Spin interactions in mineral libethenite series: evolution of low-dimensional magnetism

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Abstract

Interesting magnetic properties and spin-exchange interactions along various possible pathways in the half-integral spin quantum magnetic tetramer system: A₂PO₄OH (A = Co, Cu) are investigated. Interplay of structural distortion and the magnetic properties with the evolution of localized band structure explain the gradual transition from a three-dimensional antiferromagnet to a low-dimensional frustrated magnetic system along the series. A detailed study of the exchange mechanism in this system explores various possibilities of complex magnetic interaction. The electronic structure of this series, studied with the help of different appropriate density functional approaches such as Nth order muffin-tin orbital (NMTO) and plane-wave pseudopotential calculations incorporating onsite Coulomb repulsion (U), identifies the underlying magnetic exchange mechanism of this series. Thereafter a generalized minimal model spin-Hamiltonian is constructed for the low-dimensional system. Solution of this model Hamiltonian within first-order perturbation theory results in the evaluation of spin-gap in the spin-tetramer system. In addition, the effects of size confinement and volume reduction on the relevant exchange integrals and spin-gap of the low-dimensional system are also discussed.

(Some figures may appear in colour only in the online journal)

1. Introduction

Thorough understanding of the interrelated structural and magnetic properties of complex geometrically frustrated systems remain always interesting, as absence of long-range magnetic order in such systems opens up the possibilities of a wide range of excited state properties [1]. Such half-integral spin systems, especially the spin-1/2 low-dimensional magnetic system with a singlet ground state, attract much attention due to their fundamental quantum nature [2, 3] and are also considered to be suitable two-level systems for quantum computing [4]. Observation of a pseudospin-gap in high-Τ_c cuprates [5] has motivated intensive study of the spin-exchange mechanism of new spin-gap systems. Increasing experimental activity on complex low-dimensional magnetic systems [6–9] motivates a detailed theoretical first-principles investigation of the underlying mechanism of substitution-induced structural distortions and the resulting changes in magnetic exchange properties to understand the evolution of a long-range ordered system into a low-dimensional one. Moreover, for complex geometrically frustrated systems, identification of exchange paths relevant to the formation of a minimal spin-Hamiltonian, and thus determination of effective magnetic mechanism, can provide an insight into magnetostructural correlations.

A₂PO₄OH (A = Co, Cu), the natural mineral Libethenite, possessing emerald green and dark purple colour for Cu- and Co-based systems respectively, belongs to the phosphate mineral class [10] and is mostly used for their excellent catalytic properties [11]. The parent compound, Co₂PO₄OH is experimentally observed to possess a three-dimensional antiferromagnetic order at around 70 K. Substitution of Cu gradually in place of Co1, Co2 and finally for both Co1 and Co2 sites leads to the onset of low-dimensional magnetic
properties in this system [11, 12]. The final compound Cu$_2$PO$_4$OH, a spin-1/2(d$^5$) low-dimensional tetrameric system, being the most interesting among such class, will be investigated in more detail in the present work. Previous experimental observations on the Cu$_2$PO$_4$OH system [13, 14] predict a singlet ground state with a spin-gap $\sim$141 K. A simpler analogue of the spin-exchange mechanism were put forward via the square spin-tetramer (SQST) model [14]. In the present study, we adopt suitable methodologies based on Density Functional Theory (DFT) to first identify and then calculate the relevant exchange interactions in such systems, which appears to be more complicated than the SQST model [14]. Next, we construct the minimal Heisenberg Model for the final system and approximately solve it within first-order perturbation theory to evaluate the spin-gap between the singlet ground state and the triplet excited state. Such multistep analysis will be helpful to build a generalized spin-model Hamiltonian for the low-dimensional tetrameric systems and also provide understanding of the correlation between the magnetic and structural properties. For the last system, the effects of size reduction and cell volume reduction on the exchange mechanism are also studied.

2. First-principles analysis

A$_2$PO$_4$OH belongs to the space group Pnmm (58), with two types of the transition-metal cation A (A1 or A2, suitably replaced by Cu or Co) and four types of O-ligand (O1, O2, O3 and O4). A1 forms a distorted octahedra with O1, O2 and O4(H), whereas A2 is fivefold coordinated with O1, O3 and O4(H) (figures 1 and 5(a)). The experimental value of lattice parameters are obtained from [10]. For a detailed understanding of magnetic interactions in the tetrameric system, we have investigated all four systems in the series, namely, (I) Co$_2$PO$_4$OH, (II) CuCoPO$_4$OH (Cu replacing Co1), (III) CoCuPO$_4$OH (Cu replacing Co2) and (IV) Cu$_2$PO$_4$OH, all generated from the parent Libethenite system I. First-principles density functional investigation of this series involves three steps; namely, (1) For all four systems, lattice parameters and the atomic positions in the 36-atom unit cell are optimized using conjugate-gradient relaxation criteria as implemented in VASP [15, 16] with projector augmented wave (PAW) [17] formalism. Bond length and bond angles of the relaxed structure provide a prior idea of the effects of structural distortion on the electronic and magnetic properties due to Cu substitution. (2) With the optimized positional coordinates and lattice parameters as input, we have utilized the Nth order muffin-tin orbital (NMTO) downfolding technique [18, 19] to obtain the tight-binding hopping parameters for the Cu and Co localized d-bands. Under second-order perturbation theory, computation of these hopping parameters ($t_{ij}$), corresponding to some specific paths may lead to a quantitative comparison of the exchange couplings along them. For antiferromagnetic couplings, $4t^2/U$ is a measure of the exchange coupling $J_i$, with $U$ being the onsite Coulomb interaction strength for Co and Cu-3d bands. (3) After obtaining these relevant exchange paths, we have estimated the exchange coupling constants and the nature of exchange along these pathways by a total energy calculation for different spin configurations in various supercell configurations consisting of 72 atoms within local spin-density approximation (LSDA) + onsite Coulomb repulsion ($U$) formalism with VASP-PAW potentials. The estimated exchange coupling constants are utilized to construct an effective spin-Hamiltonian for the system considered. The following subsections describe each of the steps mentioned above.

2.1. Structural analysis of optimized system

The first step consists of the analysis of optimized structure. With gradual substitution of Cu in the parent Co$_2$PO$_4$OH system, the relaxed structure indicates that due to the smaller size of the Cu$^{2+}$ ion, there is sizeable amount of structural distortion, including changes in the bond angle and bond length around the site of substitution. The trend of significant bond length, ionic distance and bond angle modifications are presented in table 1 for...
Table 1. Important intra- and inter-tetramer distances (d) and transition-metal cation to ligand bond lengths (b) and bond angles for the relaxed structures of the libethenite series. See figure 5(a) for structure.

|                | I         | II        | III       | IV        |
|----------------|-----------|-----------|-----------|-----------|
| A1–A2 (intra)  | 3.47      | 3.43      | 3.35      | 3.30      |
| A1–A1 (intra)  | 2.78      | 2.82      | 2.90      | 2.95      |
| A1–A1 (inter)  | 2.89      | 2.91      | 2.89      | 2.95      |
| A1–O1          | 1.91      | 1.93      | 2.00      | 1.97      |
| A2–O1          | 2.03      | 1.97      | 1.87      | 1.93      |
| A2–O3          | 1.95      | 1.93      | 1.99      | 2.14      |
| A1–O4          | 2.28      | 2.40      | 1.98      | 2.32      |
| Angle (deg)    |           |           |           |           |
| O2–A1–O2      | 96.52     | 90.35     | 86.88     | 82.47     |
| O1–A1–O1      | 83.88     | 83.03     | 82.50     | 81.20     |
| A1–O2–A1      | 95.99     | 96.64     | 97.99     | 98.40     |
| A1–O1–A1      | 96.11     | 96.33     | 98.09     | 97.35     |
| A2–O3–A2      | 99.71     | 100.78    | 102.82    | 101.42    |
| A1–O1–A2      | 123.40    | 122.86    | 122.30    | 121.64    |

comparison. From system I–IV, as a combined effect of decrease in O2–A1–O2 and O1–A1–O1 and increase in A1–O2–A1 bond angles, the difference between the intra- and inter-tetramer A1–A1 z-direction distance nullifies along the series (table 1) and thereby the z-direction A1–A1 dimer chain structurally turns into a monomer chain. This also leads to a Jahn–Teller-like elongation of the distorted octahedra. Although the A1–O1–A2 angle does not change much, but as a result of increase in A1–O1–A1 and A2–O3–A2 angle, the intra-tetramer A1–A2 distance reduces and the inter-tetramer A2–A2 distance increases along the series. Interestingly, a disparity of bond lengths of A1 and A2 with O1 and O2 and H ligands leads to a competition in the cationic covalency, which also has influences on the ligand field splitting and localized band structure, as discussed in the next step. However, system (III) slightly breaks the gradual order in some structural details, namely, A1–O1–A1 and A2–O3–A2 bond angles are more than system IV, which leads to a change in the coordination of ligand O4 around A1 (dist ∼ 1.98 Å) such that A1–O4 bonds are formed for system III.

Incorporation of the H ion into the ligand coordination significantly changes the ligand field and the resulting splitting for this series of materials. The three-dimensional real structure of the system consists of A1O4(OH)2 plane-sharing infinite octahedral chains along the z-axis, edge-shared with A2O4(OH) trigonal bipyramidal dimers. This structure is distorted from the edge-shared A1O6-octahedra, corner-shared with A2O5 trigonal bipyramids, as shown in figure 1(a). Figures 1(a) and (b) depict a comparison of the distorted ligand coordination around A1 and A2 due to the H ion. The ligand field splitting for A1 and A2 3d-levels also deviate from the usual octahedral and trigonal bipyramidal ones and becomes closer to a distorted square-antiprismatic (coordination no. 8) and octahedral (coordination no. 6) coordination for A1 and A2, respectively. A closer look at figure 1(b) also reveals that the actual coordination around A2 is distorted octahedral and two plane-shared octahedra around A1 along z resembles more of a distorted antiprism. This description will be more evident in the orbital analysis of the different 3d-characters.

2.2. Fatband analysis and comparison of hopping parameters by NMTO calculation

In the second step, the relaxed structural inputs are used to extract the resulting effects of structural distortion on the localized band structure. Orbital analysis of the localized bands provides an idea about the connection between the change of ligand coordination and ligand field splitting with the magnetic properties along the series. For this purpose, we have utilized the Nth order muffin-tin orbital (NMTO) method based downfolding technique [18–20] to construct a low-energy tight-binding model Hamiltonian only for the localized manifold of the full LDA band structure. This downfolding method enables derivation of a few-orbital (Co and Cu d for the present study) effective Hamiltonian from the LDA Hamiltonian consisting of all bands. The reduced basis set is composed of the active orbitals needed to describe the low-energy physics, whereas the inactive orbitals are downfolded into the tails of the active orbitals. In this method, only renormalized effective interactions between the effective orbitals are included in the active basis. Detailed descriptions of the NMTO downfolding are available in [20].

Figures 2(a)–(d) represent the LDA all-orbital bands of the relaxed structures with the A1 and A2 3d localized NMTO-downfolded bands [18, 19] (marked in blue) around the Fermi level. It is to be noted that the downfolded Co and Cu d-bands with reduced basis set agrees nicely with all-orbital LDA bands obtained with linearized muffin-tin orbital (LMTO) within the atomic sphere approximation (ASA) [21]. Localized 3d-bandwidths for these four systems are 3.71 eV, 3.76 eV, 2.72 eV and 2.8 eV, respectively. This reduction in bandwidth of ∼ 1 eV from the first two to the last two systems can be mostly attributed to the structural distortion. The orbital projected Co and Cu 3d-fbands for systems I and IV are presented in figures 3 and 4 respectively. The nature of orbital character distribution for system II and III are similar to I and IV. The labelling of various atoms can be seen from figure 5(a).

Usually, for low-dimensional Cu2+ based dimer systems [23, 24], eight Cu 3d_{4z^2−r^2} bands localize near EF. In the present case, highly localized A1 and A2 3d_{4z^2−r^2} bands for system I and II also imply the presence of dimer interactions. For system III and IV, however, the dimer-like localization of A1 and A2 3d_{4z^2−r^2} levels smears out due to hybridization with other orbitals indicating the existence of more complex magnetic interactions. For A1, the bonding orbitals are z^2−y^2 and z^2−1, while xy, yz and xz have both bonding and antibonding contributions. The situation is just reversed for A2. A1 3d_{4z^2−r^2} orbitals form sigma-bonds with O1 and O2 p_x, rendering the respective bands to be the lowest in energy for all systems. A1 3d_{4z^2−r^2} is pi-bonded with O1 and O2 p_y and p_z and thus gets localized at a lower energy level than xy. For A1, xz and yz orbitals are highly hybridized in nature, the bonding part of which originates from the overlap of the
Figure 2. LDA band structure for all four systems (a) Co$_2$PO$_4$OH, (b) CuCoPO$_4$OH (Cu replacing Co1), (c) CoCuPO$_4$OH (Cu replacing Co2) and (d) Cu$_2$PO$_4$OH with the localized NMTO-d-bands near the Fermi level in blue. Bandwidth reduction of the localized manifold from system I and II to III and IV can be observed.

Figure 3. Orbitally projected NMTO fatbands for Co1-d and Co2-d bands for the system Co$_2$PO$_4$OH. The high-symmetry points are G, Z, T, Y, G, X, S, R, U, similar to the bands presented in figure 2. The energy axis ranges from $-3$ to $+2$ eV at an interval of 0.5 eV.

z branch of $xz$ or $yz$ with O1 and O2 $p_z$. The antibonding part is from the $x$ or $y$ branches, which due to H–O1 charge transfer, have little opportunity to interact with O1-$p_x$ or $p_y$. The occupied part of A1 3$d_{xy}$ originates due to the overlap with O4 $p_x$ and $p_y$. For A2, 3$d_{xy}$ and the $x$ and $y$ branches of 3$d_{xz}$ and 3$d_{yz}$ are sigma-bonded with O3 $p_x$ and $p_y$. 3$d_{x^2-y^2}$ and 3$d_{3z^2-1}$ is mostly of antibonding nature. However, for the third system, additional covalency with O4 $p$ lowers both of the orbital energies, especially for the 3$d_{3z^2-1}$.

In the present series, competitive cationic covalency effects are prominent from the orbital analysis. For the same O1 $p_x$ or $p_y$ orbitals, there is a competition between A1 3$d_{x^2-y^2}$, A2 3$d_{xy}$ and H-1s. For system I and II, the A1–O1 bond length is less than the A2–O1 bond (table 1), indicating greater chances for A1 3$d_{x^2-y^2}$ covalency. Thus for A1, 3$d_{x^2-y^2}$ bands localize at a lower energy compared to A2. For systems III and IV, the A1–O1 bond length is greater than the A2–O1 bond. Thus, A2 3$d_{x^2-y^2}$ levels stay at a lower energy compared to the first two systems. For the third system, additional lowering occurs due to bonding with O4 $p_x$ and $p_y$. Also, for system III, strong interaction of d-bands with the $p_x$ and $p_y$ orbitals of O3 and O4 and $p_z$ orbital of O1 and O2 pushed the filled ligand levels far below (around $-4$ eV) in comparison to the other systems (figure 2).

Extraction of the effective hopping parameters between the TM-d states of selective ions from the few-band model Hamiltonian is possible after Fourier transforming it from the reciprocal ($k$) to the direct lattice space ($R$). The magnitude of such hoppings enables us to select the significant exchange paths and also provides a rough estimate of the exchange
coupling constants by the relation \( J_i = 4t_i^2/U \), with \( U \) being the onsite Coulomb repulsion at the TM sites. In the present study, however, we have utilized NMTO-hopping parameters only to select the appropriate exchange paths by comparing the magnitude of the hopping parameters between the neighbouring sites. The coupling constants are determined in a next step after incorporating \( U \) and \( J \) parameters. Thus, NMTO calculations help to identify six significant couplings for such system, namely. The intra-tetrameric exchange \( J_1 \) and \( J'_1 \) between A1 and A2, the dimeric exchange \( J_2 \) and \( J'_2 \) along the \( z \)-axis A1-array and another in-plane dimeric exchange \( J_3 \) and \( J'_3 \) between A2. Figure 5(a) shows the exchange paths with arrows along with the structure and figure 5(b) depicts the schematic diagram of predicted exchange couplings for this system.

The detailed orbital analysis presented with the LDA localized bands implies that even before switching on the magnetic order in this system, dopant-induced (Cu) structural distortion has an important role in introducing low-dimensional magnetic behaviour. In addition, for the magnetic system, Cu also affects the spin-manipulation, as a spin \( 1/2 \) ion (Cu) is replacing a spin \( 3/2 \) ion (Co).

### 2.3. Estimation of exchange integrals

After identifying these relevant exchange paths, we have estimated the exchange coupling constants and the nature of exchange along these pathways by a total energy calculation for different spin configurations in various supercell configurations consisting of 72 atoms. Under the LSDA + \( U \) approximation, the total energy for each spin configuration is calculated with VASP-PAW potentials after ionic relaxation. The nature and magnitude of exchange couplings, however, depend on the choice of \( U \) and \( J \). Therefore, we have optimized the \( U \) and \( J \) parameters for Cu after matching the obtained spin-gap value with the experimental results \([13, 14]\) for some set of \( U \) and \( J \) values. The present values of \( U \) and \( J \) for Cu offer the closest match. For Co, these parameters are chosen from a comparative analysis, as presented in \([22]\). The best choice for optimization of \( U \) and \( J \) parameters can be obtained after comparing with the optical experiments where the electronic bandgap for this system is measured. However, such experiments are not presently available in the literature. Significant exchange coupling constants for all four systems are listed for this optimum \( U \) (5 eV for Cu and 4.5 eV for Co) and \( J \) (1 eV for Cu and 0.9 eV for Co) value in table 2. Exchange coupling constant along a specified path is computed by equating the ground-state energy difference of the anti-parallel and parallel spin combination in that path with the energy differences calculated from the model Hamiltonian (discussed in the next section) after keeping suitable terms. In our convention, \( J = 1/2(E_{AFM} - E_{FM}) \), by which AFM and FM coupling constants will have negative and positive values respectively. The insulating nature of all these four compounds are correctly represented with the LSDA + \( U \) calculation. The selective paths from the NMTO calculations are also verified with the LSDA + \( U \) calculations.

For system 1 (table 2), the tetrameric exchange is actually composed of two kinds of dimeric exchanges \( J_1 \) and \( J'_1 \)
The Co2-dimeric exchange $J_{1}$×$J_{2}$ selective paths corresponding to those exchange integrals as in place of Co1 and Co2 in system II and III, experimental results [12]. With gradual substitution of Cu order is three-dimensional, which appears to agree with the order of magnitude of the couplings also implies that the magnetic long-range magnetic order prevails in this system. The order and dimer exchange values are less than the tetrameric exchange, implying the onset of low-dimensional magnetic behaviour in this system. The magnetostructural details of this series are similar to the experimental studies performed in [11].

Evolution of local magnetic moment of Co and Cu ions at different sites along the series may be informative to understand the site-specific magnetostructural coupling. Therefore, we mention the LSDA + $U$ magnetic moments for different systems in absolute values. For system I, Co1 and Co2 spin-only moments are 2.76 and 2.78 $\mu_{B}$ respectively. For system II, Cu and Co2 moments are 0.4 and 2.76 $\mu_{B}$ respectively. As mentioned in the structural details, as the A1–O1 bond length is smaller than A2–O1, charge transfer from O1 to Cu or Co1 leads to reduction of its ideal spin-only moment value for both of these systems. For system III, the moments of Co and Cu1 are 2.77 and 0.77 $\mu_{B}$ respectively. For the final system, Cu1 and Cu2 acquire a moment of 0.81 and 0.80 $\mu_{B}$ respectively. As expected, for the latter system, the moment at site A1 is slightly less than that at site A2 due to a reversed disparity in the ligand bond length in comparison to the first two systems. The LSDA values of absolute moments are smaller than the above-mentioned values.

It may also be mentioned that for all these systems, exchange couplings extracted from LSDA calculations lead to very small energy differences between the AFM and FM configurations. For some of the exchange paths, coupling is reversed from AFM to FM or vice versa. As an example, for system IV, LSDA values for $J_{1}$, $J_{2}$, $J_{3}$ and $J_{4}$ are $-9.39$ meV, $0.8$ meV, $-0.35$ meV and $0.1$ meV respectively, which may lead to a long-range AFM ordered system with no spin-gap, as lifting the geometrical frustration of spins along some path may not lead to a zero-spin singlet ground state.

2.4. Construction of effective spin-Hamiltonian

A large number of analytical investigations are available for the spin-chain low-dimensional systems [25–30] and also for more complicated systems such as spin-trimers, tetramers [31, 32], octahedra [33] etc. We may construct a generalized minimal Heisenberg Model spin-Hamiltonian describing the low-energy spin interactions and excitations for the low-dimensional tetramer system as:

$$H = J_{1} \sum_{i,j=1, i \neq j}^{4} S_{i} \cdot S_{j} + J_{m} \sum_{i=1}^{n} S_{2i-1} \cdot S_{2i+1} + J_{d} \sum_{i=1}^{n} S_{2i} \cdot S_{2i+2}. \quad (1)$$
Here $n$ is the number of tetramer units. $J_t$, $J_m$ and $J_d$ are the tetrameric ($J_1$), monomeric ($J_2$) and dimeric ($J_3$ and $J_4$) exchange constants for system IV. For the isolated spin cluster as presented in figure 5(b), equation (1) can be simplified to involve one intra-tetrameric exchange $J_1$, three $z$-direction monomeric exchange $J_2$, one dimeric exchange $J_3$ and two dimeric exchange $J_4$. Within the first-order approximation, the degenerate $|S_{ztot}| = 1$ triplet states for this system are given by $1/\sqrt{2}(|↑↑↑↓⟩−|↑↓↑↑⟩), 1/\sqrt{2}(|↓↓↓↑⟩−|↓↑↓↓⟩)$ and $1/\sqrt{2}(|↑↑↓↑⟩−|↓↑↑↑⟩)$. The $|S_{ztot}| = 0$ degenerate singlet states are given by $1/\sqrt{2}(|↑↑↓↓⟩−|↓↓↑↑⟩)$ and $1/\sqrt{2}(|↑↑↑↑⟩−|↓↓↓↓⟩)$. Calculation of eigenvalues corresponding to these eigenstates leads to evaluation of the spin-gap, i.e., the energy difference between this singlet ground state and triplet excited states. As a next step, we will investigate the effect of volume reduction on the magnitude of the spin-gap using this simple model Hamiltonian.

3. Investigation on spin-gap

Among these four systems, presence of a spin-gap is experimentally confirmed only for Cu$_2$PO$_4$OH. Hence, we have studied this particular system under volume reduction (equivalent to the application of hydrostatic pressure) and size confinement. The volume reduction effects on the magnetic exchange coupling constants are studied in two steps. In the initial step, we intend to observe qualitatively the effects of volume reduction on the magnitude of the inter- and intra-tetramer exchange coupling constants by comparing the energy-versus-volume graph of different magnetic supercell configurations. In the next and final step, we use quantitative calculations by using the effective spin-Hamiltonian to compute the variation of the spin-gap of this particular system under volume reduction. In all of these calculations, both the lattice parameters and ionic coordinates of various supercell configurations are relaxed with a particular magnetic arrangement.

At the initial step, in a $1 \times 1 \times 2$ supercell, FM denotes the configuration where all the Cu atoms are ferromagnetically aligned. In AFM1, only the intra-tetrameric exchange $J_1$ is present. In AFM2, the monomeric exchange $J_2$ is also present along with $J_1$. With gradual volume reduction, AFM2 becomes the lowest energy configuration for the $1 \times 1 \times 2$ supercell, as seen in the upper panel of figure 6. Similarly, for a $2 \times 1 \times 1$ supercell, AFM3 is the magnetic configuration with only $J_1$. In AFM4, Cu2–Cu2 dimeric exchange $J_3$ is present along with $J_1$. In this case, AFM4 becomes the lowest energy configuration (figure 6, lower panel) with volume reduction with a very small energy difference with FM configuration. Figure 7 presents a schematic diagram of the above-mentioned magnetic configurations. Thus, this qualitative analysis implies that with gradual cell

Figure 6. Effect of cell volume reduction is equivalent to application of hydrostatic pressure. Upper and lower panel represent the comparison of lowest energy configuration for $1 \times 1 \times 2$ and $2 \times 1 \times 1$ supercells, respectively (details in text).

Figure 7. Schematic model spin configurations to understand the importance of inter-tetramer couplings as mentioned in the text. AFM1 and AFM2 are for the $1 \times 1 \times 2$ supercell whereas AFM3 and AFM4 are for the $2 \times 1 \times 1$ supercell (details in text).
Figure 8. Upper panel depicts the variation of exchange couplings with cell volume in a system where all four couplings are present. Inset shows the variation of the exchanges in a small scale. The lower panel represents the variation of spin-gap values (in K) with cell volume as computed numerically from the simplified model Hamiltonian. The red line in the figure shows the equilibrium cell volume and the corresponding spin-gap value ~150 K.

As a next step, evolution of these four effective exchange integrals with reduced volume, as presented in the upper panel of figure 8, are computed for a $2 \times 2 \times 2$ supercell, where all sorts of magnetic couplings are present. The exchange couplings are plotted with respect to an average cell volume of 72 atoms, to ease a comparison with figure 6. The equilibrium cell volume is also computed in a similar way. This figure indicates that, with reduced volume, all of the effective couplings become more and more antiferromagnetic, with $J_3$ and $J_4$ orders of magnitude smaller than the other two. Variation of the spin-gap (in K) with volume, as calculated from the model spin-Hamiltonian, is also plotted in the lower panel of figure 8. It is evident from the figure that with all four effective couplings present, a decrease from the equilibrium cell volume (denoted by red dotted line in the figure) may result in an increase in the spin-gap magnitude. The situation is slightly different with an increase of cell volume, where the spin-gap first decreases and then increases. The marked red dotted line at the spin-gap axis indicates its value (~150 K) corresponding to the equilibrium volume. The spin-gap value is quite close to the experimental observation of 141 K [14]. The increase of spin-gap with volume change is actually a manifestation of the variation of the couplings near equilibrium volume, which are shown in the inset of the upper panel of figure 8.

The effect of size confinement is also studied after confining a 36-atoms unit cell cluster and 72-atoms $1 \times 1 \times 2$ and $2 \times 1 \times 1$ supercell clusters and calculating the effective exchange integrals (table 3). A general observation not only indicates an increase of the exchange integrals but the geometric frustration of the bulk system seems to disappear as some such exchanges becomes ferromagnetic. So, in reduced dimensions, the system may show a long-range ordering.

4. Conclusion

In conclusion, for the general class of Libethenite systems, the effect of substitutional impurity-induced transformation from a three-dimensional antiferromagnet to a low-dimensional quantum spin-1/2 tetramer system is investigated with the combined effects of structural and localized band structure analysis along this series. The interplay between the structural distortion introduced by Cu substitution at the Co site and its manifestation into the spin-magnetic structure of the series of systems are investigated with the help of appropriate DFT techniques. Identification of significant exchange paths and calculation of the corresponding exchange integrals provides the input to construct the model Hamiltonian for the low-dimensional system.

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Table 3. Relevant exchange couplings constants in meV for the CuPO$_4$OH system under size reduction.

| System  | $J_1$  | $J_1'$ | $J_2$  | $J_2'$ | $J_3$  | $J_4$  |
|---------|-------|-------|-------|-------|-------|-------|
| CuPO$_4$OH | $-35.56$ | $-35.56$ | $20.32$ | $20.32$ | $16.407$ | $-10.69$ |
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