Chemical potential shift in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$: Photoemission test of the phase separation scenario

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Abstract. – We have studied the chemical potential shift in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ as a function of doped hole concentration by core-level x-ray photoemission. The shift is monotonous, which means that there is no electronic phase separation on a macroscopic scale, whereas it is consistent with the nano-meter scale cluster formation induced by chemical disorder. Comparison of the observed shift with the shift deduced from the electronic specific heat indicates that hole doping in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ is well described by the rigid-band picture. In particular no mass enhancement toward the metal-insulator boundary was implied by the chemical potential shift, consistent with the electronic specific heat data.

It is generally recognized that the manganites $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ with the perovskite structure, where $\text{R}$ is a rare-earth ($\text{R} = \text{La}, \text{Pr}, \text{Nd}$) and $\text{A}$ an alkaline-earth metal ($\text{A} = \text{Sr}, \text{Ba}, \text{Ca}$), exhibit a very rich phase diagram because of competition between the ordering and fluctuations of the spin, lattice and charge degrees of freedom. They are antiferromagnetic (AFM) insulators for undoped materials ($x = 0$) while hole doping produces a ferromagnetic (FM) metallic phase, which shows colossal magnetoresistance (CMR). Historically, the ferromagnetism in this phase has been explained by double exchange mechanism. Materials with $x$ close to 0.5 have been the focus of recent studies because most of the manganites show so-called CE-type antiferromagnetic charge- and orbital-ordered insulating state at $x = 0.5$. When this spin-charge-orbital ordering completes with metallic behavior, they also exhibit a remarkable CMR effect, which becomes the subject of intensive studies. The origin of the CMR behaviors has been debated for many years since it was pointed out that double exchange interaction alone is insufficient to explain the large resistivity change.

Recently, the possibility of phase separation as the origin of the CMR is discussed by theoretical studies. Moro et al. has pointed out the possibility of the coexistence of the antiferromagnetic or ferromagnetic insulating phase and the ferromagnetic metallic phase.
and argued that this phase separation may be responsible for the CMR effect based on their quantum Monte Carlo simulation on the double exchange model including orbital degeneracy and electron-phonon coupling. The tiny Drude weight in the optical conductivity observed in the metallic region of $R_{1-x}A_x\text{MnO}_3$ has been explained in the framework of phase separation. The phase separation picture has also been suggested by some experimental results: electron microscopy studies have shown a phase separation on a large length scale of $\sim 100$ nm for $\text{La}_{0.625-x}\text{Pr}_x\text{Ca}_{0.375}\text{MnO}_3$ ($y = 0.4$), which shows ferromagnetic metallic behavior below the Curie temperature. NMR study of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ has revealed that the system is separated into a ferromagnetic metallic state and a ferromagnetic insulating state for $0.20 \leq x \leq 0.33$.

Among the manganites, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ is expected to have the widest band width. Magnetic and transport measurements have revealed that the system becomes a ferromagnetic metal in a wide composition range of $0.175 \leq x \leq 0.6$. In the end member $\text{LaMnO}_3$, the $A$-type antiferromagnetism is accompanied by a Jahn-Teller distortion of the Mn$^{3+}$ ion with $3d^4$ configuration and the orthorhombic distortion. No clear sign of charge-ordered state has been found for $x \sim 0.5$ probably because of the wide band width of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. Very recently, however, materials with $x \sim 0.5$ have been found to show different types of ground states depending on the crystalline states. Single crystals become FM metals for $x = 0.5$ and AFM metals for $x \geq 0.54$. A study using polycrystals has suggested a signature of charge ordering for $x \sim 0.5$ from the measurements of the sound velocity. Another polycrystal study has suggested that FM and AFM domains coexist with an anomaly due to charge ordering. These results suggest that charge ordering or at least its fluctuations are important also in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. The pair-distribution function analysis of pulsed neutron diffraction data of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ has shown that local Jahn-Teller distortions are present in the metallic state up to at least $35\%$ of hole doping, in disagreement with the homogeneous picture of the double exchange model.

In general, electronic phase separation results in the pinning of the chemical potential $\mu$. The numerical studies have indeed shown the pinning of $\Delta \mu$ in the composition range where the phase separation is realized. Even if there is no phase separation on a macroscopic ($>100$ nm) scale, $\Delta \mu$ would be pinned when there exists a microscopic “phase separation”, where hole-rich and hole-poor regions coexist on a nanometer scale and the volume of the hole rich region changes proportionally to the doped hole concentration, as has been demonstrated for the “charge stripes” in the high-$T_C$ cuprates. Hence, experimentally obtained $\Delta \mu$ can be directly used to test the above theoretical predictions. Core-level photoemission spectroscopy is a suitable method for this purpose: the chemical potential shifts can be deduced from the core-level shifts since in photoemission experiments the binding energy of each core level is measured relative to the chemical potential $\mu$. We note that one can distinguish an electronic phase separation and a chemical inhomogeneity by this method because no pinning of $\Delta \mu$ is expected in the latter case. In this paper, we present the results of highly precise x-ray core-level photoemission measurements of polycrystalline $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0 \leq x \leq 0.6$) to study the chemical potential shift $\Delta \mu$.

Polycrystalline samples of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ were prepared by solid-state reaction. The sample preparation procedure is described in detail elsewhere. X-ray photoemission spectroscopy (XPS) measurements were carried out using a Mg x-ray source ($h\nu = 1253.6$ eV). All the measurements were done at liquid-nitrogen temperature except for $x = 0$. Because charging effect was observed for $x = 0$ at liquid-nitrogen temperature, it was measured at room temperature. For an accurate determination of the core-level energy shifts, we have corrected for the time-dependent fluctuations of the retarding voltage and the pass energy of the spectrometer by simultaneous measurements of the voltage of the outer hemisphere, the inner
hemisphere and the entrance slit. After the correction, the errors in the measured shifts were reduced to \( \sim 10 \) meV if the measurements were made within a day. In order to achieve this accuracy for the whole set of the samples, we performed measurements of samples of interest and a reference sample within one day. Relative core-level energy shifts were thus measured with reference to \( x = 0.5 \). The samples were repeatedly scraped in situ with a diamond file. We have adopted spectra taken within 50 minutes after scraping and the reproducibility of the spectra was confirmed by repeated scraping. We note that even with the energy resolution of XPS (~0.9 eV), we could determine the core-level shifts with an accuracy of \( \sim 10 \) meV if the spectral shape does not change with the composition as confirmed by the measurements of the gold \( 4f_{7/2} \) core-level spectrum. In the case of \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \), we have achieved the accuracy of 50–100 meV due to the spectral changes with \( x \). \[14\]

Figure 1 shows the XPS spectra of the O 1s, La 3d, Mn 2p and Sr 3d core levels. Energy shifts of those core levels were determined by comparing the positions of the spectral features whose line shapes do not change with composition as indicated by vertical lines in Fig. 1. The

Fig. 1 – XPS spectra of the (a) O 1s, (b) La 3d, (c) Mn 2p and (d) Sr 3d core levels of \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \). Energies are referenced to the chemical potential \( \mu \), i.e., the Fermi level \( E_F \).
shift $\Delta E$ of a core level with varying chemical composition, measured relative to $\mu$ is given by

$$\Delta E = \Delta \mu + K \Delta Q + \Delta V_M - \Delta E_R,$$

where $\Delta \mu$ is the change in the chemical potential, $\Delta Q$ is the change in the number of valence electrons on the atom considered, $\Delta V_M$ is the change in the Madelung potential, and $\Delta E_R$ is the change in the extra-atomic relaxation energy [14, 16]. Here, $\Delta Q$ produces changes in the electrostatic potential at the core-hole site as well as in the intraatomic relaxation energy of the core-hole final state. $\Delta E_R$ is due to changes in the screening of the core hole potential by metallic conduction electrons and polarizable surrounding ions.

One can see from Fig. 1 that the observed energy shifts with $x$ are common to the O 1s, La 3d and Sr 3d core levels, whereas the shift of the Mn 2p core level is opposite to them. The line shapes of all of the core levels do not change significantly for these compositions, however, the contribution of La MNN Auger emission is not negligible in the energy range of the Mn 2p spectra and its intensity changes with La concentration. We have estimated the shifts by the center of gravity for the Mn 2p core level, though the shift estimated from the peak positions give nearly the same result. The estimated energy shifts are shown in Fig. 2. Crosses denote the difference between the shift of the Mn 2p level and the average shift of the O 1s, La 3d and Sr 3d levels, demonstrating that the Mn 2p shift can be decomposed into two simple components, namely, the shift common to all the four levels and the shift which increases the binding energy linearly in $x$ as in the case of La$_{2-x}$Sr$_x$CuO$_4$ [14]. The extra component of the Mn 2p core-level shift would be attributed to the increase in the Mn valence with hole doping ($\propto -\Delta Q$) from Mn$^{3+}$ towards Mn$^{4+}$, i.e., to the so-called chemical shift. Then the shift common to all the four levels should reflect the chemical potential shift.
Δμ as in the case of La$_{2-x}$Sr$_x$CuO$_4$ [4]. In particular, one can exclude the effect of changes in the Madelung potential caused by the La$^{3+} \rightarrow$ Sr$^{2+}$ substitution because the changes in the Madelung potential would cause shifts of the core levels of the O$^{2-}$ anion and the La$^{3+}$ (Sr$^{2+}$) cation in different directions.

Thus we have deduced the chemical potential shift Δµ from the average of the O 1s, La 3d and Sr 3d core-level shifts as a function of Sr concentration $x$ as shown in Fig. 3. For $x = 0$ and $x = 0.05$, we adopted the average of the O 1s and La 3d core-level shifts since the Sr 3d core levels were not available or too weak to determine the shift. The most important feature in Fig. 3 is that the chemical potential monotonously decreases with hole doping ($x$); we do not find any sign of pinning of the shift over the whole composition range. This means that there is no obvious electronic phase separation proposed both experimentally and theoretically. The absence of electronic phase separation into different spatial regions with different hole concentrations over macroscopic length scale is quite reasonable because it would cost huge Coulomb energy [4]. Then the “phase separation” observed by electron microscopy [6] would be most likely due to chemical inhomogeneity. Also, electronic phase separation on a microscopic scale as in the stripe phase of the high-$T_c$ cuprates can be excluded by the absence of chemical potential pinning. We note that a recent Monte Carlo simulation has shown that the introduction of disorder (by the alkaline-earth atom substitution) replaces the chemical potential pinning by a smooth shift. In that case, cluster formation on nanometer-scale occurs while large cluster formation is still inhibited [17].

\[ \frac{\partial \mu}{\partial n} = \frac{1 + F}{N^*(\mu)}, \]

where $N^*(\mu) = (3/\pi^2)(\gamma/k_B^2)$ is the density of states (DOS) of renormalized quasiparticles (QP’s) and $F$ is a parameter which represents the effective QP-QP repulsion. Since $\gamma = (\pi^2/3)k_B^2N^*(\mu)$, one can predict $\Delta \mu$ from the measured $\gamma$, if $F$ is known. $\Delta \mu$ predicted for $F = 0$ is shown by the dotted curve in Fig. 3. One can see fairly good correspondence between

Fig. 3 – Chemical potential shift $\Delta \mu$ in La$_{1-x}$Sr$_x$MnO$_3$ as a function of Sr concentration $x$. The dotted line is calculated from the specific heat $\gamma$ using Eq. (1) with $F = 0$. For details, see the text.

Then let us further analyze the chemical potential shift in the metallic regime $x \geq 0.18$. For a metallic system, the rigid-band picture predicts that

\[ \frac{\partial \mu}{\partial n} = \frac{1 + F}{N^*(\mu)}, \]
the shift predicted by $\gamma$ and the shift obtained by the XPS for $0.2 \leq x \leq 0.4$. If we use $F \approx 1$, agreement between the calculated and measured shifts is much improved. This means that the rigid-band description is appropriate in the metallic phase. The specific heat measurement indicated that the effective mass $m^*$ of the quasiparticle is only slightly enhanced toward the metal-insulator boundary and our result supports this observation. Below $x \sim 0.15$, the $\Delta \mu$ calculated from $\gamma$ shows a rapid upturn because $\gamma$ decreases in the insulating phase. In the insulating phase ($x \leq 0.15$), a rapid shift is expected if a band gap of finite magnitude opens or the DOS at $\mu$ decreases. However, the observed shift $\partial \mu / \partial n$ is almost the same as in the metallic region. This suggests that the insulating ground state has a finite DOS at $\mu$ which are probably Anderson-localized.

In conclusion, we have studied the chemical potential shift of La$_{1-x}$Sr$_x$MnO$_3$ by means of x-ray core-level photoemission spectroscopy. The shift is monototonous with hole concentration, which suggests that there is no electronic phase separation on a macroscopic scale that has been suggested by the electron microscopy studies. On the other hand, the present observation is consistent with the formation of nano-meter scale clusters induced by chemical disorder. Comparison between the observed shift and the shift predicted by the specific heat indicates that the hole doping in La$_{1-x}$Sr$_x$MnO$_3$ is well described by the rigid-band picture. Also, the mass enhancement toward the metal-insulator boundary was not clearly observed through the chemical potential shift measurements, qualitatively consistent with the specific heat data.

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