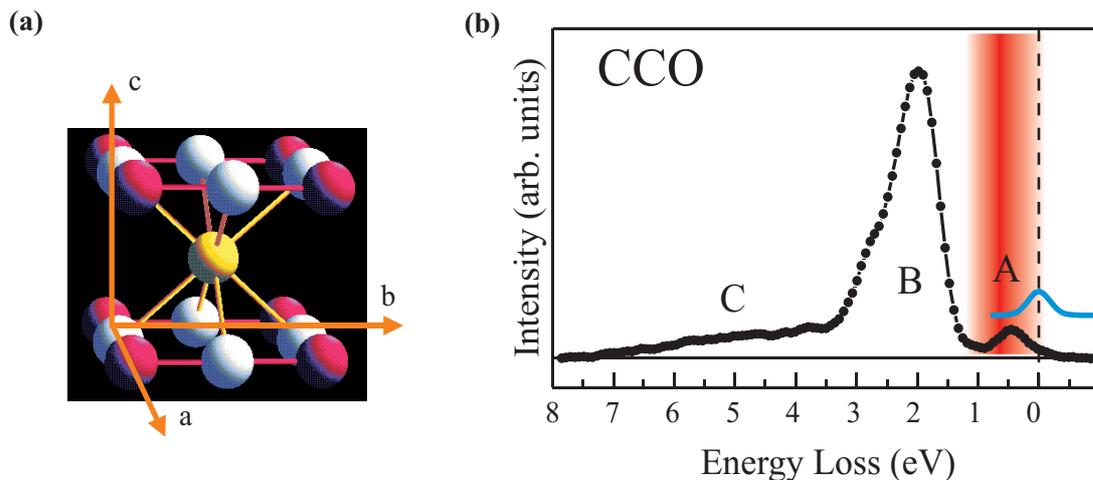


Fig. 1. (a) The unit cell of the ideal stoichiometric CaCuO_2 (CCO) and BaCuO_2 (BCO). Oxygen ion in grey, Cu in red and Ca(Ba) in yellow. (b) The RIXS spectrum of CCO with excitation at the Cu- L_3 peak. The region A containing bimagnon excitation is shaded in red.

region A contains an inelastic contribution due to a bimagnon excitation [2]. Hereafter we will concentrate on this region shaded in red in Fig. 1(b). This bimagnon region is not obscured by the tail of the elastic peak which was measured independently with scattering from silver paint (blue line in Fig. 1(b)).

The bimagnon region in CCO and BCO is presented in Fig. 2. The heavy solid black lines with white dots give the raw data with normalization to the total area of the dd -peak, the blue lines give the elastic peaks and the red lines the difference curves i.e. the bimagnon contribution on top of the background due to the tails of the main dd -peak. The position and shape of the elastic peak were determined from measurements on Silver paint and are very well fitted by the gaussian curves in blue. An important point is that already in the raw data the bimagnon peak in BCO is at much lower energy than in CCO. Due to space reasons we do not report the discussion of the self-absorption correction [14] but we mention two points. The correction is not negligible and shifts the bimagnon peak to lower energies (about 70 meV in CCO). However, the ratio of the bimagnon energies of the two compounds is rather stable against the correction giving an uncertainty smaller than $\pm 10\%$. The ratio between the bimagnon energies in the two compounds is measured by finding the rescaling of the energy scale giving the best superposition of the two bimagnon spectral functions; this does not require the independent determination of the two energies and reduces the propagation of errors. We obtain that the bimagnon energy in BCO is 0.67 ± 0.08 the CCO value. The scaling of the bimagnon energy is one of the two main experimental results. The other is the ratio of the total bimagnon spectral weights i.e. of the bimagnon areas in Fig. 2. This is more delicate since the bimagnon spectrum is on top of the background which cannot be subtracted exactly. In the figure we give simply an artist' background to guide the eye and to show that the area is certainly much smaller in BCO. In particular the ratio of the areas is surely smaller than the ratio of the bimagnon energies and is 0.5 or even less. Moreover, the chemical pressure influences also the dd -excitation. The study of this effect is outside the purpose of the present communication and will be discussed elsewhere [15]; to the present purpose it suffices to mention that CCO and BCO spectra have similar shape and that the dd -peaks shifts to lower energies in BCO by a factor 0.8 ± 0.06 . This dd -scaling factor is greater, outside the error bars, than that of bimagnon energy.

The bimagnon energy according to theory ([2,3]) is linear in the superexchange J so that the reduction of bimagnon energy is direct evidence that J is reduced by the chemical pressure expanding the lattice parameters in the basal planes. Since in CCO the renormalized J value at room temperature is 120 meV [2] we obtain in BCO $J = 85 \pm 10$ meV. Moreover, the theory ([3,4]) shows that the spectral weight of the bimagnon in the region of the BZ explored here is

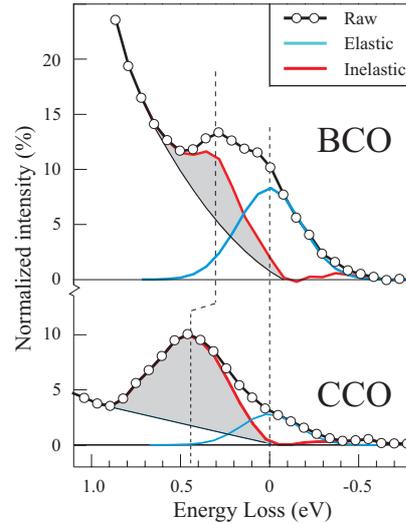


Fig. 2. The RIXS spectra of CCO and BCO in the bimagnon region with excitation at the Cu-L₃ peak. The bimagnon spectral function in red is obtained from the raw data (black) by subtracting the elastic peak (blue).

proportional to J^2 . This explains the greater reduction in the areas than in the energies. Our measured reduction of the energies is 0.67 which implies a reduction of the areas of 0.45 fully compatible with the experimental result. This is a non-negligible support for the theory ([3,4]).

The scaling of the bimagnon energy with the distance i.e. of the superexchange can be understood from the scaling of the matrix element between Cu(d) and Oxygen(p). The superexchange scales with the power 4 of this transfer integral so that our measurements indicate a scaling of the integrals of 0.905 ± 0.02 . This scaling factor is consistent with the dependence of the matrix elements on the distance. In effect the theoretical arguments by Andersen ([16–18]) goes with the power $-(l + l' + 1) = -4$ of the distance, where l and l' are the angular moments of the orbitals in the nearby sites. With the above lattice parameters this gives a scaling of the matrix elements around 0.884 in satisfactory agreement with the experiment.

In conclusion Cu-L₃ RIXS with good resolution allows the bimagnon excitation to be seen with sufficient accuracy to study the chemical pressure effect in the comparison between CCO and BCO. Moreover we have presented a rationale connecting bimagnon properties with the variation of lattice parameters in the basal plane upon chemical substitution.

References

1. J. Hill, G. Blumberg, Y.-J. Kim, D. Ellis, S. Wakimoto, R.J. Birgeneau, S. Komiya, Y. Ando, B. Liang, R.L. Greene, D. Casa, T. Gog, Phys. Rev. Lett. **100**, 097001 (2008)
2. L. Braicovich, L.J.P. Ament, V. Bisogni, F. Forte, G. Balestrino, N.B. Brookes, G.M. De Luca, P.G. Medaglia, F. Miletto Granozio, M. Radovic, M. Salluzzo, J. van den Brink, G. Ghiringhelli, Cond. Mat. (2008) [arXiv:0807.1140 v1]
3. J. van den Brink, Europhys. Lett. **80**, 47003 (2007)
4. F. Forte, L.J.P. Ament, J. van den Brink, Phys. Rev. B **77**, 134428 (2007)
5. T. Nagao, J.-I. Igarashi, Phys. Rev. B **75**, 214414 (2007)
6. F.H. Vernay, M.J.P. Gingras, T.P. Devereaux, Phys. Rev. B **75**, 020403 (R) (2007)
7. Y. Mizumo, S. Koide, Phys. Condens. Mater. **2**, 179 (1964)
8. M.E. Dinardo, A. Piazzalunga, L. Braicovich, V. Bisogni, C. Dallera, K. Giarda, M. Marcon, A. Tagliaferri, G. Ghiringhelli, Nucl. Instrum. Meth. Phys. Res. A **570**, 176 (2007) and references therein
9. G. Ghiringhelli, A. Tagliaferri, L. Braicovich, N.B. Brookes, et al., Rev. Sci. Instrum. **69**, 1610 (1998)

10. C. Aruta, G. Ghiringhelli, C. Dallera, F. Fracassi, P.G. Medaglia, A. Tebano, N.B. Brookes, L. Braicovich, G. Balestrino (to be published)
11. G. Balestrino, S. Martellucci, P.G. Medaglia, A. Paoletti, G. Petrocelli, Phys. Rev. B **58**, R8925 (1998)
12. G. Balestrino, S. Lavanga, P.G. Medaglia, P. Orgiani, A. Tebano, Phys. Rev. B **64**, 020506 (2001)
13. G. Ghiringhelli, N.B. Brookes, E. Annese, H. Berger, C. Dallera, M. Grioni, L. Perfetti, A. Tagliaferri, L. Braicovich, Phys. Rev. Lett. **92**, 117406 (2004)
14. S. Eisebitt, T. Böske, J.E. Rubensson, W. Eberhardt, Phys. Rev. B **47**, 14103 (1993)
15. G. Ghiringhelli, et al. (to be published)
16. O.K. Andersen, O. Jepsen, Physica B **91**, 487 (1977)
17. O.K. Andersen, Phys. Rev. B **12**, 490 (1975)
18. W.A. Harrison, *Electronic Structure and the Properties of Solids* (Dover Publ., New York, 1980), p. 504