Absence of magnetic ordering in NiGa$_2$S$_4$

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Triangular-layered NiGa$_2$S$_4$, contrary to intuitive expectation, does not form a noncollinear antiferromagnetic structure, as do isostructural 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 end 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.

NiGa$_2$S$_4$ 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 $t^6_{2g}e^2_{g}$, 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 conformation 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 $120^\circ$ to each other. Indeed, this is what has been observed in the above-mentioned chromates.

NiGa$_2$S$_4$, on the other hand, has attracted substantial recent interest exactly because the experiments indicate absence of any long-range magnetic ordering. Several explanations have been proposed, such as full cancellation of the nearest neighbor exchange and frustrated competition between the 2nd and the 3rd neighbor interactions, or biquadratic exchange. These, however, impose very severe quantitative restriction 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$_2$S$_4$ and found that indeed condition required by either explanation are very unlikely to be satisfied, however, the magnetic interactions are very rich and (as conjectured in Ref.) long range, so that taking into account three neighbor shells is indispensable.

For the calculations, the experimental crystal structure was used. A full potential linear augmented plane wave code was used with a gradient approximation for exchange and correlation. 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 “ferromagnetizing 90° exchange”. Note that in the DFT the Hund rule energy is approximated as $\int dr I_i m_i^2(r)/4 \approx \sum_i M_i^2/4$, where $m(r)$ is the total spin density, $I$ 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. Two Ni neighbors, when their spins are parallel, induce a magnetic moment

![FIG. 1: LDA band structure of the ferromagnetic NiGa$_2$O$_4$. The Ni character is emphasized by the size of the circles.](image-url)
of $\sim 0.2 \mu_B$ on each of the two bridging sulfurs, gaining an additional magnetic energy of $2I_5 0.2^2/4 \approx 20$ meV (The Stoner factor of the sulfur ion can be estimated as described in Ref. 7 and is about 1 eV). Defining $J$ as half of the energy for flipping a bond ($E_{nn'} = J_{nn'} S_n \cdot S_{n'}$), 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 $2t^2/I_N$, where $t$ is the effective Ni-Ni $d-d$ hopping and $I_N$ 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 4 times larger. While Ni in NiGa$_2$S$_4$ 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 overestimated.

Let us now investigate numerically the magnetic interactions in NiGa$_2$S$_4$. 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$_2$S$_4$. 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 sum over all bands of $J_{ij} S_i S_j$, $|S_i| = 1$) 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 sizeable and comparable with the nearest neighbor exchange (it was suggested already in Ref. 1 that the 3rd neighbor exchange may be anomalously large in this compound). This can be traced down to anomalously large 3rd neighbor hopping, which is in fact generic for triangular layers of transition metal oxides. 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$_x$CoO$_2$, $t_{2g} - p - t_{2g}$) 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. 3). This creates a possibility for a sizeable superexchange of the order of, as usually, $t_{eff}^2/\Delta$, where $t_{eff}$ is the effective hopping that appears after all intermediate states are integrated out and $\Delta$ is the energy required to flip the spin of a metal ion. In LDA, $t_{eff}$ is of the order of $t_{pde}^2/(E_d - E_p)/(E_{ee} - E_{t2g})$, and $\Delta$ is of the order of the Stoner (Hund) parameter, $\lesssim 1$ eV. In the Hubbard model, on the other hand, $\Delta$ 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 correlations 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 quasistatic 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 purpose it may be considered zero. Interestingly, at this value of

![FIG. 2: (color online) Different magnetic patterns used in calculating the exchange constants. Squares (circles) indicate up (down) moments within in the supercell, thin dark (thick light) line antiferro- (ferro-)magnetic bonds. The first pattern corresponds to the $\sqrt{3} \times \sqrt{3}$ supercell indicated by the dash lines, the second, third and fourth patterns to a $2 \times 1$, $3 \times 1$, and $2 \times 2$ supercells, respectively.](image)

![FIG. 3: (color online) Calculated exchange constants for the first three neighbor shells in NiGa$_2$O$_4$, in meV, as a function of the Hubbard $U$, assuming the intraatomic $J = 0.07$ Ry. The additional entry at $U = 0$ corresponds to $J = 0$.](image)
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