Electronic and magnetic excitations in the half-stuffed Cu-O planes of $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ measured by resonant inelastic x-ray scattering

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We use resonant inelastic x-ray scattering (RIXS) at the Cu L_3 edge to measure the charge and spin excitations in the “half-stuffed” Cu-O planes of the cuprate antiferromagnet $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$. The RIXS line shape reveals distinct contributions to the dd excitations from the two structurally inequivalent Cu sites, which have different out-of-plane coordinations. The low-energy response exhibits magnetic excitations. We find a spin-wave branch whose dispersion follows the symmetry of a CuO_2 sublattice, similar to the case of the “fully stuffed” planes of tetragonal CuO (T-CuO). Its bandwidth is closer to that of a typical cuprate material, such as $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, than it is to that of T-CuO. We interpret this result as arising from the absence of the effective four-spin inter-sublattice interactions that act to reduce the bandwidth in T-CuO.

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I. INTRODUCTION

The electronic properties of cuprate materials are determined largely by their strongly correlated Cu-O planes, which are assembled from CuO_4 units (plaquettes), typically connected in a corner-sharing arrangement, as shown in Fig. 1(a). The undoped parent compounds are charge-transfer insulators [1]. In the ionic limit the Cu ions have a d^9 configuration, with a single $3d$ hole in the $3d_{x^2-y^2}$ orbital, while the O $2p$ band is completely filled. The gap is defined by excitations from the O $2p$ to the Cu $3d$ band: $d^9 \rightarrow d^{10}\underline{L}$, where $\underline{L}$ represents a hole in the ligand (oxygen) band. The magnetic coupling between the local $S = 1/2$ moments on the plaquettes is antiferromagnetic (AFM), with a typical energy scale J of order 0.1 eV. When holes are introduced by chemical doping, or by removing one electron in an angle-resolved photoemission (ARPES) experiment, the lowest-energy state is not the triplet expected from the Hund rules but, rather, a “Zhang-Rice singlet” (ZRS), a symmetry-adapted $d^9\underline{L}$ superposition of a $3d_{x^2-y^2}$ hole and an O hole delocalized on the four O ions of the plaquette [2,3].

Much experimental and theoretical work has been devoted to the study of the properties of the ZRS, with ARPES playing a major role [4]. The magnetic excitations have also been studied extensively, both in theory and in experiment, with the latter investigations performed primarily by inelastic neutron scattering (INS) [5]. A recent focus in the cuprates community has been bridging the differences between some of the very different experimental techniques, in order to obtain a consistent description of the band structure, optical, and magnetic response of a single material using a single set of electronic parameters. These parameters would vary

systematically across the different families of cuprates according to factors such as coordination, layering, and the role of apical O atoms. In this context, resonant inelastic x-ray scattering (RIXS) has emerged as a new probe of both charge and magnetic excitations in the cuprates, offering the possibility of mapping both crystal-field splittings and the full magnon spectrum, even with only rather small single-crystal samples [6].

The corner-sharing arrangement of plaquettes is quite ubiquitous in cuprates containing Cu-O planes. By contrast, the alternative of edge-sharing coordination is, to a large extent, known only in quasi-1D compounds, such as CuGeO_3 and Li_2CuO_2 [7]. A notable exception is tetragonal CuO (T-CuO), which can be grown as a thin film on an STO substrate [8]. This metastable form of CuO contains square-lattice CuO_2 planes [Fig. 1(b)], built from edge-sharing CuO_4 plaquettes, which are stacked along the c axis. Each plane can be considered a superposition of two identical corner-sharing CuO_2 sublattices (which we denote Cu_A and Cu_B) with common O ions, displaced by $(0.5a, 0.5a)$ with respect to each other. It can also be seen as a CuO_2 lattice where an additional Cu ion has been added at the center of each unit cell, also known as the “fully stuffed” configuration.

The electronic structure of T-CuO has been measured by ARPES [9]. It exhibits ZRS-type quasiparticles that are compatible with moderately weak coupling between the two sublattices. RIXS measurements have shown that the spin-wave dispersion of T-CuO follows the symmetry of the magnetic Brillouin zone (BZ) of a single AFM CuO_2 sublattice [10], which is represented in Fig. 1(d). The momentum dependence is found to be qualitatively the same as for typical insulating cuprates such as $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ (SCOC) [11], with features including a weak dispersion along the $(\pi/2, \pi/2) \rightarrow (\pi, 0)$ boundary of the magnetic BZ, which has been interpreted within a pure $S = 1/2$ model as being indicative of longer-range interactions beyond the simple

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FIG. 1. (a) CuO_2 plane of a corner-sharing cuprate. (b) “Fully stuffed” Cu_2O_2 plane of T-CuO, with identical A (green) and B (red) sublattices. In both (a) and (b), the green and blue squares represent, respectively, the structural and magnetic unit cells. (c) “Half-stuffed” Cu_3O_4 plane of Ba-2342 with inequivalent Cu_A (green) and Cu_B (red) sublattices. The blue square is the structural unit cell and also the magnetic unit cell of the Cu_A sublattice. The red square is the magnetic unit cell below $T_{N,B}$, where both sublattices are ordered. (d) BZs corresponding to the same-color unit cells in (a)–(c).

nearest-neighbor (NN) Heisenberg model [11,12]. However, the magnon energies in T-CuO are approximately 30% lower than in SCOC. This suggests one of two obvious possibilities: either there are competing magnetic interactions between the Cu spins of the fully stuffed lattice or, given that the exchange energy, J , scales with the electron hopping amplitude, t , the different crystal structure of T-CuO results in a different hopping [10]. Because the two sublattices of T-CuO are identical, the quantitative analysis is not free of ambiguities. In particular, the degeneracy of the magnetic modes is lifted by the weak intersublattice coupling, but the resulting splitting is too small to be resolved with the present energy resolution of RIXS.

$\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ (Ba-2342) provides an opportunity to investigate an intermediate situation between the conventional “empty” corner-sharing CuO_2 square lattice and the fully stuffed edge-sharing square lattice of T-CuO. Ba-2342 contains Cu-O planes with a Cu_3O_4 stoichiometry, which can be seen as the superposition of two corner-sharing CuO_2 sublattices [Fig. 1(c)]. However, in contrast to T-CuO, in Ba-2342 the two sublattices have different sizes. The lattice parameter ($a = 3.90 \text{ \AA}$) of the Cu_A sublattice (shown in green in Fig. 1) is almost identical to that of typical cuprates such as SCOC ($3.97 \text{ \AA}$). The Cu_B sublattice (shown in red) is twice as large. The Cu_3O_4 plane can be obtained from the fully stuffed Cu_2O_2 plane of T-CuO by removing every second atom from one of the two identical sublattices, and it is therefore often referred to as “half-stuffed.” An ARPES study of Ba-2342

FIG. 2. The 3D structure of Ba-2342 showing the tetragonal unit cell, whose midplane coincides with the blue square in Fig. 1(c). Arrows illustrate the magnetic order in the low-temperature phase below $T_{N,B}$.

revealed two distinct ZRS bands dispersing independently and with different bandwidths on the two sublattices [13].

The BZs for the different Cu-O planes discussed above are shown in Fig. 1(d). The largest square (green) is the BZ corresponding to the primitive unit cell of the SCOC and T-CuO lattices. The smaller and 45° -rotated square (blue) is the 2D AFM BZ of SCOC and of T-CuO. It is also the 2D BZ of Ba-2342, as well as the AFM BZ of the Cu_A sublattice. The smallest square (red) is the AFM BZ of the second (red) sublattice and, also, the overall magnetic BZ of Ba-2342 in the low-temperature ordered phase.

The Cu_A and Cu_B sublattices order antiferromagnetically at quite different temperatures, $T_{N,A} = 324 \text{ K}$ and $T_{N,B} = 31 \text{ K}$, respectively [15], which already implies a weak coupling and quite different physics on the two sublattices. Below $T_{N,B}$ the ordered moments, $\sim 0.6\mu_B$ on both the Cu_A and the Cu_B sites, are collinear with and parallel to the $(1,0)$ direction, as depicted in Fig. 2. The spin waves associated with the Cu_A and Cu_B sublattices have correspondingly different energy scales, of order 300 meV for the former and 20 meV for the latter. To date, only the low-energy part of the dispersion has been studied by INS in the isostructural sister compound Sr-2342 [14]. The full spectrum of Ba-2342 was measured in a very recent INS experiment [15]. However, as a result of the weak scattering intensity, accurate determination of the magnon dispersion above approximately 250 meV by INS is challenging.

Here we present RIXS measurements of the magnetic excitation spectrum of Ba-2342 and compare them with

analogous data both from a typical cuprate parent compound, for which we use SCOC, and from T-CuO. When applied for this purpose, RIXS offers a number of advantages or complementary features compared to INS. While its ability to collect high-quality data on very small (submillimeter-sized) samples is not critical in the common cuprates, the large RIXS cross section has a wave-vector dependence quite different from that of INS. It can measure single-magnon bands and multimagnon continua at the same time and access both Raman and non-Raman features depending on the excitation energy. In particular, for cuprates it has far better statistics than INS at the upper band-edge energy around 300 meV. It is also readily capable of mapping electronic excitations, giving direct information about the local crystal environment (crystal-field excitations), which are completely inaccessible by INS.

The structure of this article is as follows. In Sec. II we discuss the details of our experimental analysis. In Sec. III we present our results, which we separate into an analysis (Sec. III A) of the higher-energy dd excitations and extraction of the tetragonal crystal-field parameters, our measurements (Sec. III B) of the low-energy magnetic excitations, and the extraction of the spin-wave spectrum (Sec. III C) combined with some theoretical considerations related to the effective modeling of the different cuprate planes in SCOC, Ba-2342, and T-CuO. In Sec. IV we present a short summary and conclusion.

II. EXPERIMENT

Single crystals of Ba-2342 were grown by the floating zone method, as described in Ref. [15], and were characterized by x-ray powder diffraction. For RIXS measurements, a crystalline plaquette (of approximate size $2 \times 2 \times 0.5 \text{ mm}^3$) was aligned by von Laue diffraction and then mounted on a cryogenic manipulator with 2 angular degrees of freedom. This assembly was inserted in the UHV system and cleaved *in situ* by the top-post method to expose the (001) surface. The sample was kept at temperature $T = 20 \text{ K}$ during all measurements.

Cu L_3 -edge ($2p_{3/2} \rightarrow 3d$; $h\nu \approx 930 \text{ eV}$) RIXS data were acquired at the ADvanced RESonant Spectroscopy (ADDRESS) beam line at the Swiss Light Source (SLS), which is located at the Paul Scherrer Institut [16]. The scattering angle was set to 130° in the horizontal plane, which contained the c axis of the sample [Fig. 3(a)]. The incident light was π polarized. The energy resolution estimated from the elastic peak of a coplanar polycrystalline Cu sample was 130 meV, which sets the measured peak widths. However, the accuracy to which the peak centers may be located is of order 40 meV over much of the BZ. The total transferred momentum was $Q = 0.85 \text{ \AA}^{-1}$. By rotating the sample around the vertical axis, its projection q on the ab plane could be varied between $-0.76 \text{ \AA}^{-1}$ (grazing incidence) and $0.76 \text{ \AA}^{-1}$ (grazing emission), with $q = 0$ corresponding to specular geometry. Following convention, the spectra were normalized to the same integrated intensity in the dd manifold. Self-absorption, i.e., absorption of the scattered beam by the sample, is significant only in the quasielastic region and near grazing emission, where it affects the intensities of the spectral features. Self-absorption-induced energy shifts

FIG. 3. (a) Experimental geometry. The scattering plane is horizontal and the sample was rotated around a vertical axis. (b) Cu L_3 XAS spectrum. (c) Typical RIXS spectrum for Ba-2342, measured as a function of the energy loss, $(h\nu_{\text{in}} - h\nu_{\text{out}})$. The elastic peak is at $E = 0$. The magnon feature (M), the dd , and the charge-transfer (CT) manifolds are indicated. A magnified ($\times 20$) version of the weak CT signal is included.

are too small to be resolved with the present energy resolution and are not considered in the discussion that follows.

III. RESULTS AND ANALYSIS

RIXS is a second-order coherent optical process, initiated by the resonant absorption of a photon by a core-level electron. Specifically, Cu L_3 RIXS from a divalent (Cu^{II}) copper ion is described schematically as $2p_{3/2}^4 d^9 + h\nu_{\text{in}} \rightarrow 2p_{3/2}^3 d^{10} \rightarrow 2p_{3/2}^4 (d^9)^* + h\nu_{\text{out}}$, where $(d^9)^*$ denotes the ground state or an excited state of the $3d^9$ configuration, while $h\nu_{\text{in}}$ and $h\nu_{\text{out}}$ are the energies of the incident and scattered photons. Figure 3(c) displays a representative RIXS spectrum measured on Ba-2342, which is shown as a function of the photon energy loss, $(h\nu_{\text{in}} - h\nu_{\text{out}})$. Here and in the following, the incident energy is tuned to the peak of the L_3 x-ray absorption spectrum, which is shown in Fig. 3(b). The prominent feature of the RIXS line shape around 2 eV is the dd manifold, representing optical transitions from the occupied crystal-field levels to the empty $3d_{x^2-y^2}$ orbital. These $\Delta L = 0$ transitions are dipole forbidden but become allowed in the second-order RIXS process. The peak at $E = 0$ contains the elastic peak, corresponding to transitions that bring the system back to the ground state, and has a quasielastic tail arising from unresolved phonon excitations. Peak M is the signature of a collective spin excitation, which is enabled by the strong (of order 20 eV) spin-orbit interaction in the intermediate $2p$ core-hole state. The weak, broad CT feature above the dd manifold is a continuum

FIG. 4. (a) Effect of a tetragonal distortion (elongation) on the energies of the Cu 3d states. Energies are relative to the $3d_{x^2-y^2}$ orbital. (b) Fit of the dd line shape of a representative spectrum to four Gaussian peaks. The blue line at the bottom is the residue.

of charge-transfer final states, mostly of $d^{10}\bar{L}$ character. These states couple to the $2p_{3/2}^3 d^{10}$ intermediate state through their minority d^9 component and their spectral weight is therefore quite small in Cu L_3 RIXS, whereas they dominate the RIXS spectral function at the oxygen K ($1s$) edge [17].

A. dd excitations

We first consider the dd excitations, which contain information concerning the local environment of the Cu ions. For a Cu^{II} ; d^9 ion in an undistorted octahedral site (cubic symmetry), a single peak would be observed at an energy equal to the separation between the e_g and the t_{2g} states [Fig. 4(a), left]. For an ion with the lower tetragonal symmetry of the Cu sites in the cuprates, both the e_g and the t_{2g} states are split, as illustrated on the right side of Fig. 4(a). For a sufficiently large tetragonal elongation, the $d_{3z^2-r^2}$ orbital can actually cross the t_{2g} manifold and become the lowest-energy orbital, a situation encountered in SCOC and in the extreme case of the infinite-layer material CaCuO_2 , where the apical O anions are missing [18]. Thus three peaks are expected, and usually observed, in cuprate materials. By contrast, the dd manifold of Ba-2342 contains four peaks, visible in the representative spectrum shown in Fig. 4(b). The extra peak reflects the presence of the two inequivalent Cu sites (Cu_A and Cu_B) in the crystal structure.

TABLE I. In-plane Cu-O ($d_{\text{Cu-O}}$) and out-of-plane Cu-anion ($d_{\text{Cu-X}}$) separations, listed together with the energies of a hole in the various Cu 3d orbitals relative to the $3d_{x^2-y^2}$ orbital, as measured by RIXS in representative cuprate materials. For Ba-2342, values for both the Cu_A and the Cu_B sites are listed.

	$d_{\text{Cu-O}}$ (Å)	$d_{\text{Cu-X}}$ (Å)	$E_{3z^2-r^2}$ (eV)	E_{xy} (eV)	$E_{xz/yz}$ (eV)	Ref. No.
La_2CuO_4	1.90	2.43	1.70	1.80	2.12	[18]
T-CuO	1.95	2.67	1.75	1.6	1.5	[10]
$\text{Sr}_2\text{CuO}_2\text{Cl}_2$	1.98	2.86	1.97	1.5	1.84	[18]
$\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$	1.95	3.43/4.94	2.04/2.44	1.57	1.78	This work
CaCuO_2	1.93	∞	2.65	1.65	1.95	[20]

The two sites have the same in-plane coordination, but Cu_A ions have two apical Cl ions with a separation $d_{\text{Cu-Cl}} = 3.43$ Å, while Cu_B ions have two apical Ba ions with a much larger separation, $d_{\text{Cu-Ba}} = 4.94$ Å.

Table I summarizes, for several representative cuprates, the in-plane Cu-O and out-of-plane Cu-anion separations, as well as the energetic separations of the different crystal-field levels, as extracted from RIXS data. Quite generally, for a given in-plane separation, changes in the apical separation have a large effect on the energy of the $d_{3z^2-r^2}$ state but a relatively small effect on the energies of the t_{2g} manifold. For Ba-2342 we may therefore expect equal energies for the d_{xy} and $d_{xz,yz}$ peaks at both the Cu_A and the Cu_B sites, but well-separated $d_{3z^2-r^2}$ peaks. The line shape illustrated in Fig. 4(b) can indeed be reproduced rather well by four peaks. From this procedure, which we assume to include both point-charge effects and covalency contributions, we obtain an accurate fit of the effective tetragonal crystal-field parameters required to obtain the measured 3d level splittings [19]. For Cu_A we obtain the parameters $10Dq = 1.57$ eV, $D_s = 0.32$ eV, and $D_t = 0.15$ eV, while for Cu_B $10Dq = 1.57$ eV, $D_s = 0.37$ eV, and $D_t = 0.18$ eV. The measured dd spectra have an angular dependence of their intensities, which is shown in Fig. 5, and also a polarization dependence. These features can be reproduced by varying the relative intensities of the four peaks, in a manner consistent with the angular dependence of the cross section predicted by a single-ion model [18], but we do not pursue these details here.

Two aspects of the analysis are noteworthy: (i) a good fit is obtained with Gaussian line shapes and (ii) the energy width of the peaks increases with the energy loss. After deconvolving the experimental resolution we obtain peak widths (FWHM) of 170 meV for $3d_{xy}$ and $3d_{xz,yz}$ and 270 and 380 meV, respectively, for the Cu_A and Cu_B $3d_{3z^2-r^2}$ orbitals. The increase in line width with energy loss is consistent with a progressively shorter lifetime of the excited hole state, but pure lifetime broadening should yield a Lorentzian contribution. The Gaussian line shape suggests an underlying dispersion of these excitonic features, which could be either of purely electronic origin or, possibly, assisted by phonons. The spin-flip and non-spin-flip final states are degenerate for the $3d_{xy}$ and $3d_{xz,yz}$ orbitals but not for the $3d_{3z^2-r^2}$ states, and therefore spin splitting can also contribute to the line width of the latter [18].

B. Magnetic excitations

Figure 5 presents RIXS data for Ba-2342 spanning most of the BZ along the high-symmetry direction from $(-\pi, 0)$

FIG. 5. Cu L_3 RIXS spectra covering nearly the whole Brillouin zone along the high-symmetry direction from $(-\pi, 0)$ to $(\pi, 0)$, as shown in the inset. The momentum interval between pairs of spectra is not uniform, with spectra being denser for positive q values. Under the specular-reflection condition, $\mathbf{q} = (0, 0)$, the large elastic peak has been reduced by a factor of 5 for clarity.

to $(\pi, 0)$, which corresponds to the direction of the Cu-O-Cu bond. The data at all angles exhibit the characteristic RIXS spectra of cuprates [11], as discussed in Figs. 3(c) and 4. Here we focus on the magnetic spectral features, which are also generic in cuprates, namely, a resolution-limited peak dispersing symmetrically from $(0, 0)$ and a broad tail at higher energies. Both features are shown in full detail in Fig. 6(a). The main peak, which is the single magnon, disperses up to an energy of 0.32 eV near the $(\pm\pi, 0)$ zone boundaries. The high-energy tail, which extends to approximately 0.6 eV, corresponds to the multimagnon continuum. The momentum dependence along this cut is also typical of the insulating cuprate parent compounds, such as SCOC [6].

Further quantitative analysis of the magnon peak reveals that its intensity is reduced upon approaching the BZ boundaries. Near $(\pi, 0)$, at the bottom of Fig. 6(a), spectra were measured at near-grazing emission, and the intensity attenuation is due to self-absorption. At the opposite end, however, spectra were measured near normal emission, where self-absorption is negligible. A similar anomalous intensity reduction was already observed by Braicovich *et al.* in L_3 RIXS data on La_2CuO_4 (LCO) [21] and was attributed tentatively to quantum corrections to the spin waves. Such corrections, predicted by theory, have been verified quantitatively by INS in the low- J material copper deuteroformate tetradeurate, which constitutes a model $S = 1/2$ square-lattice antiferromagnet [22–24].

Figure 6(b) presents data for the BZ diagonal. The magnon dispersion reaches a maximum of $E = 0.23$ eV at the

$(\pm\pi/2, \pm\pi/2)$ boundaries of the AFM BZ of the Cu_A sublattice. Figure 6(c) illustrates the dispersion between $(\pi/2, \pi/2)$ and $(0.95\pi, 0)$, along a line (inset) that almost coincides with the magnetic zone boundary. The zone-boundary dispersion is of particular significance in the theoretical interpretation of the magnetic excitation spectrum. In the simplest version of the 2D Heisenberg model, which considers only NN interactions, and in linear spin-wave theory, the magnon energy should be constant along the zone boundary. A dispersion along this cut therefore indicates longer-range magnetic interactions, or magnon interactions, or both. Coldea *et al.* observed a dispersion of some 25 meV along the magnetic BZ of La_2CuO_4 by INS measurements [12] and fitted their data with an extended Heisenberg model that included a four-spin ring-exchange interaction. A larger zone-boundary dispersion, 70 meV, was observed by RIXS measurements in SCOC [11], and this was reproduced using an extended t - t' - t'' - U Hubbard model, from which an effective spin Hamiltonian and a hierarchy of magnetic couplings can be derived [25]. From Fig. 6(c) we find that the magnon dispersion along the magnetic-zone boundary in Ba-2342 is quite similar to that of SCOC, and we pursue its theoretical analysis in Sec. III C.

The data in Figs. 6(a)–6(c) are summarized in Fig. 6(d), which shows in red the magnon dispersion data along the high-symmetry directions of the BZ. The first important conclusion to be drawn is that the A-sublattice dispersion follows the symmetry of the magnetic BZ of a single CuO_2 sublattice (the blue square in the inset in Fig. 6). In particular, for Ba-2342 we do not observe a backfolding at $(\pi/2, 0)$, which is the boundary of the magnetic BZ for the entire Cu_3O_4 plane [red square in Fig. 1(d)], even though the data were collected at 20 K, where both the Cu_A and the Cu_B sublattices are magnetically ordered. This is a strong indication that the two sublattices are not strongly coupled.

A valuable guide to understanding the RIXS dispersion of Ba-2342 [Fig. 6(d)] is provided by comparing with the RIXS dispersion of SCOC [11] (blue circles) and of T-CuO [10] (green circles), as well as with the INS dispersion measured for Ba-2342 in Ref. [15] (open circles). Clearly the magnon energies in Ba-2342 are much closer to those in SCOC, over the entire BZ, than they are to the dispersion measured in T-CuO. This observation provides important information concerning the nature of the magnetic interactions in the Cu-O planes of all three materials, as we discuss in detail in Sec. III C.

Concerning a comparison between the RIXS and the INS results, in fact the two methods are strongly complementary in cuprates. INS in Ba-2342 is not handicapped significantly by sample sizes (the authors of Ref. [15] used 8 g of coaligned crystals). However, the dispersion along the magnetic-zone boundary is generically difficult to extract because the scattering intensities here are low. By contrast, the 200- to 300-meV energy scales of these magnons in cuprates, as well as their wave vectors, have a robust RIXS cross section. A further challenge to INS is the presence of some dispersionless excitations around 300 meV arising from water in the glue used to fix the multicrystal samples, and in fact there are no reliable INS data around the $(\pi, 0)$ point of the BZ. Further, RIXS is more sensitive than INS to a hybridization between the high- and the low-energy (A and B) sublattices that would create the folded high-energy band, although as noted above this

FIG. 6. Dispersion of the magnetic excitations along (a) the direction from $(-\pi, 0)$ to $(\pi, 0)$, denoted as cut (a) in the inset (these data show in detail the low-energy regime in Fig. 5), (b) the direction from $(-\pi, -\pi)$ to (π, π) [cut (b)], and (c) the direction from $(\pi/2, \pi/2)$ to near $(\pi, 0)$ [cut (c)]. Green and blue squares in the inset are, respectively, the structural and AFM Brillouin zones of the Cu_A sublattice, as in Fig. 1(d). (d) Summary of the magnon dispersion data in Ba-2342 (red symbols) as extracted from (a)–(c). For comparison the RIXS dispersion relations obtained for SCOC in Ref. [11] (blue) and for T-CuO in Ref. [10] (blue) are shown. Open symbols show the magnon dispersion obtained by INS in Ref. [15]. The solid black line is the dispersion calculated with the model described in the text, for the parameters shown in Tables II and III.

still could not be detected in our measurements. On the other hand, the resolution of modern RIXS instruments remains too large to probe the low-energy mode associated with the Cu_B sublattice, and any understanding of this feature requires INS measurements (which established a 20-meV dispersion, also with a periodicity corresponding to the smaller magnetic BZ [15]). Finally, RIXS measurements around the $(\pi, 0)$ point display a significant continuum tail at higher energies, with a corresponding reduction in the peak amplitude [Fig. 6(c)]; in the absence of a quantitative theoretical model for this effect, a conventional fit can cause RIXS to extract a higher estimate of the magnon energy than INS [Fig. 6(d)], as documented most clearly in Ref. [26]. With these points in mind, we turn now to a theoretical analysis of the magnon dispersion in Ba-2342.

C. Model

As stated in Sec. I, coherent efforts are under way in the field of cuprate research to obtain estimates of the electronic parameters in each material that are consistent across many experimental techniques. This undertaking proceeds, of necessity, in parallel with advances in theoretical methods allowing quantitative calculations of the relevant parameters from models with decreasing levels of approximation

(specifically, magnetic-only models, those based on one- or three-band Hubbard models, and numerical schemes for an exact accounting of correlation effects in clusters). Because of the intermediate (half-stuffed) nature of Ba-2342, which provides two different types of CuO_2 lattice, our results contribute experimental information of particular value for this process.

To analyze our results for the magnon dispersion relation, we follow an approach developed to model RIXS measurements of the magnetic excitations in other insulating cuprates [25]. This description is based on a reduction of the microscopic model for the cuprate plane to an effective one-band Hubbard model, which yields significant electron-transfer (hopping) terms between first-NN (t), second-NN (t'), and third-NN (t'') Cu ions (Fig. 7), and was found to give an excellent account of the spin excitations in a number of conventional (unstuffed) cuprate parent compounds [25].

To model the half-stuffed Ba-2342 system, we introduce, in addition, the transfer term t'_3 , as defined in Fig. 7, which corresponds to NN hopping on the larger Cu_B sublattice and comment that two different second-NN terms are now required on the Cu_A sublattice, t'_1 and t'_2 , depending on the presence of a B-sublattice ion. However, to simplify the discussion of magnetic exchange, we set $t'_1 = t'_2 = t'$, a near-equality being

FIG. 7. Definition of parameters used to model the cuprate plane in Ba-2342.

expected on the grounds that the dominant microscopic cross-plaquette paths avoid the central Cu_B site. Finally, a complete description also requires a hopping term, t_d , connecting the two sublattices, but for reasons explained in detail below we proceed directly to an exchange interaction, J_d , for this function.

We derive [27] a spin-only Hamiltonian with two-, three-, and four-spin interactions, retaining terms up to order t^4/U^3 , where U is the on-site Coulomb interaction. To fit the single-magnon dispersion obtained in our RIXS measurements, we reduce this further to the effective two-spin Hamiltonian

$$\mathcal{H} = \sum_{i,j \in A} J_n^A \mathbf{S}_i^A \cdot \mathbf{S}_j^A + \sum_{i,j \in B} J_n^B \mathbf{S}_i^B \cdot \mathbf{S}_j^B + \sum_{i,j \in A,B} J_d \mathbf{S}_i^A \cdot \mathbf{S}_j^B, \quad (1)$$

where $i \in A$ denotes summation over the i th Cu_A site. Here the three- and four-spin interactions resulting from the Hubbard model are decoupled into additional effective two-spin terms, which renormalize the near-neighbor parameters and generate additional terms of longer range. All coefficients J_n^A and J_n^B are derived consistently from the Hubbard model in Fig. 7. However, the J_d term cannot be derived from a one-band treatment and is taken as a free parameter. The spin Hamiltonian in Eq. (1) was diagonalized using the SpinW library [28]. The single-magnon energy was renormalized uniformly by a momentum-independent factor, $Z_c = 1.18$ [29,30], and the optimal fit to the dispersion is shown as the solid black line in Fig. 6(d).

Clearly the theoretical framework provides an excellent fit of the measured (A-sublattice) magnon dispersion. Because our description proceeds from the Hubbard model, the fitting parameters are U , t , t' , and t'' ; the additional parameters t'_3 and J_d (Fig. 7) require knowledge of the B-sublattice dispersion and are discussed below. In practice we obtain a more statistically reliable fit by fixing U , which is known to

TABLE II. Parameters of the effective one-band Hubbard-model description, represented in Fig. 7, used to fit the magnon dispersions measured by RIXS in SCOC, T-CuO, and Ba-2342. The two parameter sets shown for T-CuO correspond to the two scenarios discussed in the text; the complete model of scenario (2) also contains an intersublattice hopping term, $t_d = 0.167$ eV [10]. The additional parameters in Fig. 7 that are required to model Ba-2342, $t'_3 = -0.086$ eV and $J_d = 10$ meV, are fixed by the low-energy B-sublattice band and are obtained from INS [15].

	U (eV)	t (eV)	t' (eV)	t'' (eV)
SCOC	3.5	0.480	-0.2	0.075
T-CuO (1)	3.5	0.425	-0.2	0.075
T-CuO (2)	3.5	0.490	-0.2	0.075
Ba-2342	3.5	0.475(11)	-0.181(9)	0.087(4)

be largely insensitive to precise structural details, to the value $U = 3.5$ eV common to all cuprates. The A-sublattice hopping parameters obtained from the fit are listed in Table II, where they are compared with the results for SCOC and T-CuO. The effective spin interactions, J_n^A and J_n^B , are obtained as an intermediate step in the process and their values, listed in Table III, provide helpful physical insight. We comment that these parameters are deduced from the full Hubbard model, not from a direct fit, and so there is no contradiction in their size, their number, or the fact that they are subject only to relative errors. Also clear from Fig. 6(d) is that the A-sublattice dispersion in Ba-2342 is qualitatively identical to that of other cuprate materials and quantitatively similar to that of SCOC, which is borne out by the close similarity of the Hubbard model and effective spin interaction parameters for the two systems (Tables II and III). This degree of quantitative accuracy serves as a benchmark for more detailed theoretical modeling, as we discuss in greater detail below.

Turning to the question of achieving a convergence of electronic parameters between INS and RIXS, the same modeling procedure was used to describe the INS measurements on Ba-2342, and the results in Tables II and III are to be compared with those in Tables II and III in Ref. [15]. As discussed above, RIXS and INS are complementary methods when applied to cuprates. At high energies, where appreciable differences are visible in the magnon dispersion along the zone boundary [Fig. 6(d)], RIXS is statistically more reliable but remains subject to its coarser energy resolution. A larger bandwidth is observed by RIXS, due not only to the higher $(\pi,0)$ energy

TABLE III. Effective spin exchange parameters for the Cu_A and Cu_B sublattices in Ba-2342, obtained from the one-band Hubbard-model parameters listed in Table II and used in Eq. (1). We state for clarity that the interaction J_4 connects a site to its A-sublattice neighbors at positions $(\pm 2, \pm 1)$ and $(\pm 1, \pm 2)$, while J_5 connects a site to those at $(\pm 2, \pm 2)$.

	n				
	1	2	3	4	5
J_n^A (meV)	165(5)	20(4)	32(2)	6.2(6)	-0.20(3)
J_n^B (meV)	8.4	0.0	—	—	—

FIG. 8. (a) Schematic of the four-spin exchange process in T-CuO, which contributes an effective FM interaction between two NN Cu ions in each sublattice. (b) In the half-stuffed Cu_3O_4 plane of Ba-2342, these terms are absent and the A-sublattice interactions are close to those of the unstuffed (SCOC) system.

(see above) but also to the lower $(\pi/2, \pi/2)$ energy, and this is reflected in larger J_1^A and, particularly, J_3^A terms. At the level of the Hubbard model, only the RIXS t' term is smaller, while t and t'' are identical within the error bars, i.e., the overall parameter sets are manifestly very similar. At low energies, INS is more reliable, and indeed the present analysis is compelled to neglect out-of-plane coupling and anisotropic exchange interactions, because these modify the magnetic spectrum on an energy scale below 10 meV [15], which is well below the resolution of RIXS. The effective model of Eq. (1) does include the magnetic fluctuations on the Cu_B sublattice, although, again, the value $t'_3 = -0.086$ eV required to account for these excitations, which are not resolvable in the present experiment, must be obtained from INS. Finally, the near-coincidence of the SCOC and Ba-2342 A-sublattice magnon bands indicates empirically that the intersublattice magnetic coupling is very weak, and indeed it is best fitted by a ferromagnetic interaction, $J_d = -10$ meV [15]. The dominant effect of this term is to produce a small spin gap at the magnetic zone center, (0,0), whose size constrains this coupling very accurately, giving a rather small value that is only 6% of J_1^A .

Comparison between the RIXS data in Fig. 6(d) and the result of our model calculations also allows us to address the evolution of the effective magnetic interactions with the stoichiometry of the Cu-O planes. We stress again that the corner-sharing CuO_2 sublattice provides the common framework in which to describe the measured dispersion relations. We have previously proposed two alternative scenarios, summarized in Table II, to explain the significant bandwidth reduction, of order 30%, between SCOC and T-CuO [10], where it is clear from the splitting of the symmetric and antisymmetric magnon bands that J_d is also very small. One scenario was a reduction in the Cu-O hybridization, which would appear as a reduction in the first-NN hopping parameter, t , in the effective Hubbard Hamiltonian [Table II; T-CuO (1)]. The other was that the near-neighbor hopping terms remain essentially unchanged [Table II; T-CuO (2)] and the reduction arises as the consequence of an effective four-spin intersublattice interaction of the type represented in Fig. 8(a), which in the Hubbard-model analysis leads to a ferromagnetic contribution, $-160t_d^2t_3^2/U^3$, that appears in the model of Eq. (1) as a ferromagnetic intrasublattice interaction. Clearly one may discard a third possibility, a band reduction due to the

ferromagnetic J_d term, as this is much too small to have such an effect.

Our results for Ba-2342 provide unequivocal evidence in favor of the second scenario. At the qualitative level, if stuffing the CuO_2 lattice were to cause a gradual reduction in Cu-O hybridization, one would expect the single-magnon bandwidth in half-stuffed Ba-2342 to lie approximately halfway between SCOC and T-CuO, which is not the case. By contrast, the effective four-spin interaction is no longer possible in the half-stuffed lattice, as depicted in Fig. 8(b), which would explain why Ba-2342 has essentially the same band width as SCOC. At a quantitative level, the interpretation in terms of a four-spin process requires that the intersublattice hopping term should take the value $t_d = 167$ meV extracted for T-CuO [10]. Here it is necessary to state that there is no inconsistency with the value of J_d required to fit the magnon bands of Ba-2342. The derivation of J_d lies beyond the single-band Hubbard model, mandating the consideration of charge-transfer terms and the energy splitting of singlet and triplet states of two electrons in orthogonal O_{2p} orbitals [31]. A complete verification of this interpretation would require the analysis of an extended multiband model containing the overlap integrals t_{pd} and t_{pp} linking the Cu_A $3d_{x^2-y^2}$, Cu_B $3d_{x^2-y^2}$, O $2p_x$, and O $2p_y$ orbitals, as well as effective Hubbard terms for Cu and O (in both spin states) and charge-transfer terms. Alternatively, *ab initio* multireference configuration interaction calculations could be attempted on clusters of several unit cells [Figs. 8(a) and 8(b)] embedded in a surrounding matrix [32]. We remark in closing that the unstuffed, half-stuffed, and fully stuffed cuprates provide an excellent case study for testing the quantitative accuracy of all such first-principles techniques, given the precision and accuracy of the structural and dynamical information available for these systems.

IV. CONCLUSION

In summary, by using Cu L_3 edge RIXS we have measured the spin-wave dispersion in the “half-stuffed” Cu-O planes of Ba-2342. Our results, which exploit a quite different probe and different set of cross sections, are complementary to data measured by INS. The experimental measurements are reproduced at a semiquantitative level by considering two independent cuprate sublattices. Our data clarify previous RIXS results on tetragonal CuO (T-CuO) and demonstrate that the substantial reduction in the magnon bandwidth in T-CuO with respect to the typical AFM layered cuprates is due to effective intersublattice four-spin interactions, which operate only in a fully stuffed system and are therefore absent in Ba-2342. Taken together, the experimental determinations of spin-wave dispersions in the series SCOC, Ba-2342, and T-CuO provide an opportunity, complementary to and, to a significant extent, more stringent than, the more common ARPES results, for an accurate comparison with state-of-the-art theoretical (multiband or *ab initio*) calculations of hopping and exchange interactions in the cuprates.

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