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Ab initio investigation of magnetic interactions in the frustrated triangular magnet $NiGa_2S_4$

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Triangular-layered $NiGa_2S_4$, contrary to intuitive expectation, does not form a noncollinear antiferromagnetic structure, as do isoelectronic $NaCrO_2$ and $LiCrO_2$. Instead, the local magnetic moments remain disordered down to the lowest measured temperature. To get more insight into this phenomenon, we have performed first principles calculations of the first, second, and third neighbors exchange interactions, and found that the second neighbor exchange is negligible, while the first and the third neighbor exchanges are comparable and antiferromagnetic. Both are rapidly suppressed by the on-site Hubbard repulsion.

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$NiGa_2S_4$ occurs in the layered structure where the main motif is a triangular layer of Ni^{2+} ions surrounded by edge-sharing *S* octahedra, forming a trilayer S-Ni-S with the rhombohedral stacking *ABC*, and the trilayers are separated by the gallium oxide layers. Ni^{2+} has the electronic configuration $t_{2g}^6 e_g^2$, and one expects it to be insulating and magnetic with $S=1$, and the magnetic moment per Ni being somewhat less than $2\mu_B$. Indeed, this is exactly what happens with structurally similar transition metal oxides with a transition metal in the d^8 configuration, such as $NaCrO_2$ or $LiCrO_2$. $3d$ metal ions in this configuration do not have an orbital moment, therefore one expects a vanishing single-site anisotropy and magnetic interactions reasonably well described by the Heisenberg model. In the nearest neighbor approximation this leads to noncollinear ground states, with neighboring spins pointing roughly at 120° to each other. Indeed, this is what has been observed in the above-mentioned chromates.

$NiGa_2S_4$, on the other hand, has attracted substantial recent interest exactly because the experiments indicate the absence of any long-range magnetic ordering.[1] Several explanations have been proposed, such as full cancellation of the nearest neighbor exchange and frustrated competition between the second and the third neighbor interactions,[1] or biquadratic exchange.[2] These, however, impose very severe quantitative restrictions on the exchange parameters, which seem quite unrealistic.

In order to elucidate magnetic interactions in this system we have performed *ab initio* density functional theory (DFT) calculations of the electronic structure and magnetic energies of $NiGa_2S_4$ and found that indeed, conditions required by either explanation are very unlikely to be satisfied, however, the magnetic interactions are very rich and (as conjectured in Ref. 1) long range, so that taking into account three neighbor shells is indispensable.

For the calculations, the experimental crystal structure[3] was used. A full potential linear augmented plane wave code[4] was used with a gradient approximation for exchange and correlation.[5] The calculations, as expected, render an insulating band structure shown in Fig. 1. As one can see, Ni $d(e_g)$ bands are fully polarized, a small gap opens (as usual, the absolute value of the gap in the DFT cannot be taken very seriously), the magnetic moment per Ni is $2\mu_B$, and in the calculations this moment, not unexpectedly, resides entirely in the NiS_2 layer. Interestingly, more than 20% of the total magnetic moment is located on the *S* sites. This creates a ferromagnetic interaction between the nearest neighbor nickels, which in the theory of strongly correlated magnetic systems is known as "ferromagnetic 90° exchange." Note that in the DFT the Hund rule energy is approximated as $\int d\mathbf{r}\, I(\mathbf{r}) m^2(\mathbf{r})/4 \approx \Sigma I_i M_i^2/4$, where $m(\mathbf{r})$ is the total spin density, I_i and M_i are the Stoner factor and the total magnetization of the atom *i*, and this energy therefore does not depend on the Ni-S-Ni bond angle. Let us estimate this interaction.[6] Two Ni neighbors, when their spins are parallel, induce a magnetic moment of $\sim 0.2\mu_B$ on each of the two bridging sulfurs, gaining an additional magnetic energy of $2I_S 0.2^2/4 \approx 20$ meV. (The Stoner factor of the sulfur ion can be estimated as described in Ref. 7 and is about 1 eV.) De-

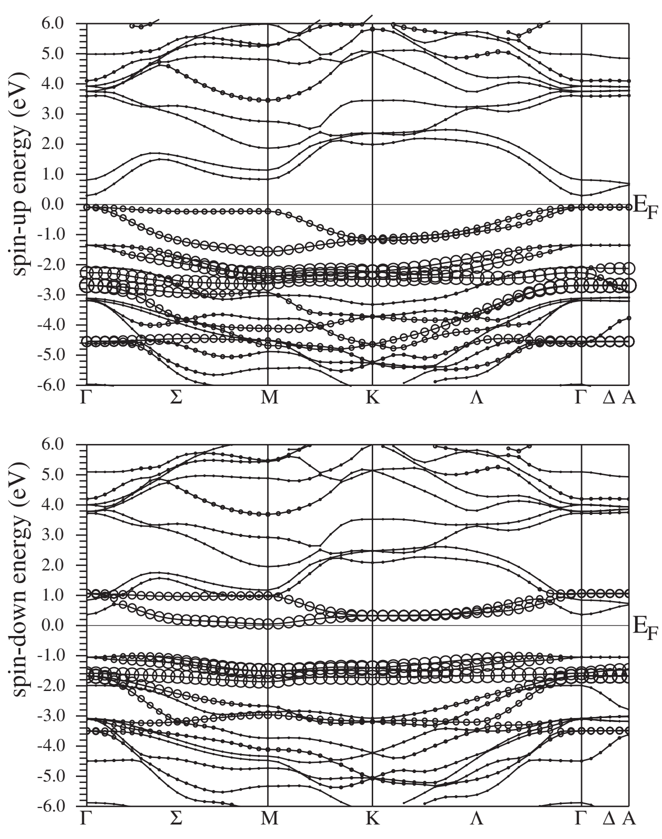

FIG. 1. LDA band structure of the ferromagnetic $NiGa_2S_4$. The Ni character is emphasized by the size of the circles.

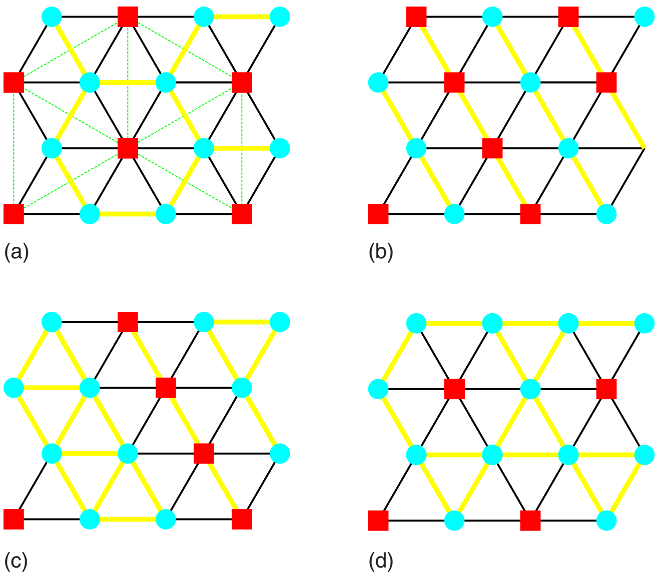

FIG. 2. (Color online) Different magnetic patterns used in calculating the exchange constants. Squares (circles) indicate up (down) moments within the supercell; thin dark (thick light) lines indicate antiferro- (ferro-)magnetic bonds. The first pattern corresponds to the $\sqrt{3}\times\sqrt{3}$ supercell indicated by the dashed lines; the second, third and fourth patterns correspond to 2×1, 3×1, and 2×2 supercells, respectively.

fining J as half of the energy for flipping a bond ($E_{nn'}=J_{nn'}\mathbf{S}_n\cdot\mathbf{S}_{n'}$), we find a ferromagnetic contribution to J of the order of 10 meV. This is not a small energy, but it has to compete with also large conventional antiferromagnetic superexchange. The latter in DFT is $2t^2/I_{\mathrm{Ni}}$, where t is the effective Ni-Ni d-d hopping and I_{Ni} is the Hund energy cost of exciting an electron with the opposite spin, $I_N\approx 0.8$ eV. However, taking into account on-site Mott-Hubbard correlation mandates substituting the Stoner I in this expression by the Hubbard U, which is at least four times larger. While Ni in $NiGa_2S_4$ is not necessarily strongly correlated, there is no doubt that the energy of adding an electron is substantially underestimated in the DFT, and hence the AFM superexchange is overestimated.

Let us now investigate numerically the magnetic interactions in $NiGa_2S_4$. First, we want to make sure that our conjecture about the absence of magnetic anisotropy is indeed correct. This can be addressed by running fully relativistic calculations imposing different magnetic field directions and comparing energies. The result is that both energies differ by at most 0.03 meV. That is to say, the single site anisotropy is not an important factor in $NiGa_2S_4$. Having established that, we have computed several different collinear magnetic structures, as shown in Fig. 2. If mapped onto a Heisenberg model with three nearest neighbor interactions, these give the exchange constants of 8.4, 0.3, and 4.1 meV (defined so that the total energy is equal to the sum over all bands of $J_{ij}S_iS_j$, $|S_i|=1$) for the first, second, and third neighbors, respectively.

Several observations are in place. First, in LDA, while the second neighbor exchange is negligible, the third one is sizable and comparable with the nearest neighbor exchange (it

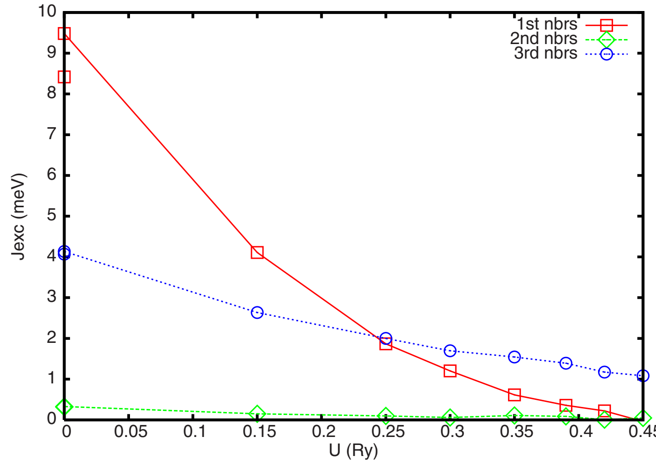

FIG. 3. (Color online) Calculated exchange constants for the first three neighbor shells in $NiGa_2S_4$, in meV, as a function of the Hubbard U, assuming the intra-atomic $J=0.07$ Ry. The additional entry at $U=0$ corresponds to $J=0$.

was suggested already in Ref. 1 that the third neighbor exchange may be anomalously large in this compound). This can be traced down to anomalously large third neighbor hopping, which is in fact generic for triangular layers of transition metal oxides (and here sulfur plays a similar role). Indeed, if the metal-oxygen bonds form precisely 90° angles, the strongest nearest neighbor hopping channel, e_g-p-e_g (or, in compounds like Na_xCoO_2, $t_{2g}-p-t_{2g}$) is forbidden by symmetry, however, a third neighbor path, $e_g-p-t_{2g}-p-e_g$ is fully allowed and in fact has the most favorable geometry (Fig. 4).[8] This creates a possibility for a sizable superexchange of the order of, as usually, $t_{\mathrm{eff}}^2/\Delta$, where t_{eff} is the effective hopping that appears after all intermediate states are integrated out and Δ is the energy required to flip the spin of a metal ion. In LDA, t_{eff} is of the order of $t_{pd\sigma}^2 t_{pd\pi}^2/(E_d-E_p)^2/(E_{e_g}-E_{t_{2g}})$, and Δ is of the order of the Stoner (Hund) parameter, $\lesssim 1$ eV. In the Hubbard model, on the other hand, Δ is set by the scale of Hubbard U $\sim 4-6$ eV. As usually, the real life is somewhat in between, meaning that the exchange constants in LDA are likely overestimated.

This can be easily demonstrated using the LDA+U method that takes into account the Mott-Hubbard correla-

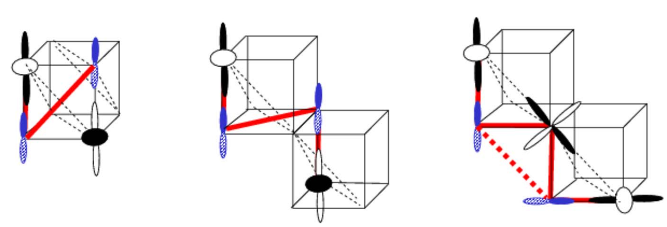

FIG. 4. (Color online) Most favorable paths for the first, second, and third neighbor superexchange in NiS_2 trilayers. Thin dashed triangles indicate the triangular Ni and (in the left panel) S layers. Thick (red online) lines show the exchange paths. The solid parts correspond to short bonds (Ni-S, 2.422 Å and the shorter S-S bond, 3.212 Å); the dashed ones correspond to the longer S-S bond, 3.626 Å.

tions in some crude approximation (Fig. 3). To get an idea of the overall scale of the picture we have estimated the value of U using the quasiatomic loop in a standard linear muffin tin orbital package, as described in Ref. 7, and obtained $U \approx 0.3$ Ry. This simplified method is known to underestimate U, therefore we have carried out calculations up to $U=0.45$ Ry. At that maximal value of U all three exchange constants practically vanish, within the accuracy of the calculation. In fact, the nearest neighbor constant at $U=0.45$ Ry becomes negative (-0.04 meV), but for all practical purposes it may be considered zero. Interestingly, at this value of U the sum of our calculated exchange constants over all (six) bonds gives $1.1 * 6 = 6.6$ meV$=76$ K, to be compared with the Curie-Weiss temperature of 78 ± 1 K (Ref. 1) (the calculated sign is antiferromagnetic, in agreement with the experiment).

What prevents the system from ordering remains unclear. Nakatsuji *et al.*[1] conjectured that the ratio of the nearest and the third neighbor exchange (no second neighbors) is ≈ -0.2, while our ratio, at large U, is essentially zero. To this point it should be mentioned that neither the accuracy of the LDA+U functional is sufficient to make firm statements with a precision of a fraction of a meV, nor the three-shell isotropic Heisenberg model is accurate to that extent. If the calculated numbers at $U=0.45$ Ry are off by ≈ 0.2 meV this would be enough to bring the calculated numbers in consistency with the Nakatsuji *et al.*'s[1] model.

Finally, one should keep in mind that the actual ordering temperature, if any, is suppressed by the 2D character of magnetic interactions. Indeed, $NiGa_2S_4$ has an extra GaS_2 layer compared to typical layer oxides of the formula ABO_2 and therefore the superexchange interaction between the layers is reduced. We have estimated this interaction by comparing the energies of the fully ferromagnetic ordered structure and the A-type antiferromagnetic one (FM layers stacked antiferromagnetically). The former is higher by about 1 meV ($J=0.5$ meV) in LDA and by about 0.3 meV ($J=0.15$ meV) in LDA+U ($U=0.3$ Ry). Importantly, this superexchange is additive with respect to all possible hopping paths between the layers that include not only hopping from a Ni to the other Ni right above, but also to a large number of neighboring Ni sites in the next plane.[9] The real exchange coupling between the two *antiferromagnetic* planes will be additionally reduced. An estimate of $J_\perp \sim 0.05$ meV seems reasonable. Of course, although a computer code calculates the numbers with arbitrary precision, the actual physical approximations used in the calculations preclude statements about energy differences of the order of 0.05 meV. For all practical purposes, it may be less than 0.01 meV, which, of course would make long-range ordering at the experimentally probed temperatures (a fraction of a Kelvin) impossible.

To conclude, we have calculated the three nearest neighbor exchange constants in $NiGa_2S_4$ by mapping LDA+U calculations onto the isotropic Heisenberg model. We found that (a) an anomalously large third neighbor coupling exists in the system that can be traced down to superexchange *via* occupied t_{2g} orbitals, (b) upon including correlation effects in terms of Hubbard U, all exchange constants decrease rapidly, according to general superexchange intuition, but the first neighbor exchange is more rapidly suppressed than the third neighbor one, (c) at $U=0.45$ Ry (6 eV) the nearest neighbor exchange is entirely suppressed (and we could not exclude, based on our calculations, that it does not become slightly ferromagnetic), while the third one is exactly the right magnitude to explain the observed Curie-Weiss temperature. On the other hand, $U=6$ eV, at least on an intuitive level, seems to be too large for Ni in such an environment. At more realistic U's, such as 3–4 eV, both interactions remain firmly antiferromagnetic. It should be kept in mind that energy differences on the order of 1 meV are on the borderline of many approximations used in our analysis. It is possible that several weak effects conspire to prevent the system from ordering. First of all, in particular, the nearest neighbor interaction results from the cancellation of two considerably stronger superexchange interactions of the opposite signs: the AFM superexchange and the FM superexchange due to the Hund rule coupling on S. Albeit we see no obvious reason for the DFT to underestimate the latter, such a possibility cannot be excluded. Second, we did not make any attempt to evaluate further exchange interactions beyond the third shell. While there is no special mechanism making them sizable (as opposed to the third neighbor interaction), again we cannot prove that numerically. Third, while the calculated onsite anisotropy is very small, other effects beyond the isotropic Heisenberg model, such as biquadratic exchange, dipole-dipole, multispin interactions, etc.[10] while small, may not be negligible on the background of the strong cancellation of the FM and the AFM superexchange, and may possibly create additional frustration in the system. Finally, fourth, interplanar coupling between the antiferromagnetic noncollinearly correlated planes is at most a fraction of a Kelvin, and possibly even smaller. This additionally suppresses long-range ordering.

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