Magnetic properties and electronic structure of S=1/2 spin gap compound $BaCu_2V_2O_8$

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(Received 7 September 2007; revised manuscript received 7 December 2007; published 28 January 2008)

A detailed experimental as well as theoretical study is carried out to elucidate the origin of the spin gap in the quasi-one-dimensional compound $BaCu_2V_2O_8$. Our experimental analysis with the aid of careful magnetic susceptibility measurements on powder samples confirms that the magnetic behavior of this compound is best described by an isolated dimer model. We have also employed first principles calculations to study the electronic structure and magnetic properties of this low-dimensional spin gap compound. Using the self-consistent tight-binding linearized muffin-tin orbital (LMTO) method, and the *N*th order LMTO method, we have identified the dominant exchange path by calculating the effective Cu-Cu hopping integrals. Our estimate of the alternation parameter α from the electronic structure calculations is consistent with that estimated from experiment confirming the validity of the isolated dimer model to explain the origin of the spin gap in this system.

DOI: 10.1103/PhysRevB.77.012410 PACS number(s): 75.10.Pq, 71.20.−b, 71.70.Gm, 75.40.Cx

INTRODUCTION

Considerable attention has been given to the physics of low-dimensional quantum spin systems in the last decade.[1] Such systems have a number of experimental realizations and exhibit a variety of phenomena, the origin of which has been attributed to quantum effects and low dimensions. In general, spin-Peierls chains, uniform or alternating-exchange antiferromagnetic spin chains, and a variety of spin ladders have been investigated. For a uniform Heisenberg antiferromagnetic (HAF) chain with half-integer spins, a gapless ground state is expected. However, a spin gap can open up in HAF spin chains either due to frustration because of next-nearest-neighbor (NNN) antiferromagnetic exchange or dimerization due to an alternating (in magnitude) exchange coupling to nearest neighbors along the chain. Exotic features related to the ground state and excitations of such gapped systems form a subject matter of current interest.[2] Copper-based compounds have had a special focus on them due to their proximity to the superconducting two-dimensional cuprates.[3]

We concentrate in this Brief Report on the proposed alternating-exchange chain compound $BaCu_2V_2O_8$. The characteristic features of this compound are Cu_2O_6 plaquettes made up from edge-sharing CuO_4 square plaquettes forming a zigzag chain along the crystallographic *c* direction. The spin Hamiltonian for such a system is given by $\mathcal{H}=J\Sigma_i(\mathbf{S}_{2i-1}\cdot\mathbf{S}_{2i}+\alpha\mathbf{S}_{2i}\cdot\mathbf{S}_{2i+1})$, where J is the nearest-neighbor (NN) exchange integral and α is the alternation parameter. Recently He *et al.*[4] reported magnetic susceptibility and heat capacity measurements on polycrystalline $BaCu_2V_2O_8$. They reported a large spin gap of 230 K. They also identified the dominant exchange path and claimed that the magnetic susceptibility was well reproduced by a strongly alternating AF chain model with $J/k_B=260$ K and $\alpha=0.2$.[4] This is at variance with ^{51}V NMR study by Lue and Xie[5] who suggested that a nearly isolated dimer model might be more suitable for the description of magnetic properties of this system. On the other hand, Koo and Whangbo,[6] based on extended Hückel tight-binding calculations, determined the dominant exchange path and found an alternation parameter close to $\alpha=0.1$. Both the parameters (exchange path and α) are different from those suggested by He *et al.*[4] The exchange path proposed by Koo and Whangbo[6] is, however, supported by a recent ^{51}V NMR study by Ghoshray *et al.*,[7] suggesting the importance of both the inequivalent vanadium ions to determine the chain topology. In view of these apparent inconsistencies, we decided to take a deeper look at the properties of $BaCu_2V_2O_8$ from both an experimental viewpoint as also via first principles electronic structure calculations.

In this Brief Report, we report on the magnetic behavior and the electronic structure of $BaCu_2V_2O_8$. The goal of the present work is to find out the magnetic exchange interactions by magnetic susceptibility measurements and also to understand and evaluate the dominant exchange path by calculating the various hopping integrals using first principles electronic structure calculations. The latter will also provide an estimate of the exchange integrals entering the magnetic Hamiltonian offering insights into the as yet unsettled nature of magnetism for this system.

CRYSTAL STRUCTURE AND MEASUREMENTS

The polycrystalline samples of $BaCu_2V_2O_8$ were prepared using the solid state reaction method using stoichiometric amounts of $BaCO_3$, CuO, and V_2O_5 as starting materials. X-ray diffraction confirmed the formation of single phase $BaCu_2V_2O_8$ with lattice parameters $a=12.7439(37)$ Å and $c=8.1480(34)$ Å and space group $I\bar{4}2d$ (No. 122) in agreement with earlier reports.[8]

A schematic diagram of the structure is shown in Fig. 1. The unit cell contains 4 f.u., where there are two inequivalent Ba [Ba(1) and Ba(2)], V [V(1) and V(2)], and four inequivalent O [O(1)-O(4)] atoms. The structure [Fig. 1(a)] is made up of Cu_2O_6 plaquettes forming a chain along the *c* axis. A pair of such chains, as illustrated in Fig. 1(a), is important for the spin-lattice model relevant for this system. For a pair of such chains, the intrachain and the interchain

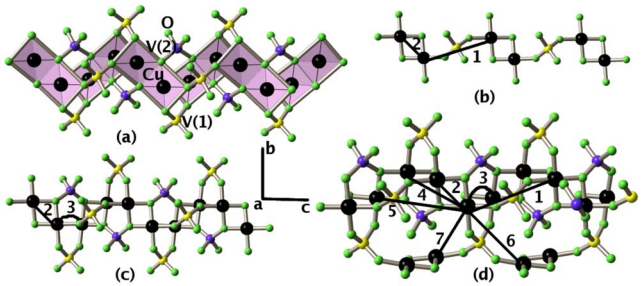

FIG. 1. (Color online) (a) The Cu_2O_6 plaquettes which form two parallel chains along the c direction bridged by V(1), V(2), and oxygens. [(b) and (c)] The dominant spin exchange paths of $BaCu_2V_2O_8$ as proposed by He *et al.* (Ref. 4) and Koo and Whangbo (Ref. 6), respectively. (d) The various hoppings t_i ($i=1-7$) between the Cu ions are shown by their respective numerical labels 1–7.

cohesion is brought about by $V(1)O_4$ and $V(2)O_4$ tetrahedra. The $V(1)O_4$ tetrahedra bridge Cu_2O_6 plaquettes along the chain and also perpendicular to the chain. However, $V(2)O_4$ tetrahedra bridge Cu_2O_6 plaquettes only between the two chains. The Ba atoms are located at the interstitial positions. The resulting NN intrachain Cu-Cu distance is 2.86 Å, while interchain distance is 3.01 Å. For the purpose of later discussion, we have shown the suggested chain topologies by He *et al.*[4] [Fig. 1(b)] and Koo and Whangbo[6] [Fig. 1(c)] and the various Cu-Cu hoppings [Fig. 1(d)]. Later, we show that the actual spin dimers arise from the Cu ions in the adjacent chains bridged by both $V(1)O_4$ and $V(2)O_4$ tetrahedra [see Fig. 1(c) label 3].

Magnetization M was measured as a function of applied field H and temperature T using a vibrating sample magnetometer of a physical property measurement system from Quantum Design. The magnetic susceptibility (M/H) of $BaCu_2V_2O_8$ is plotted as a function of temperature T from 2 to 350 K in Fig. 2. A broad maximum is observed around 280 K which is due to the low magnetic dimensionality. Below this broad maximum, the susceptibility decreases rapidly with decreasing temperature and an upturn appears below 60 K. The data between 10 and 300 K were fitted well to $\chi(T)=\chi_0+\chi_{cw}(T)+\chi_{spin}^{dimer}(T)$, as shown in Fig. 2(a), where χ_0 is the temperature independent term, $\chi_{cw}(T)=C/(T-\theta)$ is the Curie-Weiss term which models the upturn below 60 K, and $\chi_{spin}^{dimer}(T)=Ng^2\mu_B^2/[k_BT(3+e^{J/k_BT})]$, where we have taken g to be 2.2 (a typical value for Cu). The parameters obtained are as follows: $\chi_0=(4.1\pm0.1)\times10^{-5}$ cm^3/mol Cu, $\theta\approx0$ K, $C=(8.6\pm0.2)\times10^{-3}$ cm^3 K/mol Cu which amounts to about 2.3% of isolated $S=1/2$ paramagnetic moments, and $J/k_B=470\pm3$ K. The low-temperature upturn originates possibly from natural defects and or small amounts of paramagnetic impurities. Adding the core diamagnetic susceptibilities for individual ions[9] in $BaCu_2V_2O_8$, we get $\chi_{core}=-158\times10^{-6}$ cm^3/mol f.u.. The Van Vleck paramagnetic susceptibility for our sample, estimated by subtracting χ_{core} from χ_0, gives $\chi_{vv}=11\times10^{-5}$ cm^3/mol Cu which is comparable to the values found in other cuprates (e.g., χ_{vv} for Sr_2CuO_3 is 3.4×10^{-5} cm^3/mol).[10]

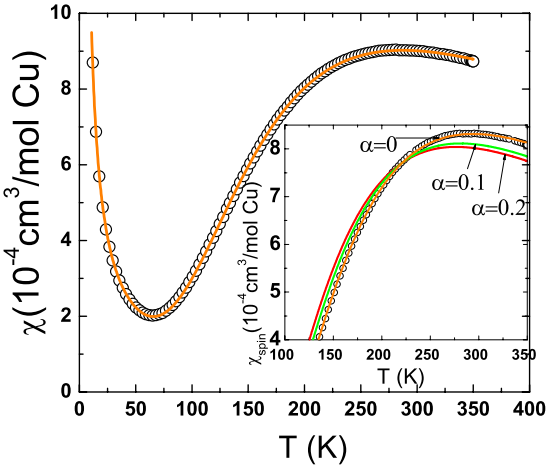

FIG. 2. (Color online) Temperature dependence of the magnetic susceptibility of $BaCu_2V_2O_8$ (open circles) with a fit to the dimer expression (orange or gray line). The inset shows $\chi(T)-\chi_0-\chi_{cw}(T)$ with fits (see text) for $\alpha=0$ (orange or gray), $\alpha=0.1$ (green or light gray), and $\alpha=0.2$ (red or dark gray).

Shown in Fig. 2 (inset) are data from which the T-independent term and the Curie-Weiss term have been subtracted. For comparison, we also show the best-fit curve with an alternation parameter $\alpha=0.1$ and $\alpha=0.2$ using Johnston's generic equation for the spin susceptibility of an alternating-exchange chain.[11] It is clear that the isolated dimer model ($\alpha=0$) fits the data better than the curves with $\alpha=0.1$ or $\alpha=0.2$. This is in contrast to the conclusion reached by He *et al.*[4] who determined $\alpha=0.2$. We note here that He *et al.*[4] analyzed their low-T data using $\chi(T)=\chi(0)+\chi_{cw}(T)+aT^{-1/2}\exp(-\Delta/k_BT)$ and obtained a gap value $\Delta/k_B=230$ K. They then analyzed their high-T data using the form given by Hatfield[12,13] to obtain the exchange coupling $J/k_B=260$ K. Note that the Hatfield expression is obtained for the spin-Hamiltonian $\mathcal{H}=2JS_iS_j$. Subsequently, they used $\Delta=J(1-\alpha)^{3/4}(1+\alpha)^{1/4}$ to obtain $\Delta/k_B=230$ K (apparently in agreement with their low-T fit) for $\alpha=0.2$. This is, however, grossly incorrect since the gap equation used by them is valid for the Hamiltonian $\mathcal{H}=JS_iS_j$. Therefore, the gap they should have obtained from their high-T data is 460 K which is grossly different from their value from the low-T fit. This indicates problems with the data analysis of He *et al.*[4] In our analysis, we have fit the susceptibility data with the expression given by Johnston *et al.*[11] which is valid in the full temperature range. We obtain a gap $\Delta/k_B\approx470$ K with $\alpha=0$ which compares closely with the gap value of $\Delta/k_B=450$ K obtained by Lue and Xie[5] by their NMR investigation. In the following, we shall corroborate our experimental results with first principles electronic structure calculations.

FIRST PRINCIPLES ELECTRONIC STRUCTURE CALCULATIONS

Our analysis of the electronic structure is carried out in the framework of the tight-binding (TB) linearized muffin-tin

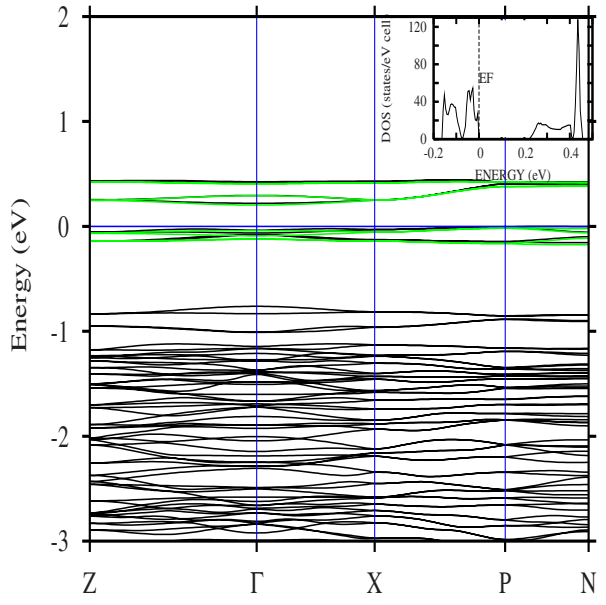

FIG. 3. (Color online) Downfolded bandstructure (shown in green or gray) projected over the full band structure (shown in black) for $BaCu_2V_2O_8$ with the density of states shown in the inset.

orbital (LMTO) method in the atomic-sphere approximation (ASA) within local density approximation (LDA) to density functional theory using the Stuttgart TB-LMTO-47 code.[14,15] The all-orbital band structure along the various high symmetry points of the body centered tetragonal Brillouin zone is displayed in Fig. 3. All the energies are measured with respect to the Fermi level of the compound. The main features of the band structure are eight bands divided into two subsets of four bands separated by a small gap (~0.2 eV) at the Fermi level. These bands that arise from eight Cu atoms in the unit cell are predominantly of Cu $d_{x^2-y^2}$ 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. This eight-band complex is separated from other occupied Cu and oxygen bands by a gap of 0.65 eV. In addition, the V bands are completely unoccupied confirming the V^{5+} character of the V states and lie far above the eight-band complex. This isolated Cu $d_{x^2-y^2}$ eight-band manifold is responsible for the low-energy physics of this material. In the absence of a gap, these bands would have been half-filled leading to a metallic state in LDA. However, the characteristic interdimer interaction primarily mediated by O-V-O bridges is responsible for the gap at the Fermi level, driving the system to an insulating state [Fig. 3 (inset)].

We expect that with the eight-band manifold so well separated from the rest, a tight-binding model with a single $d_{x^2-y^2}$ orbital per Cu site would be a good approximation to the full band structure close to the Fermi level. We have employed Nth order muffin tin orbital (NMTO) method based downfolding technique[16–18] to construct a low-energy, few-band, tight-binding model Hamiltonian for this system. The downfolding method consists of deriving few-orbital effective Hamiltonian from the all-orbital LDA Hamiltonian by downfolding the inactive orbitals into the tails of the active orbitals kept in the basis chosen to describe the low-energy physics. This method results in renormalized effective interactions between the active orbitals (here Cu $d_{x^2-y^2}$) retained in the basis. The downfolded Cu $d_{x^2-y^2}$ bands are also plotted in Fig. 3, and we note that the agreement with the full band structure is remarkable. The Fourier transform of the few-band downfolded Hamiltonian $H_K \rightarrow H_R (H_R = \Sigma_{ij} t_{ij} (c_i^\dagger c_j + \text{H.c.}))$ gives the effective hopping parameters between the Cu ions. These hoppings will determine the dominant exchange paths and also provide an estimate of the exchange interactions by the relation $J = \frac{4t_{ij}^2}{U}$, where U is the effective on-site Coulomb repulsion at the Cu site. The various hopping parameters are indicated in Fig. 1(d) and listed in Table I. We gather from Table I that, as anticipated, the dominant hopping parameter is the one mediated by the O-V-O complex [see Fig. 1(c) label 3]. In order to clarify the role of V(1) and V(2), we have also plotted in Fig. 4 the Cu $d_{x^2-y^2}$ Wannier function. We find [Fig. 4(a)] that each Cu $d_{x^2-y^2}$ orbital in the unit cell forms strong $pd\sigma$ antibonding linkages with the neighboring $O-p_x/O-p_y$ orbitals resulting in the

TABLE I. Cu-Cu distances and the hoppings associated with the various exchange paths in $BaCu_2V_2O_8$.

	Cu-Cu Distance (Å)	Hopping t (meV)
t_1	6.314	7
t_2	2.862	49
t_3	3.007	227
t_4	5.051	14
t_5	6.614	14
t_6	5.841	16
t_7	5.177	19

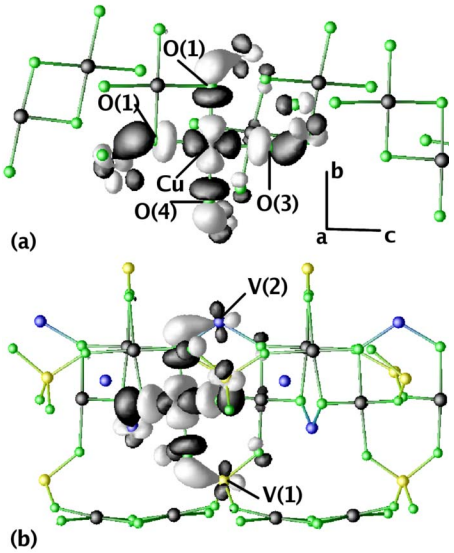

FIG. 4. (Color online) Effective Cu $d_{x^2-y^2}$ Wannier function plot showing (a) Cu $d_{x^2-y^2}$ orbital in the Cu_2O_6 plaquette and (b) the hybridization with oxygen and the vanadium to form a strongly interacting Cu-Cu dimer in $BaCu_2V_2O_8$.

eight-band complex close to the Fermi level. Figure 4(b) clearly illustrates the role of both V(1) and V(2) ions in mediating the dominant interdimer interaction. The next dominant interaction is the interaction between the two Cu ions in a Cu_2O_6 plaquette. The other hoppings are negligible. Our calculations provide a direct justification for the chain topology, as shown in Fig. 1(c) and also suggested by Koo and Whangbo.[6] Our estimation of the alternation parameter $\alpha=\frac{J_2}{J_3}=\frac{t_2^2}{t_3^2}=0.05$ is much smaller compared to that of Koo and Whangbo. With the value of α close to zero, it is clear that the isolated dimer model is the most appropriate to describe this system.

SUMMARY AND CONCLUSIONS

We have studied the quasi-one-dimensional spin gap compound $BaCu_2V_2O_8$ by means of magnetic susceptibility measurements on powder samples and using first principles electronic structure calculations. Our experimental analysis confirms that the magnetic behavior of this compound is best described by the isolated dimer model. Using the self-consistent TB-LMTO-ASA method and the NMTO method, we have analyzed in detail the various effective Cu-Cu hopping parameters and found that the Cu-Cu hopping between the NNN Cu ions is the most dominant hopping parameter. The plot of the Wannier functions suggest that the O-V-O bridges are crucial mediators of this hopping. Our estimate of the alternation parameter supports the dimer picture for this compound consistent with our experimental results.

ACKNOWLEDGMENTS

I.D. thanks DST, India (Project No. SR/S2/CMP-19/2004) for financial support. We also thank IFCPAR for financial support.

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