MAGNETIC HAMILTONIANS FOR Li_2VOSiO_4 AND Li_2VOGeO_4*

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Exchange couplings are calculated for the isostructural compounds Li_2VOSiO_4 and Li_2VOGeO_4 using LDA, suggesting the realization of a large J_2/J_1 quasi-2D spin-half Heisenberg model in both compounds. High temperature expansions for the uniform susceptibility and specific heat are used to fit the experimental data. The range and quality of unbiased fits as a function of the parameters J_1, J_2 and g are reported, confirming J_2 as the largest exchange constant for these materials.

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1. Introduction

In recent years there has been considerable theoretical interest in the square-lattice Heisenberg model with nearest neighbor (NN) exchange J_1 and second neighbor (NNN) exchange J_2. However, only very recently the materials Li_2VOSiO_4 and Li_2VOGeO_4 have been identified [1] as possible realizations of systems with substantial J_2/J_1. Here, we discuss ab initio calculations for the exchange constants of these materials based on LDA and on fits to the experimental specific heat C_P and uniform susceptibility χ data using high temperature expansions (HTE). The range and quality of unbiased fits are reported as a function of J_1 and J_2. Both the ab initio calculations and the fits to the experimental data confirm a large J_2/J_1 ratio.

2. Electronic structure calculations

Li_2VOSiO_4 (Li_2VOGeO_4) crystallizes in the tetragonal system $P4/nmm$, with $a = 6.3682$ (6.4779) Å and $c = 4.449$ (4.520) Å [2] exhibiting a layered magnetically active network of spin half V^{4+} ions. The V^{4+} arrangement suggests that both the NN and the NNN in-plane coupling should be significant.

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In order to obtain a reliable hopping part of a tight-binding (TB) Hamiltonian, band structure calculations were performed using the scalar relativistic full-potential nonorthogonal local-orbital minimum-basis scheme [3] within the LDA. V($3s, 3p, 4s, 4p, 3d$), O($2s, 2p, 3d$), Li($2s, 2p$), Si($3s, 3p, 3d$) and Ge ($3d, 4s, 4p, 4d$) states, respectively, were chosen as the basis set. All lower lying states were treated as core states. The paramagnetic calculations result in a valence band complex of about 10 eV width with two bands crossing the Fermi level E_F (see Fig. 2 in Ref. [4]) and are very similar for both compounds. The two half-filled bands at E_F originate from the two V per cell and are well separated by a gap of about 3 eV from the rest of the valence band complex. They exhibit mainly V $3d_{xy}$ and minor O(2) $2p_{x,y}$ character (oxygens of the basal plane of the VO_5 pyramid). Therefore, strong correlation effects can be expected which explain the experimentally observed insulating ground state.

Because the low-lying magnetic excitations involve only orbitals with unpaired spins corresponding to the half-filled bands, we restrict ourselves to a two band TB analysis taking into account NN transfer t_1 and NNN transfer t_2 within the [001] plane and NN hopping $t_\perp$ between neighboring planes. Our TB results are shown in the Table. The transfer integrals enable us to estimate the relevant exchange couplings. In the strongly correlated limit, valid for typical vanadates, the superexchange can be calculated in terms of the one-band extended Hubbard model $J_i^{\rm AFM} = 4t_i^2/(U_{\rm eff})$. From LDA-DMFT(QMC) studies [5] and by fitting spectroscopic data to model calculations [6], $U_{\rm eff} \sim$ 4–5 eV is estimated for typical vanadates. Therefore, we adopt $U_{\rm eff}$=4 eV and $U_{\rm eff}$=5 eV as representative values to estimate the exchange constants and their ranges. Our results are given in the Table.

TB parameters and exchange couplings for Li_2VOSiO_4 (Li_2VOGeO_4).

t_1 (meV)	t_2 (meV)	$t_\perp$ (meV)	U (eV)	J_1 (K)	J_2 (K)	$J_\perp$(K)
8.5 (12.8)	29.1 (28.0)	-4.8 (-4.1)	4	0.83 (1.88)	9.81 (9.07)	0.27 (0.20)
			5	0.67 (1.52)	7.85 (7.26)	0.22 (0.16)

Comparing our J's with the experimental findings for Li_2VOSiO_4 ($J_1 + J_2 = 8.2 \pm 1$ K [1]), we find excellent agreement for the sum $J_1 + J_2 = 9.5 \pm 1.5$ K of the in-plane couplings. In sharp contrast to Ref. [1] where they estimate $J_2/J_1 \sim 1.1 \pm 0.1$, we find a ratio $J_2/J_1 \sim 12$. In Li_2VOGeO_4 we find a considerable smaller ratio $J_2/J_1 \sim 5$.

3. Fitting the experimental data

We have developed HTE for χ and C_P of the square-lattice Heisenberg model for arbitrary values of J_2/J_1 [4]. We have previously shown that the LDA-derived exchange constants provide a good description of the experi-

mental properties of these materials [4]. Here, we provide unbiased fits to the experimental data as a function of the exchange constants J_1 and J_2 and the electron's g-factor in the material.

To judge the quality of the fit, we define [7]

$$P = \text{const.} \sum_{T_i} |A^{\text{exp}}(T_i) - A^{\text{theo}}(T_i)|\,, \tag{1}$$

where A can be χ or C_P. The constant in front is irrelevant and is adjusted to scale the plot for presentation. The variation in P with the model parameters is significant and the smallest P gives the best fit.

Figures 1 and 2 show the fits for the materials Li_2VOSiO_4 and Li_2VOGeO_4, respectively. We see that for Li_2VOSiO_4 the best fit from C_P is very close to $J_1/J_2 = 0$. The best fit parameters are $J_1/J_2 = 0.025$ and $J_2 = 5.87$ K. The shaded region gives a range of J_2 values for a given J_1/J_2. The χ data give the best fit for $J_1/J_2 = 0.45$, $J_2 = 5.85$ and $g = 1.97$. The fits have been shown in earlier publications [4]. They remain very good even when P is not at its minimum. The fits get substantially worse and P begins to increase rapidly only when J_1/J_2 approaches and exceeds unity.

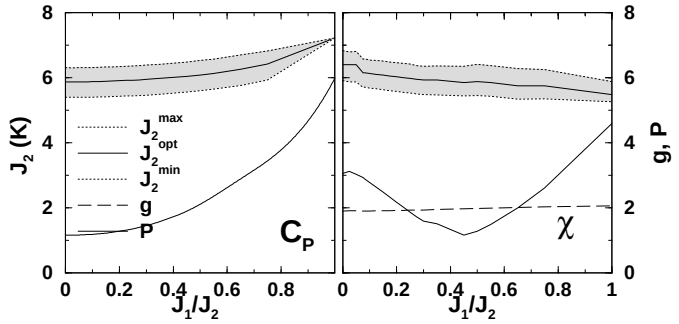

Fig. 1. Best fit parameter (J_2, J_1/J_2, g) for the compound Li_2VOSiO_4 from C_P (left) and χ (right). P gives the quality of the fit (see Eq. (1)).

For the material Li_2VOGeO_4 the best fits are obtained from C_P with parameters $J_1/J_2 = 0.75$ and $J_2 = 4.14$, whereas the best fits for χ are with parameters J_1/J_2=0.55, J_2=3.84 and g=1.83. Once again, we see that the fits get substantially worse only when J_1/J_2 approaches and exceeds unity.

These fits provide strong support for J_2 being the largest exchange interaction in these materials. The comparison between the two materials shows that J_2 is smaller for Li_2VOGeO_4whereas the J_1/J_2 ratio is somewhat larger in Li_2VOGeO_4. These results are consistent with the LDA calculations. On the whole, thermodynamic quantities are not very sensitive to the J_1/J_2 ratio and an accurate determination of these quantities may come from measurements of spin-wave spectra [4].

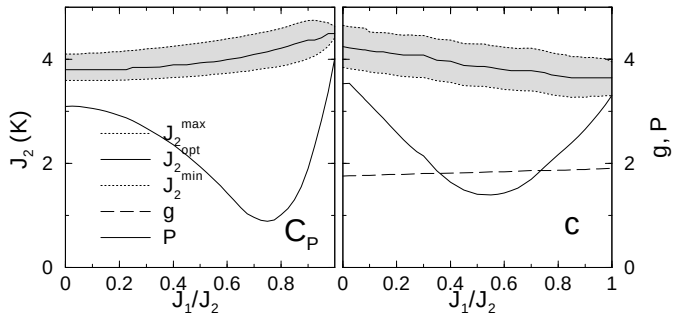

Fig. 2. The same as in Fig. 1 for Li_2VOGeO_4.

4. Conclusions

We have presented first principles calculations for the exchange constants of the materials Li_2VOSiO_4 and Li_2VOGeO_4. By comparing HTE fits for χ and C_P with the experimental data we have shown that these materials are in the large J_2/J_1 regime. Because of the demonstrated weak sensitivity of the HTE fits to the assigned parameters, we have also noted that an accurate determination of the J_1/J_2 ratio for such materials could come from the measurement of spin-wave dispersion [4].

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