Spin/Orbital Pattern-Dependent Polaron Absorption in Nd$_{1-x}$Sr$_x$MnO$_3$

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(October 29, 2018)

We investigated optical properties of Nd$_{1-x}$Sr$_x$MnO$_3$ ($x = 0.40, 0.50, 0.55,$ and $0.65$) single crystals. In the spin/orbital disordered state, their conductivity spectra look quite similar, and the strength of the mid-infrared absorption peak is proportional to $x(1-x)$ consistent with the polaron picture. As temperature lowers, the Nd$_{1-x}$Sr$_x$MnO$_3$ samples enter into various spin/orbital ordered states, whose optical responses are quite different. These optical responses can be explained by the spin/orbital ordering pattern-dependent polaron hopping.

PACS number: 75.30.-m, 78.30.-j, 72.80.Ga, 71.38.+i

Recently, lots of attention has been paid to the roles of orbital degree of freedom in the physical properties of manganites. Resonant x-ray scattering of a layered manganite provided evidences of orbital ordering [1]. Polaronic microscopy images demonstrated the existence of optical anisotropy [2], which might be due to the orbital ordering. A new elementary excitation caused by symmetry breaking of orbital ordering, called ‘orbiton’, was proposed and claimed to be observed in LaMnO$_3$ by Raman spectroscopy measurements [3]. Since the corresponding Raman peaks were observed in the energy region of a few tenth of eV, similar excitations could be observed by infrared spectroscopy.

Indeed, an anomalous incoherent absorption peak has been observed in the mid-infrared (IR) region for numerous manganites [4-9]. However, the origin of this mid-IR absorption peak is not fully understood yet. In one scenario, it was suggested that the mid-IR absorption should be due to orbital excitations [10]. Even though the observed anisotropy might be explained by this model, there have been few experimental reports to compare with the theoretical predictions even on a qualitative level [11]. In the other scenario, it has been suggested that the mid-IR absorption should arise from hopping of the Jahn-Teller (JT) polaron [7-9]. The polaron binding energy obtained from the mid-IR peak position agrees quite similar and can be explained within the JT polaron picture. At low $T$, by taking account of the effects of the S/O ordering pattern on the polaron hopping motion, the anisotropy in $\sigma(\omega)$ for the single-domain sample can be explained quite well. This S/O pattern-dependent hopping model was successfully extended to quantitatively explain the reflectivity spectra $\mathcal{R}(\omega)$ of other NSMO multi-domain crystals. This clearly demonstrates that the polaron scenario is indeed valid, and that the polaron hopping motion should be strongly affected by the S/O ordering patterns.

The NSMO single crystals were grown by the floating zone method [12]. After polishing and proper annealing, $\mathcal{R}(\omega)$ were measured by near normal incident unpolarized light over a wide photon energy region $5$ meV–$30$ eV. For the single-domain $x=0.55$ crystal, the crystal axes were determined using the neutron scattering measurement [13]. Using polarized light, we obtained $\mathcal{R}(\omega)$ for the $ab$-plane, i.e. $R_{ab}(\omega)$, and for the $c$-axis, i.e. $R_c(\omega)$. Details of the optical measurements were described in Ref. [14].

Figure 1(a) shows $\mathcal{R}(\omega)$ for NSMO multi-domain single crystals at room $T$. Note that all the samples are insulators with disordered S/O states at room $T$. Clearly, $\mathcal{R}(\omega)$ are similar for all the samples despite the different hole concentrations. On the other hand, Fig. 1(b) shows $\mathcal{R}(\omega)$ for the NSMO multi-domain samples at low $T$. $\mathcal{R}(\omega)$ show quite different characteristics for the samples with different doping level $x$. For the $x=0.40$
(i.e., F-type ordered) sample, $R(\omega)$ increases significantly below 1.2 eV and approach 1.0 in the $dc$ limit, showing metallic behavior [1]. For the $x=0.50$ (i.e., CE-type ordered) sample, $R(\omega)$ shows an insulator-like behavior with rather strong suppression below 0.2 eV. For the $x=0.55$ (i.e., A-type ordered) sample, $R(\omega)$ keeps increasing and approaches to about 0.6 as $\omega$ decreases. Finally, for the $x=0.65$ (i.e., C-type ordered) sample, $R(\omega)$ shows an insulating behavior. Such large differences in $R(\omega)$ at low $T$ are not easily understood by keeping in consideration of the similarity in $R(\omega)$ at room $T$ and the small differences in $x$. It is quite apparent that S/O ordering patterns could be playing an important role in optical properties of NSMO.

We have obtained $\sigma(\omega)$ using the Kramers-Kronig (KK) analysis of $R(\omega)$ at room $T$. Since the optical anisotropy in these disordered S/O states is expected to be small, the KK analysis can be applied at room $T$ even for the multi-domain crystals. As shown in Fig. 2(a), $\sigma(\omega)$ are quite similar for all the samples. In order to compare the polaron and the orbital excitation scenarios, we should obtain terms related to the coherent and the incoherent motions of free carriers from $\sigma(\omega)$.

In the perovskite manganites, there are numerous optical transitions. As shown in Fig. 2(b) for the $x=0.55$ sample, the room temperature $\sigma(\omega)$ below 4.0 eV was fitted with four peaks represented by the dotted lines. The first peak (Peak I) was due to either polaron hopping motions [1] [12] or orbital excitations [1]. The second peak (Peak II) located around 1.5 eV was suggested to be due to the transition between JT split $eg$ bands [17]. [A Monte Carlo simulation using a Hamiltonian with the double exchange and JT interactions also clearly predicted the existence of Peaks I and II [12].] The third peak (Peak III) was suggested to be due to a transition between the Hund’s rule exchange ($J \sim 2$ eV) split bands [18]. Finally, the fourth peak (Peak IV) was proposed to be due to the charge transfer transition between the O 2$p$ and Mn 3$d$ levels [17]. Note that the position of each peak are quite consistent with the results of other measurements [1], and the validity of those peaks has been suggested by many groups [1] [12] [20] and such analyses have already been performed quite successfully to explain the optical responses of (Bi,Ca)MnO$_3$ [1], Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ [17], and (La,Ca)MnO$_3$ [17].

In the polaron scenario, Peak I should be due to the JT polaron hopping motion. Since it can be considered as the interatomic transition from the JT distorted Mn$^{3+}$[$x$ ions per unit volume] to Mn$^{4+}$[(1-$x$) ions per unit volume], it should be proportional to $x(1-x)$. The inset in Fig. 2(a) shows the $x$-dependent strength of Peak I ($S_I$). The dotted line in the inset shows, within our fitting error bars, that the $x$-dependence of $S_I$ is well fitted with $x(1-x)$. A similar behavior was also observed in (La,Ca)MnO$_3$ [17], supporting the agreement with the polaron scenario. However, as far as we know, the $x$-dependence of Peak I in the orbital scenario, i.e., the incoherent motion of free carriers due to orbital excitations, has not been predicted yet.

To obtain further insights, we have investigated $\sigma(\omega)$ for the $x=0.55$ single-domain crystal at low $T$ in the A-type S/O ordered state. The open triangles in Figs. 3(a) and 3(b) show $\sigma(\omega)$ along the $c$-axis, $\sigma_c(\omega)$, and in the $ab$-plane, $\sigma_{ab}(\omega)$, respectively. Clearly, there exists a rather strong anisotropy of $\sigma(\omega)$ below 1.5 eV. The solid lines show the fitting curves based on the above-mentioned mode assignments. As shown in the dotted lines, the strengths of Peaks II and IV were assumed to be $T$-independent, and the strength of Peak III were assumed to be nearly zero. Since Peaks II and IV are due to the interband transitions between JT split $eg$ bands and the charge transfer transition between the O 2$p$ and Mn 3$d$ bands, respectively, they should be nearly $T$-independent. And, since Peak III is due to a transition between the Hund’s rule exchange ($J \sim 2$ eV) split bands [18], it should vanish in the spin ordered states. On the other hand, the strength of Peak I is suppressed along the $c$-axis but increases in the $ab$-plane. The enhancement factor of Peak I in the A-type S/O ordered state along the $c$-axis, $\eta_A^c$, was estimated to be about 0.4, and in the $ab$-plane, $\eta_A^{ab}$, about 1.8. The difference between $\eta_A^c$ and $\eta_A^{ab}$ for Peak I can explain the reported optical anisotropy in the S/O ordered state. It is important to note that all the parameters, except the enhancement factors, are fixed in the fitting process: namely, the solid lines in Figs. 3(a) and 3(b) are the results of single parameter fittings, keeping all other parameters the same as in the room temperature $\sigma(\omega)$ fitting.

How can we explain the difference between $\eta_A^c$ and $\eta_A^{ab}$? Recently, $\sigma(\omega)$ for the planar orbital ordered phase of the $eg$ electron with $x^2-y^2$ symmetry (the A-type orbital ordered state) were calculated based on the orbital excitation scenario [10]. This 2-dimensional model predicted that the spectral weight of the incoherent absorption, $S_I$, should decrease with decreasing $T$. On the other hand, that of the coherent absorption, corresponding to the Drude peak, should increase. Contrary to the predictions, the experimental value of $\eta_A^{ab}$ becomes larger than 1.0. Moreover, Fig. 3(b) does not show any significant Drude-like absorption term. [Note that the value of $\sigma_{ab}(\omega)$ at the $dc$ limit in Fig. 3(b) was estimated at around $2 \times 10^2 \Omega^{-1}cm^{-1}$, which is consistent with the transport experiment value on a single-domain crystal [13]]. Therefore, the model based on the orbital excitation scenario cannot explain our experimental data.

As far as we know, there are no explicit predictions on how the S/O ordering pattern will affect the polaron absorption. However, as shown in Fig. 3(c), it is quite clear that the polaron hopping motion along the $c$-axis should be suppressed since the antiparallel spin alignment in the A-type S/O ordered state will cause a large energy cost of $J$. Due to the $x^2-y^2$ $eg$ orbital ordering within the
In the spin/orbital pattern dependent polaron (SOPDP) model, the changes in \( S_I \) in the S/O ordered state should be calculated by considering the orbital contributions in the conventional polaron models, which usually include the double exchange and the JT polaron terms. However, this calculation might be quite difficult. In this paper, we made simple and crude estimations of the enhancement factors using the matrix element terms in the dipole transition. First, we considered the JT polaron absorption as a transition from a lower \( e_g \) level of a JT distorted Mn\(^{3+}\) site to one of doubly degenerate \( e_g \) levels of Mn\(^{4+}\) sites. Second, for the \( A \)-type ordered state, we evaluated the sum of possible dipole matrix elements considering the neighboring S/O configurations. For the Mn 3d \( e_g \) and the O 2p orbital wave functions, we used the wave functions of isolated ions located at corresponding sites. Third, for the disordered state, we evaluated the sum of possible dipole matrix elements, assuming that there is no preference of S/O for the initial state. Finally, we divided the summed values to obtain enhancement factors of \( S_I \) in the ordered state. Details of this estimation procedure will be published elsewhere \(^{[21]} \). We found that \( \eta_A^\circ \sim 0.7 \) and \( \eta_A^{ab} \sim 1.7 \). The estimated value of \( \eta_A^{ab} \) agrees quite well with the experimental value, suggesting the validity of the SOPDP model. The suppression of \( S_I \) along the \( c \)-axis can be explained at least qualitatively. However, the difference between the experimental and the estimated values of \( \eta_A^\circ \) might be due to the experimental errors and/or the over-simplification of our estimation.

For the other multi-domain single crystal samples, the polarized optical microscope images showed that they consist of multi-domains whose typical size is a little larger than 10 \( \mu m \). Thus, the KK analysis based on \( R(\omega) \) for multi-domain crystals may lead to errors in the positions and strengths of Peaks I and II \(^{[2]} \). To avoid such errors, we decided to analyze our \( R(\omega) \) directly. The optical responses of inhomogeneous media have been investigated extensively. In the long wavelength limit, where the wavelength \( \lambda \) of the incoming light is larger than the domain size \( L \), the medium should look homogeneous with an effective conductivity \(^{[22]} \). On the other hand, if \( \lambda < L \), the light will see the responses of individual domains, so we will obtain averaged optical responses. If the \( c \)-axes of the domains are randomly oriented along any one of the crystallographic axes, the measured \( R(\omega) \) is given by \( \frac{2}{3} R_{ab}(\omega) + \frac{1}{4} R_c(\omega) \).

To test the above argument, we have calculated \( R(\omega) \) for the multi-domain case of \( A \)-type (i.e., \( z=0.55 \)) ordering, whose polarization-dependent \( \sigma(\omega) \) were obtained experimentally. As mentioned above, the predictions of the SOPDP model are quite well matching to the real \( \sigma(\omega) \) of a single-domain crystal. From \( \sigma_{ab}(\omega) \) and \( \sigma_c(\omega) \) of the SOPDP model, as shown in Figs. 3(a) and 3(b) (solid lines), respectively, corresponding reflectance spectra for given polarization directions were obtained. Using the predicted \( R_{ab}(\omega) \) and \( R_c(\omega) \), \( R(\omega) \) were evaluated and is shown as the open triangles in Fig. 1(b). The excellent agreement between the experimental data and the SOPDP model predictions suggests that the method of obtaining the \( R(\omega) \) for a multi-domain sample using the SOPDP model is accurate for \( \lambda < L \sim 10 \mu m \).

For the \( F \)-type (i.e., \( x=0.40 \)) sample, which has isotropic S/O structure even at low \( T \), the enhancement of the mid-IR region and the metallic behavior can be explained well with the existing JT polaron model, which considers the JT distortion and double exchange interaction, as observed in La0.7Ca0.3MnO\(_3\). \(^{[6]} \) For other multi-domain samples, similar analyses based on the SOPDP model were also performed \(^{[2]} \). For the \( C \)-type ordered (i.e., \( x=0.65 \)) sample, \( \eta_C^\circ \sim 2.9 \) and \( \eta_C^{ab} \sim 0 \) can provide a good description to our experimental data. [Here we used the same method with \( \eta_A \) using \( 3z^2-r^2 \) orbital for the initial state instead of \( x^2-y^2 \) at low \( T \).] For the \( CE \)-type (i.e., \( x=0.50 \)) sample, this approach can provide a reasonable fit to the experimental \( R(\omega) \) when Peak I becomes asymmetric \(^{[2]} \). It might be due to the opening of the charge gap at the low frequency region in the S/O ordered state. As shown in Fig. 1(b), most experimental \( R(\omega) \) can be explained by the theoretical predictions using the SOPDP model with a single fitting parameter \( (\eta \circ) \). The good agreements suggest that the optical response observed in various spin/orbital ordered states of NSMO can be explained quite well within the SOPDP model.

In conclusion, we have presented the temperature-dependent spectral weight changes of Nd\(_{1-x}\)Sr\(_x\)MnO\(_3\) single crystals, which strongly depend on the pattern of the spin/orbital ordering at low temperature. These optical responses can be described quantitatively by taking account of spin/orbital pattern-dependent polaron hopping.

This work was financially supported by the Ministry of Science and Technology through the Creative Research Initiative Program. The work by Y.M. was supported by a Grant-In-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture, and from PRESTO, JST. KHK is also supported by the BK-21 Project of the Ministry of Education.

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FIG. 1. $R(\omega)$ of NSMO at (a) 300 K and (b) 15 K. In (b), solid circles, solid squares, open triangles, and open circles are the predictions of the SOPDP model for $x = 0.40, 0.50, 0.55$, and 0.65, respectively.

FIG. 2. (a) $\sigma(\omega)$ of NSMO at room $T$. The inset shows $x$-dependent $S_I$. The solid circles represent data from this study, and the open circle is from the published data by Lee et al. The dotted line in the inset represents the functional form of $x(1-x)$. (b) $\sigma(\omega)$ of NSMO ($x = 0.55$) at room $T$ (solid circles), where the solid line and dotted lines represent the fitting curves.
FIG. 3. The experimental (open triangle) and SOPDP model-predicted $\sigma(\omega)$ (solid line) of NSMO ($x=0.55$) at low $T$ for (a) the $ab$-plane and (b) the $c$-axis. (c) Schematic representation of the SOPDP model in the $A$-type ordered state.