Analysis of magnetic properties of triangular-lattice magnet $NiGa_2S_4$

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Magnetic properties of an antiferromagnet with a regular triangular lattice unit have been studied with considerable interest, since such a lattice structure with geometrical frustration generally prohibits conventional collinear spin configurations and may realize exotic spin states such as spin liquids. Among regular-triangular lattice magnets, $NiGa_2S_4$ has been considered as a possible realization of a novel exotic magnetic state with the spin quantum number $S = 1$ [1]. The crystal lattice of $NiGa_2S_4$ is constructed by stacking NiS_2 layers, each of which is a two-dimensional regular triangular-lattice formed by Ni atoms, separated by a pair of GaS layers. Based on both theoretical and experimental investigations [2], it has been revealed that the electronic and magnetic properties are dominated by the Ni d-e_g electrons near the Fermi energy. If the electron repulsive interaction among the e_g electrons is sufficiently strong, the system should be a Mott insulator with $S = 1$. Then, the nearest-neighbor spins should be coupled with an antiferromagnetic Heisenberg spin interaction $J_1 < 0$.

Results from several experiments suggest that $NiGa_2S_4$ exhibits unconventional magnetic properties [2]: Among them, neutron scattering revealed that the magnetic correlation evolves below a temperature T^* of approximately 8 K to yield the spatial spin configuration characterized by $\boldsymbol{Q} = (0.15(5), 0.15(5), 0)$ [3]. Here, it should be noted that this spin configuration is different from the so-called 120-degree ordering conventionally expected for regular triangular-lattice antiferromagnets with nearest-neighbor spin coupling. This led many researchers to take the unusual view that the long-range third nearest-neighbor spin interaction J_3 dominates over the first nearest neighbor J_1, i.e., $|J_1| < |J_3|$, in contrast to the usual intuition that J_1 is the largest $|J_1| > |J_3|$. More remarkable is that the correlation length, which is estimated from the peak width of the magnetic Bragg peak, does not diverge even at several mK, i.e., no long-range ordering can be attained even at the lowest temperature. The effective magnitude of spin moment at the Ni site was observed to be much reduced ($S = 0.51$) by approximately 49% from $S = 1$. The origin of this significant reduction has been attributed to quantum fluctuations. These observations have clearly distinguished $NiGa_2S_4$ from conventional magnets.

In this report, a theoretical analysis of these characteristic magnetic properties of $NiGa_2S_4$ is given, following [4]. First, a DFT-based first-principles electronic structure calculation is performed to obtain the precise electronic structure. Since a band structure calculation is generally not suitable to investigate arbitrary complex spin orderings, we construct a Hubbard-type model by fitting based on the so-called maximally localized Wannier functions (MLWFs). The results of the calculated bands, the fitting, and MLWFs are displayed in Fig. 1. Thus, the 17-orbital (five Ni-d and twelve S-p orbitals) tight-binding model is obtained. Through adding the Ni-site Coulomb interaction (U, U', and J) to this free-electron model, a Hubbard-type model with a realistic electronic band structure is obtained. To determine the most stable spin configuration, the Hartree-Fock (mean-field) approximation is applied to this model, allowing for spiral ordering states with an arbitrary pitch vector $\boldsymbol{Q}$, where spin moments are given by $\boldsymbol{m}(\boldsymbol{r}) = |\boldsymbol{m}|[\cos\boldsymbol{Q}\boldsymbol{r}, \sin\boldsymbol{Q}\boldsymbol{r}, 0]$ and are determined by a numerical self-consistent calculation. The most stable ordering state is the one giving the lowest stabilization energy. The calculated stabilization energies as a function of $\boldsymbol{Q}$ are displayed in Fig. 2 (a) for several strengths of the electron interaction parameter U. As a result, while the conventional 120-degree ordering ($\boldsymbol{Q} = K = (1/3, 1/3, 0)$) is obtained for weak interaction ($U = 1.6$ eV), the uniform ferromagnetic state ($\boldsymbol{Q} = \Gamma = \boldsymbol{0}$) is obtained for strong interaction $U \geq 2.8$ eV. For the intermediate $U = 2$ eV, $\boldsymbol{Q} = (0.15, 0.15, 0)$ gives the most stable state, which is consistent with the neutron scattering experiment. This value of $U = 2$ eV is quantitatively consistent with our preliminary estimation using the Bethe-Salpeter equation. The calculated ordering spin configuration is depicted in Fig. 2 (b).

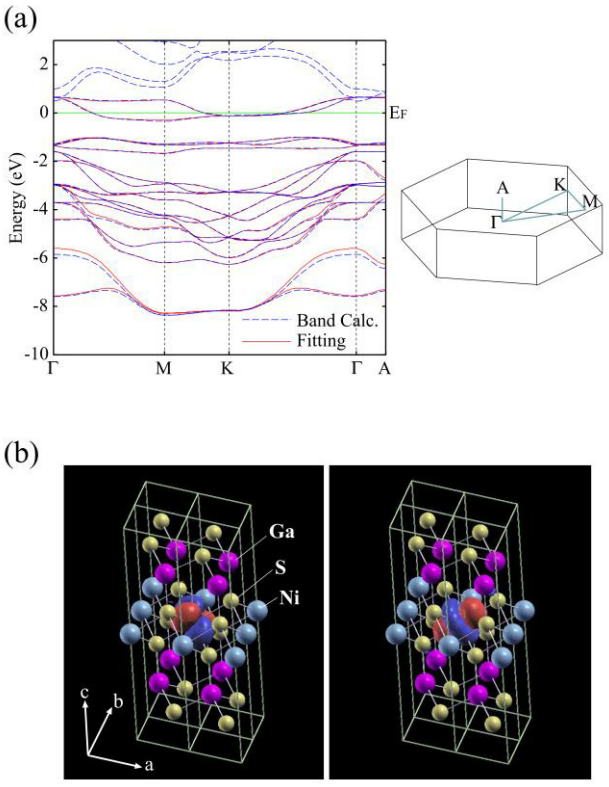

Fig. 1 (a) Calculated electronic band structure and tight-binding fit using MLWFs. On the right, the first Brillouin zone and a symmetry path are depicted. (b) The e_g-type MLWFs at the Ni site.

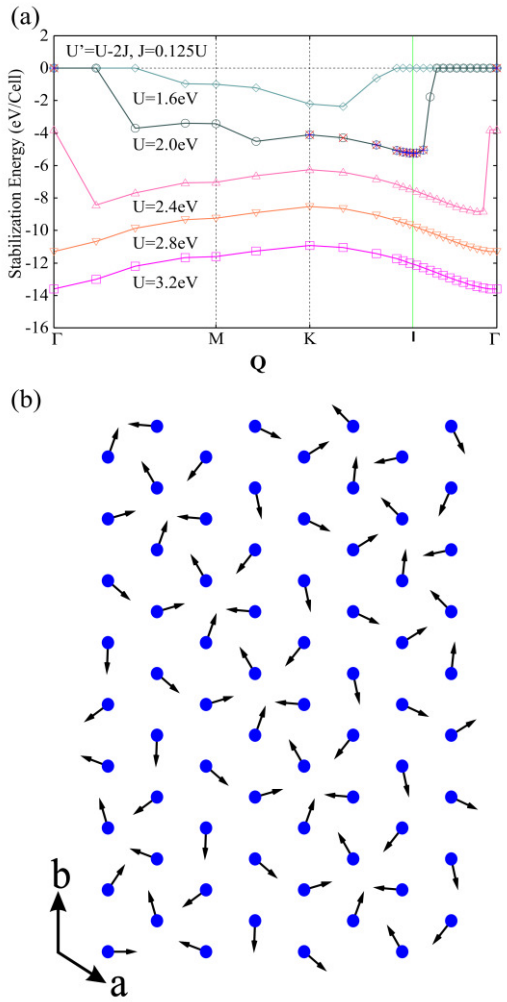

Fig. 2 (a) Calculated stabilization energies for various spin configurations characterized by the wave vector $\boldsymbol{Q}$. The vertical solid line indicates the spin configuration $\boldsymbol{Q}$ = (0.15, 0.15, 0) corresponding to the experimental observation. (b) The calculated most stable spin ordering pattern with $\boldsymbol{Q}$ = (0.15, 0.15, 0) is depicted, where the filled blue circles represent Ni atoms forming a regular triangular lattice.

The magnitude of the calculated spin moment is $|\boldsymbol{m}| = 1.16\mu_B$, corresponding to $S = 0.58$, which does not significantly deviate from the observed value of $S = 0.51$. Our calculation suggests that this significant reduction of spin moment from $S = 1$ does not originate from exotic quantum fluctuations, instead originating from the Ni-S covalent nature. Based on the mean-field results, we estimated the Heisenberg spin exchange interactions J_n, up to ninth nearest neighbors. According to the results, the first nearest-neighbor J_1 is the largest and ferromagnetic ($J_1 > |J_3| > 0$), in contrast to the results of previous studies based on the localized ionic picture.

Furthermore, the dynamical spin correlation function $S(\boldsymbol{q},\omega)$ was calculated (averaged over spin orientations: $S(\boldsymbol{q},\omega) = [2S_{ab}(\boldsymbol{q},\omega) + S_c(\boldsymbol{q},\omega)]/3$) in the magnetic state within the random phase approximation (RPA). The calculated results are displayed in Fig. 3. Here it should be noted that the excitation spectrum is quite different from that of conventional spin waves. In Fig. 3 (b), the experimental peak positions observed by neutron scattering are overlaid onto the calculated intensity map of $S(\boldsymbol{q},\omega)$ for comparison. From the results, at low energies below 1.5 meV, the central spectral peak at $\boldsymbol{q} = \boldsymbol{Q}$, accompanied by a pair of weak satellites, originates from the out-of-plane component $S_c(\boldsymbol{q},\omega)$, while above 1.5 meV, only the pair of satellites remain, which originate from the in-plane component $S_{ab}(\boldsymbol{q},\omega)$. Thus, our results suggest that the magnetic excitation structure is anisotropic and is more complex than usual antiferromagnets. To confirm these results on the spectral properties of $S(\boldsymbol{q},\omega)$, further advanced measurements are needed to carefully resolve the in-plane and out-of-plane components, using sufficiently polarized neutron scattering with high-quality single crystals.

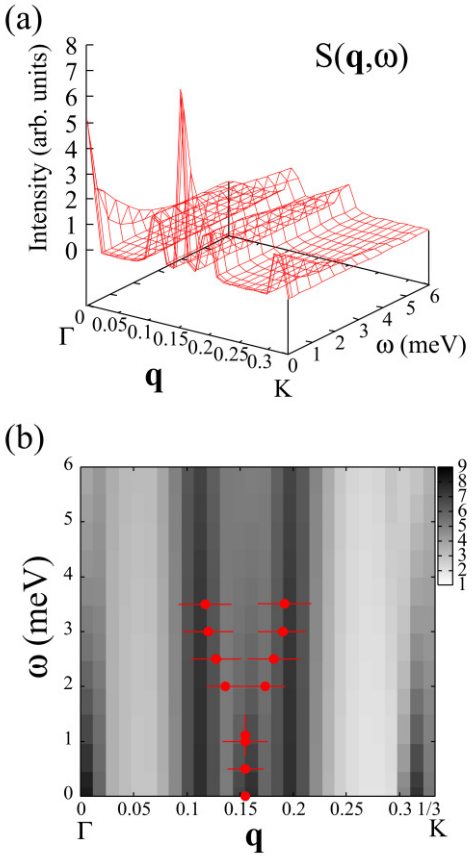

Fig. 3 (a) Calculated spin excitation spectrum $S(\boldsymbol{q},\omega)$. (b) The intensity map of $S(\boldsymbol{q},\omega)$ is overlaid with the neutron scattering data (plots with error bars) for comparison [3].

Acknowledgments

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References

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