Electronic structure of $Na_2CuP_2O_7$: a nearly 2D Heisenberg antiferromagnetic system

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Abstract
We have employed first principles calculations to study the electronic structure and the implications for the magnetic properties of $Na_2CuP_2O_7$. Using the self-consistent tight-binding linearized muffin-tin orbital method and the Nth-order muffin-tin orbital downfolding method, we have calculated the various intrachain and interchain hopping parameters between the magnetic Cu^{2+} ions. Our calculations for $Na_2CuP_2O_7$ reveal dominant intrachain hopping, but in contrast to the typical quantum spin chains the interchain hoppings are not negligible. The Wannier function plot of the Cu $d_{x^2-y^2}$ orbitals shows that the exchange interactions are primarily mediated by the oxygens and the distance between the oxygens in $Na_2CuP_2O_7$ is favorable for both intrachain and interchain interactions, suggesting the inapplicability of the one-dimensional Heisenberg model for this system, in agreement with recent experimental results.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The discovery of high-T_c superconductivity in cuprates triggered interest in oxide materials as possible progenitors of exotic magnetic phenomena. Subsequent research established the important role of the two-dimensional (2D) CuO planes concerning the magnetism and superconductivity of the cuprates. There continues to be intense experimental effort to find new one-dimensional (1D) and 2D spin $S = \frac{1}{2}$ systems with antiferromagnetic (AF) nearest-neighbor interactions. The objectives of this research have been threefold: (a) to generate a knowledge base of the properties of such quantum magnets, (b) to attempt impurity substitution and carrier doping to understand the evolution of the magnetic and possible superconducting properties, and (c) to compare the data with existing theory, which might help the theorists to come up with newer, and more refined, models. The theoretical effort on one hand has been concentrated on proposing new models and determining generic phase diagrams which might be observed in experiment, and on the other hand making detailed calculations for specific chemical systems, which

might help in resolving the intricacies of a real system. It is anticipated that a combination of the above will lead to a better understanding of the physics of low-dimensional quantum magnets.

While a sizeable number of quasi-1D $S = \frac{1}{2}$ Heisenberg antiferromagnetic (HAF) systems have been found, in most of them significant interchain interactions lead to magnetic order, thereby limiting the range of temperatures over which true 1D properties could be experimentally probed. Among the compounds in which 1D properties could be observed over a large temperature range, Sr_2CuO_3 is a prominent example, since, as inferred from susceptibility measurements, it has a large intrachain exchange coupling J/k_B of 2200 K while magnetic order was observed only below 5 K [1]. In the case of $S = \frac{1}{2}$ 2D HAF systems as well, long-range order at non-zero temperatures has been observed in virtually all the systems studied due to the existence of non-negligible inter-plane interactions.

Several new Cu-based phosphates have come to light in the recent past which have been experimentally shown to be either 1D or 2D. For instance, $(Ba, Sr)_2Cu(PO_4)_2$
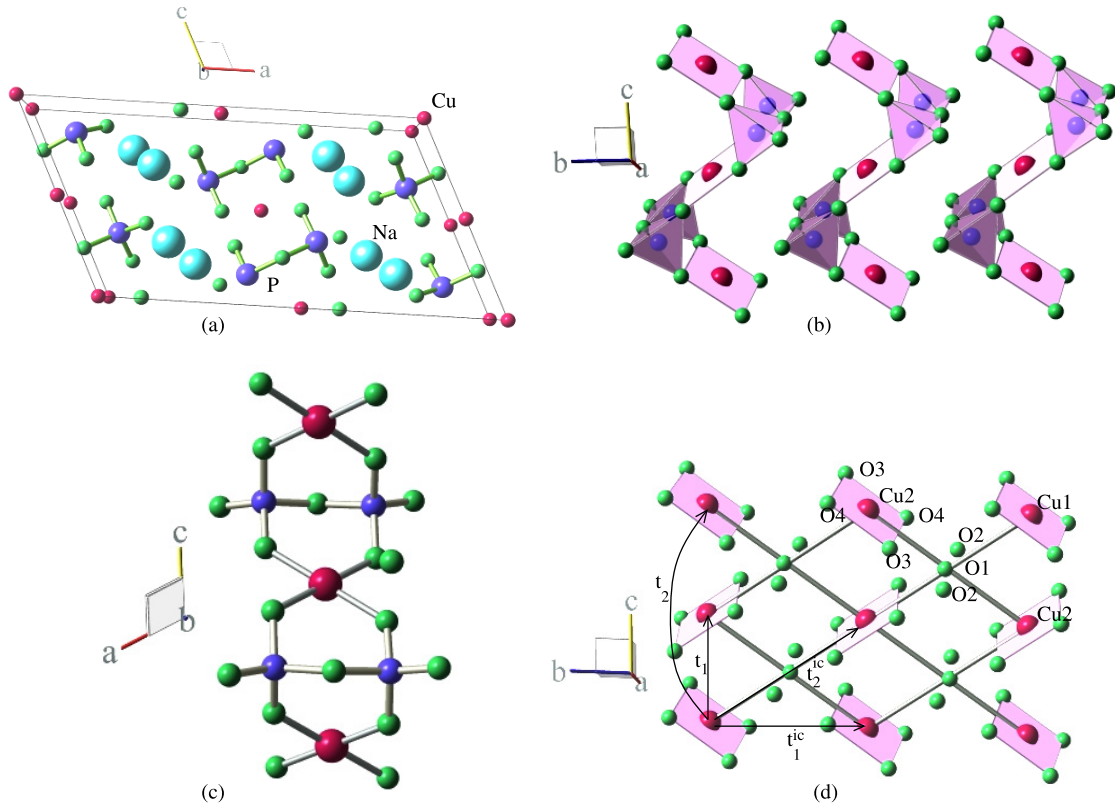
Figure 1. (a) A schematic diagram of the unit cell of $Na_2CuP_2O_7$; (b) isolated chains of Cu running along the c direction; (c) a single chain of CuP_2O_7 groups is shown for clarity; (d) the arrangement of various oxygens (O1, O2, O3 and O4) and Cu atoms in the bc-plane, resulting in a chain or a plane topology as suggested by Nath *et al* [9], and also the various hoppings between the Cu atoms.

systems were found to be quasi-1D [2, 3]. Recent electronic structure calculations [4–6] pertaining to the above compounds determined the origin of the short-range exchange interaction and the combination of factors which led to the 1D character. Other members from the phosphate family which have been investigated are $K_2CuP_2O_7$ [7], $BaCuP_2O_7$ [3, 8] and $Na_2CuP_2O_7$ [9]. While $K_2CuP_2O_7$ and $BaCuP_2O_7$ are suggested to be good quasi-1D magnets, the magnetic properties of $Na_2CuP_2O_7$ are intriguing. The magnetic susceptibility, ^{31}P NMR, and heat capacity data [9] for the high-temperature phase of $Na_2CuP_2O_7$ suggest that the 2D HAF model provides a somewhat better description for the magnetism in $Na_2CuP_2O_7$.

In this paper, we shall examine the electronic structure of $Na_2CuP_2O_7$ in some detail, and in particular identify the dominant exchange path, which in turn will clarify the magnetic dimensionality of $Na_2CuP_2O_7$. As shown in figure 1, the characteristic features of the structure of $Na_2CuP_2O_7$ are CuO_4 square plaquettes, which are connected to each other through P_2O_7 groups and run along the crystallographic c direction in a corrugated fashion. The key issue for the compound $Na_2CuP_2O_7$ is that the exchange interaction between the Cu^{2+} ions can arise due to two interaction paths, as we shall explain later. Depending on the relative importance of these two paths, the spin Hamiltonian corresponding to a chain topology or that of a 2D magnetic system might be applicable for $Na_2CuP_2O_7$.

The rest of the paper is organized as follows: in section 2 we discuss the crystal structure of $Na_2CuP_2O_7$ followed by the computational details. Section 3 is devoted to the detailed analysis of the electronic structure using the tight-binding linearized muffin-tin orbital method within the atomic-sphere approximation (TB-LMTO ASA) and extraction of a low-energy effective model Hamiltonian using the Nth-order muffin-tin orbital (NMTO) downfolding method followed by comparative study of our calculations with available experimental results. Finally, our conclusions are given in section 4.

2. Crystal structure and computational details

$Na_2CuP_2O_7$ in the high-temperature phase crystallizes in the monoclinic structure with space group $C_{2/c}$. The unit cell parameters as reported by Erragh *et al* [10] are $a = 14.728$ Å, $b = 5.698$ Å, $c = 8.067$ Å, and $\beta = 115.15°$. Etheredge *et al* [11] also reported similar results for the structural properties of $Na_2CuP_2O_7$. All the electronic structure calculations in the present work are carried out with the lattice parameters and the atomic positions as reported by Erragh *et al* [10].

The structure of $Na_2CuP_2O_7$ is shown in figure 1. The monoclinic unit cell as shown in figure 1(a) is made up of two formula units. From figures 1(b) and (c) we gather that the characteristic features of the structure of $Na_2CuP_2O_7$ are CuO_4 square plaquettes which share four corner oxygens with two
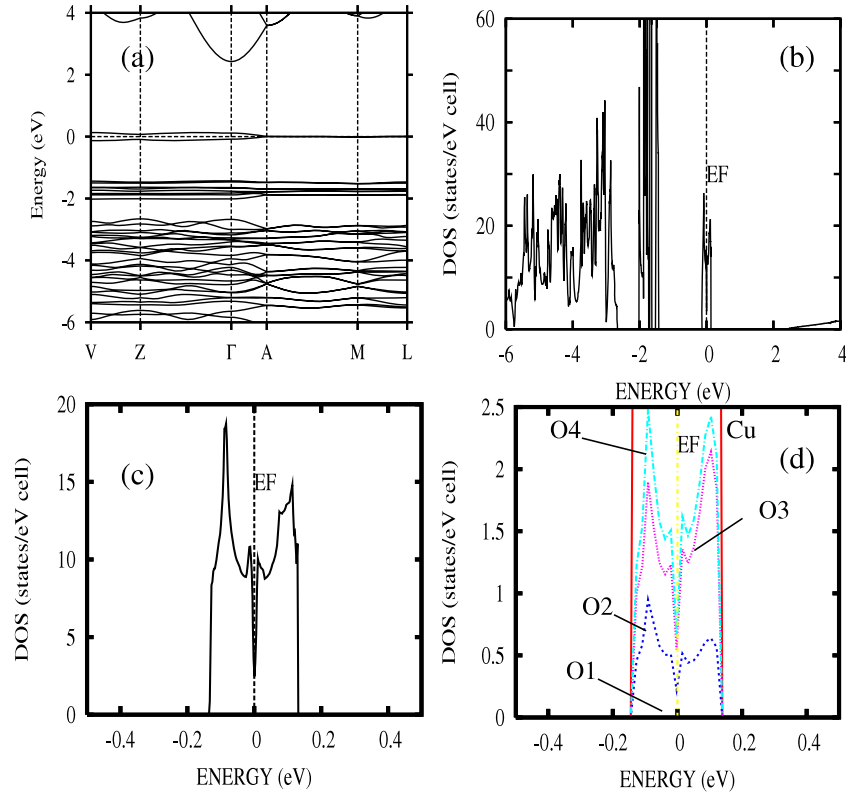
Figure 2. (a) All-orbital band structure, (b) density of states (DOS), (c) DOS near the Fermi level and (d) partial DOS of $Na_2CuP_2O_7$.

P_2O_7 diphosphate groups, forming a chain running along the c-direction in a corrugated fashion. Hence we have a structure formed of corrugated ribbons of $[CuP_2O_7]_\infty$ in the c-direction. In figure 1(d), we have shown the structure of $Na_2CuP_2O_7$ projected in the bc plane, keeping only the Cu and O (O1, O2, O3, O4) atoms. While the oxygens (O1, O2, O3, O4) are inequivalent, there are two equivalent Cu atoms in the unit cell. From figure 1(d) we note that the structure of $Na_2CuP_2O_7$ can also be regarded as sheets (bc-planes) stacked along the a-direction and bridged by Na ions. We have also indicated in the same figure the various hoppings between the Cu atoms. We note that t_1 and t_2 are the nearest-neighbor (NN) and the next-nearest-neighbor (NNN) hoppings along the chain, while t_1^{ic} and t_2^{ic} are the interchain hoppings. Depending on the relative strengths of the intrachain and the interchain hoppings, the system can be modeled as a 1D or as a 2D system. For instance, if only $t_1 \neq 0$, we will recover the uniform chain. On the other hand, if $t_1 = t_1^{ic}$ and these are the only non-zero hopping matrix elements, we will get a nearly uniform plane. So it is crucial to estimate the relative strength of these hoppings in order to understand the magnetic properties of $Na_2CuP_2O_7$.

All the electronic structure calculations presented in this work are carried out in the framework of the tight-binding linearized muffin-tin orbital (TB-LMTO) method in the atomic-sphere approximation [12] within the local-density approximation to the density functional theory. The space filling in the ASA is achieved by inserting appropriate empty spheres. The basis set for the self-consistent electronic structure calculation for $Na_2CuP_2O_7$ includes Cu(s, p, d), Na(s), O(s, p) and P(s, p) and the rest are downfolded. An

(8, 8, 8) k-mesh has been used for self-consistency. All the k-space integrations were performed using the tetrahedron method [13]. In order to derive a low-energy effective model Hamiltonian that will serve as the single-electron part of the many-body Hamiltonian necessary to model these systems, we have employed the NMTO-based downfolding method [14–16].

3. Results and discussion

The all-orbital TB-LMTO-ASA LDA band dispersion, total density-of-states (DOS) and total and partial DOS in the energy range of the conduction band for $Na_2CuP_2O_7$ are displayed in figure 2. The bands are plotted along the various high-symmetry directions of the Brillouin zone corresponding to the monoclinic lattice for $Na_2CuP_2O_7$. All the energies are measured with respect to the Fermi level of the compound. The characteristic features of the non-spin-polarized band structure displayed in figure 2 are two isolated half-filled bands at the Fermi level, arising from the two Cu atoms in the unit cell. These bands at the Fermi level arise from the antibonding linear combination of Cu $d_{x^2-y^2}$ and O pσ states from the CuO$_4$ plaquette. The bands below these Cu $d_{x^2-y^2}$ bands are other Cu d bands and further below lie the oxygen 2p states. These two isolated Cu $d_{x^2-y^2}$ conduction bands that are well localized and very close to the Fermi level are responsible for the low-energy physics of this material. We note from the plot of the oxygen partial DOS displayed in an energy range of the conduction band in figure 2(d) that the conduction band
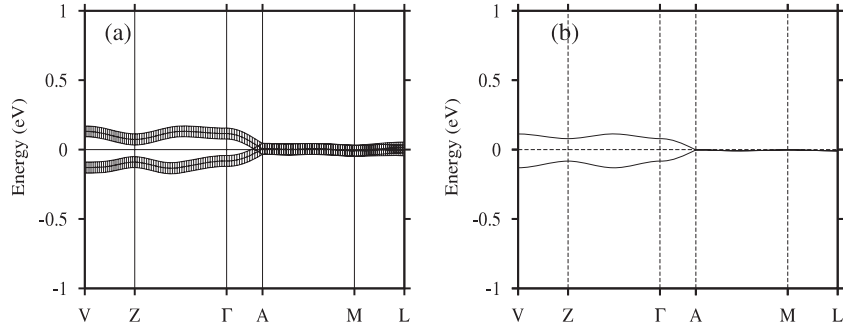
Figure 3. (a) Cu $d_{x^2-y^2}$ projected band as well as (b) the downfolded band in $Na_2CuP_2O_7$.

has contributions not only from oxygens O3 and O4 residing in the square plaquette but interestingly also from oxygen O2 that does not belong to the square plaquette. This implies that possibly Cu–O2–Cu (see t_2^{ic} in figure 1(d)) may also provide an interaction path. This would imply a tendency for 2D behavior.

Since the calculations are carried out in the framework of the LDA, the system is not insulating. The insulating state however can be recovered by inclusion of the Hubbard U in the LDA + U framework. Here we have adopted a different strategy to analyze our results. As we have argued earlier that the low-energy physics of this system is best described by the half-filled Cu $d_{x^2-y^2}$ states, so a Hubbard model $H = \sum_{i,j,\sigma} t_{ij} c_{i,\sigma}^\dagger c_{j,\sigma} + U \sum_i n_{i\uparrow} n_{i,\downarrow}$ that includes only these degrees of freedom and a strong on-site Coulomb interaction (i.e. $U \gg t$) is appropriate for this system as it maps to a Heisenberg model $H = -\sum J_{i,j}(S_i S_j)$ in this limit. The exchange integrals J_{ij} entering the Heisenberg model are in turn related to the parameters of the Hubbard model. The goal of the present work is therefore threefold: (a) extract the single electron part of the Hubbard model from the LDA calculations in a reliable way, (b) construct a relevant model as described above, and (c) utilize it to estimate and understand various exchange integrals and exchange paths leading to novel magnetism in these systems.

In the following we shall employ the NMTO downfolding method [14–16] to map our LDA results to a low-energy, orthogonal, tight-binding model Hamiltonian. The NMTO downfolding method provides an *ab initio* scheme to construct a low-energy tight-binding Hamiltonian starting from the full all-orbital LDA calculations. This method utilizes the energy selective downfolding method to integrate out high-energy degrees of freedom from the all-orbital LDA calculations. The low-energy Hamiltonian obtained in the process is defined in the basis of effective orbitals. The effective orbitals that are retained in the basis contain in their tails the states which are integrated out, with their weights being proportional to their admixture with the orbitals that are retained in the basis. It is important to note that if the low-energy sets of bands are separated from all other bands, the orthonormalized NMTO set converges to a set of Wannier functions, thereby providing a direct method to obtain Wannier functions without recourse to Bloch functions. These effective orbitals provide a direct visualization of the various interaction paths crucial to understand these systems. This method has been employed

**Table 1.** Hopping integrals (in meV) obtained from our *ab initio* analysis for $Na_2CuP_2O_7$.

	t_1	t_2	t_1^{ic}	t_2^{ic}	$t_\perp$
$Na_2CuP_2O_7$	55.8	1.4	1.4	5.4	4.1

successfully to analyze the electronic structure of a variety of materials [17–19].

In figure 3 we have displayed the band structure of $Na_2CuP_2O_7$ showing the Cu $d_{x^2-y^2}$ orbital character in the local frame of reference where Cu is at the origin and the x- and y-axes point along the oxygens residing on the same square plaquette together with the downfolded band structure, where only the Cu $d_{x^2-y^2}$ orbital is retained in the basis and the rest are downfolded. The agreement between the two is good. The Fourier transform of the downfolded Hamiltonian $H(k) \longrightarrow H(R)$ gives the effective hopping parameters for the physical (model) Hamiltonian. In table 1 we have displayed the various dominant effective hopping integrals t_{ij} (having magnitude $\geqslant 1$ meV) between the Cu^{2+} ions at sites i and j. The notations for the various hoppings are indicated in figure 1(d). $t_\perp$ refers to the hopping perpendicular to the bc-plane (i.e. along a). From table 1 we gather that, as expected, the NN hopping along the chain, i.e. along the c-direction, is dominant. The other hoppings along the chain (intrachain) as well as between the chains (interchain) are smaller than the dominant nearest-neighbor hopping but not negligible, as found in other 1D HAF systems studied in recent times [4, 7, 5]. The difference in the eigenvalues $\Delta\varepsilon(\mathbf{k})$ between the two bands displayed in figure 3 has a simple form given by

$$\Delta\varepsilon(\mathbf{k}) = 4\cos\left(\frac{c}{2}k_z\right)\left[2t_2^{ic}\cos(k_y b) - t_1\right].$$

As a consequence for $k_z = \frac{\pi}{c}$, i.e. at the points A, M, L, $\Delta\varepsilon(\mathbf{k}) = 0$ and the two degenerate bands along these direction hardly disperse due to the small magnitudes of the other hoppings. The hopping parameters listed in table 1 can be used to estimate various exchange interactions using the relation $J_{ij} = \frac{4t_{ij}^2}{U_{eff}}$, where U_{eff} is the screened Coulomb interaction. Although the total exchange constant will have a ferromagnetic and an antiferromagnetic contribution to it, for strongly correlated systems the antiferromagnetic contribution is dominant and our above estimate refers to the antiferromagnetic contribution to the total exchange constant.
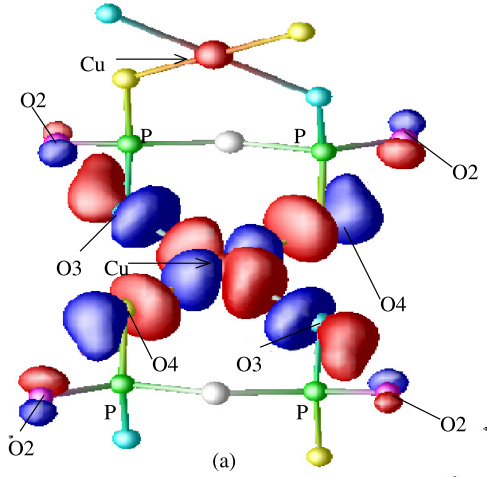
Figure 4. Cu $d_{x^2-y^2}$ Wannier function plot for $Na_2CuP_2O_7$ (the height of the isosurface is ± 0.09).

As we shall discuss later, the oxygens play a crucial role in mediating the various hoppings.

It is important to note that the dominant NN hopping (t_1) for another one-dimensional system [4, 5, 3] is about twice as large in comparison to $Na_2CuP_2O_7$ and may be attributed to the corrugated chains present in this compound. The ratio of the interchain to intrachain coupling (($\frac{t_2^{ic}}{t_1}$)^2) in $Na_2CuP_2O_7$ is ≈ 0.01, while the ratio of the interchain to dominant intrachain coupling (($\frac{t_1^{ic}}{t_1}$)^2) in other 1D systems is one order of magnitude lower. This indicates that the interchain interactions in $Na_2CuP_2O_7$ cannot be neglected, thereby putting it closer to 2D systems. For a deeper insight into the geometry and the strength of the exchange interactions in various directions, we have calculated the Wannier-like orbital for $Na_2CuP_2O_7$.

The Cu $d_{x^2-y^2}$ Wannier function has been plotted for $Na_2CuP_2O_7$ in figure 4. We note that the Cu $d_{x^2-y^2}$ Wannier function is primarily localized on one plaquette. The tails of the Cu $d_{x^2-y^2}$ orbital are shaped according to O p_x/p_y orbitals such that the Cu $d_{x^2-y^2}$ orbital forms strong pdσ antibonds with the O p_x/p_y tails. The bending of the tail of the O p_x/p_y towards the Cu atom indicates the strong hybridization of Cu with O. This antibonding linear combination results in the conduction band complex as described earlier. A small hybridization effect of the O2 atom is also seen for $Na_2CuP_2O_7$, indicating non-negligible interchain coupling. From the Cu $d_{x^2-y^2}$ Wannier function (see figure 4), we see that the Cu–Cu hopping primarily proceeds via the oxygens. As a result, as argued by Koo *et al* [6], the strength of the Cu–O$\cdots$Cu spin exchange primarily depends on the O$\cdots$O distance and Cu–O$\cdots$Cu angles rather than the Cu$\cdots$Cu distances. Thus, if the distance between the oxygens mediating the exchange interaction is large compared to the characteristic van der Waals distance 2.8 Å for oxygens, the exchange interaction becomes weak [6]. Similarly, the Cu–O$\cdots$Cu angles have a pronounced effect on the effective exchange integrals. In $Na_2CuP_2O_7$, the O–O distances are shorter than the van der Waals distance along two directions (see table 2). The O3–O4 distance along the *c*-direction is 2.521 Å, and the exchange interaction is strongest

Table 2. O–O distances along the chain direction (*c*-axis) and along the plane direction for $Na_2CuP_2O_7$.

Compound	O3–O4 (*c* direction) (Å)	O2–O4 (Cu1–O2–Cu1 path) (Å)
$Na_2CuP_2O_7$	2.521	2.512

along this path. However, as the CuO_4 planes are not parallel to each other, but corrugated along the *c* direction, the direct overlap of the neighboring Cu $d_{x^2-y^2}$ magnetic orbitals is not strong, resulting in a relatively weak intrachain hopping in comparison to other 1D HAF systems. We also note that in the *bc*-plane the O4–O2 distance along the Cu–O2–Cu path is 2.512 Å, as listed in table 2. As a result there is non-negligible interchain coupling.

As mentioned before, in real systems, there can be deviations from ideal 1D or 2D behavior due to the existence of non-negligible magnetic interactions between the chains/planes. In systems such as $(Ba, Sr)_2Cu(PO_4)_2$, it was reasonably clear from the structure itself that the system was primarily 1D (surely not 2D), while interchain interactions could lead to ordering at low temperatures [3]. On the other hand, in $Na_2CuP_2O_7$, experimental results of Nath *et al* [9] found that the spin susceptibility of $Na_2CuP_2O_7$ was somewhat better modeled considering the 2D HAF model [9], although the Cu–Cu distances involved were not comparable. Our calculations presented here suggest that the structural properties, in particular the corrugated chains in $Na_2CuP_2O_7$, and the relative O–O distances play a crucial role to determine the nature of magnetism in this system. The effective dimensionality of between 1 and 2 as observed in the experiments has then been anticipated in the theory.

4. Summary and conclusions

We have employed TB-LMTO-ASA and the NMTO downfolding method to analyze in detail the electronic structure of $Na_2CuP_2O_7$. The characteristic features of the LDA electronic structure are two isolated pair of half-filled bands at the Fermi level derived from the antibonding linear combination of Cu $d_{x^2-y^2}$ and oxygen p_σ states residing on CuO_4 square plaquettes. The various hopping integrals are calculated using the NMTO downfolding method. Although the nearest-neighbor intrachain hopping integral is dominant, the interchain hoppings are not negligible for $Na_2CuP_2O_7$. The plot of the Cu $d_{x^2-y^2}$ Wannier functions suggests that the exchange interactions between the magnetic Cu^{2+} ions are primarily mediated by the oxygens. For $Na_2CuP_2O_7$ the distance between the oxygens that mediate the exchange interaction along the chain as well as between the chains is less than the characteristic van der Waals distance, allowing for appreciable intrachain and non-negligible interchain interaction. Our estimate of the ratio of the interchain to the intrachain exchange interaction in $Na_2CuP_2O_7$ is 0.01, which is appreciable in comparison to other 1D systems, and this appears to be enough to promote a tendency towards 2D behavior in $Na_2CuP_2O_7$, as suggested in a recent experiment.

Acknowledgments

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