ELECTRONIC STRUCTURE AND EXCHANGE IN Li$_2$VOSiO$_4$

H. ROSNER, R. R. P. SINGH and W. E. PICKETT

Dept. of Physics, University of California, Davis, CA, 95616, USA

W. H. ZHENG and J. OITMAA

School of Physics, University of New South Wales,
Sydney NSW 2052, Australia

Exchange couplings are calculated for Li$_2$VOSiO$_4$ using local density approximation (LDA). From a two band tight-binding model fitted to the LDA band structure and mapped to a Heisenberg model, the in-plane and inter-plane exchange integrals are obtained. While the sum of in-plane couplings $J_1 + J_2 = 9.5 \pm 1.5$ K and the inter-plane coupling $J_\perp \sim 0.2$–0.3 K agree with recent experimental data, the ratio $J_2/J_1 \sim 12$ exceeds the reported value by an order of magnitude. Using geometrical considerations, high temperature expansions and perturbative mean field theory, we show that the LDA derived exchange constants lead to a remarkably accurate description of the properties of these materials including specific heat, susceptibility and Neél temperatures.

Keywords: Low-dimensional systems; electronic structure; exchange parameters.

Frustrated square-lattice spin-half Heisenberg antiferromagnets with nearest neighbor exchange J_1 and second neighbor (diagonal) exchange J_2 have received considerable attention recently. The properties of the model with $J_2 = 0$ (or $J_1 = 0$) are well understood at zero and finite temperature [1]. The large J_2 limit of the model is a classic example of quantum order by disorder,[2,3] where at the classical level the two sublattices order antiferromagnetically but remain free to rotate with respect to each other. This degeneracy is lifted by quantum fluctuations leading to collinear magnetic order in a columnar pattern. While there has been tremendous theoretical interest in these models, there were no known experimental realizations for intermediate to large J_2/J_1, until the investigation of Li$_2$VOSiO$_4$ by Melzi *et al.*[5] Studying ^{7}Li NMR spectra and combining several experiments, these authors derive exchange couplings well into the region where model calculations find columnar order.

However, several puzzling pieces in that excellent and detailed study remain: (i) The ratio of exchange constants was not well determined from the susceptibility and specific heat data; we will present electronic structure and many-body calculations to show that their estimate[5] $J_2/J_1 \approx 1$, is off by an order of magnitude. (ii) The order parameter exponent β at the transition was estimated to be $\beta \approx 0.25$,
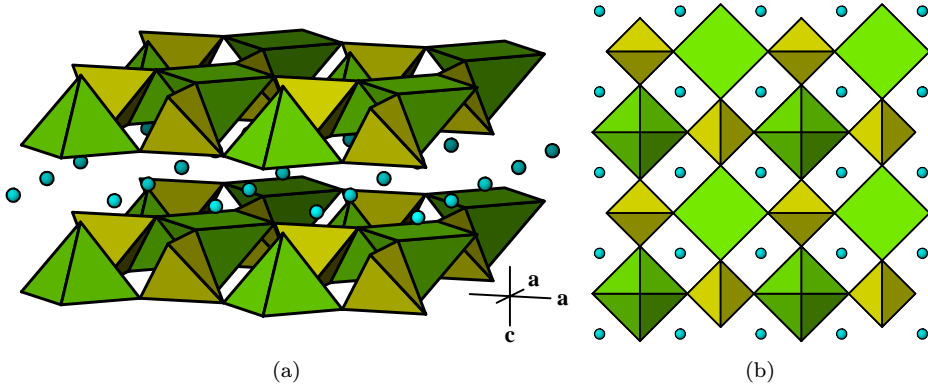
Fig. 1.   Perspective view (upper panel) of the crystal structure of Li_2VOSiO_4 and projection along [001] (lower panel). The VO_5 pyramids (large diamonds) share the corners of the basal planes with SiO_4 tetrahedra (small diamonds). The Li^+ ions are indicated by circles.

which is intermediate between 2D Ising and typical 3D exponents. (iii) The Neél temperature was nearly field independent up to a field of $9T$.

The crystal structure of Li_2VOSiO_4 is shown in Fig. 1. The magnetically active network of spin half V^{4+} ions is built up by $[VOSiO_4]^{2-}$ layers of VO_5 square pyramids sharing corners with SiO_4 tetrahedra, intercalated with Li ions. Both the nearest neighbor (NN) and the next nearest neighbor (NNN) in-plane coupling should be significant, although it is at best difficult to decide from general considerations which one is dominant.

In order to obtain a realistic and reliable hopping part of a tight-binding Hamiltonian, paramagnetic band structure calculations were performed using the full-potential nonorthogonal local-orbital minimum-basis scheme[7] within the LDA. The results show a valence band complex of about 10 eV width with two bands crossing the Fermi level (see Fig. 2). These two bands, due to the two V per cell, are well separated by a gap of about 3 eV from the rest of the valence band complex and show mainly V $3d_{xy}$ and minor O(2) $2p_{x,y}$ character (oxygens of the basal plane of the VO_5 pyramid) in the analysis of the corresponding orbital-resolved partial densities of states. The valence bands below the gap and above the Fermi level have almost pure oxygen and vanadium character, respectively. The relatively narrow bands at the Fermi level are half-filled. Therefore, strong correlation effects can be expected which explain the experimentally observed insulating ground state. Because the low-lying magnetic excitations involve only those orbitals with unpaired spins corresponding to the half-filled bands, we restrict ourselves to a two band tight-binding analysis. The dispersion of these bands has been analyzed in terms of NN transfer t_1 and NNN transfer t_2 within the [001] plane (see Fig. 1 lower panel) and NN hopping $t_\perp$ between neighboring planes. The corresponding dispersion relation of the related 2×2 problem takes the form (with $x = k_x a$, $y = k_y b$, $z = k_z c$)

$$E(\mathbf{k}) = \varepsilon_0 + 2t_2[\cos(x) + \cos(y)] \pm 4t_1 \cos(x/2) \cos(y/2) + 2t_\perp \cos(z).$$
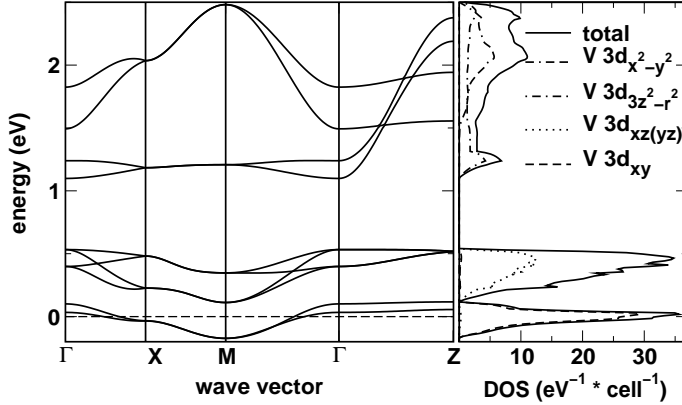
(a)
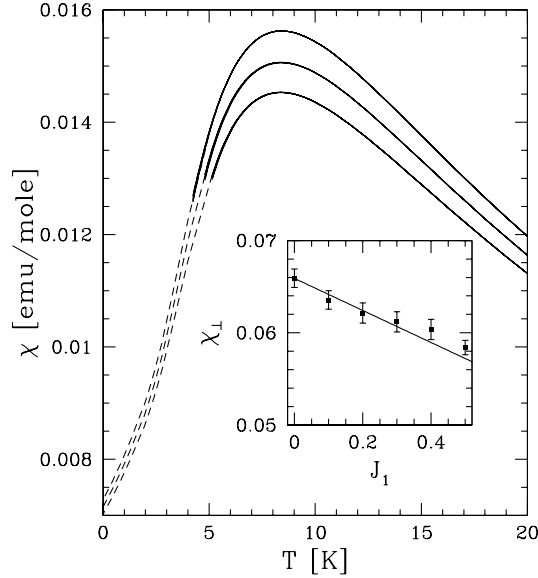
(b)

Fig. 2.   (Left) Band structure, total and orbital resolved DOS of Li$_2$VOSiO$_4$ for the V $3d$ related bands. The Fermi level is at zero energy. (Right) Susceptibility (χ, with largest χ for $J_1 = 0$) for $J_2 = 9$ K, $g = 2$ and $J_1/J_2 = 0, 0.1, 0.2$. The low-T data is obtained from QMC, while the high-T data comes from HTE. The inset shows Ising series expansion calculations for $T = 0$, $J_2 = 1$.

The parameter assignment[8] results in: $t_1 = 8.5$ meV, $t_2 = 29.1$ meV, $t_1 = -4.8$ meV. The very good agreement of the tight binding fit with the LDA bands justifies *a posteriori* the restriction to NN and NNN couplings only. The calculated transfer integrals enable us to estimate the relevant exchange couplings, crucial for the derivation and examination of magnetic model Hamiltonians of the spin-1/2 Heisenberg type $H_{\mathrm{spin}} = \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$. In general, the total exchange

J can be divided into an antiferromagnetic and a ferromagnetic contribution $J = J^{\mathrm{AFM}} + J^{\mathrm{FM}}$. In the strongly correlated limit, valid for typical vanadates, the former can be calculated in terms of the one-band extended Hubbard model $J_i^{\mathrm{AFM}} = 4t_i^2/(U - V_i)$. The index i corresponds to NN and NNN, U is the on-site Coulomb repulsion and V_i is the inter-site Coulomb interaction. Considering the fact that the VO$_5$ pyramids are not directly connected, but only via SiO$_4$ tetrahedra, ferromagnetic contributions J^{FM} are expected to be small. For the same reason, the inter-site Coulomb interactions V$_i$ should be small compared with the on-site repulsion U. From LDA-DMFT(QMC) studies[9] and by fitting spectroscopic data to model calculations,[10] $U \sim 4$–5 eV is estimated for typical vanadates. Therefore, we adopt $U = 4.5 \pm 0.5$ eV as a representative value to estimate the exchange constants, resulting in $J_1 = 0.7 \pm 0.2$ K, $J_2 = 8.8 \pm 1.3$ K, $J_\perp = 0.25 \pm 0.04$ K.[11] Comparing our calculated exchange couplings with the experimental findings,[5] we find excellent agreement for the sum $J_1 + J_2 = 9.5 \pm 1.5$ K of the in-plane couplings, reported from susceptibility data[5] to be $J_1 + J_2 = 8.2 \pm 1$ K. In contrast, we find a ratio $J_2/J_1 \sim 12$ which exceeds the experimentally derived ratio in Ref. 5 $J_2/J_1 \sim 1.1 \pm 0.1$ by an order of magnitude.

In order to understand the experiments better, we turn to high temperature expansions for the susceptibility and specific heat of the Heisenberg models. The susceptibility of the nearest-neighbor model ($J_1 = 0$) is known accurately for all T.[12] Letting $J_2 = 1$ and treating J_1 perturbatively, analogous to chain mean-field theories,[13] leads to the expression $\chi(J_1, T) = \chi_0(T)[1 - 4J_1\chi_0(T)]$ where χ_0 is the susceptibility for the Heisenberg model ($J_1 = 0$). As shown in the inset of Fig. 2, at $T = 0$ for small J_1/J_2, this expression compares very well with the susceptibility calculated from Ising series expansions.[12] Figure 2 also shows that applying Eq. (3) to the finite-T QMC data for χ_0 leads to susceptibility values which join smoothly with the high-temperature expansion results. Thus, we have accurate calculations for the susceptibility of the model with small J_1/J_2 at all T.

Rather than find a fit for the exchange constants, in Fig. 2 we show the susceptibility with $g = 2$; $J_2 = 9$ K; and $J_1/J_2 = 0, 0.1$ and 0.2. The results are close to experimental values.[5] We note that the agreement will be improved by going to the lower limit of the calculated exchange constants and slightly larger g-values.

The specific heat data was the primary source for the $J_1/J_2 \approx 1$ conclusion by Melzi *et al.*[5] They found that the peak value of the specific heat in Li$_2$VOSiO$_4$ was $0.436(4)R$ at $T^m = 3.5(1)$. We find that for the pure Heisenberg model the specific heat peaks at $T^m = 0.60(4)J$ with a peak value of $0.455(10)R$, in agreement with Ref. 14. With small J_1/J_2 the peak shifts to lower temperature and the specific heat becomes flatter. The fact that the values for the pure Heisenberg model are close to the experiments strongly favors a small J_1.

We now turn to the inter-plane couplings and the measurements of the Néel temperature, T_N. Applying the expression $T_N \approx 0.36J_\perp \xi^2(T_N)^1$ (ξ is the in-plane correlation length), to our calculated exchange constants, leads to the estimate $T_N \approx 3.6 \pm 0.4$ K, which is remarkably close to the experimental value of 2.8 K.

Furthermore, the saturation field for our calculated exchange constants is about 30 T, which is much bigger than the 9 T field applied by Melzi *et al.* At the saturation field, T_N should go to zero. However, we note that due to suppression of spin fluctuation the Neél temperature can increase slightly with field, as happens in the purely 2D model. Thus, the experimental result of very weak field dependence of the Neél temperature up to 9 Tesla is consistent with our expectations. The appreciable but still small 3D couplings should also give rise to 3D critical behavior at the finite temperature transition with strong crossover effects.

To summarize, we have used LDA to calculate exchange constants for Li$_2$VOSiO$_4$ and developed numerical studies for the Heisenberg model to show remarkable consistency with many experimental properties. Finally, we note that this material has a substantial 3D coupling, which leads to long-range order at finite T.

References

1. S. Chakravarty, B. I. Halperin and D. R. Nelson, *Phys. Rev. Lett.* **60**, 1057 (1998).
2. E. Shender, *Sov. Phys. JETP* **56**, 178 (1982).
3. P. Chandra, P. Coleman and A. I. Larkin, *Phys. Rev. Lett.* **64**, 88 (1990).
4. O. P. Sushkov, J. Oitmaa and W. H. Zheng, *Phys. Rev.* **B63**, 332 (2001).
5. R. Melzi *et al.*, *Rev. Lett.* **85**, 1318 (2000); *Phys. Rev.* **B64**, 024409 (2001).
6. P. Millet and C. Satto, *Mat. Res. Bull.* **33**, 1339 (1998).
7. K. Koepernik and H. Eschrig, *Phys. Rev.* **B59**, 1743 (1999). In the scalar relativistic calculations we used the exchange and correlation potential of Perdew and Zunger [J. P. Perdew and A. Zunger, *Phys. Rev.* **B23**, 5048 (1981)] V($3s, 3p, 4s, 4p, 3d$), O($2s, 2p, 3d$), Li($2s, 2p$) and Si($3s, 3p, 3d$) states, respectively, were chosen as the basis set.
8. The parameter-assignment has been achieved by two numerically independent procedures: By a least square fit of the two bands in all directions and by using the energy eigenvalues at selected high symmetry points. The errors can be estimated about 5% for the in-plane transfers and 15% for the inter-plane term from the differences of both procedures. These small differences can be ascribed to the influence of higher neighbors.
9. K. Held *et al.*, *Phys. Rev. Lett.* **86**, 5345 (2001).
10. A. T. Mizokawa and A. Fujimori, *Phys. Rev.* **B48**, 14150 (1993); J. Zaanen and G. A. Sawatzky, *J. Solid State Chem.* **88**, 8 (1990).
11. The specified errors results from the uncertainity of U and of t_1 and t_2 from the TB-fit.
12. C. J. Hamer, W. H. Zheng and J. Oitmaa, *Phys. Rev.* **B50**, 6877 (1994); J. Kim and M. Troyer, *Phys. Rev. Lett.* **80**, 2705 (1998); N. Elstner *et al.*, *Phys. Rev. Lett.* **75**, 938 (1995).
13. D. J. Scalapino, Y. Imry and P. Pincus, *Phys. Rev.* **B11**, 2042 (1975).
14. M. S. Makivić and H.-Q. Ding, *Phys. Rev.* **B43**, 3562 (1991).