

Ab initio determination of an extended Heisenberg Hamiltonian in CuO₂ layers

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Abstract. Accurate *ab initio* calculations on embedded Cu₄O₁₂ square clusters, fragments of the La₂CuO₄ lattice, confirm a value of the nearest neighbor antiferromagnetic coupling ($J = 124$ meV) previously obtained from *ab initio* calculations on bicentric clusters and in good agreement with experiment. These calculations predict non negligible antiferromagnetic second-neighbor interaction ($J' = 6.5$ meV) and four-spin cyclic exchange ($K = 14$ meV), which may affect the thermodynamic and spectroscopic properties of these materials. The dependence of the magnetic coupling on local lattice distortions has also been investigated. Among them the best candidate to induce a spin-phonon effect seems to be the movement of the Cu atoms, changing the Cu-Cu distance, for which the variation of the nearest neighbor magnetic coupling with the Cu-O distance is $\Delta J/\Delta d_{\text{Cu-O}} \sim 1700 \text{ cm}^{-1} \text{ \AA}^{-1}$.

PACS. 75.30.Et Exchange and superexchange interactions – 74.25.Ha Electronic structure – 74.25.Jb Magnetic properties

1 Introduction

Fifteen years after the discovery of the high- T_c superconductivity in cuprates, numerous theoretical and experimental studies pay still attention to these materials and their parent undoped compounds in an attempt to explain their electronic properties [1]. Regarding the undoped materials, the CuO₂ layers, where superconductivity takes place after doping, can be seen as two-dimensional spin lattices, where each Cu atom bears an unpaired electron, which is antiferromagnetically coupled with the nearest-neighbors (NN). The value of this NN coupling has been estimated from Raman scattering 128 ± 6 meV [2, 3] and neutron diffraction experiments 134 ± 5 meV [4–6], assuming a simple Heisenberg Hamiltonian, where only NN interactions are considered:

$$H = J \sum_{\langle ij \rangle, NN} S_i S_j \quad (J > 0) \quad (1)$$

where $\langle ij \rangle$ represents a pair of NN sites. However, this simple model does not satisfactorily reproduce the whole Raman spectra of undoped cuprates [7–12], and extended-Heisenberg Hamiltonians have been proposed [13–16].

The sophistications introduce some of the following effects:

- spin-phonon interactions,
- next-nearest neighbor (NNN) magnetic couplings, J' , and
- four-spin cyclic (4SC) exchange, K .

The spin-phonon coupling, *i.e.* the dependence of the magnetic coupling on the vibrational distortions of the lattice, has been recently invoked as possibly responsible for the asymmetry of the B_{1g} peak on the Raman spectra of cuprates [13, 17–20]. The spin-phonon interaction modifies the magnetic coupling J through the dependence of the hopping integral (t_{pd}) and the charge transfer energy (Δ_{CT}) on the Cu-O distance [21–23]. A maximum contribution of ± 54 meV to the NN magnetic coupling coming from spin-phonon interactions has been suggested [13], based on the linear dependence of J on the Cu-O distance observed in the M₂CuO₄ family [23] and the spin-wave approximation. However, the calculations explicitly including the phonon-spin interaction, using an adiabatic approximation for the phonons, [17], require unrealistic values of disorder to reproduce the width and asymmetry of the B_{1g} peak. It seems necessary to introduce additional terms (as NNN coupling and 4SC exchange) to reproduce the structure of the Raman spectra [13].

The existence of the NNN magnetic coupling J' and the 4SC exchange K can be established from a one-band Hubbard model [24–27]. The NNN interactions may be either a second order effect in form of $\sim t'^2/U$, where t' is a second-neighbor hopping integral and U is the classical

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on-site Coulomb repulsion, or fourth-order effects scaling as $\sim t^4/U^3$, where t is the NN hopping integral. The 4SC exchange is a fourth-order term in the Hubbard model, involving circulation of the electrons around the square and scaling as $\lambda t^4/U^3$, where λ is a large numerical factor ($\lambda = 40$ [24,25] or $\lambda = 80$ [26,27], depending on the formal writing of the operator), as shown in early works in quantum chemistry [24,25] and solid state physics [26,27]. Recent experiments have shown that four-spin cyclic exchange exists in the two dimensional solid ^3He [28–30], in the 2D Wigner solid of electrons formed in a Si inversion layer [31] and in the bcc ^3He [32–34].

As was previously shown, oxygen atoms play a crucial role in the spin exchange between Cu atoms in these materials [21,22,35,36]. In this context, the one-band model is not sufficient to bear all the physics of such materials as shown, for instance, by Jefferson *et al.* [37,38] and it cannot fix the ratios J'/J and K/J . The multiple parameters contained in an extended Heisenberg Hamiltonian and the spin-phonon coupling cannot be univocally fixed from the collective properties of the material and, as far as possible, a prejudiceless evaluation of them will be welcome.

In the recent past, *ab initio* quantum chemical calculations, using large basis sets and accurate treatment of the electronic correlation by means of extensive configuration interaction (CI) expansions of the wave functions, have been performed on bicentric clusters (Cu_2O_7 and Cu_2O_{11}) [21,22,39,40], properly embedded in the Madelung field of the infinite crystal, crucial to correctly represent the electronic structure of these systems [23]. These calculations, in which the metal and oxygen atoms are explicitly treated in extended basis sets, incorporate all effects of the one-band and two-band models, including the Anderson [41] and Goodenough [42] mechanisms and a lot of dynamical correlation effects. Being variational these calculations avoid the divergent behavior of the perturbative development [38]. They provide satisfactory values of J (138 meV) [21,22,39,40] and of the first-neighbor hopping integral for the hole-doped system ($t = -0.55-0.57$ eV) [21,22]. In both cases, the evaluation of the effective interaction goes through the calculation of the spectrum of the dimer.

An extension of this strategy is proposed here which provides an evaluation of J' and K from the calculation of the spectrum of four-Cu sites square embedded clusters. By the way, the transferability of the J value from the two-center to the four-center clusters will be verified. To estimate the spin-phonon coupling, the bimetallic cluster Cu_2O_7 has been used, calculating the dependence of

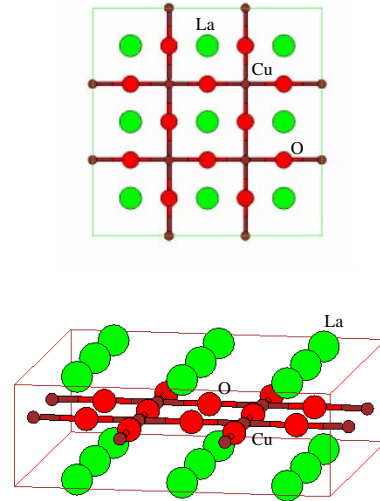


Fig. 1. Fragment of the La_2CuO_4 lattice, containing the cluster Cu_4O_{12} , which atoms are explicitly treated in the *ab initio* calculations, and its first-shell of neighbor atoms, where pseudopotentials have been placed to avoid an artificial polarization of the electronic density of the terminal oxygen atoms.

the singlet-triplet separation on different geometry distortions.

2 Next-nearest neighbor coupling and four-spin cyclic exchange

2.1 Strategy to extract the effective interactions

A square cluster containing four Cu atoms and their nearest twelve in-plane oxygen atoms (a plaquette) will be used to extract these parameters (Fig. 1). Each Cu atom contains an unpaired electron in an in-plane $dx^2 - y^2$ -type orbital. For such frame, the four center-four spin model space is spanned by six neutral determinants. If one calls a , b , c and d the magnetic orbitals, centered in each Cu atom, there are two kinds of determinants with $S_z = 0$, the fully spin-alternant determinants $|\overline{abcd}|$ and $|\overline{ab\overline{cd}}|$ and four partially-frustrated determinants $|ab\overline{cd}|$, $|\overline{abcd}|$, $|a\overline{b\overline{cd}}|$ and $|\overline{ab\overline{cd}}|$, where the common core is omitted. The effective Hamiltonian spanned by such a model space can, in full generality, be written as:

$ \overline{abcd} $	$ \overline{ab\overline{cd}} $	$ ab\overline{cd} $	$ \overline{abcd} $	$ a\overline{b\overline{cd}} $	$ \overline{ab\overline{cd}} $
$-4h - g_4$	g_4	h	h	h	h
	$-4h - g_4$	h	h	h	h
		$-2h - 2h' - g'_4$	g'_4	h'	h'
			$-2h - 2h' - g'_4$	h'	h'
				$-2h - 2h' - g'_4$	g'_4
					$-2h - 2h' - g'_4$

Energy		Symmetry
0	—	${}^5A_{1g}$
$-2(h + h' + g'_4)$	— —	3E_u
$-2h - 4h'$	—	${}^1B_{2g}$
$-4h - 2g_4$	—	${}^3B_{1g}$
$-6h$	—	${}^1A_{1g}$

Fig. 2. Spectrum of the plaquette, corresponding to an occupation of one-electron per Cu site, written in the basis of the parameters of the effective Hamiltonian. On the right, the symmetry of the different states in the D_{4h} group has been included.

where the zero of energy is that of the ferromagnetic quintet state and the equivalences between different elements are due to symmetric reasons, imposed by the structure of the plaquette. For instance, the elements $\langle \bar{a}\bar{b}\bar{c}\bar{d} | H^{\text{eff}} | a\bar{b}\bar{c}\bar{d} \rangle$ represents the exchange of the spins in b and c . In the plaquette, this interaction must be equivalent to the exchange between a and d , that is, the element $\langle \bar{a}\bar{b}\bar{c}\bar{d} | H^{\text{eff}} | \bar{a}\bar{b}\bar{c}\bar{d} \rangle$, and different from the $\langle \bar{a}\bar{b}\bar{c}\bar{d} | H^{\text{eff}} | \bar{a}\bar{b}\bar{c}\bar{d} \rangle$ element, which exchanges the spins on the diagonals.

The six eigenstates of this matrix belong to different spin-space symmetry irreducible representations. The spectrum can be easily written from the basic parameters as shown in Figure 2. There are only four energy-differences, and then the four parameters can be univocally defined. If we now perform an accurate calculation of the six lowest eigenstates of this system, employing the best *ab initio* techniques, we will obtain four level spacings which enable us to determine the four desired effective interactions.

2.2 *Ab initio* calculations

As was previously mentioned, to estimate the NNN and 4SC interactions a square cluster containing four Cu atoms and the first twelve in-plane oxygen atoms has been considered, where all the atoms are treated explicitly. The most internal electrons of the Cu atoms ($1s^2 2s^2 p^6 3s^2$) have been replaced by an effective core potential and the rest of the electrons ($3p^6 d^9$ for Cu⁺² and $1s^2 2s^2 p^6$ for O⁻², a total of 156 electrons) are explicitly treated in the basis sets of triple-*zeta* quality (double-*zeta* for O atoms) [43]. In order to model the infinite lattice, a well-established approach has been used, which consists in replacing the first-shell of neighbors (in-plane and out-of-plane) by pseudopotentials, which incorporate both electrostatic and exclusion effects of these ions, and in considering the Madelung field of the remote atoms of the periodic lattice by means of point charges, which values are chosen according to Evjen's technique [44].

A restricted open-shell self-consistent field calculation (ROHF) for the quintet state has been carried out,

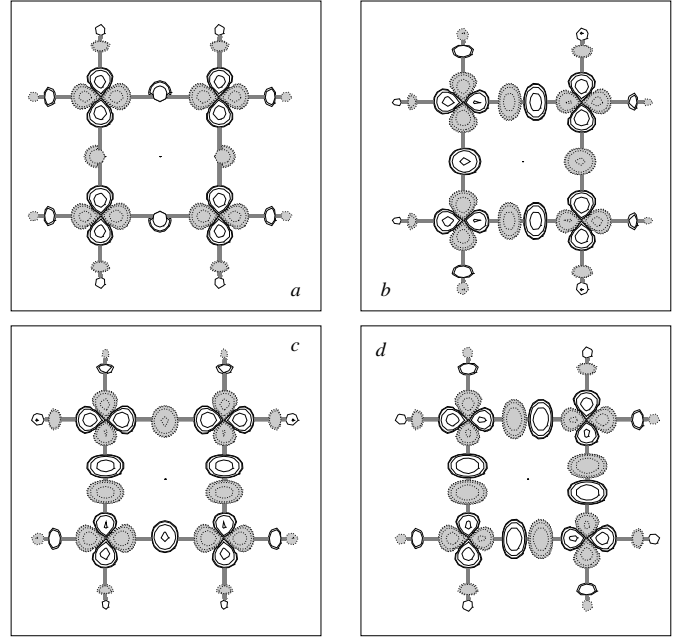


Fig. 3. Linear combinations of the $3dx^2 - y^2$ -type of orbitals, containing non-negligible delocalization tails on the neighbor oxygen atoms. These orbitals correspond to the A_{1g} (a), E_u (b and c) and B_{1g} irreducible representation of symmetry in D_{4h} group.

which determines the four magnetic orbitals (a , b , c , d or their symmetry-adapted combinations corresponding to the irreducible representations a_{1g} , e_u and b_{1g} in the D_{4h} symmetry group) (Fig. 3). These four orbitals define a valence-space with one-electron and one-orbital per site, in one-to-one correspondence with the model spaces of the Heisenberg Hamiltonian or the parent one-band Hubbard Hamiltonian.

The diagonalization of the valence CI matrix (CASCI), that is, a matrix with dimension 36 in the delocalized basis set, gives a value of -28 meV for the NN antiferromagnetic coupling, which is very far from the experimental estimation. This very limited CI only contains the Anderson mechanism in the bare one-band model. This level of description misses two important phenomena, namely intermediate charge-transfer from the oxygen atoms to the Cu atoms and the dynamical polarization effects of the internal electrons and the surrounding atoms, which react to the fluctuation of the field created by the active electrons. The treatment of these effects requires much larger CI expansions.

In order to take into account the first effect, namely the hopping between oxygen and Cu atoms, it is crucial to identify the doubly-occupied orbitals of the oxygen atoms which contribute to this mechanism. They are not necessarily canonical orbitals, *i.e.* eigenstates of the Fock operator. The most-relevant ligand-centered orbitals will be obtained as energy-difference dedicated molecular orbitals [45]. These orbitals have been obtained as follows:

- 1.- From the four-electrons in four-orbital active space, a CI calculation has been performed, limited to the

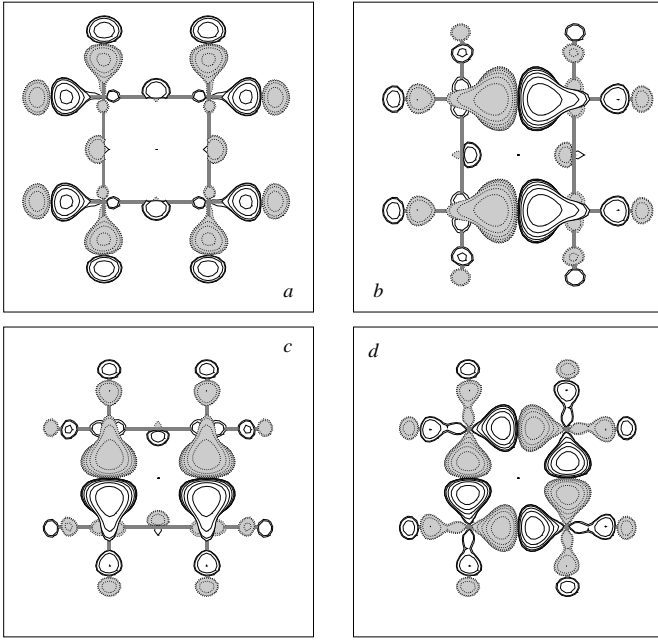


Fig. 4. Most-implicated dedicated molecular orbitals centered in the ligands. These orbitals correspond to the A_{1g} (a), E_u (b and c) and B_{1g} irreducible representation of symmetry in D_{4h} group.

single excitations on the top of all the valence space determinants.

- 2.- The density matrices, R_S and R_Q , for the lowest singlet and quintet states have been calculated. The excitation-energy dedicated MOs are the eigenvectors of the difference of the density matrices $R_S - R_Q$, restricted to the nearly doubly occupied MOs. The eigenvalues of this matrix difference, called ‘implication numbers’, give a measure of the participation of the corresponding orbital to the energy difference, hence to the antiferromagnetic mechanism responsible for the lowering of the energy of the singlet state. The MOs of largest implication numbers are essentially spanned by $2p$ atomic orbitals of the bridging oxygen atoms, as shown in Figure 4.
- 3.- Now these four orbitals will be added to the magnetic ones to define an enlarged valence space involving 12 electrons in 8 MOs, corresponding to a two-band Hubbard model since it includes both the $3d$ -like orbital of the Cu atoms and $2p$ orbitals of the bridging

oxygen directed along the Cu-O bonds, with optimized delocalization tails on the external oxygen atoms. The effect of the dynamical polarization will be taken into account by performing all the single excitations on the top of this enlarged valence space. The resulting CI vectors are expanded on a large space ($\sim 5 \times 10^6$ determinants).

When applied to the dimeric cluster Cu_2O_7 the same strategy provides a value of $J = 128$ meV, in good agreement with the experimental evaluations and our previous CI estimates 138 meV [21,22], which involved d basis functions on the bridging oxygen atoms (which had to be deleted here to make feasible the calculations on the plaquette).

The identification of the *ab initio* calculated spectrum of the tetrameric clusters with the expected spacings of Figure 2 leads to the following values of the effective interactions:

$$h = 60.22 \text{ meV}; \quad h' = 5.01 \text{ meV}$$

$$g_4 = 7.00 \text{ meV}; \quad g'_4 = 0.49 \text{ meV}.$$

From these values it is possible to establish the interactions as written in the usual spin formulation of the four-body operator [13–15]:

$$\begin{aligned}
 H = & \sum_{\langle ij \rangle NN} J(S_i S_j - \frac{1}{4}) + \sum_{\langle ij \rangle NNN} J'(S_i S_j - \frac{1}{4}) \\
 & + K \sum_{\langle ijkl \rangle} [(S_i S_j)(S_k S_l) + (S_i S_l)(S_j S_k) \\
 & - (S_i S_k)(S_j S_l) - \frac{1}{16}]
 \end{aligned}$$

where the higher multiplet energy is zero, J corresponds to the NN interaction, J' to the NNN coupling and K to the four-spin cyclic exchange. Notice that the last term produces the cyclic permutation of the four spins on the plaquette plus ordinary two-spins exchanges of all the pairs of spins of the plaquette including those on the diagonals. Written in the basis of the six $S_z = 0$ determinants of the $abcd$ configuration, this Hamiltonian has the following form:

$ \overline{abcd} $	$ \overline{a}b\overline{c}d $	$ a\overline{b}\overline{c}d $	$ \overline{a}b\overline{c}d $	$ a\overline{b}\overline{c}d $	$ \overline{a}b\overline{c}d $
$-2J$	$K/2$	$J/2 - K/8$	$J/2 - K/8$	$J/2 - K/8$	$J/2 - K/8$
	$-2J$	$J/2 - K/8$	$J/2 - K/8$	$J/2 - K/8$	$J/2 - K/8$
		$-J - J'$	0	$J'/2 + K/8$	$J'/2 + K/8$
			$-J - J'$	$J'/2 + K/8$	$J'/2 + K/8$
				$-J - J'$	0
					$-J - J'$

Identifying the two matrices and omitting the negligible g'_4 term, one obtains:

$$\begin{aligned} K &= 2g_4 && \rightarrow K = 14 \text{ meV} \\ J &= 2h + \frac{K}{4} && \rightarrow J = 124 \text{ meV} \\ J' &= 2h' - \frac{K}{4} && \rightarrow J' = 6.5 \text{ meV.} \end{aligned}$$

The value of the NN antiferromagnetic coupling (J) is in good agreement with both the previous estimation on the dimer ($J = 128$ meV) and also with the experimental evaluations (128 ± 6 meV [2,3] and 134 ± 5 meV [4-6]). Our estimate of the NNN magnetic coupling ($J' = 6.5$ meV) is in accord with the limit of $|J'| \leq 9$ meV, proposed for this compound from Raman experiments [6]. Concerning the four-spin cyclic exchange, experimental evaluations are not available and it is only possible to compare with the K/J ratios used in some recent numerical simulations of the absorption spectrum. The here-presented values of K and J give $K/J \sim 0.11$, which is lower than the value of 0.25 assumed by Honda *et al.* [15] and than the value of 0.30 taken by Lorenzana *et al.* [14] (from an earlier suggestion by Schmidt and Kuramoto [47]) but larger than the critical value, $(K/J)_c = 0.05 \pm 0.04$, estimated by Sakai and Hasegawa [16] for the appearance of a magnetization plateau at half the saturation value in the $S = \frac{1}{2}$ antiferromagnetic spin ladders. The K value here-proposed is also in accord with the value used by Matsuda *et al.* [46] (about 10% of the main NN exchange) to fit the experimental data of the $w - Q$ dispersion of the two-leg spin ladders in the La₆Ca₈Cu₂₄O₄₁ system. The ratio of the NNN and NN interactions is $J'/J = 0.051$, somewhat larger than the value accepted by Lorenzana *et al.* ($J'/J = 0.04$) [14].

3 Spin-phonon interactions

Additional calculations have been performed to evaluate the dependence of the magnetic coupling constant on local geometrical distortions of the lattice. This evaluation proceeds through *ab initio* calculations on bimetallic clusters using the same strategy as in the preceding section (same basis set, same kind of optimization of the molecular orbitals and same type of Configuration Interaction calculations).

Five different local distortions have been considered, as shown in Figure 5. Table 1 gives their corresponding force constants (f), associated frequency and the derivative $\Delta J/\Delta d_{\text{Cu-O}}$. Concerning strongly localized movements, these frequencies are different from the real frequencies of the lattice, but offer an insight on the softness of the different motions. Among the distortions, the movement of the bridging oxygen atom along the Cu-Cu bond, lengthening one Cu-O bond and shortening the other one (mode 2), has a small force constant ($\omega \sim 750$ cm⁻¹), but does not affect significantly the J value. The movements out of the Cu-Cu axis, either in-plane or along the c axis (modes 3, 4 and 5), induce strong changes on J value but the force constant and frequencies are large

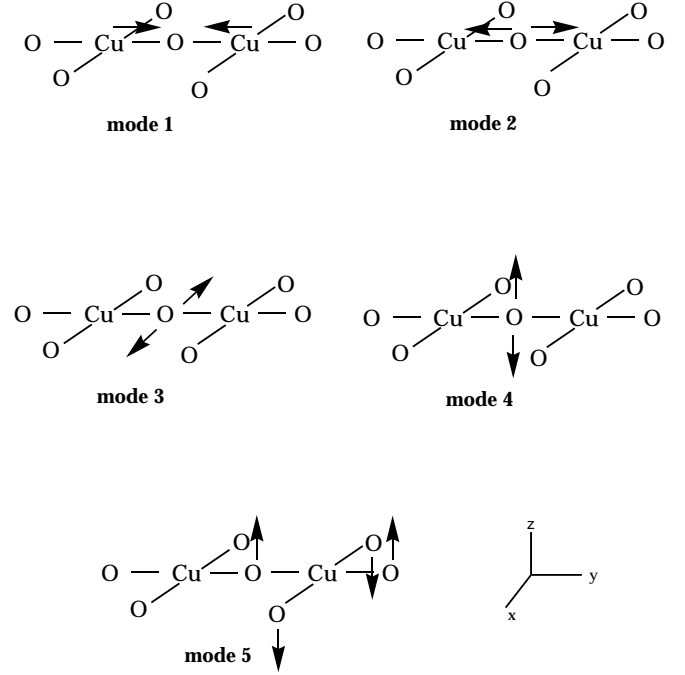


Fig. 5. Different local distortions in the Cu₂O₇ cluster. *Modes* 1, 2 and 3 correspond to the distortions in the CuO₂ plane. *Mode* 1 represents the symmetric stretching of the Cu-O_{bridge} bond. The Cu atoms have been symmetrically displaced along the y -axis. *Modes* 2 and 3 represent the displacement of the bridging oxygen atom along the y and the x axis, respectively. *Mode* 4 corresponds to the movement of the central oxygen atom out of the xy plane. *Mode* 5 represents a collective distortion, where the four oxygen atoms, coordinated to one of the Cu atoms, go out of the plane.

Table 1. Force constants (f), frequencies of vibration (ω) and variation of J with the Cu-O distance ($\Delta J/\Delta d_{\text{Cu-O}}$) of different local distortions (see Fig. 5) in La₂CuO₄.

mode	$f(\text{cm}^{-1} \text{ \AA}^{-2})$	$\omega(\text{cm}^{-1})$	$\Delta J/\Delta d_{\text{Cu-O}}$ ($\text{cm}^{-1} \text{ \AA}^{-1}$)
mode 1	6.53×10^5	833	-1693
mode 2	2.78×10^5	763	~ 0
mode 3	8.69×10^5 (*)	2549	-1246
mode 4	6.76×10^5 (*)	2246	-1213
mode 5	2.45×10^6 (*)	8568	-2098

(*) f in cm⁻¹ rad⁻².

and, then these distortions do not seem to be responsible for the dispersion of J . The movement shortening (or lengthening) the Cu-Cu bonds (mode 1) has both a significant impact on J ($\Delta J/\Delta d_{\text{Cu-O}} = 1700$ cm⁻¹ \AA⁻¹) and a low frequency ($\omega \sim 800$ cm⁻¹). These values should be compared with those assumed in a recent work [13], which takes $\Delta J/\Delta d_{\text{Cu-O}} = 4350$ cm⁻¹ \AA⁻¹ and invokes

the experimental frequencies 550 and 690 cm^{-1} . Our roughly calculated vibrational frequency is on line with the experimental one but the calculated dependence of J on the Cu-O distance is half smaller than the value previously proposed [13].

4 Conclusions

This work has evaluated the amplitudes of the different interactions generally invoked to explain the spectral features of CuO_2 layers which do not fit with the simple Heisenberg Hamiltonian restricted to nearest neighbor coupling. Neither the spin-phonon coupling nor the next-nearest neighbor magnetic interactions nor the four-body cyclic effects are negligible, they appear to be of the order of magnitude sometimes assumed in numerical simulations of the collective effects. The here-presented *ab initio* calculations are free from the simplifications of a one-band or even of a two-band model Hamiltonian. We believe that the so-obtained values of the generalized distance-dependent Heisenberg Hamiltonian are reliable enough to deserve to be used in the evaluation of the collective properties of the material. The here obtained J'/J and K/J ratios remain certainly valid for similar CuO_2 layers, in the absence of large structural distortions as those observed in $\text{YBa}_2\text{Cu}_3\text{O}_7$ compound.

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