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## **Exchange Interactions Mediated by Nonmagnetic Cations in Double Perovskites**

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Establishing the physical mechanism governing exchange interactions is fundamental for exploring exotic phases such as quantum spin liquids in real materials. In this Letter, we address exchange interactions in  $Sr_2CuTe_rW_{1-r}O_6$ , a series of double perovskites that realize a spin-1/2 square lattice and are suggested to harbor a quantum spin liquid ground state arising from the random distribution of nonmagnetic ions. Our *ab initio* multireference configuration interaction calculations show that replacing Te atoms with W atoms changes the dominant couplings from nearest to next-nearest neighbor due to the crucial role of unoccupied states of the nonmagnetic ions in the super-superexchange mechanism. Combined with spin-wave theory simulations, our calculated exchange couplings provide an excellent description of the inelastic neutron scattering spectra of the parent compounds, as well as explaining that the magnetic excitations in  $Sr_2CuTe_{0.5}W_{0.5}O_6$  emerge from bond-disordered exchange couplings. Our results demonstrate the crucial role of the nonmagnetic cations in exchange interactions paving the way to further explore quantum spin liquid phases in bond-disordered materials.

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In 3d transition metal (TM) oxides, the on-site Coulomb repulsive interactions between the electrons are strong enough to confine them to the TM sites, leading to the formation of localized spin or spin-orbital moments [1]. The manner in which these moments couple to each other is primarily governed by the underlying exchange interactions, which may be direct and/or mediated by the intermediate anions or ligands (L), the latter is also referred to as the superexchange. There are many possible ways these interactions can manifest, resulting in a plethora of magnetically ordered states such as ferromagnetic and different types of antiferromagnetic (AFM) order, magnetic spirals, or more exotic topologically protected magnetic textures such as Skyrmions [1–4].

Even more fascinating ground states that stem from exchange interactions are those which do not undergo any magnetic ordering even at absolute zero temperature, e.g., spin-liquid states in low-dimensional magnetic systems [5]. Broken-symmetry valence-bond solids and quantum spin liquids (QSLs) where symmetry is conserved are examples of such phases [5–7]. In these quantum paramagnetic phases, the long-range magnetic order is typically destroyed by frustrated exchange interactions and quantum fluctuations [8]. In the simplistic and prototypical two-dimensional spin-1/2 Heisenberg square lattice (HSL) model, the ratio of nearest-neighbor (NN)  $J_1$  and AFM next-nearest neighbor (NNN)  $J_2$  exchange interactions of ~0.5 results in magnetic frustration and a OSL ground state [7].

The exchange mechanisms in TM compounds, principally the superexchange, are reasonably well understood in the form of the Goodenough-Kanamori-Anderson (GKA) rules [1]. The highly successful GKA rules correctly predict the sign of magnetic coupling for the 180° and 90° TM-L-TM bond angles. In double perovskite compounds like  $Sr_2CuTeO_6$  and  $Sr_2CuWO_6$  the magnetic  $Cu^{2+}$  ions are separated by nonmagnetic  $Te^{6+}$  and  $W^{6+}$  cations, respectively, and the magnetic coupling is a result of the supersuperexchange (SSE) mechanism. As shown in Fig. 1, there are multiple SSE paths-the NN exchange is via two identical Cu-O-Te/W-O-Cu paths involving four bridging ligands and two nonmagnetic cations, with a 90° Cu-Te/W-Cu angle. Alternatively, the second or NNN coupling arises from only one Cu-O-Te/W-O-Cu exchange path (180° Cu-Te/W-Cu angle) involving two ligands and a nonmagnetic cation. An interesting aspect in these compounds is whether the nonmagnetic cation participates in the exchange.

In this Letter, we address the following question: do the exchange mechanisms in double perovskite compounds depend on the nonmagnetic cations and, if so, how? We compute the exchange couplings in double perovskite  $Sr_2CuTe_xW_{1-x}O_6$  with  $x = \{0.0, 0.5, 1.0\}$  compounds using ab initio many-body quantum chemistry (QC) calculations. We analyze their microscopic provenance by examining the different SSE paths involved and show that the bridging nonmagnetic cation plays a pivotal role in the exchange mechanism depending on whether it has an empty or completely filled d manifold [9–11]. Further, we decipher the possible physical origin of the features observed in the inelastic neutron scattering (INS) spectrum using spin-wave theory (SWT) while simulating the site disorder phenomena in  $Sr_2CuTe_rW_{1-r}O_6$ . Our study exposes double perovskites with nonmagnetic cations as the ideal playground to explore bond-disordered couplings and associated QSL phenomena.

The isostructural double perovskite copper oxides  $Sr_2CuTeO_6$  [12] and  $Sr_2CuWO_6$  [13] realize a quasi-twodimensional spin-1/2 HSL antiferromagnet, despite their three-dimensional crystal structures [14–16]. However, the magnetic order in the two systems is different. While a Néel AFM (NAF) ordering is observed in  $Sr_2CuTeO_6$  with large AFM  $J_1$  and small  $J_2$  of the same sign [15,17], a columnar AFM (CAF) order is stabilized in  $Sr_2CuWO_6$  with small  $J_1$ and large  $J_2$ , both AFM [16]. Interestingly, the reported  $J_2/J_1$  ratio in these two compounds differs by two orders of magnitude, 0.03 and 7.92 for  $Sr_2CuTeO_6$  and  $Sr_2CuWO_6$ , respectively.

It has been anticipated that a solid solution with equal quantities of Te and W may result in the ratio  $J_2/J_1$  close to 0.5, leading to strong magnetic frustration and possibly producing a spin-liquid ground state [11,18,19]. Interestingly, the macroscopic magnetic features of Sr<sub>2</sub>CuTe<sub>x</sub>W<sub>1-x</sub>O<sub>6</sub> for x = 0.5 show no signs of magnetic ordering, instead indicates its proximity to the highly frustrated  $J_2/J_1 = 0.5$  region. Furthermore, the specific heat behavior at low temperatures is reminiscent of a gapless QSL state with collective excitations of entangled spins [11]. Fascinatingly, the suppression of long range magnetic order is observed in a wide region of  $x \approx 0.1$ –0.6 [20].

Exchange couplings from QC calculations.—Table I compares the Heisenberg exchange couplings defined in Fig. 1 for the end compounds of  $Sr_2CuTe_xW_{1-x}O_6$  solid solution— $Sr_2CuTeO_6$  and  $Sr_2CuWO_6$ —obtained from the *ab initio* multireference difference dedicated configuration interaction (MR-DDCI) calculations [21,22]. Those obtained from INS measurements are also shown in the

TABLE I. A comparison of the Heisenberg exchange couplings obtained from *ab initio* MR-DDCI calculations (QC) and experimentally using inelastic neutron scattering (INS) for Sr<sub>2</sub>CuTeO<sub>6</sub> [15] and Sr<sub>2</sub>CuWO<sub>6</sub> [16]. The couplings obtained from INS are from fits to SWT with a renormalization factor  $Z_c = 1.18$  as the first-order correction [44] to calculated magnetic dispersion. All values are given in meV.

	Sr <sub>2</sub> CuTeO <sub>6</sub>		Sr <sub>2</sub> CuWO <sub>6</sub>	
	QC	INS [15]	QC	INS [16]
$\overline{J_1}$	7.38	7.60(3)	0.68	1.02
$J_2$	0.05	0.60(3)	8.33	8.50
$J_c$	0.003	0.04	0.005	

same table. The calculations were done on three different embedded clusters for  $J_1$ ,  $J_2$ , and  $J_c$  (see Fig. 1), respectively. For computational details see Ref. [15] and Supplemental Material [23] which includes Refs. [24–39]. In contrast to conventional density functional theory (DFT) and correlated calculations in conjunction with dynamical mean field theory (DFT + DMFT), our calculations are parameter free and accurately describe correlations within the cluster of atoms in a systematic manner. The virtual hopping processes necessary to capture the exchange interactions are well described in this approach, and this makes it the only ab initio method that has sufficient predictive capability for estimating magnetic couplings [40–43]. To extract the isotropic exchange couplings, the ab initio magnetic spectrum of two unpaired electrons in two Cu<sup>2+</sup> ions is mapped onto that of a two-spin Heisenberg Hamiltonian  $\mathcal{H}_{ij} = J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j$ . All calculations were done using the MOLPRO quantum chemistry package [38].

We have previously shown [15] that in  $Sr_2CuTeO_6$  the dominant Heisenberg coupling is the NN AFM  $J_1$ , see columns one and two in Table I. The SSE path that gives this large coupling is  $Cu^{2+}-O^{2-}-O^{2-}-Cu^{2+}$  along the two bridging TeO<sub>6</sub> octahedra and does not include the Te<sup>6+</sup> ions explicitly. On the other hand, the NNN  $J_2$  coupling with 180° Cu-Te-Cu angle is significantly smaller and is through the bridging Te atom—Cu<sup>2+</sup>-O<sup>2-</sup>-Te<sup>6+</sup>-O<sup>2-</sup>-Cu<sup>2+</sup>.



FIG. 1. (a) The crystallographic unit cell of  $\text{Sr}_2\text{Cu}(\text{Te}/\text{W})\text{O}_6$ . (b) The *ab*-plane view of  $\text{Sr}_2\text{CuWO}_6$  showing the in-plane Cu  $3d_{x^2-y^2}$  (red and blue) and W  $5d_{x^2-y^2}$  (yellow and orange) orbitals, and the different exchange couplings.

We performed QC calculations for  $Sr_2CuWO_6$  to find a strong NNN  $J_2$  and a small NN  $J_1$  resulting in the ratio  $J_2/J_1 \sim 12$ . The coupling along the *c* axis is estimated to be two orders of magnitude smaller, but nevertheless larger than in  $Sr_2CuTeO_6$ . These results are consistent with the couplings extracted from the INS data [16]. We note that the magnon-magnon interaction, not included in the linear SWT employed in Ref. [16], could have the same effect as a small NN exchange coupling. Therefore, further corrections to  $J_1$  and  $J_2$  values extracted from the INS might be necessary to account for this. However, we expect this to be small; e.g., in  $Sr_2CuTeO_6$ , this corresponds to  $(J_1, J_2)$  values being renormalized from (7.60,0.60) to (7.18,0.21) [15].

Given the qualitative similarity of the crystal structures [12,13] as well as the electronic states near the Fermi level [45], it seems surprising to find the dominant *ab*-plane exchange couplings reversed in the two compounds:  $J_1$  in  $Sr_2CuTeO_6$  and  $J_2$  in  $Sr_2CuWO_6$ . It is important to note that the states above (unoccupied) and below (doubly occupied) the Fermi level play an active role in the superexchange process, particularly, if these states belong to the ions bridging the two magnetic sites. In this respect, there is a considerable difference in the unoccupied manifold near the Fermi level in the two compounds. While there is a large density of W 5d unoccupied states in Sr<sub>2</sub>CuWO<sub>6</sub> at 4 eV above the Fermi level [45], in Sr<sub>2</sub>CuTeO<sub>6</sub> the relatively small density of unoccupied states near the Fermi level consists of Te 5p character [45]. Further, owing to the delocalized nature of W 5dorbitals, there is a considerable dp hybridization with the bridging O 2p orbitals leading to appreciable hopping matrix element across the  $W^{6+}$  ions. In contrast, the Te 5*p* orbitals are compact and little or zero pp hybridization is expected with O 2p orbitals. Thus, in  $Sr_2CuWO_6$  the W<sup>6+</sup> ions actively participate in the superexchange mechanism.

One might ask "why  $J_1$  is small in Sr<sub>2</sub>CuWO<sub>6</sub> ?" given the arguments brought forward in the previous paragraph. To gain more insight into the SSE paths involved in NN and NNN couplings, we have computed  $J_1$  and  $J_2$  by restraining the virtual hopping processes involving the W<sup>6+</sup> unoccupied orbitals. This can be achieved in QC calculations by setting the coefficients of these orbitals to zero. Although this is unphysical, it gives direct information about the role of W virtual orbitals in the exchange mechanisms.

The NN  $J_1$  coupling along two 90° Cu-W-Cu paths, see Fig. 1(b), decreases to 0.49 meV (~25% reduction) when the unoccupied orbital coefficients of the two W<sup>6+</sup> ions are eliminated. This implies that the contribution to  $J_1$  from the configurations involving W virtual orbitals is not the leading one. It turns out that the other exchange paths, particularly the Cu-O-O-Cu path, has larger contribution to  $J_1$  just as in the case of Sr<sub>2</sub>CuTeO<sub>6</sub> [15]. It should be noted that there are three different W 5*d* orbitals that participate in the SSE mechanism. While the in-plane  $5d_{x^2-y^2}$  orbitals, see Fig. 1(b), have  $\sigma$ -overlap with the bridging oxygen 2porbitals and result in an AFM coupling, the out-of-plane degenerate  $5d_{xz}$  and  $5d_{yz}$  orbitals with  $\pi$ -type overlap contribute to ferromagnetic exchange that is governed by the Hund's rule coupling of the W 5d orbitals. A competition of these two mechanisms result in an overall small AFM exchange. On the other hand, constraining the virtual hopping into a single bridging  $W^{6+}$  ion's (with 180° Cu-W-Cu angle) unoccupied orbitals results in more than ten times smaller, 0.7 meV,  $J_2$  coupling. This indicates the predominance of the W virtual orbitals in capturing the  $J_2$ coupling. Note that there is only one out-of-plane  $5d_{xz/yz}$ orbital participating in the hopping via  $\pi$  overlap which along with  $\sigma$  type hopping through  $5d_{x^2-v^2}$  orbital results in an AFM coupling.

We emphasize that in QC calculations all the virtual orbitals of the W<sup>6+</sup> ions participate in the SSE process and estimating the contributions from a particular virtual orbital is impractical. However, one can understand the SSE from a simplified Hubbard model (SSE-H) that contains two oxygen p orbitals and an additional single W  $5d_{x^2-v^2}$  virtual orbital (d - p - d - p - d) compared to a conventional d - p - d model applied for charge-transfer insulators [1]. In Fig. 2, the SSE processes in the  $J_2$  coupling within the SSE-H model are shown. There are three different possible virtual hoppings, represented schematically in Fig. 2, that lift the spin degeneracy and hence contribute to the AFM exchange coupling. In scheme I, Fig. 2(a), the electron from one  $Cu^{2+}$  ion can hop to the other and back through the intermediate configurations with a single hole (electron) in O 2p (W 5d) orbitals at a particular instance. This scheme has a dominant contribution to the  $J_2$  coupling. Two other



FIG. 2. Super-superexchange mechanisms involved in NNN  $J_2$  coupling in a five band Hubbard model. The three possible intermediate states (see text) that contribute to exchange interaction are shown as three schemes. The Cu  $3d_{x^2-y^2}$ , O 2*p*, and W  $5d_{x^2-y^2}$  levels are represented in blue, green, and orange, respectively. The sequence of virtual electron hoppings (arrows) are marked by numbers 1 to 8.

viable possibilities are shown in schemes II and III in Figs. 2(b) and 2(c). Here, configurations where both Cu  $d_{x^2-y^2}$  orbitals are doubly occupied are active. While in scheme II both oxygen atoms can contain two holes and the W  $5d_{x^2-y^2}$  orbital holds two electrons, in scheme III only one of the oxygen atoms contains two holes. The last scheme contributes twice, as either of the two oxygen atoms can accommodate two holes.

The coupling arising from scheme I can be written as

$$J_{2}^{\rm I} = 2 \frac{t_{dd}^2}{U_{dd}^{\rm Cu}}, \quad \text{with} \quad t_{dd} = \frac{t_{pd_{\rm Cu}}^2}{\Delta_{pd_{\rm Cu}}} \frac{t_{pd_{\rm W}}^4}{\Delta_{pd_{\rm W}}^2}, \qquad (1)$$

where  $t_{pd_{Cu}}$  and  $t_{pd_{W}}$  are the hopping matrix elements from O 2p to Cu  $3d_{x^2-y^2}$  and from O 2p to W  $5d_{x^2-y^2}$ , respectively,  $U_{dd}^{Cu}$  is the on-site Coulomb interaction on the Cu sites, and  $\Delta_{pd_{Cu}}$  and  $\Delta_{pd_{W}}$  are the charge-transfer energies from O 2p to Cu 3d and W 5d orbitals, respectively. Schemes II and III would involve  $U_{pp}^{O}$  $(U_{dd}^{W})$ , the Coulomb interactions when two holes (electrons) are accommodated in O 2p (W 5d) orbitals, and yield minor contributions.

*Effect of* Te/W *atom disorder on the exchange coupling* constants.—Let us consider  $Sr_2CuTe_{0.5}W_{0.5}O_6$  and assume that Te and W atoms are perfectly ordered such that every  $Cu^{2+}$  ion is surrounded by two  $Te^{6+}$  and two  $W^{6+}$  ions. In such a scenario, there are three NN  $(J_a, J_b, \text{ and } J_c)$  and two NNN  $(J_d \text{ and } J_e)$  exchange couplings as show in Fig. 3. Four of the five couplings,  $J_b$ ,  $J_c$ ,  $J_d$ , and  $J_e$ , remain the same as in the end compounds Sr<sub>2</sub>CuWO<sub>6</sub> and Sr<sub>2</sub>CuTeO<sub>6</sub> as the exchange paths are the same. On the other hand, the exchange channels corresponding to  $J_a$  are different compared to the end compounds. We estimated the coupling  $J_a$  from our *ab initio* singlet-triplet energy separation for two Cu<sup>2+</sup> ions with the neighboring environment as shown in Fig. 3. We find this coupling AFM with a magnitude, 0.3 meV, much smaller than the dominant coupling in the end compounds. To summarize, our calculations show that the average  $J_1$  and  $J_2$  can be tuned



FIG. 3. Square lattice scheme with bond disorder and different possible exchange interactions in  $Sr_2CuTe_{0.5}W_{0.5}O_6$ .

from effectively 0 to 8 meV through substitution of Te for W, opening up an interesting arena to explore bond disorder of a spin-1/2 square lattice antiferromagnet.

INS experiments and SWT calculations.—Measurements on Sr<sub>2</sub>CuTeO<sub>6</sub> were performed using the IN4 spectrometer at the ILL utilizing an incident neutron energy of  $E_i = 25.2 \text{ meV}$  [46]. The Sr<sub>2</sub>CuTe<sub>x</sub>W<sub>1-x</sub>O<sub>6</sub> for x = 0.5and 1.0 samples were studied using MERLIN at ISIS with  $E_i = 45 \text{ meV}$  [47]. Further details on Sr<sub>2</sub>CuTeO<sub>6</sub> and Sr<sub>2</sub>CuWO<sub>6</sub> INS measurements are reported elsewhere [15,16].

Figure 4 shows the inelastic neutron scattering spectra of powder  $Sr_2CuTe_xW_{1-x}O_6$  that have been collected on  $x = \{0, 0.5, 1.0\}$  compounds. A background, adjusted for the Bose thermal population factor, recorded at > 100 K has been subtracted from the spectra to remove the phonon contribution at larger  $|\mathbf{Q}|$ . The end compounds Sr<sub>2</sub>CuWO<sub>6</sub> and Sr<sub>2</sub>CuTeO<sub>6</sub> show spin waves dispersing from the CAF and NAF zone centers, respectively. A strong band of scattering around 15–17 meV is found in both compounds. This corresponds to a van Hove singularity from the top of the spin-wave dispersion. The INS spectrum of the intermediate Sr<sub>2</sub>CuTe<sub>0.5</sub>W<sub>0.5</sub>O<sub>6</sub> compound is dramatically different. There appears to be a significant smearing of the spectrum in momentum and energy transfer. The band of scattering corresponding to the van Hove singularity is absent. Weak excitations are observed up to around 20 meV. This scattering decreases with increasing  $|\mathbf{Q}|$ , as would be expected for magnetic scattering. Magnetic modes emerge from  $|\mathbf{Q}| = 0.65$  and 1.4 Å<sup>-1</sup>, much like in Sr<sub>2</sub>CuWO<sub>6</sub>, which would suggest the dominant interactions in  $Sr_2CuWO_6$  persist in the x = 0.5 compound.

To simulate the INS spectra, we need to construct an appropriate magnetic ground state from which magnetic fluctuations can be calculated. We define a  $10 \times 10$  square lattice with randomly populated W and Te atoms. The strengths of the  $J_1 - J_2$  exchange parameters are as given in Table I and the different possible exchange pathways in the mixed x = 0.5 compound are according to Fig. 3. Therefore,  $J_1$  can take values of 7.60 or 1.02 meV depending on whether two Te or W atoms are involved in the exchange process with similar arguments applying to  $J_2$ . In the case of one W and one Te atom, we take  $J_1 = 0$ . From this construction, we find the classical spin configuration which minimizes the total energy and calculate the spinwave dispersion. To account for truncation of the spin Hamiltonian at the quadratic terms when calculating the one-magnon energy, we rescale the magnon energy by a constant factor of  $Z_c = 1.18$  [44]. The calculation is repeated with different distributions of Te and W and the resulting spin-wave pattern is averaged. Figures 4(d)-4(f) show the calculated powder averaged spectra for each composition. Comparing the calculated spectra for x = 0.5to the end compounds, we observe that the simulation predicts a rather broad spectrum. The intense and sharp



FIG. 4. (a)–(c) Measured inelastic powder spectrum  $\chi''(|\mathbf{Q}|, E)$  of  $\operatorname{Sr}_2\operatorname{CuTe}_x W_{1-x}O_6$  for  $x = \{0.0, 0.5, 1.0\}$  compositions. The spectra were normalized by nuclear Bragg scattering for easier comparison. In panels (d)–(f) we present the simulations based on a random exchange-bond order. An energy broadening approximating the instrumental resolution has been applied to each calculated spectra. Solid curves in the simulations represent the range of the detector coverage in the corresponding experiment.

scattering at the top of the bandwidth in Sr<sub>2</sub>CuWO<sub>6</sub> and Sr<sub>2</sub>CuTeO<sub>6</sub> is no longer present for the intermediate compound. Therefore, the effect of the substitution for the intermediate compounds is to leave the powder spectrum featureless with the exception of excitations that emerge from Néel-like and CAF-like low-energy excitations centered at  $|\mathbf{Q}| \approx 0.7$  and 1.4 Å<sup>-1</sup>, respectively. The spectrum, despite the lack of long range magnetic order and contrary to expectations of the limitations of LSWT [48], appears to be in good agreement with the measured powder spectrum, indicating that the bond-disordered exchange couplings reproduce the INS spectrum of Sr<sub>2</sub>CuTe<sub>0.5</sub>W<sub>0.5</sub>O<sub>6</sub>.

To summarize, we have computed the NN and NNN Heisenberg exchange couplings in Sr<sub>2</sub>CuWO<sub>6</sub> and Sr<sub>2</sub>CuTe<sub>0.5</sub>W<sub>0.5</sub>O<sub>6</sub> finding excellent agreement with available experimental observations. We established that the nonmagnetic cation bridging the magnetic sites play a significant role in the SSE process. In the case of a completely filled *d*-manifold ( $Te^{6+}$ ) cation, the exchange path does not include any of its orbitals, but for the  $d^0$  $(W^{6+})$  bridging cation, the SSE process via these empty orbitals is pivotal. While these conclusions corroborate with DFT + U based studies [16,45,49], it is important to know that the computed exchange couplings strongly depend on the choice of the Coulomb repulsion parameter U. We further provided the rationale for the observed exchange interactions, justifying with numerical evidence. Our simulated INS spectra for Sr<sub>2</sub>CuTeO<sub>6</sub> and Sr<sub>2</sub>CuWO<sub>6</sub> compare extremely well with experimental data, and they give a good understanding of the measured powder spectrum for  $Sr_2CuTe_{0.5}W_{0.5}O_6$ . Although further neutron scattering studies are necessary to examine the latter compound, our calculations provide a deep insight into the nature of the interactions within the complex ground state of this system. Our work thus establishes the theoretical background for describing bond-disorder exchange couplings, highlighting site-disordered materials as a new playground for exploring QSL states.

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