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2010 New J. Phys. 12 073046

(http://iopscience.iop.org/1367-2630/12/7/073046)

New Journal of Physics
The open-access journal for physics

Resonant A_1 phonon and four-magnon Raman scattering in hexagonal $HoMnO_3$ thin film

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New Journal of Physics **12** (2010) 073046 (8pp)
Received 18 March 2010
Published 30 July 2010
Online at http://www.njp.org/
doi:10.1088/1367-2630/12/7/073046

Abstract. We present the results of resonant Raman scattering of the A_1 phonon at 680 cm^{-1} and of the four-magnon at 760 cm^{-1} in hexagonal $HoMnO_3$ thin film. We find that the A_1 phonon at 680 cm^{-1} shows a strong resonance effect near the on-site Mn d–d transition at ∼1.7 eV. Our Raman results show that the four-magnon scattering can be selectively excited with red lasers of 647 nm (1.92 eV) and 671 nm (1.85 eV), but are not detectable with green lasers of 532 nm (2.33 eV), indicating that the four-magnon scattering in hexagonal $HoMnO_3$ has an extremely strong resonance effect also near the on-site Mn d–d transition at ∼1.7 eV. Furthermore, through the analyses of our study of the resonant four-magnon Raman scattering and earlier studies of the resonant two-magnon Raman scattering, we propose a simple general model for all resonant magnon scattering. Our simple general model predicts a simple method for the investigation of the spin-flipping/spin-wave in magnetic materials, which would have significant impacts on the applications of spintronic devices.

Hexagonal $HoMnO_3$ belongs to the class of multiferroic materials characterized by the coexistence of antiferromagnetic (AFM) and ferroelectric (FE) orderings. Multiferroic materials have attracted much attention because of the prospect of controlling both the dielectric

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and the magnetic properties of these materials using electric or magnetic fields [1, 2]. This magnetoelectric coupling in a single material could lead to new applications, and new understanding of the underlying physics involved.

Hexagonal $HoMnO_3$ has a variety of AFM as well as FE phases with high FE Curie temperature $T_C \approx 900$ K. The AFM order of the Mn spins is stabilized at temperatures below the Néel temperature $T_N \approx 76$ K for single crystals [3]–[5]. Due to the AFM–FE and/or spin–phonon couplings, the Raman scattering would show new phenomena below the magnetic transition temperature, in addition to the usually reported phonons. Indeed, in our earlier Raman measurement, we observed a broad Raman peak at 760 cm^{-1} below the Néel temperature using a 647 nm red laser [6]. This broad peak is correlated with pure magnetic ordering and is due to four-magnon scattering [6].

The four-magnon peak of hexagonal $HoMnO_3$ is observed only in Raman measurements by a 647 nm red laser. However, it has not been reported in earlier measurements using a 514 nm green laser by Litvinchuk *et al* [7]. In this paper, we clearly explain that the reason for this phenomenon is due to the extremely strong resonance effect of the four-magnon scattering. In addition, we present the resonant study of the A_1 phonon at 680 cm^{-1}.

Resonant Raman scattering of the A_1 phonon at 680 cm^{-1} in hexagonal $RMnO_3$ (R = rare earth) has been reported by Litvinchuk *et al* [7] and Vermette *et al* [8]. Their studies show a strong resonance effect from 514.5 nm (2.41 eV) excitation to 632.8 nm (1.96 eV) excitation, which has been attributed to the on-site Mn d–d transition at ∼1.7 eV. In this paper, we present the resonant study of hexagonal $HoMnO_3$ in deeper resonant regime with 647 nm (1.92 eV) and 671 nm (1.85 eV) red lasers compared with the non-resonant excitation with a 532 nm (2.33 eV) green laser. We observe a stronger resonant effect, which further confirms that the resonance effect of the A_1 phonon at 680 cm^{-1} is correlated with the on-site Mn d–d transition at ∼1.7 eV.

In addition to the resonant study of the A_1 phonon at 680 cm^{-1}, we present the investigation of the resonant four-magnon Raman scattering. We show that the four-magnon scattering at 760 cm^{-1} has an extremely strong resonance effect; it can be selectively excited with red lasers of 647 nm and 671 nm, but not detectable with a green laser of 532 nm. Thus, the resonance effect of four-magnon scattering can also be attributed to the on-site Mn d–d transition at ∼1.7 eV. Therefore, the resonant four-magnon scattering in hexagonal $HoMnO_3$ occurs near the absorption edge peak, not above it. To the best of our knowledge, resonant four-magnon scattering in hexagonal $RMnO_3$ has not been investigated earlier, while resonant two-magnon scattering has been extensively investigated in cuprate AFM materials [9]–[12]. However, the studies in cuprates show that there is no resonance effect of two-magnon scattering near the absorption edge peak, but the resonance occurs well above the absorption edge peak [9]–[12]. At first sight, the resonance effect of two-magnon and four-magnon scattering is exactly opposite. Our analyses show that, actually, both the resonance effects can be explained by the same mechanism. Furthermore, we propose a simple general model for all resonant magnon scattering.

In our experiments, the hexagonal $HoMnO_3$ thin film was grown on a $Pt(111)//Al_2O_3$ (0001) substrate by the laser ablation method, which is similar to that used in previous publications [13, 14], and the physical properties of this type of sample have been investigated in [14]. Raman scattering spectra of the sample were obtained in backscattering configuration with a Jobin Yvon T64000 Raman microprobe spectrometer. Three excitation sources were used: two red lasers of 671 and 647 nm, and one green laser of 532 nm. The laser beam power densities were kept low enough to avoid laser heating. The scattered signal was detected by a

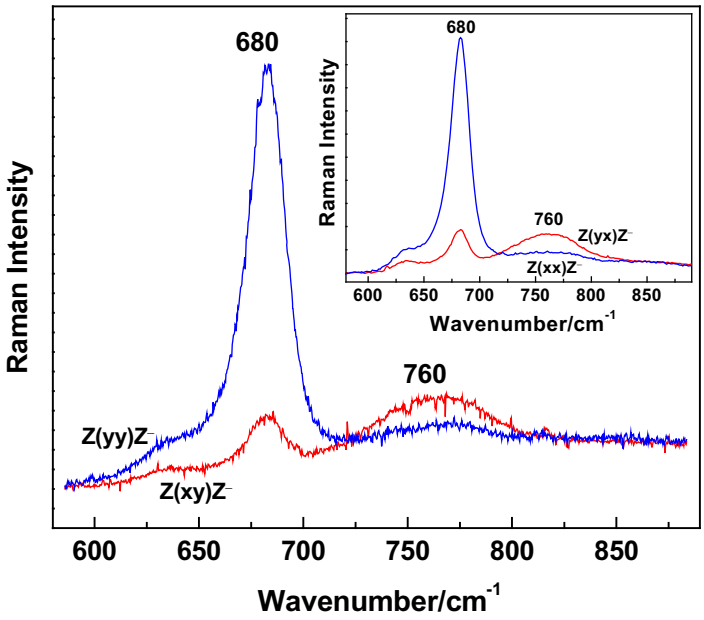

Figure 1. Polarized Raman spectra of hexagonal $HoMnO_3$ thin film at 13 K obtained in the $z(xy)\bar{z}$ and $z(yy)\bar{z}$ configurations using the 671 nm red laser. The inset is the Raman spectra obtained using the 647 nm red laser.

liquid-nitrogen-cooled CCD detector. All spectra have been corrected in the frequency using a calibrated neon source and the response using a standard white light source. The sample was mounted in a helium-closed cycle cryostat and the sample temperature was cooled to 13 K.

Figure 1 shows the polarized Raman scattering spectra of hexagonal $HoMnO_3$ thin film obtained at 13 K in the $z(xy)\bar{z}$ and $z(yy)\bar{z}$ configurations. The excitation source was a 671 nm red laser. In the parallel configuration, a strong peak at 680 cm^{-1} was observed, which can be assigned to the A_1 phonon. In the crossed configuration, the peak at 680 cm^{-1} was also observed with much weaker intensity, which should not be allowed by the Raman selection rule. This observation could be attributed to impurity disorder and departure from the exact selection rule in resonant Raman scattering, not due to misalignment of crystalline multidomains. We recorded the Raman spectra upon rotation of the hexagonal $HoMnO_3$ thin film in the x–y-plane. No measurable difference of the Raman signal was detected. Therefore, we conclude that the effect of the misalignment of crystalline multidomains is negligible. The oxygen defects in the thin film sample would have some effect on the phonon scattering. Our previous study indicates that the oxygen defects have only a weak effect on the A_1 phonon at 680 cm^{-1} [6]. Therefore, the resonance Raman condition is the main contribution to the observation of the A_1 phonon at 680 cm^{-1} in the crossed configuration. Indeed, we will show that the A_1 phonon at 680 cm^{-1} is strongly affected by the resonance condition.

The most interesting feature in figure 1 is the observation of the broad peak located at 760 cm^{-1} in the crossed configuration. This broad peak is also presented in the parallel configuration. Due to the strong A_1 phonon peak at 680 cm^{-1}, it is not well resolved. In our early study [6], this broad peak at 760 cm^{-1} was also observed using a 647 nm red laser, as shown in the inset of figure 1. The observation of this broad peak with both 647 nm and 671 nm lasers confirms its Raman origin, but not luminescence from impurity in the sample. The analyses

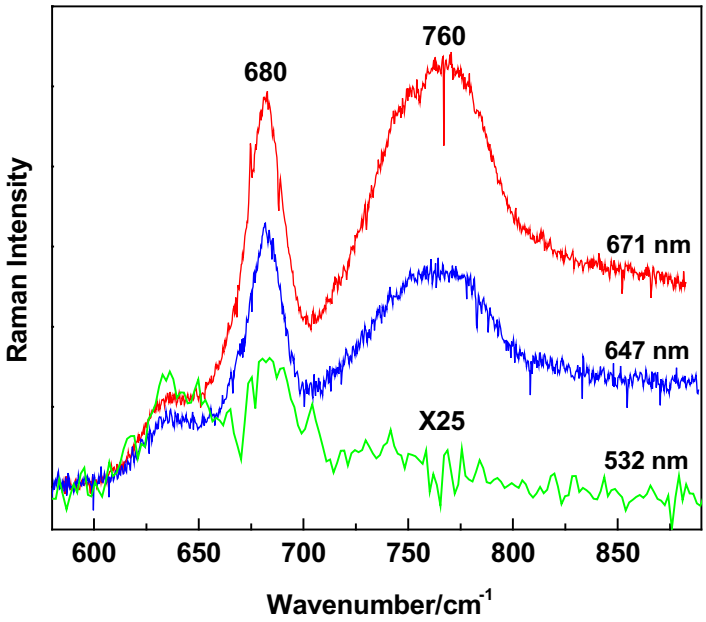

Figure 2. Raman spectra of $HoMnO_3$ thin film at 13 K obtained in the $z(xy)\bar{z}$ configuration using the following excitation sources: 671 nm (1.85 eV), 647 nm (1.92 eV) and 532 nm (2.33 eV) lasers.

of the origin of this broad peak are presented in detail in our earlier study [6]. We found that this broad peak is correlated with pure magnetic ordering, and originated from four-magnon scattering.

The spectra of the 647 nm and 671 nm lasers in figure 1 also indicate that both the A_1 phonon at 680 cm^{-1} and the four-magnon scattering at 760 cm^{-1} have a resonance effect, and the four-magnon scattering has a stronger resonance effect. In order to investigate the resonance effect in detail, we performed Raman scattering studies on the hexagonal $HoMnO_3$ thin film in the crossed configuration using three excitation sources: 671 nm (1.85 eV), 647 nm (1.92 eV) and 532 nm (2.33 eV) lasers. The results are shown in figure 2. The spectra were obtained by averaging four different spots on the sample, and the intensities of the spectra of different lasers were normalized assuming the same laser power and integration time. As can be seen in figure 2, the intensity of the A_1 phonon increases significantly from the green laser to the red lasers, and the four-magnon scattering shows an even faster intensity increase; it can be selectively excited by the red lasers, but not detectable with the green laser.

Our results show that both the A_1 phonon at 680 cm^{-1} and the four-magnon scattering at 760 cm^{-1} in hexagonal $HoMnO_3$ can be resonantly excited by the red lasers. The optical conductivity spectra of hexagonal $RMnO_3$ [15, 16] show that there are two main optical transitions: a sharp peak at ~1.7 eV and a broad band centered at ~5 eV. Although there have been debates about the origin of the sharp transition at ~1.7 eV [15]–[17], we adopt the model by Souchkov *et al* [15] for the electronic structure of hexagonal $RMnO_3$ in explaining our Raman results. In the model, the allowed optical transitions for the $E \perp c$ polarization of light are the on-site Mn d–d transitions, and the transitions from the hybridized oxygen p levels to the Mn $d_{3z^2-r^2}$ levels. In the case of $E \parallel c$ polarization of incident light, the optical matrix elements for the on-site Mn d–d transitions are zero. The on-site Mn d–d transitions correspond to the

sharp peak at ∼1.7 eV, and the transitions from O p → $d_{(3z^2-r^2)'}$ correspond to the broad band centered at ∼5 eV [15]. Therefore, we attribute the resonance effect of both the A_1 phonon at 680 cm^{-1} and the four-magnon scattering at 760 cm^{-1} in hexagonal $HoMnO_3$ to the on-site Mn d–d transition at ∼1.7 eV. Since the on-site Mn d–d transitions are allowed for the $E \perp c$ polarization, we expect that the resonance effect would occur at both the $z(xy)\bar{z}$ and $z(yy)\bar{z}$ configurations. Indeed, as we have described, the four-magnon scattering is also presented in the parallel configuration, and the A_1 phonon has been observed in the crossed configuration.

The resonant Raman scattering study of the A_1 phonon at 680 cm^{-1} in hexagonal $RMnO_3$ has been reported by Litvinchuk *et al* [7] and Vermette *et al* [8]. By comparing the $(xx)/(zz)$ polarization relative intensity, Litvinchuk *et al* [7] observed a strong resonant effect by a factor of about 10 from 514.5 nm (2.41 eV) excitation to 632.8 nm (1.96 eV) excitation. Vermette *et al* [8] also observed a strong resonant effect from 514.5 nm excitation to 632.8 nm excitation, but only qualitatively. They have attributed the resonant effect to the on-site Mn d–d transition at ∼1.7 eV. Our results show that the intensity of the A_1 phonon increased about 80 times from non-resonant excitation at 532 nm (2.33 eV) to deep-resonant excitation at 671 nm (1.85 eV), further confirming that the resonant effect of the A_1 phonon at 680 cm^{-1} is correlated with the on-site Mn d–d transition at ∼1.7 eV.

The four-magnon scattering at 760 cm^{-1} shows an extremely strong resonance effect; it can be selectively excited with red lasers of 647 nm (1.92 eV) and 671 nm (1.85 eV), but is not detectable with a green laser of 532 nm (2.33 eV). In addition, the early Raman study of hexagonal $HoMnO_3$ single crystal using a green laser of 514 nm (2.41 eV) did not observe four-magnon scattering at 760 cm^{-1} [7]. We also observed that the relative intensity of the four-magnon peak at 760 cm^{-1} is considerably larger for the 671 nm laser than for the 647 nm laser. This is consistent with the fact that the 671 nm laser has energy closer to 1.7 eV and that the four-magnon scattering at 760 cm^{-1} has a stronger resonance effect than the A_1 phonon at 680 cm^{-1}. Our results show that both the A_1 phonon and the four-magnon have a very strong resonance effect, which can be attributed to the narrow linewidth (∼0.25 eV) of the on-site Mn d–d transition at ∼1.7 eV. Furthermore, we conclude that the four-magnon scattering is strictly related to the on-site Mn d–d transition, since the four-magnon scattering can be selectively excited with red lasers of energies ∼1.7 eV.

Our results also indicate that the resonant four-magnon scattering in hexagonal $HoMnO_3$ occurs near the absorption edge peak, not above it. However, in earlier studies of the resonant two-magnon scattering in cuprate insulators, it was shown that there is no resonance effect of the two-magnon scattering near the absorption edge peak, but the resonance occurs well above it [9]–[12]. As the origin of the resonance of two-magnon scattering, several complex models have been proposed: triple resonance mechanism [9], excitonic mechanism [11] and background spins mechanism [12]. At first sight, the resonant four-magnon scattering is exactly opposite to that of the resonant two-magnon scattering. Our discussion below argues that both of them should be correlated to the same mechanism. Furthermore, we propose a simple general model for all resonant magnon scattering.

For hexagonal $HoMnO_3$, the on-site Mn d–d transitions are at lower energy than the transitions from the hybridized oxygen p levels to the Mn $d_{3z^2-r^2}$ levels. Therefore, hexagonal $HoMnO_3$ can be considered as a Mott–Hubbard-type material, in which the on-site Coulomb energy U (transition between the lower and upper Hubbard bands) is at lower energy than the charge-transfer energy Δ (transition between the oxygen p orbital and the upper Hubbard band). For cuprate insulators, they belong to the charge-transfer-type materials, in which the

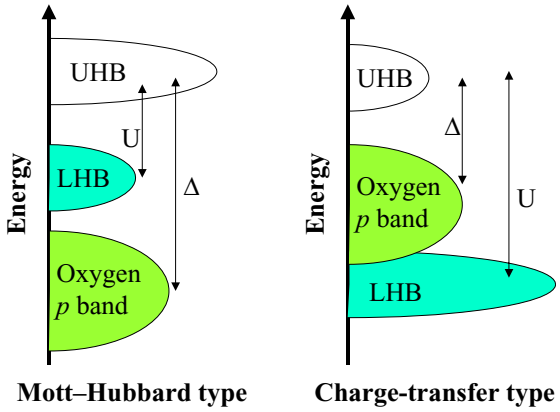

Figure 3. A schematic energy diagram of Mott–Hubbard-type materials and charge-transfer-type materials. UHB: upper Hubbard band; LHB: lower Hubbard band; U: on-site Coulomb energy; Δ: charge-transfer energy.

on-site Coulomb energy U is at higher energy than the charge-transfer energy Δ. A schematic energy diagram of Mott–Hubbard-type materials and charge-transfer-type materials is shown in figure 3.

The traditional framework for understanding magnon Raman scattering in antiferromagnets has been known as Loudon–Fleury theory [18]. From the 'Loudon–Fleury' diagrams, the magnon scattering would have resonances near the band edge [19]. The theory of Raman scattering in Mott–Hubbard systems has been presented by Shastry and Shraiman [20], which is derived from Loudon–Fleury theory. Hexagonal $HoMnO_3$ can be considered as a Mott–Hubbard-type material. Thus, it is reasonable to expect that the four-magnon scattering in hexagonal $HoMnO_3$ would have a resonant effect near the absorption edge, i.e. the four-magnon scattering resonance occurs near the on-site Coulomb energy in Mott–Hubbard systems. As expected, we observe that the resonance of four-magnon scattering in hexagonal $HoMnO_3$ does occur near the on-site Mn d–d transition at $\sim$1.7 eV, not above it. Therefore, we conclude that the four-magnon scattering has a resonance effect near the on-site Coulomb energy. However, in cuprate insulators, the resonance of the two-magnon scattering occurs well above the absorption edge peak [9]–[12], which contradicts the Loudon–Fleury theory. Several complex models have been proposed to explain this phenomenon [9, 11–12].

At first sight, the resonance of four-magnon and two-magnon scattering has a very different mechanism. However, Chubukov *et al* [9] showed that the resonance effect of two-magnon scattering in cuprate insulators occurs right at the upper end of the features in the optical data that can be interpreted as particle–hole excitations between the lower and upper Hubbard bands. Thus, the two-magnon scattering could also be classified as having a resonance effect near the on-site Coulomb energy in charge-transfer-type materials. Therefore, we conclude that the resonance effects for both two-magnon and four-magnon scattering would occur near the on-site Coulomb energy. In addition, we found that the resonance effect of four-magnon scattering in hexagonal $HoMnO_3$ is much stronger than that of two-magnon scattering in cuprate insulators. In hexagonal $HoMnO_3$, the on-site Mn d–d transition has a narrow linewidth, while in cuprate insulators, the transition between the lower and upper Hubbard bands has a much broader linewidth. Therefore, we conclude that the strength of the resonance effect of two-magnon and

four-magnon scattering would be correlated with the linewidth of the on-site Coulomb energy, narrower linewidth indicating a stronger resonance effect.

The above discussion indicates that both resonant two-magnon and four-magnon scattering occur near the on-site Coulomb energy, and the strength of the resonance effect depends on the linewidth of the on-site Coulomb energy. Therefore, we propose that, in general, all resonant magnon scattering would occur near the on-site Coulomb energy, and narrower linewidth of the on-site Coulomb energy would have a stronger resonance effect. Further confirmation of our model would need further experimental and theoretical work. Our simple model predicts a simple method for the investigation of the spin-flipping/spin-wave in magnetic materials, i.e. the spin-flipping/spin-wave could be selectively induced in certain magnetic materials. Searching for this type of magnetic material and the studies of the mechanisms of the spin-flipping/spin-wave would have significant impacts on the applications of spintronic devices.

In summary, we have presented resonant Raman scattering of the A_1 phonon at 680 cm^{-1} and of the four-magnon at 760 cm^{-1} in hexagonal $HoMnO_3$ thin film. We found that the A_1 phonon at 680 cm^{-1} is strongly enhanced with red lasers, and that the resonance effect is correlated with the on-site Mn d–d transition at ∼1.7 eV. More interestingly, we observed that the four-magnon scattering in hexagonal $HoMnO_3$ can be selectively excited with red lasers but is not detectable with a green laser. The resonance effect of four-magnon scattering is also correlated with the on-site Mn d–d transition at ∼1.7 eV. Furthermore, through the analyses of the resonant four-magnon Raman scattering and the resonant two-magnon Raman scattering, we propose that all resonant magnon scattering would occur near the on-site Coulomb energy, and the narrower linewidth of the on-site Coulomb energy would have the stronger resonance effect.

Acknowledgment

This work was supported by the National Research Foundation of Korea Grant funded by the Korean Government (2009-0063320).

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