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Localized spin-flip excitations in hexagonal $HoMnO_3$

Ji-Yeon Nam[1] | Seung Kim[1] | Hien Thi Minh Nguyen[2] | Xiang-Bai Chen[3] | Mahn-Soo Choi[4] | Daesu Lee[5,6,7] | T.W. Noh[5,6] | In-Sang Yang[1]

[1]Department of Physics, Ewha Womans University, Seoul 03760, South Korea

[2]Graduate University of Science and Technology / Institute of Physics, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Hanoi, Vietnam

[3]Hubei Key Laboratory of Optical Information and Pattern Recognition, Wuhan Institute of Technology, Wuhan 430205, China

[4]Department of Physics, Korea University, Seoul 02841, South Korea

[5]Center for Correlated Electron Systems, Institute for Basic Science (IBS), Seoul 08826, South Korea

[6]Department of Physics and Astronomy, Seoul National University, Seoul 08826, South Korea

[7]Department of Physics, Pohang University of Science and Technology (POSTECH), Pohang 37673, South Korea

Correspondence
Xiang-Bai Chen, Hubei Key Laboratory of Optical Information and Pattern Recognition, Wuhan Institute of Technology, Wuhan 430205, China.
Email: xchen@wit.edu.cn

In-Sang Yang, Department of Physics, Ewha Womans University, Seoul 03760, South Korea.
Email: yang@ewha.ac.kr

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Abstract

Growing demands for ultra-fast switching of spins have turned attention to optically controlled spintronics, which indeed has recently been demonstrated promising. Here we report localized spin-flip excitations revealed by resonance inelastic light scattering on hexagonal holmium manganite thin films with the magnetic manganese ions substituted by the nonmagnetic gallium ions ($HoMn_{1-x}Ga_xO_3$). Our analyses on a broad Raman peak support that the corresponding spin excitation is associated with flipping of all three Mn^{3+} spins in the elementary trimer of manganese ions and hence maintains the same excitation energy determined by the intrinsic spin–spin interaction between Mn^{3+} ions. The nonmagnetic gallium ions only reduce the population of the spin excitations by breaking the spin-frustrated triangular network. Such localized spin-flip excitations show another promise towards optically controlled spin devices.

KEYWORDS

hexagonal $HoMnO_3$, multiferroics, resonance Raman spectroscopy, spin-flip excitations, spin-frustrated triangular network

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1 | INTRODUCTION

Spintronics is one of the most fertile grounds for basic research aimed at future applications.[1] Spintronics uses spin states to carry and process information. Manipulation and control of spin state is the main issue in current technology. Magnetoelectric multiferroics, which possess coexisting magnetic and ferroelectric phases, can potentially be used to control the spin state by electric fields. Optical control of the spin state is now promising for future spin-control devices. Hexagonal manganite $R\mathrm{MnO_3}$ (R = rare earths), an important type of magnetoelectric multiferroics,[2] does show interesting spin excitations through resonance Raman scattering. Among them, $\mathrm{HoMnO_3}$ is an intriguing material and is widely studied because it has complex magnetic properties: magnetic ordering,[3] spin frustration, and spin–lattice coupling.[4–6]

Broad low-energy excitations near 0.1 eV ($\sim$760 $\mathrm{cm^{-1}}$) were first found in the Raman spectroscopy of the hexagonal $\mathrm{HoMnO_3}$ below the Néel ordering temperatures[7] and their strong resonance with the 671nm excitation laser ($\sim$1.85 eV) was observed and interpreted to be resonant with the Mn *d-d* transition.[8] The broad Raman scattering peaks near 0.1 eV were also found in other $R\mathrm{MnO_3}$ (R = rare earths) and some basic characters of the peaks; scattering symmetry, temperature dependence, broadness of the peaks, and so forth, indicated that the scattering peaks are due to spin excitations in the Mn planes.[9–11]

The temperature dependence of the spin excitations offers useful information about the magnetic ordering and the phase diagram of $\mathrm{LuMnO_3}$.[12] The magnetic orderings in the hexagonal $R\mathrm{MnO_3}$ (R = rare earths) are rather complicated due to the presence of the rare-earth ions. Large paramagnetic moment of the *4f* electrons of the rare earths make it difficult to be investigated by the usual magnetization measurements and neutron scattering.[3,13–15] On the other hand, the strong resonance of the spin excitation with the Mn *d-d* transition itself render us an opportunity to investigate the magnetic ordering and spin excitations related with Mn ions out of the large paramagnetic moment of the *4f* electrons of the rare earths.

In previous studies, we have investigated basic behaviors of the spin excitations in pure hexagonal manganite systems $R\mathrm{MnO_3}$ (R = rare earths), and conjectured that these were spin waves associated with Mn *d-d* transition even though the energy is much higher than the typical energies of the magnon in $R\mathrm{MnO_3}$.[16,17] In the present study, we investigate the microscopic origin of the spin excitations by studying how nonmagnetic-ion substitution affects the relative intensities and energies of the spin excitations in the hexagonal $\mathrm{HoMn_{1-x}Ga_xO_3}$ system. The Ga^{3+} ion (0.620 Å) substitution for the Mn^{3+} ion (0.645 Å) does not change the crystal structure symmetry. Ga^{3+} ion has full d^{10} electronic configuration with no net spin, while Mn^{3+} ion has d^4 electronic configuration with S = 2 in the high-spin state.[18] Spin-flip excitations assisted by the resonance Raman process are attributed to explain the prominent spin excitation peak $\sim$760 $\mathrm{cm^{-1}}$ in hexagonal $R\mathrm{MnO_3}$ below the Néel ordering temperatures.

2 | EXPERIMENT

2.1 | Synthesis and characterization

The hexagonal $\mathrm{HoMn_{1-x}Ga_xO_3}$ thin films were grown by pulsed laser ablation, which is similar to that used in previous publications.[19,20] The $\mathrm{HoMnO_3}$ thin film was grown on Pt (111)//$\mathrm{Al_2O_3}$ (0001) substrate, while the Ga substituted $\mathrm{HoMn_{1-x}Ga_xO_3}$ (x = 0.05, 0.10, and 0.33) thin films were on (111)-oriented yttria-stabilized zirconia (YSZ) single-crystal substrate for better lattice matching. During deposition of these thin films, the chamber oxygen partial pressure was kept at 350 mTorr. Under this oxygen partial pressure, the number of oxygen defects could be minimized. The X-ray diffraction (XRD) measurements showed that the Ga substitution did not change the hexagonal structure of $\mathrm{HoMnO_3}$, consistent with reported studies.[21,22] We note that the lattice parameters of $\mathrm{HoMn_{1-x}Ga_xO_3}$ (x = 0 to 0.33) change systematically by $\sim$0.5%, and the optical band gap changes from $\sim$1.4 eV (x = 0) to $\sim$1.5 eV (x = 0.33), as described in detail in an earlier work.[18]

2.2 | Raman scattering

Polarized Raman scattering spectra of the $\mathrm{HoMn_{1-x}Ga_xO_3}$ thin films were obtained in backscattering configuration with LabRam HR800 Raman spectrometer. A 671-nm laser was used as the excitation source with laser power of less than 1 mW on the surface of the thin films to avoid laser heating. The beam diameter on the thin films was $\sim$100 μm. The laser beam power density was kept low to

avoid laser heating. The propagation of laser beam is along the *c*-axis of $HoMn_{1-x}Ga_xO_3$ thin films, that is, the polarized Raman experiments were performed under $z(xx)\bar{z}$ and $z(yx)\bar{z}$ configurations. The scattered signal was detected by a liquid-nitrogen-cooled charge-coupled device (CCD) detector. All the spectra have been calibrated in wavenumber by using a standard neon source and the Si 521-cm^{-1} peak. The thin films were mounted in a helium closed-cycle cryostat, and the temperature of the samples was varied from 15 to 150 K.

The peaks of Raman spectra were fit with Lorentzian function to find the intensity, peak position and the full-width at the half-maximum (FWHM) values. The intensity in this work is not the peak height but the integrated area of the peak. Care was taken in calibrating the relative intensities of different set of measurements as described in the text.

3 | RESULTS AND DISCUSSION

Figure 1a shows polarized Raman spectra of hexagonal $HoMn_{1-x}Ga_xO_3$ ($x = 0$, 0.05, 0.10, and 0.33) thin films at 20 K obtained in the $z(yx)\bar{z}$ configuration. The Raman spectra at different temperatures 20–150 K in the range of 200–1200 cm^{-1} are presented in the Figure S1. The narrow peak ~680 cm^{-1} is the forbidden A_1 phonon mode, and the broad peaks ~500, 760, and 920 cm^{-1} are originated from the spin excitations.[7–12] The A_1 phonon intensities are scaled according to the Ga-content x dependence of the A_1 phonon intensities in the unpolarized Raman spectra of $HoMn_{1-x}Ga_xO_3$ ($x = 0$, 0.05, 0.10, and 0.33), which were measured independently. Please refer to Figure S2 in the Supporting information.

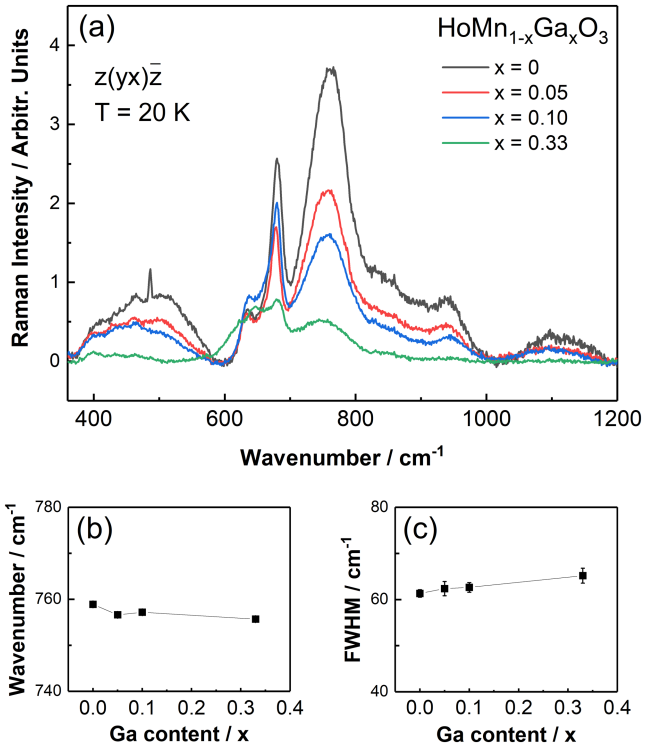

FIGURE 1 (a) Polarized Raman spectra of hexagonal $HoMn_{1-x}Ga_xO_3$ ($x = 0$, 0.05, 0.10, and 0.33) thin films at 20 K obtained in the $z(yx)\bar{z}$ configuration. (b) The wavenumbers and (c) the full-width at the half-maximum (FWHM) values of the 760 peak versus Ga content. Error bars are similar to the height of the squares or indicated otherwise

The peak positions in wavenumber correspond to the energies of the spin excitation. Figure 1b shows that the energies of the spin excitations do not change significantly as the Mn site is substituted by Ga ions. It is striking that Ga-substitution for the Mn site, which affects the lattice parameters about 0.5% by $x = 0.33$ (Ga content), does not affect the spin excitation energy (wavenumber) much. This suggests that the Mn^{3+} spin–spin interaction is not affected by the Ga substitution below $x = 0.33$. The broadness, the FWHM values (Figure 1c) also do not change as the Ga ion content increases, which means that the integrity of the origin of the spin excitation is not altered by the Ga-substitution below $x = 0.33$. On the other hand, the intensities of the spin excitation peaks drastically reduced by the Ga ion substitution. These experimental facts are supporting the idea that the spin excitation peak is from the intact region of the Mn-triangular network in $HoMn_{1-x}Ga_xO_3$, and details of arguments are following.

Figure 2 shows the intensity change of the ~760 cm^{-1} peak at 20 K as the Ga-ion content varies (squares). For hexagonal $RMnO_3$ (R = rare earths), the in-plane (a–b plane) antiferromagnetic exchange is the dominant spin

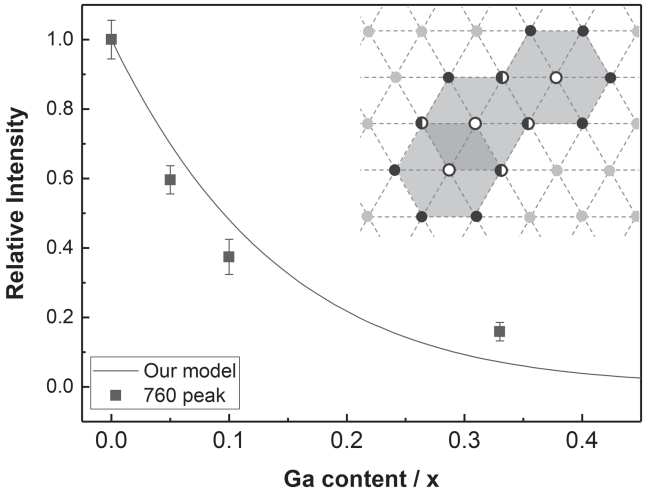

FIGURE 2 Normalized intensities (squares) of the 760 peak at 20 K versus Ga content fit by our model calculation (solid line). Inset shows the triangular network of an Mn layer in which Ga ions (empty circles) are randomly substituted. Details are in the text

exchange interaction, while the interplane spin exchange interaction is about two orders of magnitude weaker, which is often considered negligible.[23,24] In a simple model, the in-plane Mn^{3+} ions of pure hexagonal $RMnO_3$ are assumed to form a perfect triangular network in which each Mn^{3+} ion has six nearest neighbors. The first fact that the spin excitation energy is affected negligibly by the Ga-ion substitution indicates that the excitation is associated with the spins in the Mn-ion triangular network unaffected by the Ga substitution. The FWHM values of the spin excitation peaks do not change significantly by Ga-ion substitution, which means that the integrity of the spin excitation is not influenced by the Ga-ion substitution for the Mn sites. These facts indicate that the spin excitations that we observe in the Raman spectra are local ones associated with the unaffected Mn-ion triangular network, not global one like spin waves propagating over the whole Mn (Ga) planes.

The intensities of the spin excitations ~760 cm^{-1}, on the other hand, strongly decreased by Ga-ion substitution, as seen in Figure 2. The intensities dropped by ~40% and 60% for 5% and 10% Ga substitution, respectively. This dramatic intensity drop indicates that the intensities of the spin excitations are not affected by the Ga-ion content linearly. According to our model, the spin excitation intensity is affected by the breaking of the triangular network of the magnetic Mn^{3+} ions in the $HoMn_{1-x}Ga_xO_3$ system. The crystal structure of hexagonal $RMnO_3$ below T_N is in $P6_3cm$ space group, in which the Mn ions in a basal plane form a triangular network. For more details, please refer to Figure S3. We suppose that the spin excitation intensity is proportional to the number of intact Mn–Mn–Mn triangles in a Mn plane (solid line). Figure 2 inset depicts one Mn layer with Mn ions in gray. Suppose a Mn ion is replaced by a Ga ion (empty circle). Then there are six nearest neighbor Mn ions (black circles) directly affected by the nonmagnetic Ga^{3+} ion. These Mn ions are broken from the Mn-ion triangular network. However, there are Mn ions that are doubly affected by the nearest Ga ions (half-filled circles). We calculated the fraction of the Mn ions affected by the presence of the Ga ions taking into account the double counting (solid line). In our calculation, the positions of the substituting Ga ions were randomly selected in a virtual 100 × 100 Mn-ion plane. Please refer to Figure S4 and the details of the calculation in the Supporting information. Our one-plane model fits the data well, which shows that the effect of Ga-ion substitution is limited in one Mn plane. This indicates that the spin excitation responsible for the 760 cm^{-1} peak is also limited in the Mn plane. We extended the similar analyses to higher temperatures (30, 40, and 50 K), results are presented in the Figure S5. It is found that the effect of Ga-substitution on the spin excitation is stronger at higher temperatures. This is reasonable because the spin ordering at higher temperatures would be weaker so that the perturbation by the nonmagnetic Ga-ion in the Mn-triangular network would be stronger.

Figure 3a shows the temperature dependences of the integrated intensities of the 760 cm^{-1} peak of hexagonal $HoMn_{1-x}Ga_xO_3$ (x = 0, 0.05, and 0.10) thin films. The intensity of the 760 cm^{-1} peak of pure $HoMnO_3$ thin film at 20 K is set to be 1.0 in arbitrary unit, and those for x = 0.05 and 0.10 thin films at 20 K are scaled according to the values given in Figure 2. The inset in (a) shows the Néel ordering temperatures (T_N) obtained from the

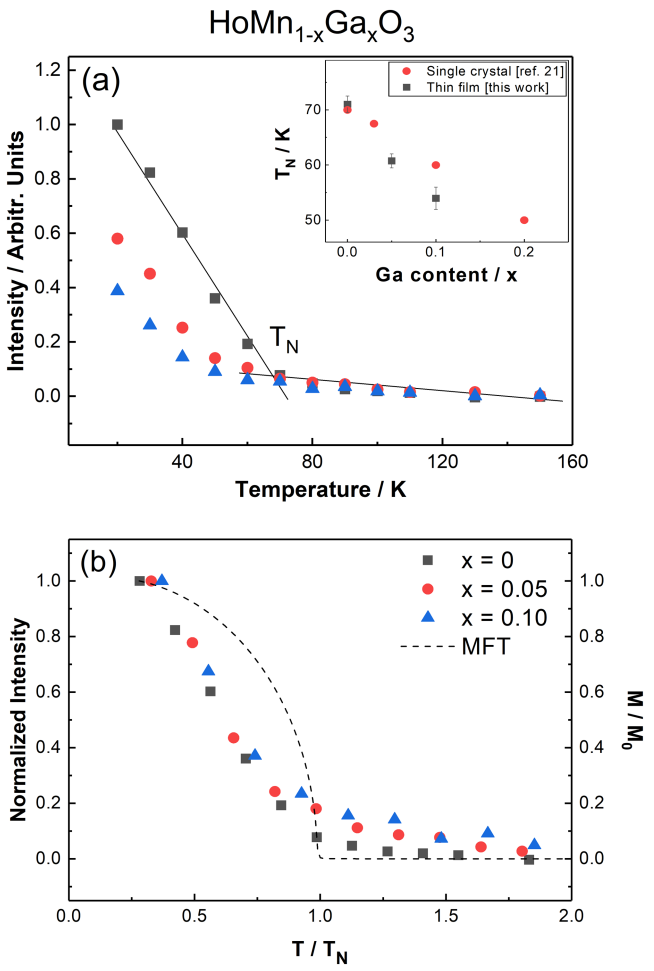

FIGURE 3 (a) Temperature dependence of the integrated intensities of the 760 cm^{-1} peak of hexagonal $HoMn_{1-x}Ga_xO_3$ (x = 0, 0.05, and 0.10) thin films. The inset in (a) shows the Néel ordering temperatures obtained from the intensity slope changes along with previous results[21] on single crystalline $HoMn_{1-x}Ga_xO_3$ samples. (b) Normalized intensities of the 760 cm^{-1} peak versus T/T_N for $HoMn_{1-x}Ga_xO_3$ (x = 0, 0.05, and 0.10) thin films. The dashed line is normalized "antiferromagnetic order parameter" M (see Equation 2 in text, not to be confused with net magnetization) calculated by the mean-field theory (MFT) based on the Bogoliubov variational principle

intensity slope changes as indicated in the figure. Previous results on single crystalline $HoMn_{1-x}Ga_xO_3$ samples are also plotted for comparison.[21] Both results are in fairly good agreement. The decrease of the Néel ordering temperatures as the Ga content increase seems to reflect the weakening of the magnetic-ordering robustness against thermal fluctuation. This is consistent with the stronger effect of Ga substitution on the spin excitation at higher temperatures as seen in Figure S5. In Figure 3b, the intensities of the 760 cm^{-1} peak at 20 K are normalized to 1.0, and the temperatures are scaled by the Néel ordering temperatures obtained in (a) for the three $HoMn_{1-x}Ga_xO_3$ ($x = 0$, 0.05, and 0.10) thin films. The three data sets fall in an almost universal line. This strongly supports that the spin excitation responsible for the 760 cm^{-1} peak is limited in the Mn-triangular network unperturbed by the nonmagnetic Ga-ion substitution. In other words, the spin excitation responsible for the 760 cm^{-1} peak is a local excitation, not a global excitation as a spin wave.

We can describe the magnetic interaction in the hexagonal $RMnO_3$ (R = rare earths) materials with the antiferromagnetic Heisenberg model.[25]

$$H = \sum_{<i,j>} J_{ij} \boldsymbol{S}_i \cdot \boldsymbol{S}_j + \sum_{<i,j>} \boldsymbol{d}_{ij} \cdot \boldsymbol{S}_i \times \boldsymbol{S}_j + \sum_j \boldsymbol{S}_j \cdot \boldsymbol{A}_j \cdot \boldsymbol{S}_j, \quad (1)$$

where $\boldsymbol{S}_j$ is the spin $S = 2$ operators of Mn^{3+} ions at site j. Here, J_{ij} are responsible for the isotropic exchange interaction, the vector $\boldsymbol{d}_{ij}$ for the Dzyaloshinskii–Moriya (DM) interaction, and the matrix $\boldsymbol{A}_j$ for the on-site spin anisotropy. We ignore the interlayer couplings of exchange and DM type. The symmetry of the space group $P6_3cm$ below T_N allows two types of nearest neighbor exchange couplings: $J_{ij} = J_1$ when the sites i and j both belong to the same elementary triangle, which forms an Mn trimer, and $J_{ij} = J_2$ otherwise. The on-site spin anisotropy tensors $\boldsymbol{A}_j$, with $\boldsymbol{A}_j{}^T = \boldsymbol{A}_j$ and Tr $\boldsymbol{A}_j = 0$, favor energetically the spins primarily parallel to the hexagonal plane and in all-in or all-out directions (for $HoMnO_3$) within an Mn trimer. It plays a crucial role in the ordered phase of otherwise isotropic exchange model, and the ground state has the same all-in or all-out spin configuration.[25] The DM coupling vector $\boldsymbol{d}_{ij}$ is mainly out of the hexagonal plane. It is typically 100 times smaller than the exchange coupling and its effect is ignorable. Motivated by the ground-state spin configuration, we take the *antiferromagnetic order parameter* (not to be confused with net magnetization) as

$$M = \sum_j C_j^z \langle \boldsymbol{S}_j \rangle \left(C_j^z \right)^\dagger, \quad (2)$$

where C_j^z are the symmetry operators corresponding to sixfold rotational symmetry. To calculate the order parameter, we have used the cluster mean-field theory (MFT) based on the Bogoliubov variational principle,[26] where the quantum and thermal fluctuations within single Mn trimers are fully incorporated. The normalized order parameter as a function of T/T_N is shown in Figure 3b (dashed line), where we assumed the parameter values, $J_1 = 3$ meV, $J_2 = 2$ meV, $A^{xx} = -0.06$ meV, $A^{yy} = -0.09$ meV. We note that the experimental data below T_N drops faster with temperature than the MFT result. This discrepancy may come from the strong fluctuation effects due to low dimensionality of the system,[27] as manifested by the existence of the short range spin order even above the Néel temperature. With the aforementioned parameter values, the MFT gives the critical temperature by $k_B T_N/J_1 \sim 3.6$, which is 1.5 times bigger than the ratio estimated experimentally. It is not surprising because MFT typically overestimates the critical temperature (with respect to the exchange coupling), especially, in lower dimensions.[27] Recall that the Mermin–Wagner theorem prevents systems of two or lower dimensions with continuous symmetry from having a long range order.[28–30] The weak interlayer coupling does allow the $RMnO_3$ (R = rare earths) materials for Néel-like ordering, but nevertheless, they are subject to strong fluctuations.

In Figure 4, we suggest a scenario of spin-flip excitation assisted by the Mn d-d transition through spin-3d orbit coupling. The incident light of energy similar to that of the Mn d-d transition is absorbed by a Mn^{3+} ion and the Mn $3d_{xy}$ or $3d_{x^2-y^2}$ orbital (in-plane orbital) is excited to the Mn $3d_{3z^2-r^2}$ orbital (out-of-plane orbital). Upon returning to the in-plane orbital, the Mn^{3+} spin state can be excited to a higher energy state. On the right-hand side, an energy diagram for the resonant Raman scattering through the Mn d-d transition is depicted. The incident light of ~1.85 eV is resonant with the Mn d-d transition and thus the spin-flip excitation (~0.1 eV) is created. Assuming that the 760 cm^{-1} peak corresponds to the spin flip of the three Mn spins in one Mn trimer (satisfying total $\Delta S_z = 0$), we estimate the spin exchange integral J_2 value is ~2 meV, consistent with the neutron scattering results.[6]

Local spin excitation has important advantage in application for stable and high-density spin-based devices, such as qubits and memories in quantum computers. Solid-state spin-control quantum devices are desirable for future spintronics due to scalability and its compatibility to existing Si nano-technology. The spin excitation responsible for the 760 cm^{-1} peak is excited (write) optically and is detected (read) optically. Optical write-and-read capability of stable spin excitations in high density could

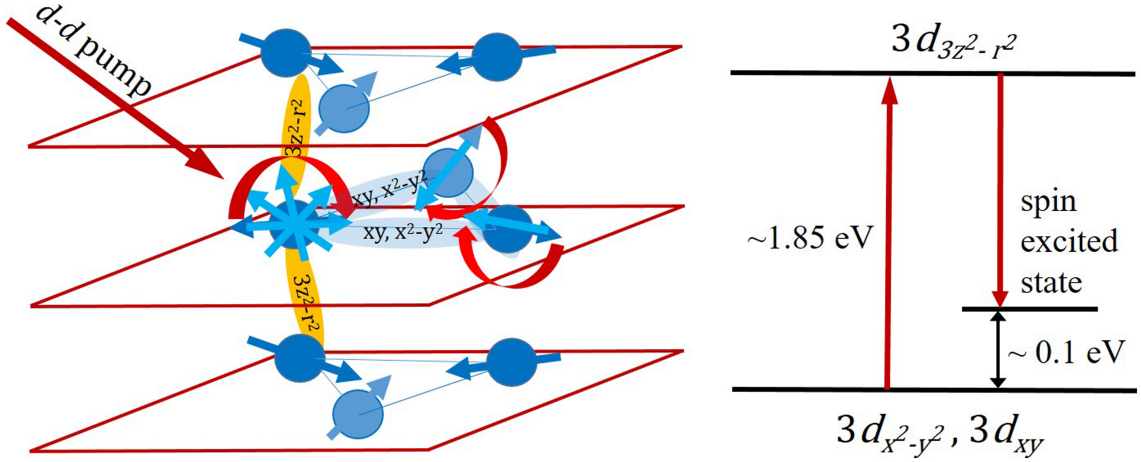

FIGURE 4 (left) A scenario of spin-flip excitation assisted by the Mn *d*-*d* transition through spin-3*d* orbit coupling. (right) Energy diagram for the resonant Raman scattering through Mn *d*-*d* transition

play crucial role in future spin-control devices. Relatively high energy of ~0.1 eV compared with the thermal energy at room temperature (~23 meV) makes the spin excitation robust against thermal agitations.

4 | CONCLUSION

We have investigated the nature of the spin excitations observed in hexagonal $RMnO_3$ (R = rare earths) through Raman spectroscopy based on the effects of the nonmagnetic Ga-ion substitution in the $HoMn_{1-x}Ga_xO_3$ (x = 0, 0.05, 0.10, and 0.33) system. The intensities of the spin excitations strongly decreased by Ga-ion substitution; they dropped by ~40% and 60% for 5% and 10% Ga substitution, respectively. Our analyses show that the spin excitation intensities are affected by the breaking of the triangular network of the magnetic Mn^{3+} ions in the $HoMn_{1-x}Ga_xO_3$ system. Normalized intensities of the spin excitation peak near 760 cm^{-1} (~0.1 eV) against the temperature scaled by the Néel ordering temperature (T/T_N) for three $HoMn_{1-x}Ga_xO_3$ (x = 0, 0.05, and 0.10) thin films fall in a universal line. Through mean-field-theory analysis, we conclude that the spin excitation near 0.1 eV is localized spin-flip excitation limited in the Mn-triangular network unperturbed by the nonmagnetic Ga-ion substitution. Relatively high energy of ~0.1 eV compared with the thermal energy at room temperature makes the spin excitation robust against thermal disturbance. Such localized spin-flip excitations may have important advantage in application for optically controlled spin devices.

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CONFLICT OF INTEREST

The authors declare no competing financial interests.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon request.

ORCID

Xiang-Bai Chen https://orcid.org/0000-0002-2784-9237
In-Sang Yang https://orcid.org/0000-0003-4956-2197

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