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Influence of $[VO_4]^{3-}$ Bridges on Magnetic Coupling in $Ba_2V_3O_9$ Studied by Molecular Orbital Calculations

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A molecular orbital study is presented of the magnetic coupling in the one-dimensional vanadium oxide $Ba_2V_3O_9$ with a bridge formed by two different types of VO_4 tetrahedra. The concept of complementary versus counter-complementary effect has been used to explain the structural origin of the magnetic behavior of the compound. Namely, the observed antiferromagnetic coupling is dominated by the orbital complementarity of the V(1) tetrahedra sharing only one oxygen corner with two adjacent VO_6 octahedra. The second type of V(2) tetrahedra does not provide a noticeable contribution to the magnetic coupling due to the orbital counter-complementarity of the bridging ligand.

Key Words : Vanadyl vanadate, Magnetic coupling, Extended Hückel calculations

Introduction

Mixed valence vanadium oxides have attracted the interest of researchers due to a wide variety of their structural and physical properties. Most of the structures have magnetic V^{4+} (d^1) ions and form low-dimensional spin systems.[1]

The structure of $Ba_2V_3O_9$ consists of infinite chains of $V^{4+}O_6$ octahedra.[2] These distorted octahedra are connected with each other through the two $V^{5+}O_4$ tetrahedra. The magnetic properties of these chains were studied in detail by Kaul and co-workers.[3] The temperature dependence of the susceptibility for the solid revealed an antiferromagnetic coupling with a sizeable strength of the magnetic intrachain exchange J of –94 K.[3] The origin of the magnetic exchange is likely a result of superexchange interaction through the VO_4 tetrahedra linking the two relatively distant paramagnetic V^{4+} centers. Recently, Canadell and co-workers[4] reported a first-principles density-functional theory study for the discrete molecular units of this spin system. However, the magnetic interactions mediated by each VO_4 bridge have not yet been discussed in the literature, based on the overlap between the bridging VO_4 orbitals and the paramagnetic V^{4+} d orbitals.

We analyze herein the different magnetic contribution of the two VO_4 bridges by employing extended Hückel molecular orbital (EHMO) calculations.[5,6] The molecular orbital analysis will be made to understand the relative importance of the two VO_4 bridges for the magnetic exchange interaction between the V^{4+} ions. The atomic parameters used in the calculations are given in Table 1.

Table 1. Atomic parameters used in EH calculations

Atom	Orbital	H_{ii} (eV)	ζ_1	C_1	ζ_2	C_2
V	4s	-8.81	1.697	1.0		
V	4p	-5.52	1.260	1.0		
V	3d	-11.0	5.052	0.3738	2.173	0.7456
O	2s	-32.3	2.688	0.7076	1.675	0.3745
O	2p	-14.8	3.694	0.3322	1.659	0.7448

Crystal Structure and Molecular Models

$Ba_2V_3O_9$ consists of infinite $[V_3O_9]^{4-}$ chains.[2] This stoichiometry supposes a presence of one V^{4+} ion (six coordinated) and two V^{5+} ions having a tetrahedral coordination, leading to the structural formula of $[VO(VO_4)_2]^{4-}$. The chains are not connected to each other. Each chain is formed by VO_6 octahedra linked *via* two VO_4 tetrahedra and an oxygen atom unshared with the tetrahedra (Figure 1(a)). The paramagnetic vanadium(IV) centers are all in an octahedral geometry, in which the six coordination sites are occupied with oxygen atoms from vanadyl V=O groups and the $[VO_4]^{3-}$ bridges. All VO_6 octahedra are significantly distorted with the vanadium atom displaced towards one of the oxygen atoms. This leads to the formation of a short V-O bond (1.69 Å indicating the typical distance for vanadyl bond in the V^{4+} polyhedra), an opposite long V-O bond (2.24 Å), and four equatorial V-O_{eq} bonds (average length of 2.00 Å).

This feature leads to the splitting of the t_{2g} levels of the

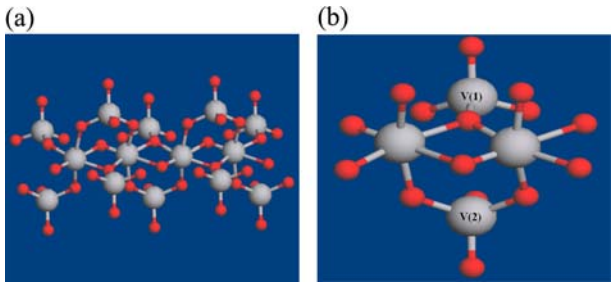

Figure 1. (a) Segment of the octahedral chain structure of $Ba_2V_3O_9$ and (b) its binuclear vanadium(IV) model. The light gray and small red circles represent the V and O atoms, respectively.

vanadium atom destabilizing the d_{xz} and d_{yz} orbitals above the d_{xy} orbital (we assume a local coordinate system such that the *z*-axis is taken parallel to the vanadyl bond with the *x*- and *y*-axis approximately along the V-O_{eq} directions). This implies that the unpaired electrons of the V^{4+} ions occupy the d_{xy} orbitals. Consequently, the vanadium $3d_{xy}$ orbitals of two adjacent octahedra make π-antibonding interactions with the oxygen 2p orbitals of the shared edge of the bridging tetrahedra which provide a good superexchange interaction along the chain.

There are two different types of VO_4 tetrahedra in the structure. One type of the VO_4 tetrahedra [V(1)] links octahedra by sharing only one oxygen corner whereas another type [V(2)] connects two adjacent octahedra *via* the two oxygen atoms. Within tetrahedra the V-O distances to oxygen atoms shared with VO_6 octahedra are longer than the V-O distances to unshared oxygen atoms. The average V-O bond lengths for V(1) and V(2) atoms are 1.72 and 1.71 Å, respectively. The adjacent V^{4+}-V^{4+} separation is 3.01 Å. The significant antiferromagnetic coupling may be explained by a superexchange interaction through each of the two bridging tetrahedra which connect the two V^{4+} octahedra. The contribution of the oxygen atom from vanadyl V=O group is almost nil, since the p orbitals of the axially bridged oxygen are not of the correct symmetry to overlap with the d*xy* orbital of V(IV). Thus, we conclude that a sizeable magnetic exchange between the V^{4+} ions along the chain is mostly mediated by the bridging VO_4 tetrahedra.

We have adopted appropriate molecular models to analyze the different magnetic contribution of the two VO_4 bridges to the magnetic coupling for this compound. The dimer model used is shown in Figure 1(b). The model was taken from the crystal structure (model 1). In order to analyze independently the role of each VO_4 bridge, we also built single VO_4-bridged models 2 and 3 by removing one of the two VO_4 tetrahedra. In the dimer unit, the V^{4+} ions are linked by V-O-V and V-[V(2)O_4)-V bridges in model 2 and by V-O-V and V-[V(1)O_4]-V bridges in model 3. In the two situations, the magnetic exchange is propagated principally *via* the d_{xy} orbitals of the V^{4+} ions which interact with the appropriate 2p orbitals of the oxygen atoms of the VO_4 bridge.

Results and Discussion

The strength of the exchange coupling is mainly associated with the overlap interactions between the magnetic orbitals of the metal centers and the highest occupied molecular orbitals (HOMOs) of the bridging ligands. By symmetry, the HOMO and HOMO-1 of a given bridging ligand mix with the symmetric (d_S) and antisymmetric (d_A) combinations of magnetic orbitals ($d_{xy} \pm d_{xy}$, in this binuclear V^{4+} complex) to give the corresponding SOMOs (singly occupied molecular orbitals) φ_S and φ_A. The interactions of these filled ligand orbitals with the metal d_{xy} orbitals are, of course, antibonding. Hoffmann and coworkers[7] have analyzed exchange interactions in bimetallic complexes in terms of pairwise interactions of these molecular orbitals. According to Hoffmann's approach, the magnetic coupling constant *J* is built by a ferromagnetic and an antiferromagnetic contribution. The latter one is considered to be proportional to the square of the energy gap (Δe) between the two SOMOs. When the energy gap is very small, the ferromagnetic coupling interaction is dominant.

Table 2. $(\Delta e)^2$ values [in $(meV)^2$ units] for the three models with different active bridges in $Ba_2V_3O_9$

Active bridge	$(\Delta e)^2$	J/k_B
$V(1)O_4$	9450 (97.2)[a]	-52.8 K [4]
$V(2)O_4$	1750 (41.8)	-7.2 K [4]
both	9600 (98.0)	-76.6 K [4]

[a]Δe values [in meV units] are given in parentheses.

To quantify the relative effectiveness of the two VO_4 bridges to magnetically couple the V^{4+} ions, we have performed a computational experiment in which we calculate Δe with one of the bridges completely deactivated. First, the whole molecule is divided in two fragments, the VO_4 bridge (fragment A) and the rest of the model (fragment B). Subsequently, the molecular orbitals of the isolated fragments are calculated and superimposed to form the AB molecule. All the covalent interactions between the V^{4+} centers and the V(1) bridge are completely eliminated by freezing the V(1) bridge and the calculated energy difference between the two SOMOs is solely due to the coupling over the V(2) bridge. The same procedure is applied taking the V(2) bridge as a frozen fragment and activating only the coupling through the V(1) bridge. Results calculated for the three models are listed in Table 2.

The first obvious conclusion that can be extracted from Table 2 is that the V(1) bridge is by far more effective in the coupling of the magnetic moments of the V^{4+} ions than the V(2) bridge. This is reflected in the calculated Δe values. Furthermore, an antisynergistic effect of the two bridges can be readily explained with the theory of orbital complementarity and counter-complementarity of Nishida *et al.*[8] and McKee *et al.*[9] The explanation is based on the Hoffmann's model,[7] which relates the energy gap (Δe) of the magnetic orbitals to the coupling parameter: the larger the energy separation, the stronger the antiferromagnetic coupling interaction between the two V^{4+} centers. The exchange interactions in magnetic solids of transition metal ions are well described by the $(\Delta e)^2$ values obtained from EHMO calculations.[10]

As mentioned, model 1 represents the real situation in the solid. The overall exchange interaction for the solid is found to be antiferromagnetic with a coupling constant of –94 K.[3] We make a comparison of the magnetic contribution of the two VO_4 bridging ligands in this model. First, comparison of the results obtained for models 1 and 2 allows evaluating the role of the V(1)-centered tetrahedra. Since its removal from model 1 results in a large reduction in the antiferromagnetic contribution Δe we conclude that the V(1) tetrahedra provide a substantial antiferromagnetic coupling. As can be seen in

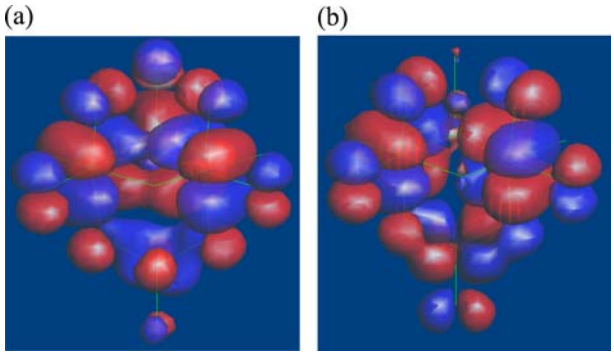

Figure 2. Magnetic orbitals (a) φ_S and (b) φ_A of the binuclear vanadium(IV) model.

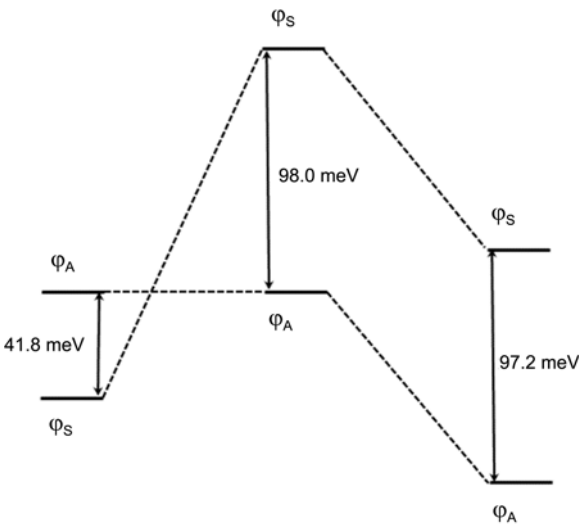

Figure 3. Orbital energy diagrams for a binuclear vanadium(IV) unit with a $V(2)O_4$ (left), a $V(1)O_4$ (right), and both VO_4 bridging ligands (center) relating to models 2, 3, and 1, respectively.

Figure 2, the interaction of the magnetic orbital d_S of the V^{4+} centers with the p orbital (HOMO-1) of the bridging oxygen from V(1) terahedra leads to a large destabilization of the symmetric combination d_S due to the antibonding interaction through the π pathway, which results in the raising of the energy of φ_S. However, for the antisymmetric magnetic orbital d_A, the HOMO of the $V(1)O_4$ bridging ligand does not have the correct symmetry to interact with d_A orbital, so no change in the energy of φ_A is expected. As a result, the symmetric (φ_S) and antisymmetric (φ_A) orbitals are split by Δe = 98.0 meV (Figure 3), thereby leading to relatively strong antiferromagnetic exchange coupling. This is in line with the larger Δe (and hence *J*) when the interaction with both bridges is considered in comparison to the $V(2)O_4$-bridge only calculation.[4] There exists an orbital complementarity by the $V(1)O_4$ bridging ligand.

If we now compare models 1 and 3, we can evaluate the role of the V(2) centered tetrahedra. Since its removal results in a very small decrease in Δe (0.8 meV), we have a weak antiferromagnetic contribution through the V(2) tetrahedra to the magnetic coupling. Because of symmetry, the magnetic orbitals d_S and d_A of V^{4+} centers interact with the HOMO and HOMO-1 of the $V(2)O_4$ bridge through the π pathway, respectively. The energies of the symmetric (φ_S) and antisymmetric (φ_A) orbitals are both raised, as shown in Figure 3. Consequently, a change in the energy gap that separates the φ_S and φ_A orbitals becomes very small, which leads to the weak antiferromagnetic contribution. This is due to an orbital counter-complementarity phenomenon of the $V(2)O_4$ bridge.

Obviously, there is a significant difference of the magnetic contributions between the two VO_4 bridging ligands; *i.e.*, one is a very weak antiferromagnetic and the other is rather strong antiferromagnetic contribution to the coupling. This indicates that the antiferromagnetic coupling interaction in the two VO_4-bridged divanadium(IV) model is mainly determined by the $V(1)O_4$ bridging ligand. In addition, the magnetic exchange parameter is predicted to be more than 5 times larger for $V(1)O_4$ than for $V(2)O_4$ bridge (*i.e.*, 9450/1750 = 5.4), which is consistent with the tendency in the calculated *J* values (see Table 2).

Conclusion

In order to explore the essential reason for the difference between the magnetic contributions of the two VO_4 ligands bridging V^{4+} ions in $Ba_2V_3O_9$, the molecular orbital analysis was made. The magnetic properties can be understood in an EHMO picture by considering the interaction of the symmetric and antisymmetric magnetic orbitals with the HOMO and HOMO-1 (mainly O 2p orbitals) of the VO_4 bridges. The isolated exchange interaction of the $V(1)O_4$ bridge is more than 5 times larger than that of the $V(2)O_4$ bridge, illustrated by the square of SOMO gap (97.2 meV and 41.8 meV) in the models 2 and 3 freezing one of the two bridges. The global magnetic coupling in $Ba_2V_3O_9$ is dominated by the orbital complementary interaction between the V^{4+} octahedra through the $V(1)O_4$ tetrahedra sharing one oxygen atom with the octahedra. The $V(2)O_4$ tetrahedra bridging two adjacent V^{4+} octahedra and the oxygen atoms unshared with tetrahedra have a very small influence on the magnetic coupling. It can be concluded that the antiferromagnetic coupling in $Ba_2V_3O_9$ is almost exclusively due to the $V(1)O_4$ bridge and the $V(2)O_4$ bridge is only of secondary importance.

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References

1. Ueda, Y. *Chem. Mater.* **1998**, *10*, 2653.
2. Dhaussy, A.-C.; Abraham, F.; Mentre, O.; Steinfink, H. *J. Solid State Chem.* **1996**, *126*, 328.
3. Kaul, E. E.; Rosner, H.; Yushankhai, V.; Sichelschmidt, J.; Shpanchenko, R. V.; Geibel, C. *Phys. Rev. B* **2003**, *67*, 174417.
4. Rodriguez-Fortea, A.; Llunell, M.; Alemany, P.; Canadell, E. *Phys. Rev. B* **2010**, *82*, 134416.
5. Whangbo, M.-H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 6093.

6. Whangbo, M.-H.; Hoffmann, R.; Woodward, R. B. *Proc. R. Soc. A* **1979**, *366*, 23.
7. Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.
8. (a) Nishida, Y.; Kida, S. *J. Chem. Soc., Dalton Trans.* **1986**, 2633. (b) Nishida, Y.; Takeuchi, M.; Takahashi, K.; Kida, S. *Chem. Lett.* **1983**, 1815. (c) Nishida, Y.; Takeuchi, M.; Takahashi, K.; Kida, S. *Chem. Lett.* **1985**, 631.
9. (a) McKee, V.; Zwagulis, M.; Dagdigian, J. V.; Patch, M. G.; Reed, C. A. *J. Am. Chem. Soc.* **1984**, *106*, 4765. (b) McKee, V.; Zwagulis, M.; Reed, C. A. *Inorg. Chem.* **1985**, *24*, 2914.
10. Whangbo, M.-H.; Dai, D.; Koo, H.-J. *Solid State Sci*. **2005**, *7*, 827.