Temperature dependence of optical conductivity in double-exchange ferromagnet $La_{1-x}Sr_xMnO_3$

Paulo Eduardo de Brito* and Hiroyuki Shiba
Department of Physics, Tokyo Institute of Technology, Oh-Okayama, Tokyo 152, Japan
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The optical absorption observed in ferromagnetic metal $La_{1-x}Sr_xMnO_3$ shows a strong temperature dependence. Assuming that the temperature dependence comes mainly from the spontaneous magnetization, we study theoretically how the optical conductivity is affected by the decrease of spontaneous magnetization. The coherent-potential approximation is used to describe the effect of t_{2g} spin disorder on the optical conductivity, which consists of intraband and interband transitions within e_g bands. The result explains well some important features of the experimental data. [S0163-1829(98)04503-2]

I. INTRODUCTION

The discovery of high-T_c superconducting oxides has led researchers to reinvestigate a wide class of oxides, in which magnetism and conduction are coupled. The $3d$ transition-metal oxides of perovskite type are such materials. Various combinations have been studied extensively: $R_{1-x}A_xMO_3$ where $R=$ La, Pr, Nd, Sm (a rare-earth element), $A=$ Ca, Sr, Ba (a divalent alkaline earth), and $M=$ Sc to Cu (a transition metal with an incomplete $3d$ shell). Some of the materials listed above exhibit colossal magnetoresistance when carriers are doped. This problem has attracted much interest not only from the viewpoint of strongly correlated systems, but also from its potential application.

$La_{1-x}Sr_xMnO_3$ is a typical material in this group. It is believed that the ferromagnetic metallic state in these compounds is stabilized mainly by the double-exchange mechanism.[1–3] This originates from the strong Hund coupling between the charge carriers and local spins which are both dominantly of the $3d$ orbital character.

Recently, measurements of the optical conductivity of $La_{1-x}Sr_xMnO_3$($x=0.175$ and 0.3) (Ref. 4) have shown that the excitations are present in a wide energy range from ~ 0.02 to ~ 1 eV, whose intensity increases with the decrease of temperature and appears to be finite even at zero temperature. This absorption is sometimes called ''incoherent absorption,'' whose origin has been a matter of controversy among researchers.[5,6]

In a recent paper,[5] it was shown that the anomalous optical absorption ranging from ~ 0.02 to ~ 1 eV, which is present even at $T=0$ K, is presumably related to the interband transition within e_g bands. By using the simplest tight-binding model for Mn e_g electrons on the cubic lattice, it has been found that the optical absorption consists of intraband (i.e., Drude) and interband contributions. The latter contribution ranges continuously from 0 to the e_g-band-width. The interband transitions become allowed due to the orbital dependence of the transfer integral, which one naturally expects from the overlap of Mn e_g and O p wave functions.[7]

As a continuation of Ref. 5, in this work we examine the temperature dependence of the optical absorption due to the intraband and interband transtions within e_g orbitals. Experimentally a drastic and characteristic change is observed in the spectrum when the temperature is raised from the $T=0$ ferromagnetic phase to the paramagnetic phase above the Curie temperature. It is noteworthy that the absorption in the range $\omega=0.2-1$ eV decreases with the increase of temperature. The temperature dependence of optical conductivity was already studied by Furukawa,[8] who could correctly reproduce the spectral weight transfer to high-energy region as the temperature is raised. However, the temperature dependence of the optical conductivity below ~ 1 eV was just opposite to what the experimental results show. As shown in Ref. 5, the orbital degeneracy in e_g orbitals, which Furukawa ignored, is actually very important for the energy region below 2 eV. Therefore, taking properly into account the orbital degeneracy and assuming that the main source of the temperature dependence is the magnetization of t_{2g} electrons which are Hund coupled with e_g electrons, we examine in this paper the temperature dependence of the optical spectrum. For simplicity we treat the disorder of t_{2g} spins by using the coherent-potential approximation,[9] which captures the essence of Furukawa's dynamical mean-field treatment.[8] The result shows that the interband absorption is strongly temperature dependent, consistent with the experiment. The total optical conductivity for $2e_g$ orbitals is much different from that for the single-orbital case, particularly in the energy region where the interband transitions are important.

II. MODEL AND METHOD

We use the simplest Hamiltonian for e_g electrons,

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_K, \tag{1}$$

where $\mathcal{H}_0$ is the tight-binding model to describe the electrons in the e_g orbitals:

$$\mathcal{H}_0=\sum_{\substack{\langle ij\rangle\sigma\\ \gamma\gamma'}} t_{ij}^{\gamma\gamma'}(c_{i\gamma\sigma}^{\dagger}c_{i\gamma'\sigma}+\text{H.c.}). \tag{2}$$

The operator $c_{i\gamma\sigma}^{\dagger}$ creates an electron with spin $\sigma(=\uparrow,\downarrow)$ in the orbital γ at site i. The transfer integral $t_{ij}^{\gamma\gamma'}$ depends sensitively on the orbitals, since the overlap integral between the Mn $3d$ and O $2p$ orbitals is involved.[7] If $3z^2-r^2$ and x^2-y^2 orbitals are used for two e_g orbitals, we obtain

$$t_{ij}^{\gamma\gamma'} = -t\begin{pmatrix} \frac{1}{4} & -\frac{\sqrt{3}}{4} \\ -\frac{\sqrt{3}}{4} & \frac{3}{4} \end{pmatrix}, \quad -t\begin{pmatrix} \frac{1}{4} & \frac{\sqrt{3}}{4} \\ \frac{\sqrt{3}}{4} & \frac{3}{4} \end{pmatrix}, \quad -t\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \tag{3}$$

for $\vec{r}_j = \vec{r}_i \pm \hat{x}$, $\vec{r}_j = \vec{r}_i \pm \hat{y}$, $\vec{r}_j = \vec{r}_i \pm \hat{z}$, respectively. Here $\hat{x}$, $\hat{y}$, and $\hat{z}$ are the nearest-neighbor distances along x, y, and z directions, respectively.

The second term in Eq. (1) is the Hund coupling of e_g electrons with localized t_{2g} electrons,

$$\mathcal{H}_K = -J\sum_i \vec{S}_i^{t_{2g}} \cdot \vec{s}_i, \tag{4}$$

where $\vec{S}_i^{t_{2g}}$ is the localized spin and $\vec{s}_i$ is the spin of itinerant e_g electron. In this paper, we approximate $\vec{S}^{t_{2g}}$ by an Ising spin for simplicity:

$$\mathcal{H}_K = -J\sum_{i\sigma} S_i \sigma n_{i\sigma}. \tag{5}$$

The electron-electron interaction within the e_g orbitals is ignored here; its possible effect will be discussed later.

In the momentum representation $\mathcal{H}_0$ is expressed as

$$\mathcal{H}_0 = \sum_{\substack{\vec{k}\sigma \\ \gamma\gamma'}} \varepsilon_{\gamma\gamma'}(\vec{k})(c^\dagger_{\vec{k}\gamma\sigma} c_{\vec{k}\gamma'\sigma} + \text{H.c.}), \tag{6}$$

where $\varepsilon_{\gamma\gamma'}(\vec{k})$ is the Fourier transform of $t_{ij}^{\gamma\gamma'}$:

$$\varepsilon_{\gamma\gamma'}(\vec{k}) = \varepsilon_0 \delta_{\gamma\gamma'} + \varepsilon_1 \tau^z_{\gamma\gamma'} + \varepsilon_2 \tau^x_{\gamma\gamma'}. \tag{7}$$

Here τ^z and τ^x are Pauli matrices in the orbital subspace,

$$\tau^z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \tau^x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

$\varepsilon_0(\vec{k})$, $\varepsilon_1(\vec{k})$, and $\varepsilon_2(\vec{k})$ are given by

$$\varepsilon_0 = t(\cos k_x + \cos k_y + \cos k_z), \tag{8}$$

$$\varepsilon_1 = \tfrac{1}{2} t(\cos k_x + \cos k_y - 2\cos k_z), \tag{9}$$

$$\varepsilon_2 = -\frac{\sqrt{3}}{2} t(\cos k_x - \cos k_y). \tag{10}$$

The lattice constant a as well as $\hbar$ is taken to be unity.

The ferromagnetic metal $La_{1-x}Sr_xMnO_3$ is fully spin polarized at $T=0$. As the temperature is raised, the ferromagnetic moment decreases. That is, the t_{2g} spins gradually become disordered with the increase of temperature. It is natural to think that this is the most important effect of temperature on optical properties. As a first approximation to describe the effect of spin disorder we use the coherent-potential approximation (CPA),[9] which is the same as the dynamical mean-field (DMF) theory[10] in its spirit. Basically the CPA as well as DMF assumes that the spin disorder is a local one: each t_{2g} spin takes $\uparrow$ (or $\downarrow$) with probability $p_\uparrow$ (or $p_\downarrow$). Intersite correlations are not taken into account in this treatment. This assumption may be too crude to be realistic for $La_{1-x}Sr_xMnO_3$, since we expect the spatial change of magnetization to be gradual. In fact later we shall see some consequences of this assumption in optical conductivity.

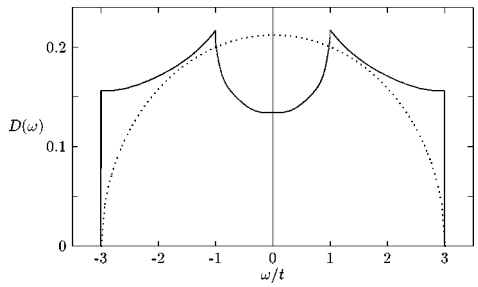

FIG. 1. The density of states (DOS) $D(\varepsilon)$ of the tight-binding model in Eq. (6) is shown with a solid line and semielliptic form in Eq. (17) with dotted line.

According to the CPA one assumes a local (i.e., momentum-independent), frequency-dependent self-energy, $\Sigma_\sigma(\omega + i\delta)$ to describe an average effect of t_{2g} spins on the e_g spin-σ electrons. It is related to the local Green function as

$$\widetilde{G}_\sigma(z) = \int_{-\infty}^{\infty} d\varepsilon \frac{D(\varepsilon)}{z - \Sigma_\sigma(z) - \varepsilon}, \tag{11}$$

where $D(\varepsilon)$ is the density of states for the tight-binding model $\mathcal{H}_0$, which is shown in Fig. 1.

Local fluctuations from $\Sigma_\sigma(\omega + i\delta)$, which are given by $-JS\sigma - \Sigma_\sigma(\omega + i\delta)$, causes a scattering of e_g electrons. $\Sigma_\sigma(\omega + i\delta)$ is determined in such a way that the average of the scattering due to the local fluctuations from $\Sigma_\sigma(\omega + i\delta)$ should vanish:

$$\left\langle \frac{-JS_i\sigma - \Sigma_\sigma(\omega + i\delta)}{1 - \widetilde{G}_\sigma(\omega + i\delta)(-JS_i\sigma - \Sigma_\sigma(\omega + i\delta))} \right\rangle_{\text{average over } S_i} = 0. \tag{12}$$

Let us assume that S_i takes either S or $-S$ with probability $p_\uparrow$ or $p_\downarrow$, respectively. Then Eq. (12) reduces to the following self-consistency equation:

$$p_\uparrow \frac{-JS\sigma - \Sigma_\sigma}{1 - \widetilde{G}_\sigma(-JS\sigma - \Sigma_\sigma)} + p_\downarrow \frac{JS\sigma - \Sigma_\sigma}{1 - \widetilde{G}_\sigma(JS\sigma - \Sigma_\sigma)} = 0. \tag{13}$$

The t_{2g} spin S is $\frac{3}{2}$, and $p_\uparrow + p_\downarrow = 1$ holds. The average magnetization is given by

$$M = S(p_\uparrow - p_\downarrow). \tag{14}$$

Then the self-consistency equation (13) is written as

$$\widetilde{G}_\sigma \Sigma_\sigma^2 + \Sigma_\sigma - \widetilde{G}_\sigma (JS)^2 - \sigma JM = 0. \tag{15}$$

Coupled equations (11) and (15) are solved self-consistently by using the density of states $D(\omega)$ in Fig. 1. The resulting density of states for spin σ e_g electrons,

$$\widetilde{D}_\sigma(\omega) = -\frac{1}{\pi} \text{Im} \widetilde{G}_\sigma(\omega + i\delta) \tag{16}$$

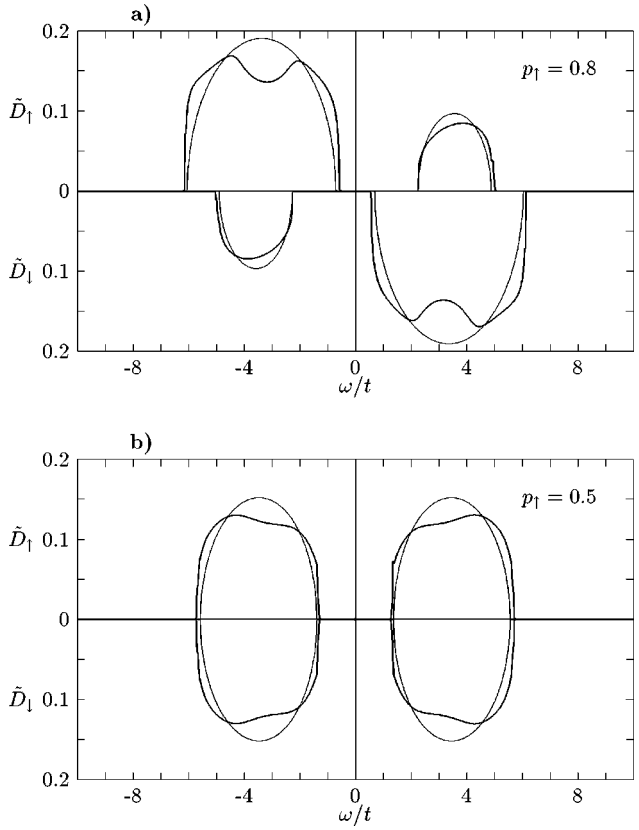

FIG. 2. The density of states $\widetilde{D}_\sigma(\omega)$ for (a) $p_\uparrow=0.8$ and $p_\downarrow=0.2$ and (b) $p_\uparrow=p_\downarrow=0.5$. The solid line shows the result for DOS of the tight-binding model in Eq. (6), whereas the thin line represents the result for the semielliptic band. $S=\frac{3}{2}$ and $J/t=2.2$ are assumed to describe $La_{1-x}Sr_xMnO_3$.

is shown in Fig. 2 for spin $\sigma=\uparrow$ above the frequency axis and spin $\sigma=\downarrow$ below the axis. $\widetilde{D}_\downarrow(\omega)$ can be obtained simply by taking a reflection of $\widetilde{D}_\uparrow(\omega)$ with respect to $\omega=0$.

Figure 2 shows that the density of states $\widetilde{D}_\sigma(\omega)$ is broadened due to the spin disorder, as naturally expected. Second, $\widetilde{D}_\uparrow(\omega)$ consists of two parts due to the exchange splitting: the low-energy part comes mainly from hopping via sites with $\uparrow t_{2g}$ spin, whereas the high-energy part is due to hopping via sites with $\downarrow t_{2g}$ spin. The splitting of the spectrum is approximately $2JS$. The magnitude of the parameters relevant to ferromagnetic $La_{1-x}Sr_xMnO_3$ is as follows. The exchange splitting $E_{\rm ex}=2JS(S=\frac{3}{2})$ is estimated as ~ 3 eV.[11] The hopping integral t can be estimated by comparing the tight-binding model with a band-structure calculation;[12] it leads to $t=0.3$–0.4 eV (i.e, the total bandwidth $6t=1.8$–2.4 eV). These estimations are taken into account in Fig. 2, where $2JS$ is larger than the total bandwidth in $D(\varepsilon)$. This is the reason for the splitting of the two bands. When $2JS$ is smaller than the total bandwidth $2W(=6t)$, the splitting does not occur. The relative weights of the two parts depend on M (i.e., $p_\uparrow=1-p_\downarrow$). The weight of the low-energy part is larger in $\widetilde{D}_\uparrow(\omega)$ when the system is partially polarized as $p_\uparrow=0.8$ and $p_\downarrow=0.2$. For the fully polarized case $M=S$ (i.e., $p_\uparrow=1$), which corresponds to $T=0$, we obtain $\widetilde{D}_\uparrow(\omega)=D(\omega+JS)$ and $\widetilde{D}_\downarrow(\omega)=D(\omega-JS)$.

For a comparison we also show the density of states $\widetilde{D}_\uparrow(\omega)$, which has been obtained by using the semielliptic form for $D(\varepsilon)$,

$$D(\varepsilon)=\frac{2}{\pi}\frac{1}{W^2}\sqrt{W^2-\varepsilon^2}, \tag{17}$$

instead of the density of states (DOS) for the tight-binding model. In Fig. 1 we show the density of states from these cases. Here W is chosen as $3t$, which gives the same total width as the DOS from the tight-binding model. It is clear that because of the broadening due to spin disorder both densities of states are not so different except for a small dip in the central region.

III. OPTICAL CONDUCTIVITY

The optical conductivity is calculated from the Kubo formula

$$\sigma_{\mu\mu}(\omega+i\delta)=\frac{-i}{\omega+i\delta}[K_{\mu\mu}(\omega+i\delta)-K_{\mu\mu}(0)], \tag{18}$$

where $K_{\mu\mu}(\omega+i\delta)$ can be obtained from the standard thermal Green function

$$K_{\mu\mu}(i\omega_m)=-\frac{1}{\beta}\sum_n\sum_{\vec{k},\sigma}\mathrm{Tr}\{J_\mu G^\sigma_{\vec{k}}(i\omega_m+i\varepsilon_n)J_\mu G^\sigma_{\vec{k}}(i\varepsilon_n)\} \tag{19}$$

via analytic continuation. ω_m is the Matsubara frequency: $\omega_m=2m\pi k_BT$ (m is an integer). The current operator along the $\mu(=x,y,z)$ direction is given by

$$J_\mu=\sum_{k\alpha\beta} j^{\alpha\beta}_\mu(\vec{k})c^\dagger_{\vec{k}\alpha}c_{\vec{k}\beta}, \tag{20}$$

where $j^{\alpha\beta}_\mu(\vec{k})=(-e)\partial\varepsilon^{\alpha\beta}(\vec{k})/\partial k_\mu$. From Eq. (7), we have

$$j^{\alpha\beta}_\mu(\vec{k})=j_{\mu0}(\vec{k})\delta_{\alpha\beta}+j_{\mu1}(\vec{k})\tau^z_{\alpha\beta}+j_{\mu2}(\vec{k})\tau^x_{\alpha\beta}. \tag{21}$$

Within the CPA, which is a single-site approximation, the effect of spin disorder is described by the self-energy Σ_σ in the Green function as

$$G^\sigma_{\vec{k}\beta\beta'}(i\varepsilon_n)=\left(\frac{1}{i\varepsilon_n-\Sigma_\sigma(i\varepsilon_n)-\mu-\hat{\varepsilon}(\vec{k})}\right)_{\beta\beta'}. \tag{22}$$

The Green function can be divided into two contributions corresponding to the two e_g bands:

$$\frac{1}{z-\hat{\varepsilon}(\vec{k})}=\frac{\hat{A}_+(\vec{k})}{z-E_+(\vec{k})}+\frac{\hat{A}_-(\vec{k})}{z-E_-(\vec{k})}, \tag{23}$$

where the two e_g bands and their weights are given by

$$E_{\pm}(\vec{k})=\varepsilon_0\pm\sqrt{\varepsilon_1^2+\varepsilon_2^2},\quad \hat{A}_{\pm}(\vec{k})=\frac{1}{2}\pm\frac{1}{2}\frac{\varepsilon_1\tau^z+\varepsilon_2\tau^x}{\sqrt{\varepsilon_1^2+\varepsilon_2^2}}. \tag{24}$$

ε_0, ε_1, and ε_2 are defined in Eqs. (8), (9), and (10), respectively.

Because of the two e_g bands the conductivity can be divided into intraband and interband contributions:

$$\begin{aligned}\mathrm{Re}\sigma_{\mu\mu}^{\mathrm{intra}}(\omega+i\delta)&=\int_{-\infty}^{\infty}d\varepsilon\frac{f(\varepsilon)-f(\varepsilon+\omega)}{\omega}\\&\times\sum_{\vec{k}\sigma}\left[\left(j_0+\frac{j_1\varepsilon_1+j_2\varepsilon_2}{\sqrt{\varepsilon_1^2+\varepsilon_2^2}}\right)^2\right.\\&\times\tilde{D}_{\sigma}^{(+)}(\varepsilon)\tilde{D}_{\sigma}^{(+)}(\varepsilon+\omega)+\left(j_0-\frac{j_1\varepsilon_1+j_2\varepsilon_2}{\sqrt{\varepsilon_1^2+\varepsilon_2^2}}\right)^2\\&\left.\times\tilde{D}_{\sigma}^{(-)}(\varepsilon)\tilde{D}_{\sigma}^{(-)}(\varepsilon+\omega)\right],\end{aligned} \tag{25}$$

$$\begin{aligned}\mathrm{Re}\sigma_{\mu\mu}^{\mathrm{inter}}(\omega+i\delta)&=\int_{-\infty}^{\infty}d\varepsilon\frac{f(\varepsilon)-f(\varepsilon+\omega)}{\omega}\sum_{\vec{k}\sigma}\frac{(j_1\varepsilon_2-j_2\varepsilon_1)^2}{\varepsilon_1^2+\varepsilon_2^2}\\&\times[\tilde{D}_{\sigma}^{(-)}(\varepsilon)\tilde{D}_{\sigma}^{(+)}(\varepsilon+\omega)+\tilde{D}_{\sigma}^{(+)}(\varepsilon)\tilde{D}_{\sigma}^{(-)}(\varepsilon+\omega)],\end{aligned} \tag{26}$$

where

$$\tilde{D}_{\sigma}^{(\pm)}(\varepsilon)=-\frac{1}{\pi}\mathrm{Im}\left(\frac{1}{\varepsilon-\Sigma_{\sigma}(\varepsilon+i\delta)-E_{\pm}(\vec{k})}\right) \tag{27}$$

is the density of states for band $\pm$ and spin σ. The results in Eqs. (25) and (26) reduce to that in Ref. 5, when the system is completely polarized at $T=0$.

In Fig. 3 we show the total optical conductivity

$$\mathrm{Re}\sigma(\omega+i\delta)=\mathrm{Re}\sigma^{\mathrm{intra}}(\omega+i\delta)+\mathrm{Re}\sigma^{\mathrm{inter}}(\omega+i\delta) \tag{28}$$

for various values of magnetization M at $n=0.7$ (corresponding to $x=0.3$ in $La_{1-x}Sr_xMnO_3$). Together with the total conductivity the intraband and interband contributions are also shown separately. For simplicity, we used Σ_{σ} for semielliptic $D(\varepsilon)$, since it is not much different from the true density of states as demonstrated in Fig. 2.

Figure 3 shows the following.

(1) The interband absorption is modified by spin disorder. The latter effect generally relaxes the momentum conservation in the transition process, so that the absorption between $\omega\sim 2t$ and $4t$ decreases with the decrease of magnetization, whereas the absorption around $\omega\sim 0$ and $\omega\sim 2JS$ increases.

(2) The intraband absorption is also strongly affected by spin disorder. The sharp Drude absorption at $\omega=0$ is broadened appreciably as the magnetization decreases; at the same time the absorption at $\omega\sim 2JS$ grows. The peak at $\omega\sim 2JS$ corresponds to the excitation process from the lower band to the upper band of the exchange-split density of states. Physically it originates from the transfer of an e_g electron from a site, on which the t_{2g} spin is parallel to the e_g electron, to a nearest-neighbor site, on which the t_{2g} spin is antiparallel. As far as this process of spectral weight transfer is concerned, the present result for the intraband absorption is similar to Furukawa's work, in which the orbital degeneracy in e_g is ignored.

(3) The total optical conductivity is just a sum of the two contributions described above. At $T=0$, where the magnetization is completely aligned, the optical conductivity consists of the Drude peak at $\omega=0$, and the interband absorption ranging from $\omega=0$ to $\omega=4t$.[5] As the magnetization decreases, the Drude peak becomes broad and interband ab-

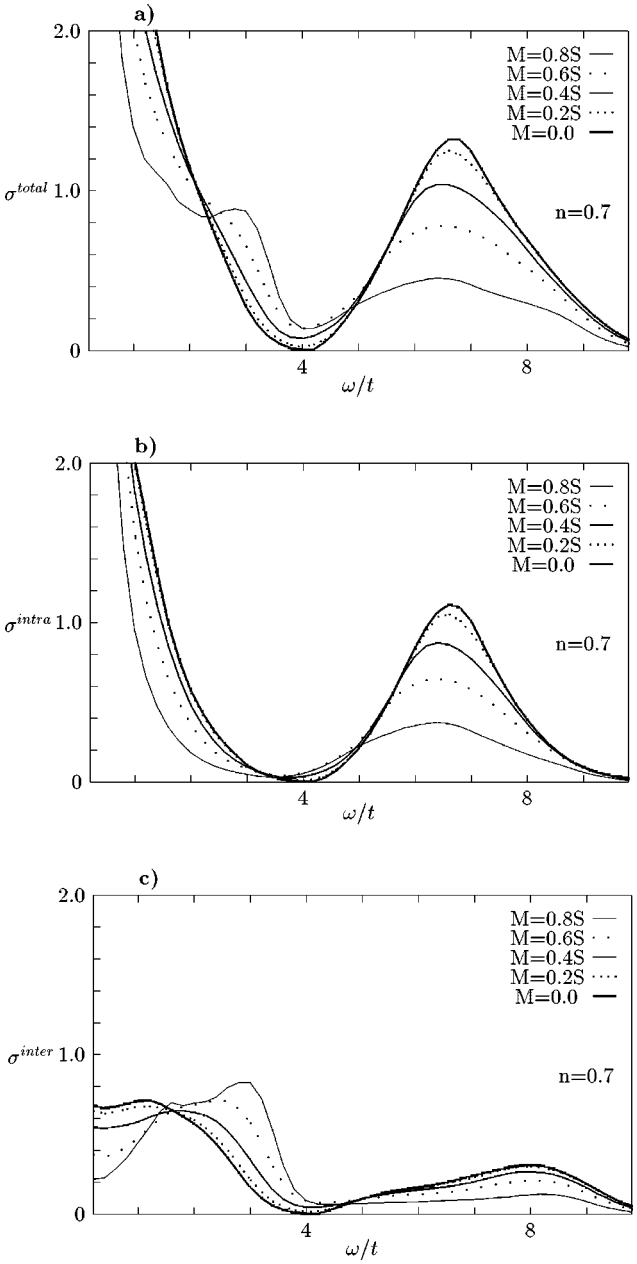

FIG. 3. The optical conductivity as a function of ω for various magnetizations. The electron density n is 0.7. (a) Total conductivity (σ^{total}). (b) Intraband conductivity (σ^{intra}). (c) Interband conductivity (σ^{intra}).

sorption between $\omega \sim 2t$ and $4t$ decreases. It is accompanied by a spectral weight transfer to high frequency at $\omega \sim 2JS$.

IV. COMPARISON WITH EXPERIMENTS AND DISCUSSION

The experimental optical conductivity of $La_{1-x}Sr_xMnO_3$ ($x=0.175$ and 0.3) (Ref. 4) shows that, in the high-frequency region, the peak increases as the magnetization decreases (i.e., with the increase of temperature), whereas the absorption in the intermediate-frequency region decreases as the magnetization decreases. Our results described in Sec. III explain well these experimental features.

Comparing the present result with the experiments more closely, we find a disagreement on the width of the Drude part centered around $\omega=0$. It is simply too large in our result. This is presumably due to the single-site nature of the CPA, in which intersite correlations of t_{2g} spins are totally ignored. This also applies to the dynamical mean-field theory of Furukawa. Physically speaking, t_{2g} spins must change gradually in space. Then a longer ''transport relaxation time,'' is expected compared with the ''one-particle relaxation time,'' which is determined by the imaginary part of Σ_σ; thus it must result in narrower Drude peak. In fact, if the Drude width were smaller in our intraband absorption, the total conductivity becomes closer to experimental data.

The effect of electron-electron interaction among e_g electrons is not taken into account in this paper. It would modify the optical spectrum even at $T=0$; a quantitative calculation on this point is underway. However, as far as the temperature dependence is concerned, we do not expect any strong temperature dependence from the electron-electron interaction among e_g electrons.

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*Permanent address: International Center of Condensed Matter Physics, Universidade de Brasilia, Brazil.

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