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Evidence for polaronic Fermi liquid in manganites

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The modern multipolaron theory predicts a polaronic Fermi-liquid state, but such a state has not been unambiguously confirmed by experiment so far. Here we report theoretical and experimental studies of the isotope effects on the low temperature kinetic properties of the doped ferromagnetic manganites. Our results provide clear evidence for a polaronic Fermi-liquid state in doped ferromagnetic manganites.

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Over the past decades, very interesting phenomena such as high-temperature superconductivity and colossal magnetoresistance have been discovered in several doped oxides. These doped oxides are characterized by significant carrier densities (\( \approx 10^{21} \) cm\(^{-3} \)) and low mobility of the order or even less than the Mott-Ioffe-Regel limit (\( ea^2/\hbar \sim 1\) cm\(^2\)/Vs, where \( a \) is the lattice constant) at room temperature. The very nature of the low-temperature “metallic” state of these materials can be hardly understood within the framework of the canonical theory of metals. However, it has been known for many decades starting from the pioneering work by Landau\(^1\) that the local lattice deformation can transform electrons into “self-trapped” polarons in doped ionic insulators. Further extensive theoretical studies (for review, see Refs. 2 and 3) have shown that polarons behave like heavy particles, and can be mobile with metallic conduction at sufficiently low temperatures. Under certain conditions\(^4\) they form a polaronic Fermi liquid with some properties being very different from ordinary metals. One of them is the effective mass of polarons. It is well known that electrons can change their mass in solids due to the interactions with ions, spins, and themselves. The renormalized (effective) mass of electrons is independent of the ion mass \( M \) in ordinary metals where the Migdal adiabatic approximation is believed to be valid. However, if the interactions between electrons and nuclear ions are strong and/or the adiabatic approximation is not applied electrons form polarons (quasi-particles dressed by lattice distortions), so their effective mass \( m^* \) will depend on \( M \). This is because the polaron mass \( m^* = m \exp(A/\omega) \),\(^5\) where \( m \) is the band mass in the absence of the electron-phonon interaction, \( A \) is a constant, and \( \omega \) is a characteristic phonon frequency which depends on the masses of ions. Hence, there is a large isotope effect on the carrier mass in polaronic metals, in contrast to the zero isotope effect in ordinary metals.

The total exponent of the isotope effect on \( m^* \) is defined as \( \alpha_m = \sum -d \ln m^*/d \ln M_i \) (\( M_i \) is the mass of the \( i \)th atom in a unit cell). From this definition and the expression for the polaron mass \( m^* \) mentioned above, one readily finds

\[
\alpha_m = -\frac{1}{2} \ln(m^*/m) .
\]

Interestingly, the same isotope exponent is predicted for the intersite bound pairs of polarons (i.e., bipolarons).\(^5,6\) The underlying assumption used to obtain this equation is the harmonic approximation for phonons and the inverse coupling perturbation expansion based on the Lang-Firsov canonical transformation, which is valid in a wide region of the coupling with high-frequency optical phonons.\(^4\)

A large isotope effect on the effective mass of supercarriers has been observed in the high-temperature cuprate superconductors,\(^7-9\) which suggests that polarons and/or bipolarons should be involved in high-temperature superconductivity. Furthermore, in doped manganites, the polaronic nature of the carriers in the high-temperature paramagnetic insulating state has been shown by several independent experimental results such as the sign anomaly of the Hall effect,\(^10\) the Arrhenius behavior of the drift and Hall mobilities,\(^10\) the giant oxygen-isotope shift of the Curie temperature \( T_C \),\(^11\) and the electron paramagnetic resonance linewidth which is proportional to the conductivity.\(^12\)

On the other hand, the very nature of the charge carriers in the low-temperature metallic state of doped manganites has not been understood. In a theory of colossal magnetoresistance for ferromagnetic manganites\(^13\) polarons are considered as the carriers even in the low-temperature metallic state, while others\(^14\) believe that polaronic effects are not important at low temperatures. Some experimental studies\(^15\) concluded that polaronic effects may be involved in the ferromagnetic metallic state of the low \( T_C \) compounds, while many others explained their unusual behavior in terms of a percolative conduction mechanism.\(^16\)

Theoretically it has been demonstrated that the coherent motion of small polarons can lead to metallic conduction at low temperatures.\(^2,17,4\) In order to provide decisive evidence for the “metallic” polaronic liquid in doped ferromagnetic manganites, it is essential to study the isotope effects on the low-temperature kinetic and thermodynamic properties. These properties are dominated by the impurity and electron-electron scatterings, so the only source of the isotope effect might be the polaron mass dependence on the ion mass. For example, replacing \(^{16}\)O with \(^{18}\)O will increase the polaron mass, leading to the changes in the residual resistivity, and in other kinetic and thermodynamic properties. Here we provide clear evidence for the polaronic liquid in doped ferro-
magnetic manganites at low temperatures from theoretical and experimental studies of the isotope effects on kinetic and thermodynamic properties.

We first define and calculate three exponents: $\beta_C = d \ln C_{el} / d \ln m^*$, $\beta_p = d \ln \rho_p / d \ln m^*$, and $\beta_S = d \ln S / d \ln m^*$ in the polaronic liquid. Here $C_{el}$ is the electronic specific heat at low temperatures, $\rho_p$ is the residual resistivity, and $S$ is the low-temperature thermopower. We assume that the Fermi level (chemical potential) lies above the mobility edge, so polarons propagate in the Bloch states as heavy fermions$^{17,4}$ scattered by the short-range impurity potential. The polaronic band structure might be quite complicated in manganites involving a few different orbital states of oxygen and manganese and electron-electron correlation effects. While our further consideration is largely independent on the band structure details, we choose a simple model of the polaron spectrum supported by the site selective experiments. Several experiments$^{18,19}$ have shown that doped holes in manganites mainly reside on the oxygen orbitals for the doping level less than 0.4. Within a tight binding approximation, the oxygen hole energy spectrum consists of three bands formed by the overlap of $p_x$, $p_y$, and $p_z$ orbitals, respectively (see the schematic picture in the inset of Fig. 1). These bands are quasi-one-dimensional (1D) due to a large anisotropy in the hopping integrals $[i.e., t_{ppp} = -(1/4)t_{ppp}]$. The polaronic mass enhancement is normally larger along the directions with a much smaller hopping integral$^{20}$ This will increase the anisotropy further so that the polaron bands become practically 1D. Three different bands are not mixed because the off-diagonal hopping integrals (e.g., $t_{p_x, p_y}$) are zero for the nearest neighbors. The random potential does not mix them either if it varies smoothly on the atomic scale. Therefore, there are three degenerate 1D-like polaronic oxygen hole bands in a cubic perovskite compound. Such a model allows us to derive the isotope exponents analytically. The polaronic propagator, $G(k,E) = [E-k^2/2m^* - \Sigma(k,E)]^{-1}$ is found with the self-energy, which is momentum ($k$)-independent in the noncrossing ("ladder") approximation,

$$\Sigma(E) \simeq \sum_k G(k,E).$$

Taking the integral in Eq. (2) one obtains the algebraic cubic equation for $\Sigma(E)$ with a solution:

$$\sigma(e) = \frac{e}{3} - \left( \frac{1-3/2}{2} \right) \left[ \frac{1}{16} + \frac{e^3}{27} + \frac{1}{256} + \frac{e^3}{216} \right]^{1/3}$$

Here we introduce the dimensionless energy, $e = E/\epsilon_0$, and the self-energy $\sigma(e) = \Sigma(E)/\epsilon_0$ using the scattering rate $\epsilon_0 = (D^2 m^*/h^2)^{1/3}$ as the energy unit. The constant $D$ is the second moment of the Gaussian white-noise potential, $D = 2(n_{im} v^2/a^2)$, where $n_{im}$ is the impurity density, and $v$ is the coefficient of the $\delta$-function impurity potential. This self-energy is almost exact above the mobility edge as shown with the exact solution for a one-dimensional particle in a random white-noise potential.$^{21}$

The specific heat is proportional to the density of states (DOS) at the (dimensionless) Fermi level, $\mu = E_F/\epsilon_0$. Assuming three degenerate spin-polarized oxygen bands, we find

$$C_{el} / T = 2\pi k_B^2 S / \hbar a^2 c^2 \epsilon_0 \Sigma(\mu) \epsilon_0,$$

with $S = \frac{e^2}{2\pi^2 m^* c^2} \int_{-\infty}^{\infty} dk k^2 [\text{Im} \ G(k,\mu)]^2$.

If there coexist electronlike and holelike polarons, Eq. (6) must be multiplied by a factor $f_x$ with $|f_x| \leq 1$. We would like to mention that Eq. (5) should be underestimated due to the fact that the bands are not strictly one-dimensional and that the transport relaxation rate is generally smaller than $\epsilon_0$. While the scattering rate and the transport relaxation rate are equal in the noncrossing approximation, they are different for any finite-range scattering potential due to the vertex corrections. Calculating the integral in Eq. (5) leads to

$$\rho_o^{-1} = \frac{\epsilon}{2\pi^2 m^* c^2 \hbar a^2} F(\mu),$$

where

$$F(\mu) = \frac{3}{g [\mu + (\mu + g^2)^{1/2}]^{1/2}} [\mu + (\mu + g^2)^{1/2}]^{1/2},$$

and $g = |g(\mu)|$. These expressions allow us to calculate the exponents $\beta_C$, $\beta_p$, and $\beta_S$. The number of carriers does not depend on the isotope substitution,$^{22}$ so that the chemical potential itself
we finally obtain the logarithmic dependence on the mass ratio $m$, keeping in mind that in the order of unity. At large filling, i.e., negligible isotope effect on density of states in the random potential, we find even a sizable isotope effects on all thermodynamic and kinetic properties with the exponents $b$, $s$, and $m$. Interestingly, if the doping is not so high, the same for any dimension of the polaron spectrum in this approximation for the impurity scattering. The ratio remains a good agreement with the measured values: $C_{22}^{O} = 0.5$, $C_{22}^{O} = -1.6$, $C_{22}^{O} = 0.0$, (12)

i.e., negligible isotope effect on $S$, and more than 3 times lower isotope effect on $C_{el}$ than on $\rho_{o}$. Applying the exact density of states in the random potential, we find even a somewhat lower exponent $\beta_{C}$ for $\mu \leq 0$ than that in Fig. 1. All these findings are in sharp contrast with those in ordinary single crystals. Furthermore, the value of $\epsilon_{0}$ is in good agreement with the measured transport relaxation rate ($\sim 24$ meV) for La$_{0.75}$Ca$_{0.25}$MnO$_{3}$. This justifies the choice of $\mu = 0.25$ and $\alpha_{m}^{O} = -1.1$ for Nd$_{0.67}$Sr$_{0.33}$MnO$_{3}$. For La$_{0.75}$Ca$_{0.25}$MnO$_{3}$, we calculate $C_{el}/T = 7.5$ mJ/mol K$^2$ and $\rho_{o} = 150 \mu\Omega$ cm by setting $\mu = 0.70$ and $\alpha_{m}^{O} = -0.7$. The measured $\rho_{o}$ for La$_{0.75}$Ca$_{0.25}$MnO$_{3}$ is 120–150 $\mu\Omega$ cm [see Fig. 2(a) and discussion in Ref. 23]. From our specific-heat data for La$_{0.75}$Ca$_{0.25}$MnO$_{3}$, we estimate $C_{el}/T = 7$ mJ/mol K$^2$, which is slightly lower than the one ($\sim 8$ mJ/mol K$^2$) for La$_{0.8}$Ca$_{0.2}$MnO$_{3}$. With $\mu = 0.70$ and $\alpha_{m}^{O} = -0.7$, we have $\alpha_{C}^{O} = 0.5$, $\alpha_{O}^{C} = -1.2$, $\alpha_{S}^{O} = 0.17$. (13)

Experimentally, the oxygen-isotope effect on the intrinsic low-temperature resistivity has been studied in high-quality thin films of La$_{0.75}$Ca$_{0.25}$MnO$_{3}$ and Nd$_{0.75}$Sr$_{0.25}$MnO$_{3}$. Our thin films were thick (2000 Å), and were annealed at 940 °C for 10 h, so no strains could remain in the films. We did back-exchange, and we knew precisely the oxygen-isotope enrichment (more details can be found in Refs. 23 and 31). In Fig. 2 we plot the low-temperature resistivity of the oxygen-isotope exchanged films of (a) La$_{0.75}$Ca$_{0.25}$MnO$_{3}$ and (b) Nd$_{0.75}$Sr$_{0.25}$MnO$_{3}$. In both cases, the residual resistivity $\rho_{o}$ for the $^{18}$O samples is larger than for the $^{16}$O samples by 15% (Ref. 23). The oxygen-isotope exponent $\alpha_{O}^{P}$ was calculated from the definition: $\alpha_{O}^{P} = -d \ln \rho_{o}/d \ln M_{O}$ ($M_{O}$ is the oxygen mass).
\( \alpha_{p}^{O} = -1.4(2) \) for Nd\(_{0.75}\)Sr\(_{0.33}\)MnO\(_{3}\), and \( \alpha_{p}^{O} = -1.2(2) \) for La\(_{0.75}\)Ca\(_{0.25}\)MnO\(_{3}\). These values are in excellent agreement with Eq. (12) and Eq. (13), respectively.

The quantitative agreement between the resistivity data and the theory indicates that the low-temperature metallic state in doped manganites is a polaronic Fermi liquid. To further confirm this, one should experimentally demonstrate that \( \alpha_{S}^{O} \) is negligible and that \( \alpha_{C}^{O} \) is rather small in these materials. Our preliminary results of the oxygen-isotope effect on the low-temperature specific heat in La\(_{1-x}\)Ca\(_{x}\)MnO\(_{3}\) are consistent with Eq. (12) within the experimental uncertainty. Here we show the data of the thermopower \( S \) for the isotope-exchanged La\(_{1-x}\)Ca\(_{x}\)MnO\(_{3}\).

Figure 3 shows the thermopower \( S \) below 60 K for the \(^{16}\text{O}\) and \(^{18}\text{O}\) samples of La\(_{1-x}\)Ca\(_{x}\)MnO\(_{3}\) with \( x = 0.20 \) and 0.25. The isotope-exchanged samples are the same as those reported in Ref. 31. It is apparent that the oxygen-isotope effect on \( S \) is negligible below 20 K for both compositions (\( \alpha_{S}^{O} \approx 0.0 \)). The negligible \( \alpha_{S}^{O} \) and the substantial \( \alpha_{p}^{O} \approx -1.3 \) observed in these samples are in quantitative agreement with the theoretical prediction [Eq. (12) and Eq. (13)]. Therefore, the present theoretical and experimental studies of the low-temperature kinetic and thermodynamic properties provide strong evidence for the existence of polaronic Fermi liquid in manganites.

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