Homopolar Bond Formation in $\mathrm{ZnV_2O_4}$ Close to a Metal-Insulator Transition

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(Received 8 May 2008; published 19 December 2008)

Electronic structure calculations for spinel vanadate $\mathrm{ZnV_2O_4}$ show that partial electronic delocalization in this system leads to a structural instability, with the formation of V-V dimers along the [011] and [101] directions, and readily accounts for the intriguing magnetic structure of this material. The formation of V-V bonds is a consequence of the proximity to the itinerant-electron boundary and is not related to orbital ordering. We discuss how this mechanism naturally couples charge and lattice degrees of freedom in magnetic insulators close to such a crossover.

DOI: 10.1103/PhysRevLett.101.256403 PACS numbers: 71.27.+a, 71.30.+h, 75.25.+z

The transition between an antiferromagnetic (AF) insulator and a paramagnetic metal is associated with some of the most intriguing experimental observations in solid state physics. Unconventional forms of superconductivity, electronic phase separation, and a variety of non-Fermi liquid behavior are well-known examples. Although not completely understood, it is however becoming clear that a strong coupling between charge, spin, orbital, and lattice degrees of freedom is an essential ingredient to explain many of these phenomena. Thus, it is important to define the properties and conditions under which this coupling among different degrees of freedom takes place and to explore their consequences. Especially interesting phenomena may occur in a regime intermediate between localized and itinerant electrons, i.e., close to the insulator-metal (Mott) transition. One such possibility is that this crossover can occur via *partial delocalization* of electrons, not in the whole system right away, but first in certain clusters, e.g., in dimers [1]. Below, we prove that this scenario can indeed be realized in one specific system, the spinel $\mathrm{ZnV_2O_4}$, and argue that this effect can also take place in other similar systems close to Mott transition.

The spinel $\mathrm{ZnV_2O_4}$ is an excellent candidate for such study, being a magnetic insulator close to the itinerant-electron limit. *Ab initio* calculations with structural optimization could be very useful to study possible lattice instabilities, and this is what is done in the present Letter. We will show that for small values of the electron-electron (Hubbard's) repulsion U, the most stable structure always consists of V-V dimers along the [011] and [101] directions, with ferromagnetic bonds becoming shorter [2] that helps to understand the intriguing magnetic structure of this material. There is no orbital ordering in our solution, except higher occupation of the d_{xy} orbital. The dimerization obtained is a dramatic example of a strong electron-lattice coupling due to the partial electronic delocalization in the proximity of the itinerant-electron limit.

$\mathrm{ZnV_2O_4}$ crystallizes in a cubic spinel structure, where the V atoms form a pyrochlore lattice of corner-sharing tetrahedra. Because of the geometry of the pyrochlore lattice, the AF interactions between the V atoms are highly frustrated. The material undergoes a magnetic transition and a structural transition to a low-temperature tetragonal phase ($c/a < 1$) below 50 K [3]. The lattice formed by the V atoms can be described as built up by V-V chains running along the [110], [011], and [101] directions (we use below the cubic setting). The magnetic structure, found by neutron diffraction [4,5], is AF along the [110] direction (within the ab plane), but along the [101] and [011] (off-plane) directions the V moments order ↑↑↓↓↑↑ (see Fig. 1).

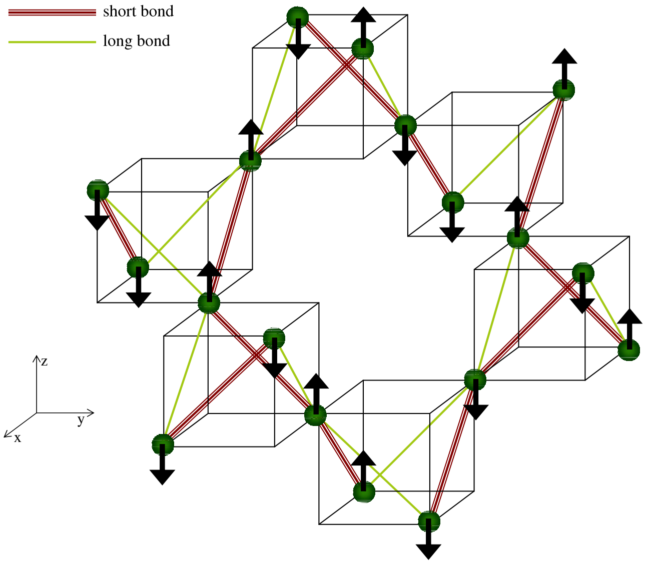

FIG. 1 (color online). Schematic representation of the "dimerized" structure resulting from our *ab initio*, all-electron calculations for realistic values of U in $\mathrm{ZnV_2O_4}$. Bold (thin) line represents short (long) in-chain bonds. The magnetic structure is indicated by arrows.

0031-9007/08/101(25)/256403(4)

The electronic structure of the V^{3+} ion (d^2) has an orbitally degenerate configuration. Several types of orbital orderings were proposed for ZnV_2O_4 recently [6–10]. One is an "antiferro-orbital" picture [9], with the full occupation of a d_{xy} orbital at each site and with an alternation of d_{xz} and d_{yz} orbitals along the c-axis. Also, a "ferro-orbital" ordering of complex orbitals ($d_{xz} \pm i d_{yz}$) [6] and an "orbital-Peierls" ordering [7] with the orbitals in a $d_{yz} - d_{yz} - d_{xz} - d_{xz}$ pattern along the tetragonally compressed c-axis were suggested. In the *ab initio* calculations, including spin-orbit effects [8], the most stable solution is the same as in Ref. [6]. Most of these works assume that U/W (W being the bandwidth) is large, i.e., use a purely localized picture, which seems to contradict recent experimental findings [1]. In many of these works, the lattice symmetry found in the existing experiments (space group $I4_1/amd$) [3] was imposed as a rigid constraint. However, in general, electronic structure may have lower symmetry. Below, the structure derived from the tetragonal distortion described above will be called the "standard" structure, and the relaxed structure with lower symmetry will be referred to as "dimerized" structure, to signal the formation of V-V dimers along the chains.

Full-potential, all-electron, electronic structure calculations based on the density functional theory, utilizing the APW + lo method [11] were performed using the WIEN2K software [12]. We have used various exchange-correlation functionals and the LDA + U scheme [13] to model strong correlation effects in the system, these being controlled by an effective U ($U_{\text{eff}} = U - J$), U being the on-site Coulomb repulsion and J the Hund's rule exchange constant. Spin-orbit effects have been introduced as a second variation using the scalar relativistic approximation [14]. All our calculations were fully converged with respect to the parameters used, with a cutoff of 200 eV for the plane wave expansion and a $7 \times 7 \times 7$ mesh in the irreducible wedge of the Brillouin zone. Local orbitals were used to improve the flexibility in dealing with semicore states (Zn $3p$, V $3s$ and $3p$, and O $2s$). The geometry optimization was carried out minimizing the forces on the atoms and the total energy of the system, relaxing the system from an initial trial state with reduced symmetry, allowing for having unequal V-V distances along the [011] and [101] directions.

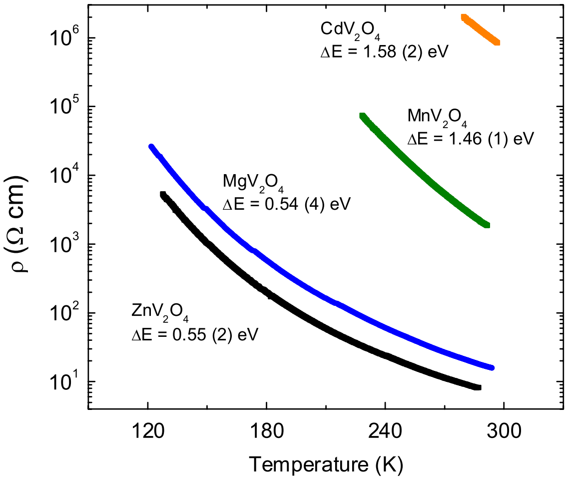

FIG. 2 (color online). Temperature dependence of the resistivity in the $A^{2+}V_2O_4$ series. Small differences in the resistivity for MgV_2O_4 and ZnV_2O_4 could be due to intergrain boundary scattering in the ceramic pellets (their room temperature resistivity differs only by $\simeq 8$ Ω cm). In any case, their activation energy (ΔE) is practically identical, as it should be, given the similar V-V distance in both compounds.

As mentioned above, the anomalous variation found in the pressure dependence of T_N along the series $A^{2+}V_2O_4$ [1] has been interpreted as the consequence of a variation of U/W, which first becomes progressively reduced by pressure, and then collapses close to the itinerant limit. According to this, even though MgV_2O_4 and ZnV_2O_4 are still semiconducting, a partial electronic delocalization along the V-V bonds leading to the formation of short-range cation clusters and to a lattice instability can be anticipated. In Fig. 2, we present experimental resistivity curves for different vanadates in which the divalent cation at the tetrahedral site has been used to tune the V-V distance (the details of sample preparation and characterization are given in Ref. [1]). The results show how the activation energy decreases with the decrease of V-V distance as the metal-insulator transition is approached from the insulating side. This confirms the reduction of U/W in this series, which could lead to a partial delocalization of electrons [1]. In order to check the possibility of a lattice instability due to this electronic effect, we performed a structural optimization using the experimentally observed magnetic structure [4,5] (↑↓↑↓↑↓ spins in [110] chains, ↑↑↓↓↑↑ in [101] and [011] directions). As a starting point, we selected an artificially deformed structure that would give rise to V-V dimers (distances along the [101] and [011] chains get short-long-short-long) and let the system relax until forces on the atoms are smaller than 4 mRy/a.u. (small enough to consider the system is relaxed) [15]. The system relaxes to a structure away from the "standard" one, forming chains with an alternation of short-long V-V distances (Fig. 1). The same relaxed structure is obtained starting from different artificially deformed structures, including the one with the chains having short-intermedite-long-intermediate V-V distances along the [101] and [011] chains (proposed in Ref. [7]). This shows we have found a stable (it is the ground state) and reproducible structure. We have performed structural relaxations using the LDA + U method for several values of U_{eff} (up to 6 eV). For small values of U_{eff} (up to 3.0 eV), this leads to the same relaxed structure as obtained with GGA (the difference in V-V distances is less than 1%), but a relaxation for large values of ($U_{\text{eff}} > 3$ eV) leads to the "standard" V positions without dimerization. For $U_{\text{eff}} =$ 3.0 eV, the "dimerized" structure obtained would be only 3 meV/V more stable than the "standard" one. Figure 3

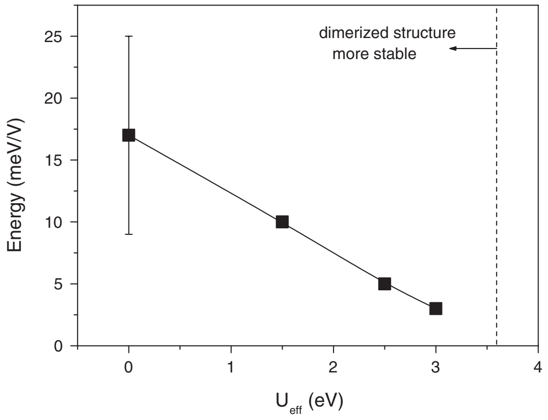

FIG. 3. Stabilization energies (in meV/V) of the “dimerized” structure with respect to the “standard” one as a function of U_{eff}. Our proposed “dimerized” structure is more stable for values of $U_{\mathrm{eff}} \lesssim 3$ eV. Error bars for $U_{\mathrm{eff}} = 0$ account for the various functionals used (see text).

shows the total energy differences, for various values of U_{eff}, between the structures optimized with LDA + U, both of them in the experimentally found magnetic structure. For $U_{\mathrm{eff}} = 0$, we have obtained values using various exchange-correlation functionals for optimizing the structure. This gives that such a “dimerized” structure is more stable than the “standard” one (by 30 meV/V with the Perdew-Burke-Ernzerhoff GGA [16], by 14 meV/V using the Wu-Cohen GGA [17] and by 8 meV/V using the LDA [18]). For $U_{\mathrm{eff}} > 3$ eV, the “standard” structure is obtained as a result of a structure optimization.

For carrying out this computational experiment, one needs to reduce the symmetry of the compound from the “standard” $I4_1/amd$ [19,20] to the $P4_12_12$ space group [19], that allows having different V-V distances along the chains and, at the same time, keeping the same magnetic unit cell. The lattice parameters (unit cell volume) were not optimized, they were taken from Ref. [4]. They are usually given by experiment quite accurately. However, the internal positions are much more difficult to obtain experimentally, especially in the case of small distortions as the one we describe here. For that reason, the internal optimization we have carried out computationally becomes necessary.

For relatively small values of U_{eff} (below about 3 eV) the “dimerized” structure is more stable than the “standard” one. Such small values of U_{eff} would be consistent with our experimental findings of the system being close to the itinerant-electron limit. In such cases, LDA + U method is known to overestimate correlation effects, and in the itinerant case LDA or GGA calculations may be more appropriate. To model the intermediate situation, we have to reduce the values of U/W; thus, values of $U_{\mathrm{eff}} \lesssim$ 3 eV seem quite reasonable for ZnV_2O_4 (for which W is calculated to be 2 eV). It is remarkable that in the “dimerized” structure, even the GGA calculation is enough to open a tiny gap in the density of states (~0.05 eV). This occurs because in the “dimerized” structure, spin-parallel V atoms move closer to allow two halves of d_{xz} (d_{yz}) electrons to fill up a bonding molecular orbital along the [101] ([011]) direction (see Fig. 1). Then the bonding-antibonding splitting opens the gap and stabilizes this “dimerized” structure, without the need of orbital ordering.

Thus, from our calculations, we conclude that as U_{eff}/W is reduced on approaching the itinerant behavior, a strong coupling between charge and lattice degrees of freedom takes place leading to the obtained dimerization and determining the low-temperature properties of the system. Detailed experiments, preferably on single crystals, should be carried out to check our new proposed picture of ZnV_2O_4. It is remarkable that no special constraints have been introduced in the calculations, so the specific results obtained for ZnV_2O_4 may be a manifestation of a general trend which may exist also in other systems close to a localized-itinerant crossover, in particular, in other V spinels.

Table I shows the V-V distances in the “dimerized” structure, so we can compare them with the other members of the series. The shortest V-V distance is below the critical distance for electron itineracy (~2.94 Å), as estimated by Goodenough for a direct $V^{3+} - V^{3+}$ bond across a shared octahedral edge in an oxide [21]. This is in agreement with the experimental prediction of the formation of V-V molecular orbitals close to a metal-insulator transition in ZnV_2O_4 [1], and is similar to the case of $MgTi_2O_4$, where a tetramerization of the Ti chains has been observed [22].

As mentioned above, for the “standard” structure it is possible to stabilize different orbital orderings. Among them, the most stable one has an unquenched orbital angular momentum of about $0.7\mu_B$ per V site antiparallel to the spin moment at each site. However, if we analyze the electronic structure of the “dimerized” structure, such an orbital ordering is not found. In fact, in our solution, we do not observe any orbital ordering (except higher occupation of the d_{xy} orbital, common for all the models). The occupations of the levels d_{xz} and d_{yz} are almost identical, but the orbital angular momenta are fairly small (about $0.1\mu_B$). If we use a basis set with the real combination of orbitals: $d_{xz} \pm d_{yz}$, they are also equally populated. Hence, there is no trace of orbital ordering left once dimerization of the V

TABLE I. V-V distances (in Å) along the different directions in the “standard” (experimental values from Ref. [4]) and the “dimerized” (our calculations) structure of ZnV_2O_4 and also for the other members of the series AV_2O_4 in the cubic phase (our experimental results).

	in-plane	off-plane short	off-plane long
“standard”	2.98	2.97	2.97
“dimerized”	2.98	2.92	3.01
CdV_2O_4	3.07	3.07	3.07
MnV_2O_4	3.01	3.01	3.01
MgV_2O_4	2.97	2.97	2.97

chains occurs. The dimerization of the structure is caused by a spin-lattice coupling without orbital ordering being involved, the only necessary ingredient being the reduction of U_{eff}/W in the vicinity of a metal-insulator transition.

We have carried out total energy calculations in various magnetic structures to calculate the different exchange constants in the material. We have fitted the total energies obtained for $U_{\text{eff}} = 1.7$ eV to a Heisenberg model ($H = -\sum_{i,j} J_{ij} S_i S_j$) to calculate $J_{\text{in}} = -16$ meV (the in-plane exchange constant), $J_s = 10$ meV (out-of-plane exchange constant for the short FM bonds) and $J_l = -3$ meV (a much smaller out-of-plane AF exchange constant for the long bonds). Thus, the dimerized structure removes the magnetic frustration and readily explains the experimentally observed off-plane ↑↑↓↓↑↑ magnetic structure (see Fig. 1). Our work resolves the difficulty in obtaining the correct magnetic structure met in other approaches [6,9,10]. A possible physical picture explaining why there occurs dimerization in the ↑↑↓↓↑↑ chains close to the itinerant regime is that in this case the exchange interaction resembles double exchange. Shortening of ↑↑ bonds leads to a larger hopping and to a gain in double exchange energy, stabilizing this spin ordering.

Summarizing, our *ab initio* calculations demonstrate that in ZnV_2O_4, the system close to localized-itinerant crossover, there occurs partial delocalization of electrons in pairs of V ions, analogous to the formation of homopolar V-V covalent bonds. This V-V bonding occurs simultaneously with corresponding lattice distortion and is caused by the strong interplay of charge, spin, and lattice degrees of freedom in a regime when electron correlations gradually weaken. We want to emphasize that it is the nature of the chemical bond that changes at the electronic transition, and hence dramatic changes in the physical properties of the system can be expected. The unusual properties of many localized-electron systems that are close to the itinerant crossover should be revisited on the light of the results presented in this Letter.

The authors thank the CESGA (Centro de Supercomputacion de Galicia) for the computing facilities and the Ministerio de Educación y Ciencia (MEC) for the financial support through the projects MAT2006/10027 and HA2006-0119 and also the Xunta de Galicia through the project PXIB20919PR. S. B.-C. and F. R. also acknowledge MEC for support under programs FPU and Ramón y Cajal, respectively. The work of D. Kh. and H. W. was supported by DFG via the project SFB 608, and by the European Project COMEPHS.

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