

Unusual electronic structure of the pseudoladder compound CaCu_2O_3

T. K. Kim,¹ H. Rosner,^{1,2,*} S.-L. Drechsler,¹ Z. Hu,^{1,†} C. Sekar,¹ G. Krabbes,¹ J. Málek,^{1,‡} M. Knupfer,¹ J. Fink,¹ and H. Eschrig¹

¹Leibniz-Institute for Solid State and Materials Research Dresden, P.O. Box 270116, D-01171 Dresden, Germany

²Department of Physics, University of California, Davis, California 95616

(Received 8 August 2002; published 29 January 2003)

Experimental and theoretical studies of the unoccupied electronic structure of CaCu_2O_3 single crystals have been performed using polarization-dependent x-ray absorption spectroscopy and band-structure calculations. The measured hole distribution shows an unusual large number of holes in orbitals parallel to the interlayer direction which is in agreement with the theoretical analysis. CaCu_2O_3 deviates significantly from the standard $pd\sigma$ cuprate picture. The corresponding strong interlayer exchange is responsible for the missing spin gap which is generic for other two-leg ladder cuprates.

DOI: 10.1103/PhysRevB.67.024516

PACS number(s): 71.27.+a

I. INTRODUCTION

The electronic structure and magnetic properties of cuprates exhibiting various interesting physical properties have been intensively studied in recent years. In particular, considerable attention has been attracted by so called spin ladders.¹⁻³ Their study might contribute to a complete understanding of spin and charge excitations in high- T_c superconductors since in the presence of a spin gap d -wave superconductivity might occur in spin-ladder compounds.¹ Superconductivity under high pressure has been reported in $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$.^{4,5} So far, only a few studies were carried out for CaCu_2O_3 (belonging structurally to the ladder family, see Fig. 1). However, the magnetic susceptibility $\chi(T)$ is^{6,7} quite different from that of the prototype two-leg ladder system SrCu_2O_3 .⁸ From $\chi(T)$ an antiferromagnetic ordering below a Néel temperature $T_N \approx 25$ K was concluded. In order to contribute to the understanding of ladder compounds, in general, and to clarify the character of the hole distribution in CaCu_2O_3 , polarization-dependent x-ray absorption spectroscopy (XAS) studies of single-crystalline samples were performed. We report the experimentally studied unoccupied electronic structure together with that derived from band-structure calculations within the local-density approximation (LDA) and show that at variance with usual ladder compounds, the hole distribution in CaCu_2O_3 has a strong non-planar nature.

II. EXPERIMENT

The CaCu_2O_3 single crystals were grown by the traveling solvent floating zone method. The as-grown crystals were found to be phase pure as confirmed by x-ray diffraction, energy dispersive x-ray (EDX), and thermogravimetric analysis.⁹ Further, the EDX results indicate a deficiency of Ca, with a balancing excess in Cu corresponding to a nonstoichiometric composition $\text{Ca}_{0.86}\text{Cu}_{2.14}\text{O}_{2.93}$ in agreement with the structure refinement by Ruck *et al.*⁷ The space group and the corresponding lattice constants were determined to be P_{mmn} and $a = 9.946$ Å, $b = 4.079$ Å, and $c = 3.460$ Å, respectively, in agreement with the values found in the literature.¹⁰ Single crystal samples with the size of about 5

$\times 5 \times 2$ mm³ were cut from the grown rod for the XAS measurements. The determination of the sample orientation was carried out by taking Laue images (image plate), followed by a simulation of the surface orientation. The crystal structure of this material, shown in Fig. 1, is similar to that of SrCu_2O_3 .¹¹ It consists of an array of ladder-like structures with quasi-one-dimensional copper oxide chains extending along the crystallographic b direction. However, in the Sr compound the Cu-O-Cu bond angle within the straight rungs is 180°, whereas in CaCu_2O_3 the rungs turn out to be “kinked” at about 123°.

The XAS experiments were carried out using linearly polarized light from the U49/1-PGM beam line at the synchrotron light source BESSY II in Berlin.¹² The energy resolution of the monochromator was set to be 280 and 660 meV at the O 1s and Cu 2p absorption thresholds, respectively. A core-level excitation whose absorption coefficient is small compared to the total absorption, as in the case for the O 1s edge, leads to a very poor signal-to-background ratio in total electron yield (TEY), but has the distinct advantage that self absorption effects in the fluorescence yield (FY) mode remain small. The situation is just reversed in the case of the relatively strong Cu 2p absorption. Therefore, for the O 1s and the Cu 2p absorption spectra, we choose the FY and TEY detection mode, respectively. The fluorescence was de-

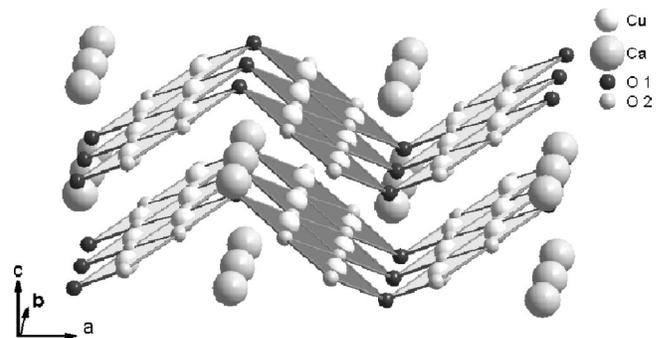


FIG. 1. The crystal structure of CaCu_2O_3 . The corner-shared CuO_2 zigzag chains running along the b axis are alternately tilted by nearly 28.55° forming positively and negatively buckled ladders with “kinked” rungs in a direction.

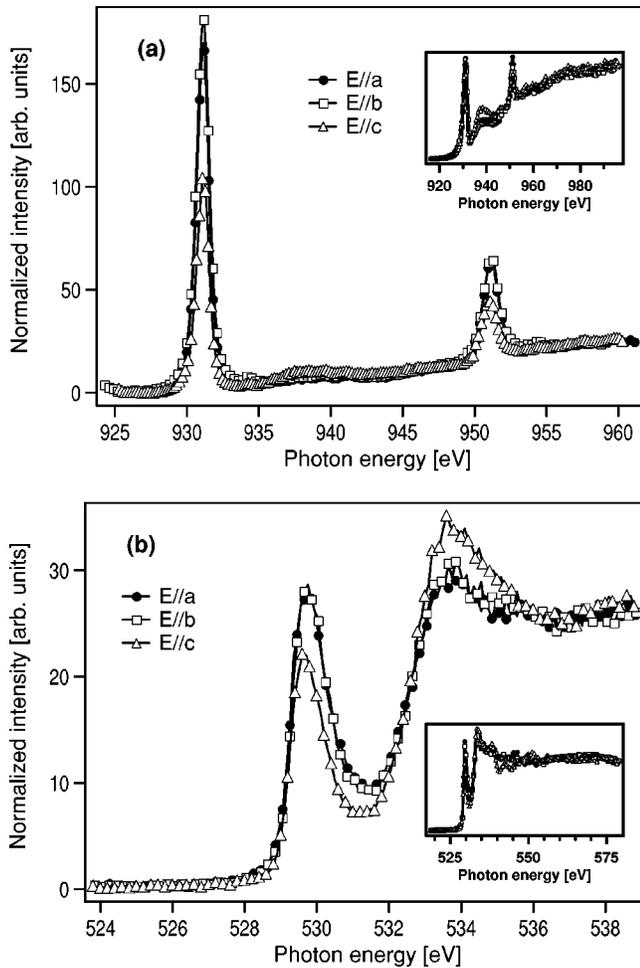


FIG. 2. Polarization dependent XAS spectra at the (a) Cu $2p$ and (b) O $1s$ absorption edges of CaCu_2O_3 . The insets show the XAS raw data in a wider energy range that includes the energy region where the spectra have been normalized.

tected by a solid state Ge detector, placed at 45° angle with respect to the incident photon beam. A total electronic yield was measured by means of a sample current amplifier. The sample was mounted on a two-axis rotatable sample holder, which allowed us to measure spectra with the light polarization vector \mathbf{E} set parallel to one of the crystallographic a , b , or c axes. Energy calibration was performed by comparison of the O $1s$ and Cu $2p$ XAS signal of a CuO sample with corresponding electron energy-loss data.¹³ In all cases, the data were corrected for the energy-dependent incident photon flux and, in the case of O $1s$, for self-absorption effects following a procedure described elsewhere.¹⁴ The spectra for different crystal orientations are normalized 60 eV above the absorption threshold, where the final states are nearly isotropic free-electron-like. All measurements were performed at 300 K with the vacuum in the chamber better than 10^{-9} mbar during the measurements.

III. RESULTS AND DISCUSSIONS

Figure 2(a) shows the polarization dependent Cu $2p$ XAS spectra of CaCu_2O_3 for \mathbf{E} parallel to all three crystallo-

graphic axes. As transitions into Cu $4s$ states are weak,¹⁵ these measurements probe mainly the hole distribution in the Cu $3d$ orbitals. All spectra show a narrow peak at 931.1 eV and 951.2 eV (the so called “white line”), which is associated with excitations from the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ levels into Cu $3d$ contributions to the upper Hubbard band (UHB).¹⁶ While the data for $\mathbf{E}\parallel\mathbf{a},\mathbf{b}$ are very similar, a clear variation in intensity is found going to $\mathbf{E}\parallel\mathbf{c}$. The white line is suppressed for $\mathbf{E}\parallel\mathbf{c}$, but the features at 936–943 eV are higher in intensity compared to the other polarization directions.

The polarization dependent O $1s$ XAS edges are shown in Fig. 2(b). These measurements probe empty electronic states located in the O $2p_x$ ($\mathbf{E}\parallel\mathbf{a}$), O $2p_y$ ($\mathbf{E}\parallel\mathbf{b}$), and O $2p_z$ ($\mathbf{E}\parallel\mathbf{c}$) orbitals. The features directly above the absorption onset (i.e., below 531 eV) can be assigned to transitions to the UHB resulting from hybridization of O $2p$ orbitals with Cu $3d$ states. The O $1s$ absorption is considerably different for $\mathbf{E}\parallel\mathbf{a}, \mathbf{b}$ and $\mathbf{E}\parallel\mathbf{c}$. For $\mathbf{E}\parallel\mathbf{c}$ the preedge peak intensity is lower and the feature at 534 eV, which most likely arises from a combination of O and Ca states, is more pronounced. As for the Cu $2p$ edge, for the O $1s$ absorption a relatively big fraction of holes was found in \mathbf{c} direction compared to the planar one-leg ladder compound SrCuO_2 ¹⁷ and the two-leg-ladder $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$.¹⁸ This unusual behavior will be discussed below together with our LDA results.

In order to get insight into the projected density of states in the different directions, band-structure calculations were performed using the full-potential nonorthogonal local-orbital minimum-basis scheme¹⁹ within the LDA. In the scalar relativistic calculations, we used the exchange and correlation potential of Perdew and Zunger.²⁰ Cu ($3s, 3p, 4s, 4p, 3d$), O ($2s, 2p, 3d$), and Ca ($3s, 3p, 4s, 4p, 3d$) states, respectively, were chosen as the basis set. All lower lying states were treated as core states. The inclusion of Cu and Ca ($3s, 3p$) states in the valence states was necessary to account for nonnegligible core-core overlaps. The O $3d$ states were taken into account to increase the completeness of the basis set. The spatial extension of the basis orbitals, controlled by a confining potential²¹ $(r/r_0)^4$, was optimized to minimize the total energy. The results of the paramagnetic calculation (see Fig. 3) show a valence-band complex of about 8 eV width with four bands crossing the Fermi level ($E_F=0$) according to the four copper atoms per unit cell. An analysis of partial densities of states (not shown) shows that the valence-band is mainly built by Cu $3d$ and O $2p$ states with small contributions of Cu $4s$ and $4p$ states at the bottom of the valence band due to hybridization. The contribution of Ca states is negligible.

The two band complexes at E_F (see Fig. 3) have the typical bandwidth of CuO_3 chain derived compounds of about 2 eV and are nearly half-filled.²⁸ Furthermore, strong correlation effects are present which explain the experimentally observed insulating ground state. As one would expect, the main dispersion of these two antibonding Cu $3d$ –O $2p$ band complexes (with respect to the Cu–O bonds) occurs along the Γ –Y direction, corresponding to the crystallographic \mathbf{b} direction of the CuO_2 double chains (legs). The upper band along

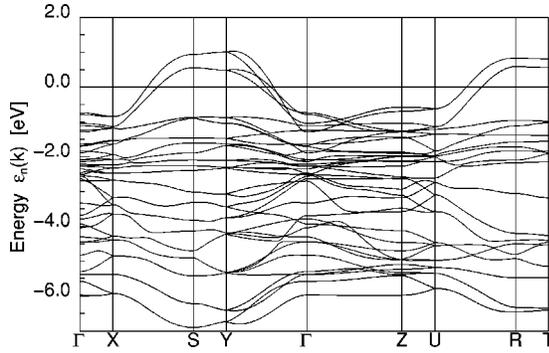


FIG. 3. The LDA band structure of CaCu_2O_3 near E_F . The notation of the symmetry points is as follows: $\Gamma=(0,0,0)$, $X=(1,0,0)$, $Y=(0,1,0)$, $Z=(0,0,1)$, $S=(1,1,0)$, $U=(1,0,1)$, $T=(0,1,1)$, and $R=(1,1,1)$ (in units of $\pi/a, \pi/b, \pi/c$). The full Brillouin zone for the point group $Pmmn$ is a simple cuboid.

Γ -X, X-S, S-Y, U-R, R-T, and the group with stronger dispersion along Γ -Y is antibonding in nature whereas their counter part is bonding (now with respect to the rung Cu-Cu bond of the ladder). They are split by about 0.5 eV due to the interactions t_{\perp} via the rung. The weak interladder coupling causes a further small splitting along the Γ -X, Γ -Y, Γ -Z, and Z-U lines. Within the corresponding zigzag representation the shift of the neighboring leg by $b/2$ in real space results in a doubling of the Brillouin zone (BZ) along the \mathbf{b} axis: $-2\pi/b \leq k_y \leq 2\pi/b$. The secondary splitting can be understood as a band defolding in the original twice as short BZ. Surprisingly, the “interlayer” dispersions along Γ -Z (crystallographically parallel to the \mathbf{c} -axis) are quite strong for a cuprate compound being of the *same* order as that along the rungs as mentioned above, i.e., of the order of ~ 500 meV. The strong buckling of our pseudoladder compound causes a sizable admixture of the $2p_z$ O(1) orbitals in the bonding bands. The corresponding “molecular” rung orbital exhibits here local odd parity (under reflection along the \mathbf{c} axis) in good approximation. As a consequence an “anomalous” negative dispersion along the Γ -Z direction occurs.

Contrary the usual positive cosine like dispersion of the antibonding band is caused by predominant Cu $3d$ contributions with even parity and a much smaller admixture of O $2p_z$ states. The dispersion along \mathbf{a} is rather small due to the weak coupling between the subchains of the double “zigzag” chain (shaded structural blocks in Fig. 1). The reason for the weak inter-sub-chain coupling is nearly 90° Cu-O-Cu bond between neighboring Cu in different sub-chains. The relative number of holes in the O $2p$ and Cu $3d$ orbitals pointing along the respective crystal directions can be derived from the intensity of the lowest lying absorption feature in the O $1s$ and Cu $2p$ absorption edges, respectively. These numbers are listed in Table I and compared to those obtained for the projected density of states from our band-structure calculations.

Table I demonstrates that the XAS and the theoretically derived numbers are in good agreement. Both reveal that about 40% of the holes occupy orbitals along the \mathbf{a} and \mathbf{b} directions. Strikingly, a relatively big portion (about 20%) of

TABLE I. Relative number of holes for different polarization directions from XAS experiment and LDA calculations.

n_h (%)	\mathbf{a}	\mathbf{b}	\mathbf{c}
O_{theory}	35	44	21
O_{exp}	37	36	27
Cu_{theory}	47	36	17
Cu_{exp}	36	41	23

holes is found in orbitals along the \mathbf{c} direction. At first glance, this anomalous large number of nonplanar holes as compared to the “normal ladder”¹⁸ could be understood considering simply projections due to the buckled structure of CaCu_2O_3 . From the measured relative O hole number 0.37 in \mathbf{a} direction one has a local in plane (plaquette) nominal hole concentration of $0.37/\cos^2\theta=0.48$, where $\theta \approx \pm 28.55^\circ$ is the local tilting angle (see Fig. 1). Projecting this number on the \mathbf{c} axis, a contribution of only 0.11 nominal O holes would be expected in contrast with the observed 0.27 nominal ones. Hence, there are about 0.16 nominal holes from orbitals which usually do not enter the ground state of a local CuO_4 ⁻⁶ plaquette configuration. In order to illustrate the absolute charge distribution, we adopt a typical Cu-O hole distribution ratio with 2.4 Cu and 1.6 O holes per unit cell. Then one has about 0.26 absolute holes residing in nonstandard plaquette O $2p$ orbitals. Within the LDA one arrives at about 0.104 nominal anomalous O $2p_z$ holes which reside mostly (71%) in the O(1) $2p_z$ states on the rung. Remarkably, just these states yield an important contribution to the coupling in \mathbf{c} direction as discussed above for the bonding band. While the Cu-O(1)-Cu bond angle ($180^\circ - 2\theta$) at the rungs decreases from 180° , as it would be in the case of a “normal” planar ladder (e.g., SrCu_2O_3), the coupling of the electronic states of two legs within the ladder through the rung oxygen is reduced, and above some critical angle $\theta=45^\circ - \delta$ in approaching the almost “decoupled” chain limit at 45° it might become even smaller than that in \mathbf{c} direction. Considering the Cu holes, we arrive at about 0.12(0.3) anomalous nominal (absolute) holes. Thus, in total about 0.56 (Cu + O) anomalous holes of four holes per unit cell are moved into \mathbf{c} axis oriented orbitals. This is much more than the usually observed approximately 0.05 holes per Cu atom in various planar cuprates which is mainly attributed to the experimentally available slightly nonideal polarization in the present day XAS experiments; see, e.g., Refs. 18 and 22. This clear effect then also leads to more isotropic spin interactions for CaCu_2O_3 which is consistent with the observation of a three-dimensional Néel like transition at $T_N \approx 25$ K in the measurements of the magnetic susceptibility,^{6,7} while SrCu_2O_3 stays in the spin gapped nonmagnetic state down to $T=0$.⁸ As our LDA results point to a comparable rung and interlayer hopping integral $t_{\perp} \sim 250$ meV and $t_z \sim \pm 125$ meV, comparable antiferromagnetic exchange integrals $J_{\perp} \sim 50$ meV and $J_z \sim 20$ meV within a simple bilinear antiferromagnetic spin-1/2 Heisenberg model picture can be expected.²³ The consideration of a ferromagnetic contribution of the same order as J_z due to Hund’s rule coupling between O(1) $2p_x$ and $2p_z$ orbitals introduced by the rung buckling,²⁹ would bring both

exchange integrals still closer to each other. Then, the critical regime expected near $J_z \sim 0.3\sqrt{J_{\parallel}J_{\perp}}$ is arrived (compare for instance Ref. 26). In this way, the standard ladder picture becomes invalid and we arrive at a picture of coupled ordered chains whose ground state is a Néel-like state (with a period doubling along the **b** and **c** directions but an incommensurate ordering in the **a** direction due to the frustrated ladder arrangement). The numbers given above should be compared with those of the spin gaped planar ladder compound SrCu_2O_3 ,³ where at a comparable large $J_{\parallel} \approx 130$ to 150 meV, a larger $J_{\perp} \approx 72$ meV has been found. But most importantly, only a tiny $J_z \sim 1$ meV can be expected.²⁷ Thus, CaCu_2O_3 is only a pseudoladder compound which differs markedly from standard two-leg ladders. Since the interladder exchange along *a* is weak, we arrive at a picture which is essentially in line with that put forward by Kiryukhin *et al.*⁶ who suggested that CaCu_2O_3 can be described as an array of 2D “*b-c* double planes” in which spins-1/2 are coupled by spatially anisotropic antiferromagnetic exchange interactions described by the isotropic (in spin space) Heisenberg model.

IV. SUMMARY

In conclusion, we have studied the unoccupied electronic structure of the pseudoladder compound CaCu_2O_3 . The experimental XAS data of the relative hole numbers is in good agreement with the LDA values. Further calculations to study correlation and impurity effects are necessary to ad-

dress some remaining small deviations. At variance with the normal ladder picture (and more generally also with all other known cuprates comprised from isolated or shared CuO_4 -plaquettes in straight or planar networks) the hole distribution has a less pronounced local Cu $3d-O 2p\sigma$ character. Here, it is related to the missing spin gap and the antiferromagnetically ordered Néel-like state below 25 K. A broad study of the properties of this unique cuprate, including doping, is of interest for the ladder and the cuprate physics, in general. Since the relationship of pressure induced superconductivity and a possible suppression of the spin gap in the planar combined ladder-chain compound $\text{Sr}_2\text{Ca}_{12}\text{Cu}_{24}\text{O}_{41}$ is still under debate,³² the investigation of a related compound clearly *without* a spin gap, such as our title compound, is of considerable interest. In particular, here any doping induced superconductivity would be obviously different from the spin gap based scenario proposed for planar two-leg ladder cuprates.^{1,2}

ACKNOWLEDGMENTS

We thank N. M. Plakida, A. S. Moskvina, and R. R. P. Singh for helpful and stimulating discussions and A. Teresiak for the crystallographic analysis of our samples. Financial support by the DFG (under Projects Nos. Fi-439/10-1, Es-85/8-1, Kr-1241/3-1), the DAAD (H.R.) and the Grant Agency of the Czech Republic (Project No. 202/01/0764; J.M.) is gratefully acknowledged.

*Corresponding author, Email address: helge@maugre.ucdavis.edu
Present address: Max-Planck Institute for Chemical Physics of Solids, Nöthnitzer Straße 40, D-01187 Dresden, Germany.

[†]Present address: II. Physikalisches Institut, Universität zu Köln, Zülpicher Strasse 77, D-50937 Köln, Germany.

[‡]On leave from Institute of Physics, ASCR, Na Slovance 2, CZ-18221 Prague, Czech Republic.

¹T.M. Rice *et al.*, Europhys. Lett. **23**, 445 (1993).

²E. Dagotto, Rep. Prog. Phys. **62**, 1525 (1999).

³T.F.A. Müller *et al.*, Phys. Rev. B **57**, R12 655 (1998).

⁴M. Uehara *et al.*, J. Phys. Soc. Jpn. **65**, 2764 (1996).

⁵M. Isobe *et al.*, Phys. Rev. B **57**, 613 (1998).

⁶V. Kiryukhin *et al.*, Phys. Rev. B **63**, 144418 (2001).

⁷K. Ruck *et al.*, Mater. Res. Bull. **36**, 1995 (2001).

⁸M. Azuma *et al.*, Phys. Rev. Lett. **73**, 3463 (1994).

⁹C. Sekar *et al.*, Physica C **378**, 678 (2002).

¹⁰Chr. Teske *et al.*, Z. Anorg. Allg. Chem. **370**, 135 (1969); R. Arpe *et al.*, *ibid.* **426**, 1 (1976).

¹¹Z. Hiroi *et al.*, J. Solid State Chem. **95**, 230 (1991).

¹²H. Petersen *et al.*, Rev. Sci. Instrum. **66**, 1 (1995); C. Jung *et al.*, Proc. SPIE **3150**, 148 (1997).

¹³N. Nücker *et al.*, Z. Phys. B: Condens. Matter **67**, 9 (1987).

¹⁴L. Tröger *et al.*, Phys. Rev. B **46**, 3283 (1992).

¹⁵Transitions into unoccupied Cu *4s* states are also allowed, but show a reduced transition probability by a factor of 20 compared to Cu *3d* final states: B.K. Teo and P.A. Lee, J. Am. Chem. Soc. **101**, 2815 (1979)

¹⁶J. Fink *et al.*, J. Electron Spectrosc. Relat. Phenom. **66**, 395 (1994).

¹⁷M. Knupfer *et al.*, Phys. Rev. B **55**, R7291 (1997).

¹⁸N. Nücker *et al.*, Phys. Rev. B **62**, 14 384 (2000).

¹⁹K. Koepf *et al.*, Phys. Rev. B **59**, 1743 (1999).

²⁰J.P. Perdew *et al.*, Phys. Rev. B **23**, 5048 (1981).

²¹H. Eschrig, *Optimized LCAO Method and the Electronic Structure of Extended Systems* (Springer, Berlin, 1989).

²²R. Neudert *et al.*, Phys. Rev. B **62**, 10 752 (2000).

²³A more sophisticated mapping including also cyclic four-spin and anisotropic two-spin interactions (Refs. 24 and 25) both are affected by the buckling, is left for future work.

²⁴S. Brehmer *et al.*, Phys. Rev. B **60**, 329 (1999).

²⁵R. Citro and E. Orignac, Phys. Rev. B **65**, 134413 (2002).

²⁶L. Capriotti *et al.*, Phys. Rev. **65**, 092406 (2002), showed that for coupled isotropic ladders ($J=J_{\perp}=J_{\parallel}$) at $T=0$ a quantum phase transition from a spin gap to a Néel phase occurs near strong interladder (IL) coupling $J_{IL}=0.3J$.

²⁷As it also has been estimated for the strongest interchain exchange in the closely related single chain compound Sr_2CuO_3 (Ref. 28). This value rises to about 3 to 4 meV for the isomorphic Ca_2CuO_3 due to the reduced interchain distance (Ref. 28) which is of interest in the present context.

²⁸H. Rosner *et al.*, Phys. Rev. B **56**, 3402 (1997).

²⁹The value of this ferromagnetic contribution depends on the on-site energy difference between the two involved O *2p* orbitals, the direct ferromagnetic exchange interaction between O and Cu orbitals, as well as on the Cu-O (1)-Cu bond angle. To estimate the total ferromagnetic contribution, we mention that in CuGeO_3 with a nearly 99° Cu-O-Cu bond angle it amounts to about 15

meV (Ref. 30). In the corner-shared $\text{BaCu}_2\text{Si}_2\text{O}_7$ with a Cu-O-Cu bond angle of 124° very close to our case, a total exchange integral of 24 meV has been estimated (Ref. 31) which is in accord with our estimate given above.

³⁰H. Rosner *et al.*, Phys. Rev. B **63**, 073104 (2001).

³¹M. Poirier *et al.*, Phys. Rev. B **66**, 054402 (2002).

³²N. Fujiwara, Y. Uwatoko, N. Mori, T. Masumoto, T. Motoyama, and S. Uchida, *Proceedings of 23rd International Conference on Low Temperature Physics, Hiroshima, Japan, August 20-27 2002* [Physica B (to be published)].