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Citation: [Applied Physics Letters](#) **99**, 052506 (2011); doi: 10.1063/1.3622768

View online: <http://dx.doi.org/10.1063/1.3622768>

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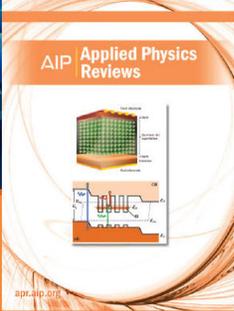
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# Spin exchange interactions in hexagonal manganites $\text{RMnO}_3$ (R = Tb, Dy, Ho, Er) epitaxial thin films

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(Received 7 April 2011; accepted 11 July 2011; published online 3 August 2011)

We present the results of an optical method of quantitatively estimating the spin exchange interactions in hexagonal manganites  $\text{RMnO}_3$  (R = Tb, Dy, Ho, Er) epitaxial thin films. The two in-plane (a-b plane) spin exchange integrals  $J_1$  (intratrimer Mn-Mn interaction) and  $J_2$  (intertrimer Mn-Mn interaction) are deduced from the magnon scattering peak wavenumbers. We found that  $J_2$  decreases systematically when the R ionic radius increases, while  $J_1$  is nearly independent of R ionic radius, contrary to the expectation in single crystals. We show that the R dependence of  $J_1$  could be understood in terms of the stress in the thin films. Our result indicates that the stress has stronger effect on the atomic displacement of the intratrimer Mn-Mn distance than the intertrimer Mn-Mn distance. © 2011 American Institute of Physics. [doi:10.1063/1.3622768]

Magnetic exchange interaction is one of the main concepts of magnetism in solids. Recently, spin exchange interaction was found to mediate magnetoelectric coupling in multiferroics – materials with coexisting magnetic and ferroelectric orders.<sup>1–3</sup> Multiferroic hexagonal manganites have attracted much interest because of their promising properties and potential applications.<sup>4–14</sup> Hexagonal  $\text{RMnO}_3$  (R = rare earth) have ferroelectric properties with fairly large remnant polarization and quite high Curie temperature ( $T_C$ ), typically above 590 K. Hexagonal  $\text{RMnO}_3$  also exhibit antiferromagnetic behaviors, with Néel temperature ( $T_N$ ) of 70–120 K. Below  $T_N$ , the antiferromagnetic exchange between Mn moments leads to their  $120^\circ$  ordering in the basal a-b plane.<sup>15,16</sup> The in-plane (a-b plane) antiferromagnetic exchange is the dominant spin exchange interaction, while the inter-plane exchange interaction is about two orders of magnitude weaker,<sup>17,18</sup> which often be considered negligible.

In a simple model, the in-plane  $\text{Mn}^{3+}$  ions of hexagonal  $\text{RMnO}_3$  are assumed to form a perfectly hexagonal network, in which the spin exchange interactions can be described by a Heisenberg Hamiltonian as:  $H = J \sum_{\langle i,j \rangle} (S_i \cdot S_j)$ , where  $S_i$  is the spin on site  $i$  and the summation is over the nearest-neighbor  $\text{Mn}^{3+}$  ion pairs and  $J$  is the exchange integral which quantitatively characterizes the exchange interaction. However, it has been reported that because of the distortion in the triangular lattice of the Mn moments, the equal distance of the Mn-O bonds in the a-b plane splits into two different bonds below  $T_N$ , in which the  $\text{Mn}^{3+}$  ions forming nearly triangular networks. Thus each  $\text{Mn}^{3+}$  ion has two nearest neighbors and four next nearest neighbors, and the splitting naturally leads to two different exchange interactions  $J_1$  (nearest neighbor: intratrimer Mn-Mn interaction) and  $J_2$  (next nearest neighbor: intertrimer Mn-Mn interaction).<sup>5,18</sup> Figure 1 shows a schematic diagram of the  $\text{Mn}^{3+}$  ion trian-

gular network, in which the exchange interactions can be described by  $H = J_1 \sum_{\langle i,j \rangle} (S_i \cdot S_j) + J_2 \sum_{\langle i,k \rangle} (S_i \cdot S_k)$ , the summation on  $j$  is over the nearest-neighbor  $\text{Mn}^{3+}$  ion pairs, and the summation on  $k$  is over the next-nearest-neighbor  $\text{Mn}^{3+}$  ion pairs.

The measurements of  $J_1$  and  $J_2$  values can be performed by neutron scattering studies, which were reported for hexagonal  $\text{YMnO}_3$  single crystal only.<sup>5,18</sup> The accurate measurements of  $J_1$  and  $J_2$  by neutron scattering are rather difficult and tedious, and thus, there is no reported study on the R dependence of  $J_1$  and  $J_2$ . In this letter, we present an optical method for estimating  $J_1$  and  $J_2$  of hexagonal  $\text{RMnO}_3$  (R = Tb, Dy, Ho, Er) thin films using Raman scattering spectroscopy. The  $J_1$  and  $J_2$  values are deduced from the magnon scattering peak wavenumbers, and we investigated the R dependent behaviors of  $J_1$  and  $J_2$ .

In our experiments, high-quality hexagonal  $\text{RMnO}_3$  (R = Tb, Dy, Ho, Er) thin films were grown on Pt(111)// $\text{Al}_2\text{O}_3$  (0001) substrates by pulsed laser deposition techniques, similar to that used in previous publications.<sup>8–12</sup> Note that in the bulk form,  $\text{TbMnO}_3$  and  $\text{DyMnO}_3$  are in orthorhombic phases. We used the epistabilization technique to convert these materials into hexagonal form. All the thin films were grown epitaxially with their  $c$  axis perpendicular to the film surface, and all the thin films have similar thickness.

Raman spectra were obtained in back-scattering with a Jobin-Yvon T64000 micro-Raman spectrometer in the single mode. A 647.1 nm laser was used as the excitation source, with laser power of  $\sim 1$  mW and beam diameter of  $\sim 50 \mu\text{m}$  on the surface of the samples. The beam power density was low enough to avoid laser heating. The samples were cooled to 13 K in a helium closed-cycle cryostat. In order to measure the Raman peak wavenumbers precisely, all the spectra have been calibrated in the frequency by using a standard neon source just before and after the measurements.

Figure 2 shows the Raman spectra of the hexagonal  $\text{RMnO}_3$  (R = Tb, Dy, Ho, Er) thin films obtained at 13 K in

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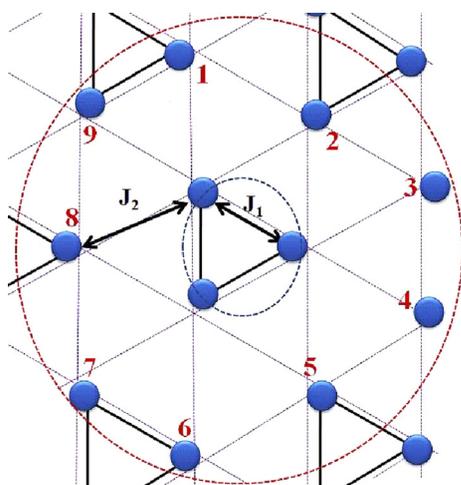


FIG. 1. (Color online) Schematic diagram of the  $\text{Mn}^{3+}$  ion triangular network in the  $a$ - $b$  plane of hexagonal  $\text{RMnO}_3$ . Each  $\text{Mn}^{3+}$  ion has two nearest neighbors ( $J_1$ ) and four next nearest neighbors ( $J_2$ ); each  $\text{Mn}^{3+}$  ion triangular has nine neighbors.

the crossed polarization. The strong broad peak  $\sim 760 \text{ cm}^{-1}$  is originated from four-magnon scattering, the weak broad peak  $\sim 950 \text{ cm}^{-1}$  is from six-magnon scattering; the strong narrow peak  $\sim 685 \text{ cm}^{-1}$  is assigned to  $A_1$  phonon, the weak narrow peak  $\sim 640 \text{ cm}^{-1}$  is assigned to  $E_1$  phonon.<sup>19–21</sup> In antiferromagnets, two-magnon scattering usually has the strongest intensity, while higher order magnon scattering has extremely weak intensity. In hexagonal  $\text{RMnO}_3$ , we found that four-magnon has the strongest intensity, and six-magnon intensity is not negligible. We attributed these phenomena to the special triangle spin network of  $\text{Mn}^{3+}$  ions.<sup>19–21</sup> The observation of both four-magnon and six-magnon in hexagonal  $\text{RMnO}_3$  provides us a simple method to estimate the  $J_1$  and  $J_2$  values.

The energies of multi-magnon scattering could be simply estimated through assuming spin flipping on neighboring sites,<sup>22</sup> which predicts results in reasonable agreement with the more sophisticated quantitative method of Green-function calculation.<sup>23</sup> In our previous study,<sup>19</sup> we estimated multi-magnon energies in hexagonal  $\text{RMnO}_3$  through a sim-

plified Heisenberg model of spin flipping on neighboring sites. Our simplified model predicted multi-magnon energies that agreed well with the experimental results. In our model, four-magnon scattering would be corresponding to the spin flipping of three  $\text{Mn}^{3+}$  ions in one triangle and one  $\text{Mn}^{3+}$  ion in the neighboring triangle, and six-magnon scattering would be corresponding to the spin flipping of six  $\text{Mn}^{3+}$  ions in two neighboring triangle. Due to the special triangle network of hexagonal  $\text{RMnO}_3$ , the spin flipping of all three  $\text{Mn}^{3+}$  ions in one triangle would induce spin reorientation of the neighbors; therefore, only the total number of neighbors would be counted for the magnetic interaction. We estimated that the energy of four-magnon would be  $13J_1 + 26J_2$ , and the energy of six-magnon would be  $18J_1 + 30J_2$  (Ref. 19).

As can be seen in Figure 2, the energies of four-magnon and six-magnon are strongly dependent on rare earth R. From the four-magnon and six-magnon peak wavenumbers, we can deduce the values of  $J_1$  and  $J_2$  optically and thus investigate the R dependent behavior of  $J_1$  and  $J_2$ . Our results are presented in Figure 3. As R changes from Er to Tb, the R ionic radius increases systematically. Figure 3 shows that  $J_2$  decreases systematically when the R ionic radius increases, while  $J_1$  is nearly independent of R ionic radius. In hexagonal  $\text{RMnO}_3$ ,  $J_1$  is strongly dependent on the intratrimer Mn-Mn distance, and  $J_2$  is strongly dependent on the intertrimer Mn-Mn distance. Therefore, the knowledge of the R dependence of the intratrimer and intertrimer Mn-Mn distances would be helpful for understanding the R dependence of  $J_1$  and  $J_2$ .

Although there is no reported study on neither the R dependence of  $J_1$  and  $J_2$  nor the R dependence of the intratrimer and intertrimer Mn-Mn distances, Zhou *et al.*<sup>24</sup> reported that for hexagonal  $\text{RMnO}_3$  single crystals, the lattice constant  $a$  decreases systematically when the R ionic radius decreases. Therefore, it would be reasonable to expect that for hexagonal  $\text{RMnO}_3$  single crystals, both the intratrimer and intertrimer Mn-Mn distances would decrease systematically when the R ionic radius decreases. For our hexagonal  $\text{RMnO}_3$  thin films, Figure 3 suggests that the intertrimer Mn-Mn distance would decrease systematically when the R ionic radius decreases, which agrees with the expectation in single

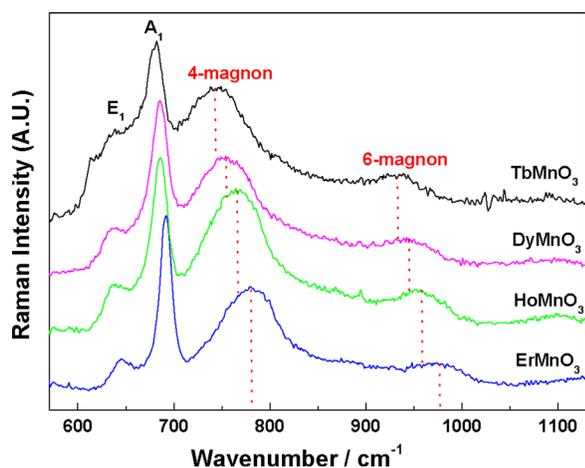


FIG. 2. (Color online) Raman spectra of hexagonal  $\text{RMnO}_3$  ( $R = \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}$ ) thin films at 13 K obtained in the  $z(yx)z^-$  polarization. The spectra are shifted in  $y$ -direction for clarity. The red dotted lines are indicating peak positions of the magnon peaks.

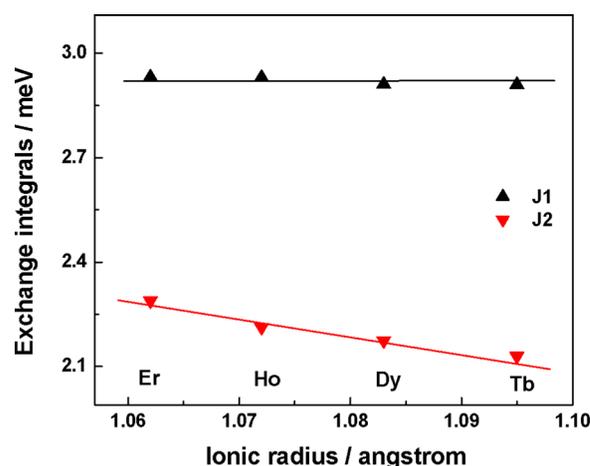


FIG. 3. (Color online) The R ionic radius dependence of the spin exchange integrals  $J_1$  and  $J_2$  of hexagonal  $\text{RMnO}_3$ . The solid lines are guides for the eye.

crystals, while the intratrimer Mn-Mn distance would be independent of the R ionic radius, contrary to the expectation in single crystals. We show in the later discussion that this difference could be understood in terms of the stress in the thin films.

The spin exchange integrals change rapidly with the lattice distances. Our study of the R dependence of  $J_1$  and  $J_2$  would be helpful to understand the atomic displacement in hexagonal RMnO<sub>3</sub>. When the atoms move, the electric structure of the solid changes, leading to different physical properties. Therefore, the study of the atomic displacement is important for understanding the physical properties and thus leading to new applications of the solid. The atomic displacement in a solid responds to either temperature or stress. The atomic displacement responding to temperature in hexagonal RMnO<sub>3</sub> was investigated by Lee *et al.*<sup>5</sup> Their study showed that atomic displacement of the Mn atoms behaves unusually below  $T_N$ . Because of this unusual movement of the Mn atoms, the equal distance of Mn-O bonds on the a-b plane splits into two different bonds: Mn-O3 and Mn-O4 (Fig. 3 of Ref. 5) and the splitting increases with further decreasing temperature. It is this splitting that leads to two different exchange interactions  $J_1$  and  $J_2$ .

In our experiments, the Raman spectra of all thin film samples were measured at the same temperature. Thus, the unusual R dependent behavior of  $J_1$  would not be originated from the unusual atomic displacement of the Mn atoms due to temperature differences in the thin films. While for thin films, due to the mismatch with the substrates, generally they are grown under strained condition. Therefore, we may expect that the unusual R dependent behavior of  $J_1$  could be due to the stress differences in the hexagonal RMnO<sub>3</sub> thin films.

The hexagonal RMnO<sub>3</sub> thin films used in our experiments were grown on the same kind of substrates and have similar film thicknesses to each other. Thus, as R changes from Er to Tb, the lattice mismatch would vary systematically; therefore, the stress in the thin films would also vary systematically. Earlier studies<sup>21,25</sup> did indicate that the stress in the thin films varies systematically with R ionic radius. Taking into account the R dependence of the stress in the thin films, we then could understand the unusual R dependent behavior of  $J_1$ . As R changes from Er to Tb, without stress, both the intratrimer and intertrimer Mn-Mn distances would decrease; while in the thin films, the stress would change the intratrimer and intertrimer Mn-Mn distances at the same time, if the stress induces stronger change of the intratrimer Mn-Mn distance than the intertrimer Mn-Mn distance. Then it would explain our predictions from  $J_1$  and  $J_2$  measurements that the intratrimer Mn-Mn distance is nearly independent of R ionic radius and the intertrimer Mn-Mn distance decreases systematically as R ionic radius increases. In this letter, we have studied thin films of similar thickness, thus we have assumed that the stress difference induced by different film thicknesses would be negligible. A preliminary study of the film thickness dependence of Raman scattering is presented in the supplementary material,<sup>26</sup> which further confirms our assumption.

Above discussion indicates that the stress would have stronger effect on the atomic displacement of the intratrimer Mn-Mn distance than the intertrimer Mn-Mn distance. Our result predicts that the atomic displacement of the Mn atoms would behave unusually under stress. This phenomenon is similar as the unusual behavior of the atomic displacement of the Mn atoms responding to temperature reported by Lee *et al.*<sup>5</sup> Thus, we may conclude that for hexagonal RMnO<sub>3</sub>, the atomic displacement of the Mn atoms behaves unusually responding to both temperature and stress. Lee *et al.*<sup>5</sup> reported that the unusual behavior of the atomic displacement of the Mn atoms produces the antiferromagnetic moment and strong magneto-electric coupling. Therefore, a systematic study of the atomic displacement of the Mn atoms responding to high pressure would be necessary, and we propose that an antiferromagnetic transition and a strong magneto-electric coupling could be induced under high pressure in hexagonal RMnO<sub>3</sub>.

In conclusion, we presented the rare earth dependence of the spin exchange interactions in hexagonal manganites thin films. We estimated the two a-b plane exchange integrals  $J_1$  and  $J_2$  and investigated the R dependent behaviors of  $J_1$  and  $J_2$ . We found that  $J_2$  decreases systematically when the R ionic radius increases. Due to the stress in the thin films,  $J_1$  is nearly independent of R ionic radius. Our results indicate that the stress in the thin films has stronger effect on the atomic displacement of the intratrimer Mn-Mn distance than the intertrimer Mn-Mn distance.

We thank the National Research Foundation of Korea Grant Nos. 2009-0063320 and 2010-0022857. The work at Seoul National University was supported by the National Research Foundation of Korea Grant Nos. 2009-0080567 and 2010-0020416.

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<sup>26</sup>See supplementary material at <http://dx.doi.org/10.1063/1.3622768> for a preliminary study of the film thickness dependence of Raman scattering.