DIELECTRICS

Anomalous Thermodynamics of the Doped Mott−Hubbard Insulators

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Abstract—The concentration dependence of the entropy of doped Mott−Hubbard insulators has been considered within the $t−J$ model. It has been shown that a change in the type and statistics of charge carriers as compared to the Fermi gas leads to a radical change in the entropy s, in particular, to the giant growth of the entropy upon doping. The quantity $\partial s/\partial x \approx k_B$ is approximately consistent with the experimental data for HTSC cuprates in the pseudogap phase.

1. INTRODUCTION

The doped Mott−Hubbard insulators include such topical classes of materials as HTSC cuprates, manganites, and cobaltites with colossal magnetoresistance. As a rule, their doping causes metallic conductivity. In the area of small doping concentrations x, however, there are anomalies of the conducting state, in particular, pseudogap states and deviations from the Fermi-liquid behavior. One of such anomalies was found in HTSC cuprates with the entropy variation [1, 2]; specifically, an increase in entropy upon addition of one hole appeared to be abnormally large: $\Delta s \approx k_B$, where k_B is the Boltzmann constant. Recall that for the Fermi gas with concentration of particles n, we have

$$\Delta s = -\left(\frac{\pi}{3}\right)^{2/3} \frac{m k_B^2 T}{3 n^{\frac{2}{3}}}, \tag{1}$$

which at $n \approx 10^{28}–10^{29}$ m^{-3}, m equal to the electron mass, and $T \approx 10–100$ K yields the value of about $10^{-3}–10^{-2} k_B$. One can see that, in the Fermi gas, the changes are smaller by 2−3 orders of magnitude; in addition, they are of the opposite sign. Addition of a hole is equivalent to removal of an electron, at which entropy of the electron gas decreases.

In this study, we will show that such a large difference in the properties of the doped Mott−Hubbard insulator and the Fermi gas consists in the strong electron correlations (SECs). In the systems with the SECs, the definition of electrons, as such, changes. The part of the Hilbert space containing two-particle states is excluded at the expense of the SECs. This known limitation on occupation of the two-particle states is named the constraint condition. As a result, the Fermi quasiparticles (Hubbard fermions) are described not by the operators of creation and annihilation of free electrons but by the Hubbard operators working in the limited Hilbert space and having complex algebra. Already this fact in itself leads to the large values $\frac{\partial s}{\partial x}$, which we demonstrate by an accurate calculation in the atomic limit at $t/U = 0$ in Section 2. Here, U is the Hubbard energy and t is the parameter of interatomic hopping. The account for the hoppings yields dispersion of the Hubbard fermion band. In Section 3, we present the calculation of entropy with regard of dispersion in the simplest Hubbard-1 approximation. Generally speaking, in this case, the value of the derivative $\frac{\partial s}{\partial x}$ changes quantitatively as compared to the atomic limit, but the order of its magnitude remains the same. Thus, the giant growth of entropy upon addition of one hole is not the consequence of an order of the theory of perturbations in the parameter $t/U \ll 1$; it occurs from the change in the definition and statistics of electrons in the strongly correlated systems.

2. ELECTRONIC ENTROPY IN THE ATOMIC LIMIT

The local basis set of the eigenstates of one atom in the $t−J$ model contains three states: a vacuum singlet $|0\rangle$ with the number of electrons $n_e = 0$ and a single-

particle doublet $|\sigma\rangle = a^+_{f\sigma}|0\rangle$ $\left(\sigma = \pm\frac{1}{2}\right)$ with the number of electrons $n_e = 1$. By virtue of the SECs, the two-particle state $|2\rangle = a^+_{f\uparrow}a^+_{f\downarrow}|0\rangle$ is forbidden by the constraint condition. In this basis set, the operator of creation of an electron equals to the Hubbard operator $X^{pq} = |p\rangle\langle q|$:

$$a^+_{f\sigma} = X^{\sigma 0}_f. \tag{2}$$

The commutation properties of such an operator do not at all coincide with those of the free electrons [3]:

$$a^+_{f\sigma}a_{m\sigma} + a_{m\sigma}a^+_{f\sigma} = \delta_{fm}(X^{00}_f + X^{\sigma\sigma}_f) = \delta_{fm}(1 - X^{\bar\sigma\bar\sigma}_f).$$

Here, $\bar\sigma = -\sigma$ and the last equality follows from the completeness condition

$$X^{00}_f + X^{\sigma\sigma}_f + X^{\bar\sigma\bar\sigma}_f = 1.$$

The Hamiltonian of the t–J model in the representation of the Hubbard operators can be written as [4, 5]

$$H = H_0 + H_1, \tag{3}$$

where

$$H_0 = \sum_{f\sigma}(\varepsilon - \mu)X^{\sigma\sigma}_f, \tag{4}$$

$$H_1 = -\sum_{fm\sigma}t_{fm}X^{\sigma 0}_f X^{0\sigma}_m$$
$$+ \frac{1}{2}\sum_{fm\sigma}J_{fm}(X^{\sigma\bar\sigma}_f X^{\bar\sigma\sigma}_m - X^{\sigma\sigma}_f X^{\bar\sigma\bar\sigma}_m). \tag{5}$$

In expression (4), ε is the energy of an electron on the site and μ is the chemical potential; in expression (5), t_{fm} is the integral of hopping from site $\mathbf{f}$ to site $\mathbf{m}$ and J_{fm} is the exchange integral between sites $\mathbf{f}$ and $\mathbf{m}$.

In the atomic limit, we have $t = 0$ and $H = H_0$. Hamiltonian H_0 describes the set of individual sites. The partition function for the system describing Hamiltonian H_0 is given by

$$\Xi_0 = 1 + 2\exp\left(-\frac{\varepsilon - \mu_0}{k_B T}\right). \tag{6}$$

Using Eq. (6), it is easy to obtain the thermodynamic potential

$$\Omega_0 = -k_B T\ln\left(2\exp\left(-\frac{\varepsilon - \mu_0}{k_B T}\right) + 1\right). \tag{7}$$

From this expression, using the well-known thermodynamic formula $s = -\left(\dfrac{\partial\Omega}{\partial T}\right)_\mu$, we find the expression for electronic entropy in the atomic limit:

$$s_0 = k_B\left[\ln\left(2\exp\left(-\frac{\varepsilon - \mu_0}{k_B T}\right) + 1\right)\right.$$
$$\left. + \frac{2(\varepsilon - \mu_0)\exp\left(-\dfrac{\varepsilon - \mu_0}{k_B T}\right)}{k_B T\left(2\exp\left(-\dfrac{\varepsilon - \mu_0}{k_B T}\right) + 1\right)}\right]. \tag{8}$$

To find the chemical potential, we note that the mean number of electrons per site is, on the one hand, $n_e = 1 - x$, where x is the doped hole concentration and, on the other hand, $n_e = -\left(\dfrac{\partial\Omega_0}{\partial\mu_0}\right)_T$. Using the latter circumstance, we obtain

$$\mu_0 = \varepsilon - k_B T\ln\frac{2x}{1 - x}. \tag{9}$$

As a result, we have the entropy

$$s_0 = k_B[(1 - x)\ln 2 - (x\ln x + (1 - x)\ln(1 - x))]. \tag{10}$$

From expression (10) at $x = 0$ the well-known result $s_0 = k_B\ln 2$ follows; i.e., the entropy is determined by the localized spins $\sigma = \dfrac{1}{2}$. Expression (10) has a simple interpretation based on the Boltzmann formula, according to which $s = -k_B\overline{\ln w} = -k_B\sum_k w_k\ln w_k$, where w_k is the probability of implementation of the quantum state with number k in the system. In the doped case, the number of occupation is $n_e = 1 - x$ for the single-particle state and $n_h = x$ for the vacuum state. Therefore, the spin contribution to entropy decreases to $k_B(1 - x)\ln 2$, but the configuration contribution $-k_B(x\ln x + (1 - x)\ln(1 - x))$ adds. According to Eq. (2), annihilation of a hole (creation of an electron) is caused by the transitions between the two configurations $|0\rangle$ and $|\sigma\rangle$, so that the configuration entropy is of electron origin. Analogously, for electron doping with the number of electrons $n_e = 1 + x$, the t–J model can be applied for the upper Hubbard band formed by the excitations from $|\sigma\rangle$ to the two-particle term $|2\rangle$ with the spin $s = 0$. As a result, formula (10) remains, but now x equals to the concentration of added electrons. Figure 1 presents a scheme of the configuration space and the contributions from different parts of this space to total entropy. The dependence of electronic entropy on the hole concentration is shown in Fig. 2 (curve 4).
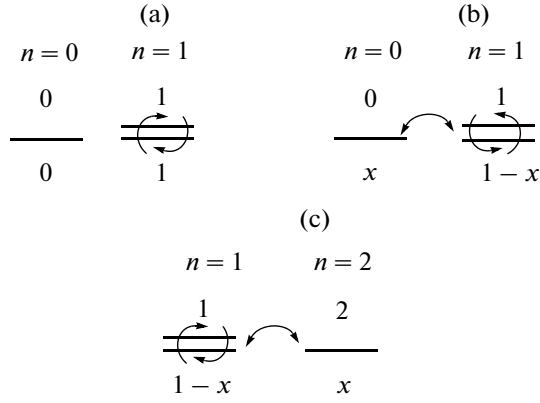
Fig. 1. Scheme of the configuration space and contributions to the entropy for (a) undoped cuprates, (b) cuprates doped by holes, and (c) cuprates doped by electrons. The occupation numbers x and $1 - x$ of terms with different n in the case of doping are shown in the figure.

Fig. 2. Dependences of the entropy s on the hole concentration x ($t = 0.5$ eV and $J = 0.5$ eV) according to (*1–3*) calculations with inclusion of the dispersion at different temperatures: (*1*) >0.004, (*2*) 0.001, and (*3*) 0.0005 eV; and (*4*) dependence of the entropy on the hole concentration in the atomic limit.

Another interesting interpretation of formula (10) can be obtained by calculation of number g of the ways of seating N_e electrons on N sites within the $t–J$ model:

$$g = \frac{2^{N_e} N!}{N_e!(N - N_e)!} \cong \frac{2^{(1-x)N}}{x^{xN}(1-x)^{(1-x)N}}. \tag{11}$$

Comparing Eqs. (10) and (11), we conclude that

$$s_0 = k_B \frac{\ln g}{N}, \tag{12}$$

i.e., we obtain the well-known Boltzmann formula.

From Eq. (10), we find that at $x = 0.1$ the derivative $\frac{\partial s_0}{\partial x}$ equal to the entropy jump upon addition of one hole to the system is $\frac{\partial s_0}{\partial x} = 1.5k_B$. So, already in the atomic limit, a jump value close to the experimental one is obtained. In the next section, we will discuss the entropy behavior with regard of perturbation H_1 taking into account the hoppings and the exchange interaction.

3. CONTRIBUTION OF THE INTERATOMIC INTERACTIONS TO THE THERMODYNAMICS OF THE $t–J$ MODEL

In order to find a correction to the thermodynamic potential of the $t–J$ model caused by the hoppings and the exchange interaction, we used the integration over the interaction constant. Along with Hamiltonian (3), we will introduce one more Hamiltonian
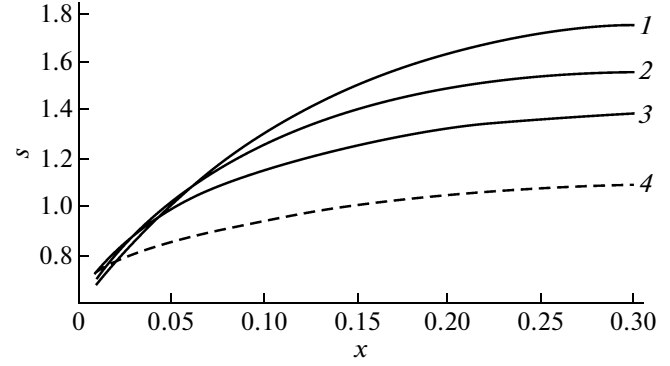
$$H = H_0 + \lambda H_1, \tag{13}$$

where H_0 and H_1 are given by expressions (4) and (5), respectively, and the interaction constant is $0 \leq \lambda \leq 1$. The correction to the thermodynamic potential is [6]

$$\Delta\Omega = -\frac{a^2}{4\pi^2} k_B T \int_0^1 \frac{d\lambda}{\lambda} \int_{\substack{\text{first zone} \\ \text{of Brillouin}}} d^2\mathbf{k} \sum_{\omega_n} G^{(0)-1}(\mathbf{k}, \omega) \tag{14}$$

$$\times (G(\lambda, \mathbf{k}, \omega) - G^{(0)}(\mathbf{k}, \omega)),$$

where the internal integral is taken over the first Brillouin zone for a two-dimensional square lattice with parameter a, summation is made over the Matsubara frequencies $\omega_n = (2n + 1)\pi k_B T$ ($n = 1, 2, 3, ...$), $G(\lambda, \mathbf{k}, \omega)$ is the electron Green's function for the system described by Hamiltonian (13), and $G^{(0)}(\mathbf{k}, \omega)$ is the electron Green's function of the system at $\lambda = 0$. Note that $G(\lambda, \mathbf{k}, \omega)$ is the Fourier transform of the function $G_{ij}(E) = \langle\langle X_i^{0\sigma} | X_j^{\sigma 0} \rangle\rangle$. In the Hubbard-1 approximation,

$$G(\lambda, \mathbf{k}, E) = \frac{F_{0s}}{E - \varepsilon(\lambda, \mathbf{k})}, \tag{15}$$

where $\varepsilon(\lambda, \mathbf{k}) = \varepsilon - \mu(\lambda) - \lambda(F_{0s}t(\mathbf{k}) + \mathbf{J_0 n_s})$, $\mu(\lambda)$ is the chemical potential for the system described by Hamiltonian (13), $F_{0s} = \langle X_i^{00} + X_i^{\sigma\sigma} \rangle = \frac{1+x}{2}$ is the spectral weight of quasiparticles, $t(\mathbf{k})$ is the Fourier transform of hopping integral $t_{\mathbf{fm}}$, J_0 is the Fourier transform at $\mathbf{q} = 0$ of exchange integral $J_{\mathbf{fm}}$, $J(\mathbf{q}) = \sum_{\mathbf{f-m}} J_{\mathbf{fm}} \exp(-i\mathbf{q}(\mathbf{f} - \mathbf{m}))$, and $n_s = \langle X_i^{\sigma\sigma} \rangle = \frac{1-x}{2}$.

To obtain the final result, it is necessary to solve the equation with respect to the chemical potential. Using

the spectral theorem for the Green's functions, we obtain the following equation:

$$(1 + x)\frac{a^2}{4\pi^2} \int\limits_{\substack{\text{first zone} \\ \text{of Brillouin}}} \frac{d^2\mathbf{k}}{\exp\left(\dfrac{\varepsilon(\lambda, \mathbf{k})}{k_B T}\right) + 1} = 1 - x, \quad (16)$$

where the integral is taken over the first Brillouin zone and the band spectrum $t(\mathbf{k})$ was taken in the approximation of the nearest neighbors:

$$t(\mathbf{k}) = 2t(\cos(k_x a) + \cos(k_y a)). \quad (17)$$

At fixed λ, x, and T, Eq. (16) has the only root. The roots of Eq. (16) at different λ, x, and T must be substituted into the final expression for the entropy correction that we obtain differentiating the correction to the thermodynamic potential with respect to the temperature with the minus sign before the derivative:

$$\Delta s = \frac{a^2}{4\pi^2} k_B \int\limits_0^1 d\lambda \int\limits_{\substack{\text{first zone} \\ \text{of Brillouin}}} d^2\mathbf{k}$$

$$\times \frac{\varepsilon(\lambda, \mathbf{k})(\varepsilon(\lambda, \mathbf{k}) + \mu_0 - \varepsilon)\exp\left(\dfrac{\varepsilon(\lambda, \mathbf{k})}{k_B T}\right)}{\lambda k_B^2 T^2 \left[\exp\left(\dfrac{\varepsilon(\lambda, \mathbf{k})}{k_B T}\right) + 1\right]^2}, \quad (18)$$

where μ_0 is calculated by formula (9).

4. CONCLUSIONS

The problem on finding the dependence of entropy on the hole concentration can be solved only numerically. The results obtained by us are presented in Fig. 2. We found that at $x = 0.1$ and $k_B T \geq 0.002$ eV, the partial derivative is $\dfrac{\partial s}{\partial x} \approx 3.47 k_B$, i.e., the entropy increase upon addition of one hole to the system is $\Delta s \approx 3.47 k_B$. It is interesting to note that at $T = 0$ the right-hand side of expression (18) for the correction to the entropy becomes zero. Thus, at $T = 0$ the curve $s(x)$ coincides with the curve described by expression (10), i.e., with entropy s_0 in the atomic limit.

REFERENCES

1. J. W. Loram, J. Luo, J. R. Cooper, W. Y. Liang, and J. L. Tallon, J. Phys. Chem. Solids **62**, 59 (2001).
2. J. R. Cooper and J. W. Loram, J. Phys. (Paris) **10**, 214 (2000).
3. J. C. Hubbard, Proc. R. Soc. London, Ser. A **285**, 542 (1965).
4. V. I. Belinicher, A. L. Chernyshev, and V. A. Shybin, Phys. Rev. B: Condens. Matter **53**, 335 (1996).
5. N. M. Plakida and V. S. Oudenko, Phys. Rev. B: Condens. Matter **59**, 11949 (1999).
6. A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinskii, Methods of *Quantum Field Theory in Statistical Physics* (Pergamon, London, 1965; Dobrosvet, Moscow, 1998), 2nd ed.

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