Origin of the 2 eV peak in optical absorption spectra of LaMnO$_3$: an explanation based on the orbitally degenerate Hubbard model

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Abstract. We investigated the temperature-dependent optical absorption spectra of LaMnO$_3$ and NdMnO$_3$ epitaxial thin films. We found that both spectra have strong absorption features around 2 eV, and that the 2 eV peak of LaMnO$_3$ has a weak temperature dependence. As the La ions are replaced with Nd ions, the spectral weight of the peak becomes suppressed. From careful comparisons with the orbitally degenerate Hubbard model, we could explain most of the spectral features of the 2 eV peak observed in the absorption spectra. We also found a fine structure of three sub-peaks in the 2 eV peak, whose origin was considered based on currently available ideas.

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1. Introduction

LaMnO$_3$ is a prototype material where the couplings among the charge, spin, orbital and lattice degrees of freedom are strong. Note that the ground state of this material shows an orbital ordering, where the Mn ions in the $xy$-plane have an $e_g$ electron with $d_{3z^2-r^2}$ or $d_{xy}$ orbitals alternately. This orbital ordering can be accompanied by cooperative Jahn–Teller distortion, which results in elongation and shortening of the Mn–O bond lengths in the $xy$-plane. The superexchange interaction between the $e_g$ electrons and the strong Hund’s rule coupling can provide the $A$-type magnetic ground state. These properties are rather complicated phenomena due to the strong interplay among the charge, orbital, spin and lattice degrees of freedom.

Optical investigation can prove characteristic energy scales, related to these physical phenomena. The optical conductivity spectra of LaMeO$_3$ ($Me = Sc$, Ti, V and Cr) show a systematic change of absorption features below 5 eV, which are supposed to originate from the electron–electron correlation [1]. It was shown that the Mott gap increases as the atomic number of the metal ion increases from Sc to Cr [1]. In the study by Arima et al [1] LaMnO$_3$ was considered to be located in the vicinity of the borderline where the optical gap changes from the Mott gap to the charge transfer gap. The 2 eV peak in optical conductivity spectra of LaMnO$_3$ was assigned to a charge transfer transition peak between O 2p and Mn 3d bands by early workers [1]. However, it was noticed that the spectral weight of the 2 eV peak could be fitted reasonably well to follow a functional form of $(1 - x)^2$ in La$_{1-x}$Ca$_x$MnO$_3$, which suggested that the 2 eV peak should be mainly due to the intra-atomic transition on a Mn$^{3+}$ ion or the inter-atomic transition between neighbouring Mn$^{3+}$ ions [2]. This is inconsistent with the charge transfer picture which assigned the 2 eV peak as a charge transfer peak.

There have been several experimental and theoretical studies on the optical properties of this material [3]–[9]. Tobe et al [7] still claimed that the 2 eV peak should come from a charge transfer...
transition. However, other workers considered other possibilities, such as on-site \[6\] transition among JT split Mn \(e_g\) orbitals, inter-band \[4\]–\[8\] transition or Mott–Hubbard type inter-site transition \[9\] among degenerate d-orbitals. A proper understanding on the 2 eV absorption peak of LaMnO\(_3\) is still lacking.

Recently, intense theoretical and experimental investigations on LaMnO\(_3\) have been revived from a somewhat different context. Unusual phonon-like features in the resonant Raman spectra were reported \[10\]. These low-energy excitations have attracted a lot of interest, since they were suggested to be a new kind of elementary excitation, the so-called ‘orbiton’ \[10\]. It was claimed that the orbiton should be a continuous excitation, i.e. the Goldstone mode, of a particular orbital ordering. At this moment, the origin of the resonant Raman peaks is still the subject of controversy and debate \[11\]–\[14\]. In spite of this situation, it is clear that the excitations in the Raman spectra should be closely related to the 2 eV absorption peak, since the resonance of the Raman peaks does occur around 2 eV. Therefore, reinvestigation of the origin of the 2 eV absorption peak should be a timely study, since it can provide us with some important clues in solving the controversy related with the ‘orbiton’ issue.

In this paper, we will present the temperature-dependent optical absorption spectra \(\alpha(\omega)\) of epitaxially grown thin films of LaMnO\(_3\) and NdMnO\(_3\). From \(\alpha(\omega)\), the energy scales of the interaction among charge, orbital and spin could be deduced. On the basis of these parameters, we will dispute the previous theoretical and experimental efforts on the 2 eV absorption peak of the manganites. In addition, we also observed interesting fine structures in the 2 eV absorption peak, and will discuss a few important aspects of these intriguing fine structures.

### 2. Experimental methods

Epitaxial\(^2\) LaMnO\(_3\) and NdMnO\(_3\) thin films were grown on double-side polished (001) cut plane of LSAT ((LaAlO\(_3\))\(_{0.3}\)(SrAl\(_{0.5}\)Ta\(_{0.5}\)O\(_3\))\(_{0.7}\)) substrates using the pulsed laser deposition (PLD) technique. Their physical properties were found to be very sensitive to oxygen stoichiometry, so careful post-annealing treatments were needed. The LaMnO\(_3\) thin films were post-annealed at 800 °C in Ar 96% + H\(_2\) 4% gas to reduce excess oxygen. The NdMnO\(_3\) films were annealed in O\(_2\) gas at 900 °C for 12 h. Their basic properties, such as x-ray diffraction pattern, temperature \((T)\)-dependent resistivity and magnetization curves were measured. All the films were found to be epitaxial with their \(c\)-axes oriented perpendicular to their film surfaces. Details of the thin film growth and the characterization methods can be found elsewhere \[15, 16\].

The out-of-plane lattice parameter of the LaMnO\(_3\) film is 3.94 Å. This is slightly larger than the pseudo-cubic out-of-plane lattice parameter of bulk samples by about 2.5%. This means that the films are under slight compressive strain in the \(ab\)-plane. One might consider that the physical properties can be changed due to the strain \[17, 18\]. However, it should be noted that the \(A\)-type spin/orbital structure survives under severe lattice deformation unless the spontaneous orthorhombic strain in the \(ab\)-plane is less than about 9% \[19, 20\]. So our films are worthy enough to compare with the optical properties of a single crystalline material despite the substrate strain.

\(^2\) Epitaxial growth is a growth process by which a thin layer of single crystalline material is deposited on single-crystal substrate, so the epitaxial growth occurs in such a way that the crystallographic structure of the substrate is reproduced in the growing material. In our case, it means that only (001) planes of the LaMnO\(_3\) and NdMnO\(_3\) have grown on LSAT (001) substrate and that has been verified by the structural analysis of the films.

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Transmission spectra of the LaMnO$_3$ and NdMnO$_3$ thin films were measured from 0.5 to 5.5 eV using a grating-type spectrophotometer. Note that the optical transmission method is quite useful to observe small changes in absorption coefficients. From the transmission spectra, the absolute value of the absorption coefficient could be obtained using values of the film thicknesses, which were measured from cross-sectional field emission scanning electron microscopy (FE-SEM) pictures. Since we used a geometry where the light entered normal to the sample surface, we could obtain the $ab$-plane responses from our transmission spectra.

3. Results

3.1. Temperature-dependent spectral weight change

Figure 1(a) shows the $T$-dependent absorption spectra of LaMnO$_3$ thin film. At 10 K, there is a strong absorption peak centred around 2 eV, which is the main topic of this paper. The higher energy feature above 3.25 eV is supposed to come from the tail of the Mn 3d–O 2p charge transfer peak [2]. As $T$ increases, the spectral weight of the 2 eV peak decreases, which is consistent with previous reports for single-crystal samples [5, 7]. In particular, the spectral weight decreases...
in the spectral region between 0.7 and 2.7 eV. This decrease seems to be compensated by the increased spectral weight higher than 2.7 eV. To show the \( T \) dependence more quantitatively, the values of spectral weight of the 2 eV peak were evaluated by integrating the absorption coefficients from 0.7 to 2.7 eV. Figure 1(b) shows the \( T \) dependence of the 2 eV peak. Around 120 K, the spectral weight shows a distinct suppression, as \( T \) increases. This change should be related with the magnetic ordering of our thin films. The Néel ordering temperature \( T_N \) of this compound is known to be \( \sim 140 \) K [19]. Above \( T_N \), the sample is in a paramagnetic state. Below \( T_N \), it is in the A-type antiferromagnetic state, where spins are ordered ferromagnetically within the \( ab \)-plane but antiferromagnetically stacked along the \( c \)-axis.

As shown in figure 1(a), the 2 eV peak has fine spectral features, which will be called as the sub-peak structure from now on. With our best knowledge, the details and origins of this spectral features have not yet been addressed in previous studies. At low \( T \), the 2 eV peak looks like a single broad peak; however, the fine peak structure emerges and becomes prominent as \( T \) increases above \( \sim 100 \) K. Note that value of \( T \) where the sub-peak features become evident is close to the reported value of \( T_N \). The positions for the first, second and third peaks are located around 1.9, 2.3 and 2.6 eV at room temperature, respectively. There is a weak \( T \) dependence of the first sub-peak; as \( T \) increases, its peak position moves slightly towards a lower energy. Due to the broad features, the \( T \) dependences of the other sub-peaks are difficult to be determined.

### 3.2. Difference between \( \text{LaMnO}_3 \) and \( \text{NdMnO}_3 \)

\( \text{RMnO}_3 \) (\( R \) = rare earth ion from La to Sm) belong to a family of manganites, whose \( e_g \)-electron orbitals are ordered below the ordering \( T \) (\( T_{\text{OO}} \)). This orbital ordering is accompanied by the cooperative Jahn–Teller effects. According to a recent systematic study, \( T_{\text{OO}} \) (or Jahn–Teller transition \( T \)) increases monotonically as \( R \) ion size (\( r_R \)) decreases: \( T_{\text{DD}} \sim 800 \) K for \( \text{LaMnO}_3 \) and \( T_{\text{DD}} \sim 1100 \) K for \( \text{NdMnO}_3 \) [19]. This suggests that the Jahn–Teller distortion due to strong electron–lattice coupling can be more stabilized in \( \text{NdMnO}_3 \) than in \( \text{LaMnO}_3 \).

Figure 2 shows the absorption coefficient spectra of \( \text{LaMnO}_3 \) and \( \text{NdMnO}_3 \) at room temperature. We can find two interesting points. Firstly, as \( r_R \) decreases from La to Nd, the
spectral weight of the 2 eV peak becomes significantly suppressed. This behaviour cannot be simply understood in terms of the changes in the Mn–O–Mn bond angle or Mn–O bond length, since the structural differences between LaMnO$_3$ and NdMnO$_3$ are rather small [20]. Secondly, the 2 eV peak for NdMnO$_3$ is located at a slightly lower position than that for LaMnO$_3$. The Jahn–Teller distortion for NdMnO$_3$ is larger than that for LaMnO$_3$ [20]. If the 2 eV peaks are related to the Jahn–Teller distortion, the NdMnO$_3$ peak should have a higher position than that the LaMnO$_3$, contrary to our observation.

4. Discussion

4.1. Comparison with currently available models for the 2.0 eV peak

4.1.1. The tight-binding band calculation. A recent model based on the tight-binding calculation predicted anisotropic optical conductivity spectra for LaMnO$_3$ [4]. In this model, the Hund rule, electron–electron and electron–lattice couplings were treated with the mean-field approach to obtain the full optical conductivity of LaMnO$_3$ as a function of $T$. The 2 eV peak was assigned to an inter-band transition between the Mn e$_g$ bands. The optical anisotropy comes from the difference of the spin alignments in the \textit{ab}-plane and along the \textit{c}-axis. Since the difference is quite large in the $A$-type antiferromagnetic spin ground state, the anisotropy in the optical spectral weight should also be large. However, in the paramagnetic state above $T_N$, the optical anisotropy should be diminished. Therefore, there should be a strong $T$ dependence on spectral weight change. In this model, the spectral weight change was evaluated to be about 30% at $T_N$. However, our experimental results are not consistent with the theoretical predictions. As shown in figure 1(b), the spectral weight change around $T_N$ is much smaller, i.e. by about 3%. Note that this result did not take into consideration the orbital ordering and its coupling with the spin ordering.

4.1.2. The intra-molecular transition model based on the Frank–Condon process. Another model for the 2 eV absorption peak was proposed by Allen and Perebeinos [6]. They interpreted the intriguing absorption feature in terms of the intra-molecular transition due to the Frank–Condon process between the Jahn–Teller split e$_g$ levels. In this model, the value of $U$ was assumed to be very large, so it suppresses any inter-site hopping of the e$_g$ electrons. Instead, they considered the Jahn–Teller type electron–phonon coupling as a candidate which could give rise to a strongly self-trapped exciton. This kind of optical transition has been frequently observed in absorption spectra of numerous molecules [21]. However, it has been considered that this transition should be suppressed in solid, since such an excitation can be easily delocalized in solids.

In the model, it was argued that the Gaussian broadening of the pure electronic transition could occur even in solid when excited states were self-localized by the strong Jahn–Teller electron–lattice coupling. Then, the signature of such effects could be detected in the optical spectra of LaMnO$_3$ [6]. If the excited states are self-localized and can stay in a reasonably long time scale, we can think about vibrational–electronic levels for the excited as well as the ground states. Then the optical transition can occur via the Frank–Condon process, since the electronic transition can take place so rapidly that the nuclei do not move significantly during the transition [21]. Between numerous vibrational–electronic levels in the ground and the excited states, the
optical transition can occur, which can be determined by the overlap integral between the initial and the final states. Due to the involvement with numerous vibrational–electronic levels, the absorption peak could be broad and positioned around a frequency which is larger by about four times than the Jahn–Teller stabilization energy. With the experimentally measured value (i.e. about 0.5 eV) of the Jahn–Teller stabilization energy [22], the broad 2 eV peak could be explained.

Unfortunately, this model cannot provide a reasonable explanation of the \( T \) dependence of our experimental data. In this model, the \( T \) dependence of the spectra should come from the population changes in the vibrational states of the electronic ground state. At a given \( T \), its population changes will be determined by the Maxwell–Boltzman statistics. Since the Jahn–Teller phonon frequency, \( \omega_{JT} \), of the LaMnO\(_3\) is around 80 meV. At room temperature, \( \omega_{JT} / k_B T \approx 3.2 \) and the Boltzman factor \( \exp(-\omega_{JT} / k_B T) \) for room temperature is about 0.041, which is too small to explain the size of the observed spectral weight change in figure 1(b). Actually, the calculated spectra, i.e. in figure 2 of [6], showed little \( T \) dependence between the 0 and the 300 K spectra. In addition, the theory predicted the decrease in the spectral weight at the low \( T \), which is opposite to the observed spectral weight change. Furthermore, this model cannot explain the reason why the spectral weight change occurs rather abruptly near \( T_N \).

Let us also discuss on the \( r_{R} \)-dependent spectral weight change, observed in figure 2. According to a neutron scattering experiment result, as \( r_{R} \) decreases, the lattice distortion increases, which means that the distortion of the oxygen octahedra becomes stronger [20]. Within the intra-molecular transition model, as distortion of the oxygen octahedra becomes stronger, the Jahn–Teller gap should be larger. This increase in the Jahn–Teller gap makes the equilibrium position difference between the ground and the excited states larger. Then, the overlap between the initial and the final vibrational wavefunctions becomes reduced, resulting in the decrease in the spectral weight. Therefore, the observed spectral weight suppression could be understood. However, the increase in the equilibrium position should make the optical transition frequency larger, which is opposite to our experimental observations.

4.2. Explanations of the 2.0 eV peak based on the orbitally degenerate Hubbard model (ODHM)

The single-band Hubbard model has been commonly used as a starting point to explain optical properties of transition metal oxides [23]. According to this model, the transition between the lower and the upper Hubbard bands, called the correlation-induced peak, can occur. However, as we demonstrated recently, this model cannot explain multiple structures and/or broad spectral features, experimentally observed in the correlation-induced peaks of numerous transition metal oxides [24]–[26]. To overcome these shortcomings and to take account of the effects of the orbital degeneracy, we introduced the optical transitions in the ODHM [24]–[26]. It was demonstrated that the correlation-induced peak could occur at different frequencies depending on spin or orbital correlations between nearest-neighbour metal ions [24]–[26].

Let us look into the possibility that the 2 eV peak might come from the inter-atomic transition (i.e., \( d^4 + d^4 \rightarrow d^3 + d^5 \)). Several kinds of inter-atomic transitions can occur depending on the nearest-neighbour spin/orbital configurations [24, 25]. On the basis of ODHM picture, four distinct spin/orbital configurations for the neighbouring Mn e\(_g\) electrons can be considered. Figures 3(a)–(d) show possible inter-site transitions in each configuration schematically. When the same (different) e\(_g\) orbitals are occupied between the nearest-neighbour electrons, we call
it ferro- (antiferro-)orbital ordering, which will be abbreviated as FO (AFO). Since the overlap integral between the $x^2 - y^2$ orbital of one Mn site and the $3z^2 - r^2$ of the other neighbouring Mn site is negligible, the optical transition between these orbitals should not be allowed, which will work as a kind of a selection rule for the inter-atomic transitions between the neighbouring sites. As shown in figure 3(a), for the FM/FO configuration, all the inter-atomic transitions are forbidden either by the Pauli exclusion principle or by the selection rule. As shown in figure 3(b), for the FM/AFO configuration, the $e_g$ electron can hop into the other site with the energy cost of $U_{\text{eff}} - 3J_H$, where $U_{\text{eff}}$ is the effective on-site Coulomb repulsion energy in the same orbital. The group theory shows that the excited state (i.e. two electrons with the same spin on one site) has the $6A_1$ symmetry [27]. As shown in figure 3(c), for the AFM/FO configuration, there will be two kinds of excited states, i.e. the $4E_\epsilon$ and the $4A_2$ symmetries, whose corresponding energy costs are $U_{\text{eff}} + 8/3J_H$ and $U_{\text{eff}} + 16/3J_H$, respectively. Finally, as shown in figure 3(d), for the AFM/AFO configuration, there will be two kinds of excited states, i.e. the $4A_1$ and the $4E_\theta$ symmetries, whose corresponding energy costs are $U_{\text{eff}} + 2J_H$ and $U_{\text{eff}} + 8/3J_H$, respectively. In this picture, the 2 eV peak can be assigned to the inter-atomic transition with the smallest energy cost, i.e. of $U_{\text{eff}} - 3J_H$. Namely, this corresponds to the optical transition in the FM/AFO configuration [27, 28].

Numerous features of the 2 eV absorption can be explained in terms of the correlation peak in the FM/AFO configuration. Firstly, this assignment agrees with the values of $U_{\text{eff}}$ and $J_H$, measured by other experimental techniques. Using the energy values of $U_{\text{eff}} = 5.5$ eV and $J_H = 0.8$ eV [29], the $U_{\text{eff}} - 3J_H$ peak should be located around 2.5 eV. In addition, from a photoemission and x-ray absorption spectroscopy, the energy separations between the one electron removal ($N \rightarrow N - 1$) and addition ($N \rightarrow N + 1$) excitation peak of LaMnO$_3$ was estimated to be around 3.5 eV [30]. Note that an optical transition results in an electron–hole
pair, which is called the exciton effect. This effect usually lowers the experimental optical transition frequency than the required energy cost by the exciton binding energy. Considering this exciton effect, it is reasonable that the 2 eV peak should be originated from the $U_{\text{eff}} - 3J_H$ peak.

Secondly, the FM/AFO configuration, where the 2 eV peak should occur, does agree with the ground state of LaMnO$_3$, which has the A-type ordering. In this ordering state, the $e_g$ orbitals have the long-range ordering where the $3x^2 - r^2$ and the $3y^2 - r^2$ orbitals are alternately occupied in the $ab$-plane. Once the $3x^2 - r^2$ orbital of a Mn site is occupied, then the $x^2 - z^2$ orbital of the nearest-neighbour site should be empty. The overlap between these orbitals are quite large. Therefore, the correlation peak between the neighbouring Mn electrons with the FM/AFO configuration should have large weight within the $ab$-plane.

Thirdly, the inter-atomic transition for the FM/AFO configuration should result in a strong optical anisotropy. Along the $c$-axis, the spins are antiferromagnetically ordered and the overlap between the $e_g$ orbitals should be quite small. Therefore, the correlation peak between the neighbouring Mn electrons with the FM/AFO configurations should have little spectral weight along the $c$-axis. This simple prediction based on the spin and the orbital configurations does agree with the experimental fact that there should be little spectral weight of 2 eV peak along the $c$-axis of a LaMnO$_3$ single crystal [7].

Fourthly, the $T$-dependent spectral weight changes could be explained in terms of the $T$-dependent changes of the spin and orbital correlations between the neighbouring Mn electrons with the FM/AFO configuration. As shown in figure 1(b), around 120 K, the spectral weight shows a distinct suppression, as $T$ increases. This change should be related to the A-type antiferromagnetic ordering transition, which occurs at $T_N = 140$ K. Another important point of figure 1(b) is that, in spite of the suppression around $T_N$, most of the spectral weights still remain above $T_N$ and become slowly decreasing as $T$ increases. Above $T_N$, the long-range antiferromagnetic spin ordering along the $c$-axis should disappear. However, within the $ab$-plane, the long-range orbital ordering of LaMnO$_3$ can survive up to 800 K [7]. Since the spins are strongly coupled to orbital ordering, it is highly probable that the short-range spin ordering can survive within the $ab$-plane much above $T_N$, which will provide the 2 eV peak.

Finally, $r_R$-dependent change of the 2 eV peak could be explained in terms of the correlation peak between the neighbouring Mn electrons. As shown in figure 2, the spectral weight of the 2 eV peak in NdMnO$_3$ is smaller than that of LaMnO$_3$. The peak energy, however, remains almost the same. According to the ODHM picture, the peak energy corresponds to $U_{\text{eff}} - 3J_H$. It is natural to consider that both $U_{\text{eff}}$ and $J_H$ cannot be changed with the different rare-earth ion substitution. The little difference in the peak energies for NdMnO$_3$ and LaMnO$_3$ can be explained. In addition, the substitution of Nd ions will cause the reduction in the hopping integral by reducing the Mn–O–Mn bond angle and bond distance. The decrease in the hopping integral will cause the suppression of the spectral weight, observed in figure 2.

4.3. Comparison with the resonant inelastic x-ray scattering (RIXS) data

Recently, Inami et al [8] performed RIXS experiments and reported that there are three peaks located around 2.5, 8.0 and 11.0 eV. They claimed that the low lying peak, i.e., the 2.5 eV peak, should come from the transition from the lower Hubbard band to the upper Hubbard band. They claimed that the electron correlation effect should play an important role in the low-energy excitation of LaMnO$_3$. 

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To explain these experimental data, Kondo et al. provided a theoretical framework, based on the ODHM, to investigate the charge and orbital excitations in LaMnO$_3$ [31]. To get the theoretical RIXS spectra, they counted the individual charge and orbital excitations caused by the electron transitions from occupied to unoccupied electronic states across the Mott gap, i.e., the electron–hole excitation from the effective lower Hubbard band to the upper Hubbard band. The RIXS spectra were calculated numerically as functions of momentum, polarization and type of the orbital ordered states. From these calculations, they proposed that the correlation peak due to the Coulomb interaction can explain the 2.5 eV peak in the RIXS spectra [31]. Although the microscopic mechanism of RIXS is different from that of optical transition, it can be assumed that the lowest electron excitation might cost nearly the same energies in both RIXS and optical processes. Considering the exciton effect in the optical spectra, the value seems to agree with the observed peak value of 2 eV for the correlated peak in our optical spectra.

### 4.4. The sub-peak structure

As shown in figure 1(a), there are three fine peaks in the 2 eV peak. Up to this point, there has been little effort to understand this sub-peak structure. Although our understanding is still far from complete, there are a few experimental facts which should be considered for complete understanding of these peaks. (i) The sub-peak structures could be observed at room temperature, not below 100 K. The disappearance of the fine peak structure at low $T$ is quite unique. In most of the ordinary fine peak structures, the low $T$ spectra should show sharp features. (ii) The sub-peak features become evident near $T_N$. (iii) The positions for the first, second and third sub-peaks are located around 1.9, 2.3 and 2.6 eV at room temperature. (iv) The $T$ dependences of the sub-peak positions are very weak.

The seemingly natural approach to explain the sub-peak structure is to use the optical transitions in the ODHM, which have different energy costs depending on the spin/orbital configurations. As discussed in section 4.2, it could be argued that, much above $T_N$, the peaks at $U_{\text{eff}} + 2J_H$, $U_{\text{eff}} + 8/3J_H$, and/or $U_{\text{eff}} + 16/3J_H$ might be allowed, resulting in the sub-peak structure. It should be noted that similar multiple structures have been observed in the optical conductivity spectra of other transition metal oxides, such as LaVO$_3$ [26]. In LaVO$_3$, the sub-peaks were assigned to inter-atomic transitions between d orbitals of neighbouring V sites, which were discussed in a similar manner to those in section 4.2. Unfortunately, the value of $J_H$ in manganites is close to 1.0 eV, so this approach cannot explain the sub-peaks, whose separations are about 0.3–0.4 eV.

Let us look at the possibility that these structures could be related to the elementary excitation, the so-called ‘orbiton’, observed in the Raman spectra by Saitoh et al [10]. Note that the $T$ dependence of the sub-peak shifts resembles that of the ‘orbiton’ observed in the Raman spectra. There are also three peaks in the $ab$-plane data of Raman spectra, which are centred at 120, 140 and 160 meV. Interestingly, the frequency and spectral weight of the lowest Raman peak are reported to be sensitive to $T$, while the other two peaks are not so sensitive to the $T$ change up to the room temperature, which are very close to the behaviours of the sub-peaks in figure 1(a). In addition, the Raman scattering also shows a strong resonant behaviour with 2 eV incident laser beam [11]. It is possible that the sub-peaks might be related to the ‘orbiton’; however, we believe that the origin of the controversial Raman feature should be clearly understood first.

It would be also interesting to look at the theoretical RIXS spectra, calculated based on the ODHM by Kondo et al [31]. In the spectra, shown in figure 1 of [31], there are three peaks.
at 5.0\(t\), 6.0\(t\) and 7.5\(t\) at the \(\Gamma\) point, where \(t\) is the hopping integral of an electron used in their calculation. These fine structures come from the momentum dependence of the electron energy band used in their calculation. With \(t \sim 0.35\) eV, the theoretical position seems to be in reasonably good agreement with the experimentally observed sub-peak positions. Further investigations are highly desirable to find the origin of the sub-peak structures in the ODHM.

5. Summary

In summary, a possible mechanism to explain the 2 eV peak of LaMnO\(_3\) was suggested. It was found that the combination of the orbital degeneracy and the correlation effects can provide reasonable explanations on the peak energy, temperature-dependent spectral weight changes and rare-earth ion substitution-dependent spectral weight changes. By applying the orbitally degenerate Hubbard model, it was shown that the 2 eV peak could be originated from the inter-atomic transition in the A-type spin/orbital ordering. In addition, the fine structure of the 2 eV peak was observed and discussed with a few possible scenarios.

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References

[1] Arima T, Tokura Y and Torrance J B 1993 Phys. Rev. B 48 17006
Arima T and Tokura Y 1995 J. Phys. Soc. Japan 64 2488
[2] Jung J H, Kim K H, Eom D J, Noh T W, Choi E J, Yu Jaejun, Kwon Y S and Chung Y 1997 Phys. Rev. B 55 15489
Jung J H, Kim K H, Noh T W, Choi E J and Yu Jaejun 1998 Phys. Rev. B 57 11043
[3] Solovyev I, Hamada N and Terakura K 1996 Phys. Rev. B 53 7158
[4] Ahn K H and Millis A J 2000 Phys. Rev. B 61 13545
[5] Quijada M A, Simpson J R, Vasiliu-Doloc L, Lynn J W, Drew H D, Mukovskii Y M and Karabashev S G 2001 Phys. Rev. B 64 224426
[6] Allen P B and Perpeinos V V 1999 Phys. Rev. Lett. 83 4828
[7] Tobe K, Kimura T, Okimoto Y and Tokura Y 2001 Phys. Rev. B 64 184421
[8] Inami T et al 2003 Phys. Rev. B 67 045108
[9] Kovaleva N N, Boris A V, Bernhard C, Kulakov A, Pimenov A, Balbashov A M, Khaliullin G and Keimer B 2004 Phys. Rev. Lett. at press
[10] Saitoh E, Okamoto S, Takahashi K T, Tobe K, Yamamoto K, Kimura T, Ishihara S, Maekawa S and Tokura Y 2001 Nature 410 180
[11] Krüger R, Schulz B, Naler S, Rauer R, Budelmann D, Bäckström J, Kim K H, Cheong S-W, Perebeinos V and Rübhausen M 2004 Phys. Rev. Lett. 92 97203
[12] Grüninger M, Rückamp R, Windt M, Reutler P, Zobel C, Lorenz T, Freimuth A and Revcolevschi A 2002 Nature 418 39

New Journal of Physics 6 (2004) 156 (http://www.njp.org/)
[13] Saitoh E, Okamoto S, Tobe K, Yamamoto K, Kimura T, Ishihara S, Maekawa S and Tokura Y 2002 Nature 418 40
[14] Martin-Carron L and Andres A 2004 Phys. Rev. Lett. 92 175501
[15] Murugavel P, Lee J H, Yoon J-G, Noh T W, Chung J-S, Heu M and Yoon S 2003 Appl. Phys. Lett. 82 1908
[16] Parashar S et al to be published
[17] Konishi Y, Fang Z, Izumi M, Manako T, Kasai M, Kuwahara H, Kawasaki M, Terakura K and Tokura Y 1999 J. Phys. Soc. Japan 68 3790
[18] Okimoto Y, Konishi Y, Izumi M, Manako T, Kawasaki M and Tokura Y 2002 J. Phys. Soc. Japan 71 613
[19] Kimura T, Ishihara S, Shintani H, Arima T, Takahashi K T, Ishizaka K and Tokura Y 2003 Phys. Rev. B 68 60403
[20] Alonso J A, Martinez-Lopez M J, Casais M T and Fernandez-Diaz M T 2000 Inorg. Chem. 39 917
[21] Fox M 2001 Optical Properties of Solids (Oxford: Oxford University Press)
[22] Kaplan M D and Vekhter B G 1995 Cooperative Phenomena in Jahn–Teller Crystals (New York: Plenum)
[23] Cooper S L 2001 Struct. Bond. 98 161
[24] Lee J S, Lee Y S, Noh T W, Oh S-J, Yu J, Fukazawa H and Maeno Y 2002 Phys. Rev. Lett. 89 257402
[25] Kim M W, Lee Y S, Noh T W, Yu J and Moritomo Y 2004 Phys. Rev. Lett. 92 27202
[26] Miyasaka S, Okimoto Y and Tokura Y 2002 J. Phys. Soc. Japan 71 2086
[27] Feiner L F and Oles A M 1999 Phys. Rev. B 59 3259
[28] Lee J S et al to be published
[29] Mizokawa T and Fujimori A 1996 Phys. Rev. B 54 5368 and references therein
[30] Park J-H, Chen C T, Cheong S-W, Bao W, Meigs G, Chakarian V and Idzerda Y U 1996 Phys. Rev. Lett. 76 4215
[31] Kondo H, Ishihara S and Maekawa S 2001 Phys. Rev. B 64 014414