Charge Ordering Fluctuation and Optical Pseudogap in $La_{1-x}Ca_xMnO_3$

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Optical spectroscopy was used to investigate the optical gap (2Δ) due to charge ordering (CO) and related pseudogap developments with x and temperature (T) in $La_{1-x}Ca_xMnO_3$ ($0.48 \leq x \leq 0.67$). Surprisingly, we found $2\Delta/k_BT_{CO}$ is as large as 30 for $x \approx 0.5$, and decreases rapidly with increasing x. Simultaneously, the optical pseudogap, possibly starting from T^* far above T_{CO} becomes drastically enhanced near $x = 0.5$, producing non-BCS T-dependence of 2Δ with the large magnitude far above T_{CO}, and systematic increase of T^* for $x \approx 0.5$. These results unequivocally indicate systematically enhanced CO correlation when x approaches 0.5 even though T_{CO} decreases.

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It is one of the key problems of current condensed matter physics to understand the mysterious nature of charge/spin stripes in strongly correlated materials [1]. Some exotic, but complex, physical phenomena such as high T_c superconductivity in cuprates and colossal magnetoresistance (CMR) in manganites can be intimately linked to the striped charge/spin correlations. However, in the cuprates it is still under debate how dynamic and/or short-range charge/spin stripes are related to the pseudogap phenomena at high temperatures [2]. In the manganites [3,4], it has recently been recognized that dynamic or spatially fluctuating correlations of charge/spin/orbital can play an important role in the CMR phenomena [4–6]. In particular, neutron scattering experiments showed that short-range correlation of the so-called CE-type charge ordering (CO) exists in ferromagnetic (FM) manganites, $La_{1-x}Ca_xMnO_3$ for $x \approx 0.30$, above the Curie temperature T_C, explaining its large resistivity and magnetoresistance near T_C [5]. Therefore, it is fundamentally important to better understand the roles of dynamic or short-range charge/spin stripes, in relation to the physical properties of those correlated materials.

Historically, the "CE-type" CO in manganites was named for representing the special CO pattern observed in $La_{0.5}Ca_{0.5}MnO_3$ below $T_{CO} \approx 180$ K. A recent transport and structural study indicated that the short-range CE-type CO correlation can be robust even to very high temperature (T) regions above T_{CO} in $La_{1-x}Ca_xMnO_3$ for $x \approx 0.50$. However, an origin of the strong CE-type correlation and its presence over the other doping ranges are still enigmatic, partly due to intrinsic experimental difficulties in measuring fluctuating and short-ranged physical objects. Optical spectroscopy has been powerful to probe fluctuating order parameters of solids because the frequency of the electromagnetic wave can be much higher than that of the fluctuating sources. Thus, it has successfully probed a phase-correlation time of superconducting order parameter of $Bi_2Sr_2CaCu_2O_{8+\delta}$, an optical pseudogap in $Nd_{2-x}Ce_xCuO_4$ in the normal states [9], and fluctuating charge-density-wave order parameters of $K_{0.3}MoO_3$ and $(TaSe_4)_2I$ at high temperatures [10,11]. However, there are few optical conductivity studies probing short-range CO fluctuation in strongly correlated materials.

In this Letter, we present systematic optical conductivity spectra $\sigma(\omega)$ of $La_{1-x}Ca_xMnO_3$ ($0.48 \leq \boldsymbol{x} \leq 0.67$) revealing evidence of the short-range CO fluctuation at high temperatures. We find an optical pseudogap in $La_{1-x}Ca_xMnO_3$ ($0.50 \leq x \leq 0.67$) due to a spatially fluctuating CO correlation, which presumably starts at a characteristic temperature T^* far above T_{CO}. This optical pseudogap is greatly enhanced near $x = 0.50$ and systematically diminishes as x increases. Furthermore, the systematic pseudogap evolution with x is well correlated with T-dependence of charge gap evolution with x, which deviates from the conventional BCS functional form for $x \simeq 0.50$ and recovers the form for $x \simeq 0.67$. These results are in contrast with a previous optical transmission study with powdered samples in a limited photon energy range (0.05–0.19 eV) [12], interpreting the BCS functional form for the charge gap behavior of $x = 0.50$.

Single crystals of $La_{1-x}Ca_xMnO_3$ with high Ca concentration are difficult to grow. And, thus, high density polycrystalline specimens of $La_{1-x}Ca_xMnO_3$ ($x = 0.48$, 0.50, 0.52, 0.60, and 0.67) were prepared with the standard solid state reaction method. T_{CO} and/or T_C of the samples were determined from magnetization (M) studies. For $x = 0.48$, a FM metallic state is dominant below $T_C \approx 220$ K, possibly with a small CO phase emergent below 180 K [the inset of Fig. 1(a)]. However, the antiferromagnetic long-range CO becomes a dominant phase at low T for $x \geq 0.50$ so that T_{CO} values of $x = 0.50$, 0.52, 0.60, and 0.67 were 180, 190, 250, and 257 K, respectively. Because the $\boldsymbol{x} = 0.50$ sample is located at the phase boundary between FM metallic and CO insulating states, it shows also $T_C \approx 220$ K. All of the ordering temperatures were quite consistent with the established phase diagram

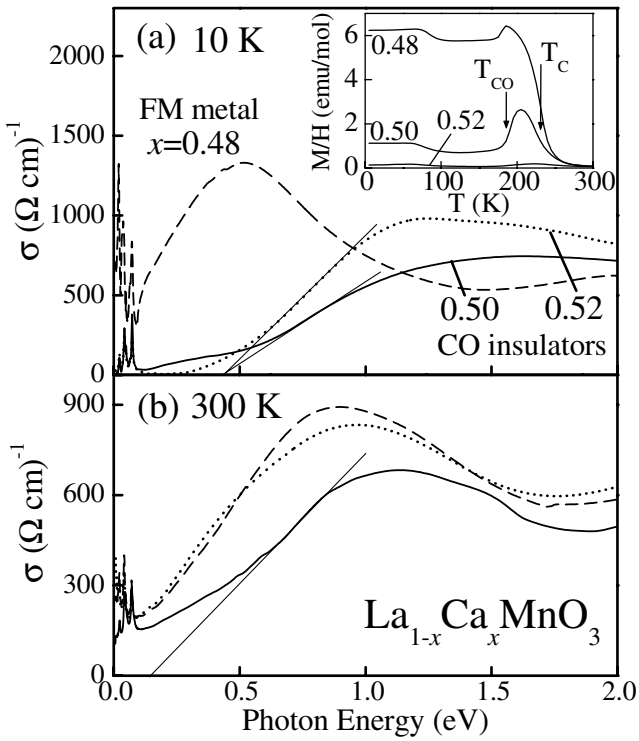

FIG. 1. Optical conductivity spectra $\sigma(\omega)$ of $x = 0.48$, 0.50, and 0.52 at (a) 10 K and (b) 300 K. The crossing points between the x-axis and linear extrapolation lines give an estimate of the charge gap 2Δ. The inset of (a) shows that M/H values measured at 2 kOe after zero field cooling.

of $La_{1-x}Ca_xMnO_3$ [3]. Near normal incident reflectivity spectra $R(\omega)$ of those samples were measured from 6 meV to 30 eV in a T range between 10 and 300 K during a heating cycle. To subtract surface scattering effects from $R(\omega)$, after measuring reflectivity of the sample surface, a $\sim$1000 Å layer of gold is evaporated onto the sample and the reflectivity is measured again and used for normalizing $R(\omega)$ of the samples [13]. From the normalized $R(\omega)$, $\sigma(\omega)$ were calculated by the Kramers-Kronig transformation. The resultant $\sigma(\omega)$ matched well the $\sigma(\omega)$ from the spectroscopic ellipsometry between 1.5 and 4.5 eV. High T-resistivity measurements were performed in a flowing inert gas condition up to $\sim$1000 K.

Figure 1(a) shows $\sigma(\omega)$ of the $x = 0.48$, 0.50, and 0.52 samples at 10 K. $\sigma(\omega)$ of $x = 0.48$ have a large absorption band centered at $\sim$0.5 eV, which can be related to an incoherent hopping motion of polarons from Mn^{3+} to Mn^{4+} sites in the metallic state [14]. On the other hand, an optical gap due to the long-range CO, namely, a charge gap, is clearly observed in $\sigma(\omega)$ of $x = 0.50$ and 0.52 at 10 K. We define a charge gap, 2Δ, as an onset energy of the steeply rising part of $\sigma(\omega)$, which can be determined from a crossing point between the x abscissa and a linear extrapolation line drawn at the inflection point of $\sigma(\omega)$. This procedure has been a common practice to evaluate 2Δ of various CO materials [15], resulting in $2\Delta(10\ \mathrm{K}) \simeq 0.45$ eV for both $x = 0.50$ and 0.52 samples. The charge gap energy at the ground state, $2\Delta(0) \approx 0.45$ eV, is the largest among numerous CDW systems [11] and charge-ordered oxides [15]. This large $2\Delta(0)$ can be a peculiar characteristic of the CE-type CO, indicating unusual stability of the special CO pattern.

On the other hand, $\sigma(\omega)$ of $x = 0.50$ at 10 K show significant in-gap absorption below 0.5 eV, while in-gap absorption of $x = 0.52$ is negligible at 10 K. One key finding from our experiments is that the spectral weight of the in-gap absorption is proportional to the amount of FM phase inside the samples. For example, a decrease of M/H values at 10 K from $x = 0.48$ to 0.52 [the inset of Fig. 1(a)] is well correlated with a decrease of spectral weight of $\sigma(\omega)$ below 0.5 eV at 10 K. In addition, the larger M/H values of $x = 0.50$ than $x = 0.52$ are consistent with the increased FM regions in $x = 0.50$, located near the CO/FM phase boundary [16]. Therefore, the in-gap absorption of $x = 0.50$ is attributed to a FM phase coexisting with a CO phase at low T.

In Fig. 1(b), $\sigma(\omega)$ of $x = 0.50$ at 300 K reveal anomalous spectral features; $\sigma(\omega)$ below 1.0 eV are smaller than those of neighboring compounds. Furthermore, $\sigma(\omega)$ increase steeply with ω, showing a positive curvature at low photon energy, which is very similar to the gap feature observed at 10 K. It is noted that this spectral response is not compatible with a single polaron absorption model [14]. Instead, the gap feature at 300 K suggests the presence of short-range CO or correlated multipolarons even far above T_{CO}. We note that it is not yet known if a theory for correlated multipolaron absorption could account for the peculiar $\sigma(\omega)$ of $x = 0.50$ above T_{CO}.

To understand further the anomalous $\sigma(\omega)$ of $x = 0.50$, we systematically investigated $\sigma(\omega)$ of $La_{1-x}Ca_xMnO_3$ with $x = 0.50$, 0.52, 0.60, and 0.67 (Fig. 2). It is noted that T-dependence of the charge gap for $x = 0.50$ is also

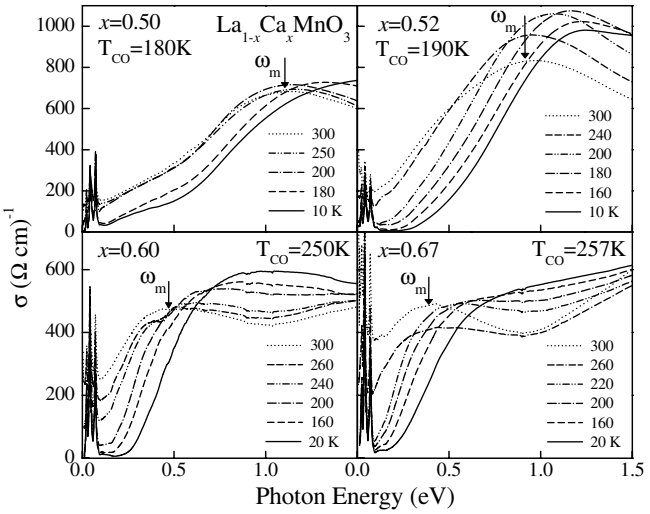

FIG. 2. $\sigma(\omega)$ of $La_{1-x}Ca_xMnO_3$ ($0.50 \le x \le 0.67$) at various T. The arrow for each x represents an energy of maximum $\sigma(\omega)$, ω_m, at 300 K. With decreasing x from 0.67 to 0.50, 2Δ at the lowest T increases (while T_{CO} decreases), and the suppression of spectral weight below ω_m, i.e., the optical pseudogap feature, is systematically enhanced.

peculiar; at 10 K $\leq T \leq$ 180 K, large 2Δ values are observed in $\sigma(\omega)$ of $x = 0.50$. In particular, 2Δ values at $T = 250$ and 300 K still remain finite, remarkably having almost the same magnitude with 2Δ at 200 K. The $\sigma(\omega)$ of $x = 0.52$ with $T_{CO} \approx 190$ K also show that 2Δ remains nonzero up to $T \approx 240$ K. These observations strongly suggest that the strong fluctuations of short-range CO (or correlated multipolaron) can be responsible for the finite charge gap far above T_{CO} in the $x = 0.50$ and 0.52 samples.

Even at high $T > 240$ K, where 2Δ is no longer finite, there exists significant suppression of spectral weight below an energy of maximum $\sigma(\omega), \omega_m$ (arrows in Fig. 2). This suppression of spectral weight is accompanied by a pseudogap in $\sigma(\omega)$, i.e., decreasing $\sigma(\omega)$ below ω_m at each T. This pseudogap is also observed in the $\sigma(\omega)$ of $x = 0.60$ and 0.67 at temperatures up to at least 300 K, even if 2Δ of $x = 0.60$ and 0.67 becomes zero just above T_{CO}. Surprisingly, it is found that the pseudogap feature shows systematic doping dependence. First, ω_m at 300 K systematically increases as $x \rightarrow 0.50$ from above (see Fig. 2). Second, the suppression of spectral weight below ω_m at 300 K becomes more evident as x approaches 0.50, which finally produces a nonzero 2Δ even at 300 K. This systematic enhancement of the pseudogap feature and its proximity to the finite 2Δ far above T_{CO} near $x = 0.50$ consistently suggest that the optical pseudogap can be attributed to the spatially fluctuating CO correlation of $La_{1-x}Ca_xMnO_3$ ($x \geq 0.50$) at the high T region.

To investigate the charge gap and its pseudogap developments quantitatively, we determined T-dependent suppressed spectral weight, $\Delta\sigma(T) \equiv \sigma(\omega_m)\omega_m - \int_0^{\omega_m} \sigma(\omega)\, d\omega$ and $2\Delta(T)$ for each x, as shown in Figs. 3(a) and 3(b), respectively. Below T_{CO}, the $\Delta\sigma(T)$ values of $x = 0.50$ are smaller than those of $x = 0.52$. The proximity to FM phase boundary at $x = 0.50$ may be responsible for the reduction of $\Delta\sigma(T)$ of $x = 0.50$ at low T. It is noted that high-T $\Delta\sigma(T)$ values of all the samples are clearly nonzero up to at least 300 K. In particular, $\Delta\sigma(T)$ values at 300 K increase systematically as $x \rightarrow 0.50$. At the same time, $2\Delta(0)$ values in Fig. 3(b) increase as $x \rightarrow 0.50$; $2\Delta(0) \approx 0.2$, 0.26, 0.45, and 0.45 eV for $x = 0.67$, 0.60, 0.52, and 0.50, respectively [17]. This increase of the $2\Delta(0)$ is well correlated with the increase of $\Delta\sigma(T)$ at 300 K as x approaches 0.50. These findings indicate that the strength of CO stability is clearly maximized for $x \approx 0.50$, being responsible for the enhanced CO fluctuation at high temperature. On the other hand, T_{CO} of these compounds decreases as x approaches 0.50. Therefore, $2\Delta(0)/k_BT_{CO}$ values systematically increase: $2\Delta(0)/k_BT_{CO} \approx 9$, 12, 28, and 30 for $x = 0.67$, 0.60, 0.52, and 0.50, respectively. This $2\Delta(0)/k_BT_{CO}$ increase up to 30, an unusually large value among many charge-ordered oxides, indicates strongly enhanced electron correlation near $x = 0.50$ [15].

Related with the enhanced pseudogap feature and large $2\Delta(0)/k_BT_{CO}$ value for $x \approx 0.50$, $2\Delta(T)/2\Delta(0)$ vs T/T_{CO}

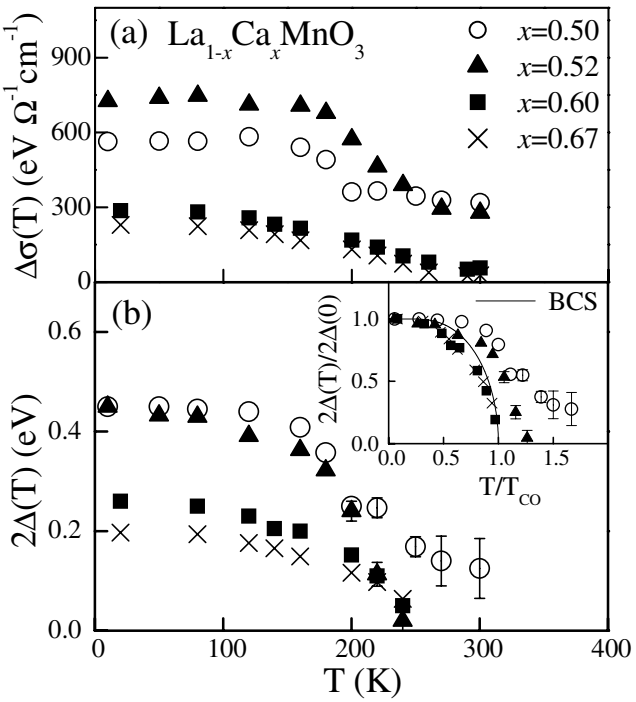

FIG. 3. (a) $\Delta\sigma(T) \equiv \sigma(\omega_m)\omega_m - \int_0^{\omega_m} \sigma(\omega)\, d\omega$ and (b) $2\Delta(T)$ plots of $La_{1-x}Ca_xMnO_3$ ($0.50 \leq x \leq 0.67$). The inset shows $2\Delta(T)/2\Delta(0)$ vs T/T_{CO} plot. The solid line represents the BCS functional form.

curves of $x = 0.50$ and 0.52 clearly deviate from the BCS functional form [the inset of Fig. 3(b)]. For example, $2\Delta(T)/2\Delta(0)$ values of $x = 0.50$ are still about 0.25 at $T/T_{CO} \approx 1.7$ ($T = 300$ K) and those values of $x = 0.52$ are nonzero up to at least $T/T_{CO} \approx 1.2$ ($T \approx 240$ K). These unique $2\Delta(T)/2\Delta(0)$ curves of non-BCS-type are quite consistent with the greatly enhanced spatial and/or temporal CO fluctuation near $x = 0.50$ at high temperature regions. However, as x is increased, $2\Delta(T)/2\Delta(0)$ curves recover the BCS form for $x = 0.60$ and 0.67, as observed in most of the CO materials [15].

To gain insights on how high temperatures this CO fluctuation survives, we studied high-T resistivity of $La_{1-x}Ca_xMnO_3$ with $x \geq 0.50$, as shown in Fig. 4(a). The $x = 0.50$ sample shows insulating behavior up to above ~850 K, where orthorhombic (low T) to rhombohedral (high T) structural transition occurs. Surprisingly, for $x \geq 0.52$, there exists a crossover from metallic to insulating states as T decreases. Moreover, the crossover temperature defined as T^* decreases systematically as x increases from 0.50. This T^* evolution with x is well correlated to $2\Delta(0)$ and $\Delta\sigma(300\text{ K})$ behaviors for $0.50 \leq x \leq 0.67$. Furthermore, in Fig. 4(b), T^* decreases as T_{CO} does above $x = 0.67$. Our previous study of $x = 0.80$ showed $2\Delta(0) \approx 0.08$ eV, indicating that both T_{CO} and $2\Delta(0)$ decrease together above $x = 0.67$ [18]. Therefore, T^* of charge-ordered $La_{1-x}Ca_xMnO_3$ is clearly linked to $2\Delta(0)$. This observation supports that T^* can be the temperature where high T-CO correlation starts and thus optical pseudogap appears.

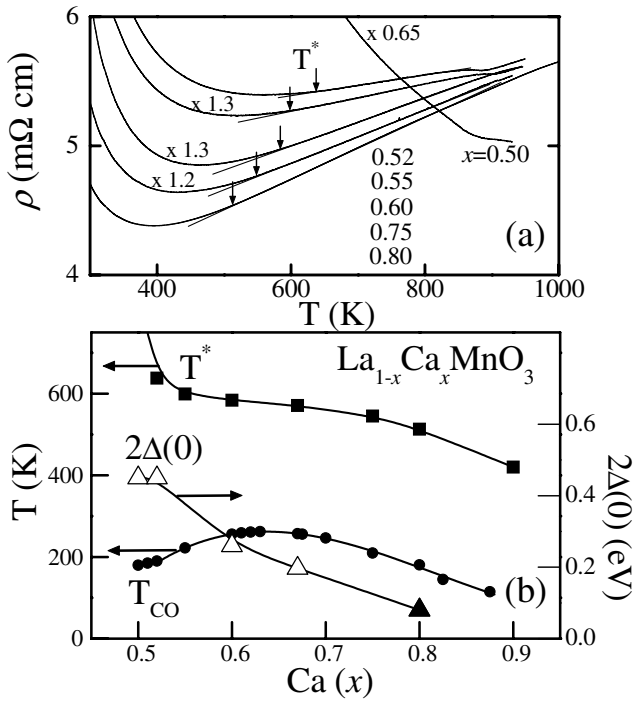

FIG. 4. (a) High $T - \rho$ data for $La_{1-x}Ca_xMnO_3$ for $x \geq 0.50$. T^* (arrow) for each x was determined as the T where the linear metallic resistivity starts to deviate. (b) Phase diagram of $La_{1-x}Ca_xMnO_3$ with $x \geq 0.50$ showing T^*, T_{CO}, and $2\Delta(0)$. The solid lines are guides to the eye. A solid triangle represents a $2\Delta(0)$ value of $x = 0.80$ from Ref. [19].

One convincing explanation for the enhanced CO fluctuation for $x \approx 0.50$ can be a competition of order parameters in $La_{1-x}Ca_xMnO_3$ ($x = 0.50$). Obviously, the commensurate 1:1 ratio of Mn^{3+} and Mn^{4+} ions is compatible with the strong CO tendency at $x = 0.50$. At the same time, the double exchange mechanism predicts that the strength of the FM correlation in $La_{1-x}Ca_xMnO_3$ should be varied as $x(1 - x)$ and optimized at $x = 0.50$ [19]. Indeed, $La_{1-x}Ca_xMnO_3$ ($x = 0.50$) has a thermodynamic bicritical point, where the FM metallic and the CO insulting states meet with the paramagnetic insulating state. Therefore, near the critical point, competing order parameters can lead to the suppression of ordering temperatures as well as increased spatial/temporal fluctuation among those phases. This scenario is further supported by a recent computational study, predicting that large charge fluctuations could be a generic feature of the mixed-phase systems at or near the regimes where a phase separation occurs as $T \rightarrow 0$ [20].

In conclusion, using systematic optical conductivity and transport studies, we determined doping dependent evolutions of charge ordering gap and its pseudogap in $La_{1-x}Ca_xMnO_3$ ($0.50 \leq x \leq 0.67$). With decreasing x from 0.67 to 0.50, the low temperature charge gap systematically increased while the charge ordering temperature decreased. Simultaneously, the optical pseudogap, indicating charge ordering fluctuation at high temperatures, is greatly enhanced as x approaches 0.50. This $\sigma(\omega)$ study provided a convincing evidence that short-range charge ordering fluctuation is anomalously strong in manganites.

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