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Features of the Low-Temperature Specific Heat in Underdoped $YBa_2Cu_3O_{6+x}$ Single Crystals

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The behavior of the low-temperature specific heat $C(T)$ for $YBa_2Cu_3O_{6+x}$ single crystals with the doping level corresponding to the normal phase has been studied by the relaxation technique at different values of the applied magnetic field. It has been found that the $C(T)/T$ plot exhibits such an anomaly as a steep increase with decreasing temperature from T about 4 K down to $T \le 2$ K (the minimum temperature value accessible in the experiment). The applied magnetic field as high as 9 T inverts this anomaly and leads to a sharp drop in $C(T)/T$ during cooling within the same temperature range. A model involving the Schottky-type centers formulated in this work and the data on spin correlation functions has allowed us to calculate the temperature dependence of the specific heat, which fits the experimental curves quite well.

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In spite of the intensive studies of the high-T_c superconductor $YBa_2Cu_3O_{6+x}$ that have been carried out since its discovery [1], the electronic and thermal properties of this compound still remain enigmatic in many respects. In particular, the mechanisms underlying the evolution of the low-energy elementary excitation spectrum under the effect of the applied magnetic field are not properly understood. The data on the low-temperature specific heat play an important role in analyzing the characteristic features of this spectrum.

In this paper, we present the results on the temperature dependence of the specific heat for high-quality $YBa_2Cu_3O_{6+x}$ single crystals. The measurements were taken at the applied magnetic field ranging from zero to 9 T. We studied three samples annealed at different temperatures. By comparing the experimental data with the model calculations, we found the values of the characteristic parameters for this model interpreting the origin of the Schottky anomaly in $YBa_2Cu_3O_{6+x}$.

1. The studies of the temperature dependence of the specific heat at low temperatures were performed using high-quality $YBa_2Cu_3O_{6+x}$ single crystals grown at the Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences (Novosibirsk). The crystals 35.7 mg in weight had no visible traces of the block structure. The changes in the oxygen content were achieved by the variation of the annealing temperature at the fixed partial pressure of oxygen [2]. The annealing was performed during 48 h at $T = 825$, 850, and 890°C. After that, the samples were quenched in liquid nitrogen and remained there just until the measurements to avoid an exchange with atmospheric oxygen. As a result, we obtained samples with $x = 0.34$, 0.32, and 0.28. All of the samples were nonsuperconducting; this was checked by the measurements of the temperature dependence of the dc magnetization, which gave no indications of the superconducting transition down to 1.9 K.

The low-temperature specific heat $C(T)$ was studied using the Quantum Design PPMS-6000 setup. The $C(T)$ temperature dependence was measured by the relaxation technique on heating from 1.9 to 10 K at a fixed applied magnetic field ranging from zero to 9 T. To increase the accuracy, all of the measurements were taken at two stages. At the first stage, we measured the specific heat of the empty sample holder with thermal grease applied onto it, whereas at the second stage, we measured the heat capacity of the empty sample holder with the sample. Using the obtained data, we calculated the specific heat of the sample.

In Fig. 1, we illustrate the change in the temperature dependence of the specific heat under the effect of the applied magnetic field $H = 9$ T for the sample with $x = 0.28$. It is seen that at the lowest temperature values, the magnetic field reduces the heat capacity, while in the temperature range near 5 K, an appreciable increase in the specific heat is observed. Upon further

heating, the change in the specific heat becomes smaller. A similar effect of the applied magnetic field on the temperature dependence of the specific heat was also observed for the samples with $x = 0.32$ and 0.34.

To separate the electron and phonon contributions to the specific heat and to demonstrate the Schottky anomaly in the $YBa_2Cu_3O_{6+x}$ single crystals under study, Fig. 2 shows the plots of the $C(T)/T$ ratio against T^2 at three values of the applied magnetic field. The shape of these curves exhibits three main features:

(a) at zero magnetic field, the $C(T)/T$ curve has a minimum at T of about 4 K. Below the temperature corresponding to this minimum, $C(T)/T$ increases rapidly;

(b) the applied magnetic field $H \sim 9$ T qualitatively changes the shape of the $C(T)/T$ curve. The steep increase in $C(T)/T$ is changed to its fast decrease. The crossover in the $C(T)/T$ behavior occurs at intermediate values of the magnetic field;

(c) at relatively high temperatures, the magnetic field leads to a displacement of the $C(T)/T$ curve.

The last feature gives an indication of the renormalization of the electronic contribution to the specific heat. Such a renormalization can be naturally interpreted in terms of the strong correlation between the electronic and spin degrees of freedom (see below).

The low-temperature anomaly in the specific heat at $H = 0$ was earlier reported for the $YBa_2Cu_3O_{6+x}$ compound [3]. To explain this anomaly, Alexeevskii et al. [3] suggested the presence of Schottky-type centers in the studied compounds. The transformations in the behavior of $C(T)/T$ under the effect of the applied magnetic field is determined by the characteristic features of the low-energy spectrum of the system and their changes after the switching-on of the magnetic field. In addition to the phonon contribution, the total specific heat in the low-temperature range is also determined by the contributions from the local excitations in the CuO_x chains. Below, we will demonstrate that the number of oxygen atoms in these chains depending on the annealing temperature T^* for the given sample affects the magnitude of the Schottky-type anomalies. The inclusion of these factors is assumed as the basis for the interpretation of the aforementioned experimental findings.

2. To formulate the model of the Schottky-type centers, we take into account that oxygen atoms are nominally bivalent (O^{2-}), while copper ions can have either the completely filled $3d$ shell corresponding to Cu^{1+} or the underfilled shell like in Cu^{2+} [4].

Figure 3 schematically illustrates the scenario for the formation of copper–oxygen complexes leading to the Schottky anomaly. If the annealing temperature is high enough, we obtain the $YBa_2Cu_3O_6$ compound having no oxygen in the chains; i.e., all copper ions are

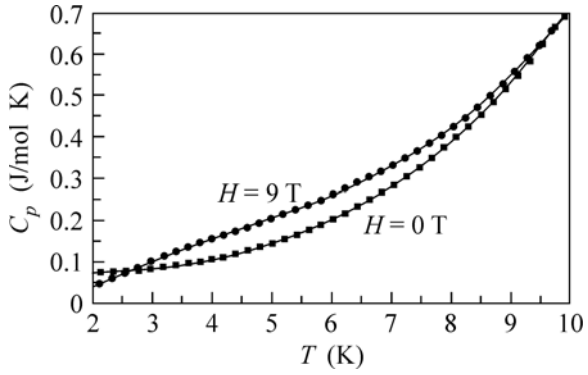

Fig. 1. Low-temperature behavior of the specific heat $C(T)$ for the $YBa_2Cu_3O_{6+0.28}$ sample at two values of the magnetic field.

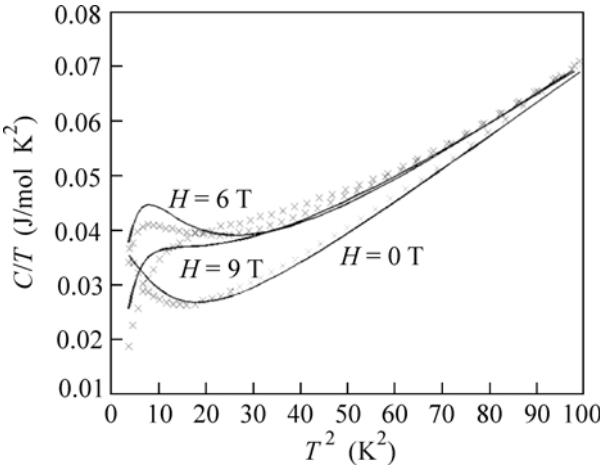

Fig. 2. Low-temperature behavior of the $C(T)/T$ ratio for the $YBa_2Cu_3O_{6+0.28}$ sample at different values of the magnetic field. The crosses are the experimental data and the solid lines are the theoretical curves.

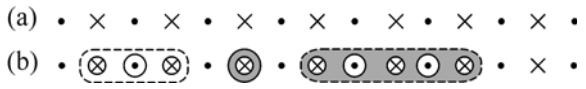

Fig. 3. Formation of Schottky centers in chains.

univalent. Schematically, this situation is shown in Fig. 3a. The points denote vacant oxygen positions and the crosses correspond to Cu^{1+} ions. In this case, there are no Schottky-type centers in the chains. As the annealing temperature decreases, oxygen occupies the vacant positions giving rise to the $YBa_2Cu_3O_{6+x}$ compound. At small x values, oxygen ions occupying

the positions between two copper ions form the three-ion complexes (Cu–O–Cu) so that the oxygen positions both on the left and right sides from such complexes remain empty (see the left unshaded complex in Fig. 3b). The formation of chemical bonds in the three-ion complexes gives rise to divalent copper ions with the spin moment $s = 1/2$. The Anderson superexchange [5] involving O^{2-} leads to the singlet state in Cu–O–Cu. Hence, these complexes are not involved in the formation of the Schottky anomaly.

With a further reduction of the annealing temperature and an increase in x, five-ion complexes appear in the chains. In these complexes, oxygen ions occupy only two nearest-neighbor vacancies (see the right shaded complex in Fig. 3b). The concentration of such complexes is proportional to $\sim x^2(1 - x)^2$. The total number of energy levels in a Cu–O–Cu–O–Cu complex including the orbital states ($l = 2$) is equal to 1000. However, due to the odd number of copper ions with $s = 1/2$, such a complex can form the Schottky anomaly.[1]

Note that it is necessary to have an additional electron to form a five-ion complex with the nominal valence of the ions. There are two possibilities. In the first case, the electron comes from CuO_2 planes. This leads to the creation of holes in these planes. In the second case, the missing electron is taken from the $3d$ shell of a univalent copper ion. Such a mechanism implies the formation of an isolated (without oxygen ions both on its left and right) Cu^{2+} ion (see the shaded single-ion complex in the middle of Fig. 3b) having spin $s = 1/2$. It is easy to see that such isolated ions can play the role of the Schottky-type centers.

If not all ions in the five-ion complex correspond to the nominal valence, there should exist a hole moving within this complex. Since the hole introduces an additional spin $s = 1/2$, the ground state in this case is singlet. Therefore, such a complex is also not involved in the formation of the Schottky anomaly. This means that only a certain part of five-ion complexes will contribute to the Schottky anomaly. As a result, in the calculation of the contributions from the Schottky-type centers to the total specific heat, we should include a correction factor to take into account the concentration of five-ion complexes contributing to the Schottky anomaly. Let us emphasize that the contribution of the Schottky anomaly calculated neglecting this effect is overestimated as compared to that deduced from the experimental data.

3. A divalent copper ion is characterized by the spin ($s = 1/2$) and orbital angular momentum ($l = 2$). The set of its energy levels emerges under the effect of the crystal field, spin–orbit interaction, and applied magnetic field. The corresponding Hamiltonian for a Cu^{2+} ion located at the fth site can be written as

$$H_0(f) = -\frac{K}{2}(l_{fx}^4 + l_{fy}^4 + l_{fz}^4) - \lambda(\mathbf{s_f l_f}) + \Delta(l_{fx}^2 - l_{fy}^2) - \mu_B H(2s_{fz} + l_{fz}), \quad (1)$$

where the first term describes the interaction with the cubic-symmetry component of the crystal field, the second term takes into account the spin–orbit interaction, and the third term reproduces the effect of the orthorhombic anisotropy. The last term in this Hamiltonian corresponds to the Zeeman energy at the applied magnetic field H.

In the five-ion complex, where copper ions occupy sites f_1, f_2, and f_3, it is necessary to take into account the exchange interaction between the spin moments $\mathbf{S}_{f_i}$ of these ions. Hence, the total Hamiltonian for this complex has the form

$$H = \sum_{i=1}^{3} H_0(f_i) + I(\mathbf{S}_{f_1}\mathbf{S}_{f_2} + \mathbf{S}_{f_2}\mathbf{S}_{f_3}), \quad (2)$$

where I is the exchange integral. Using these Hamiltonians, we determined the energies of single- and five-ion complexes. The variation of the model parameters K, λ, and Δ provided an opportunity to describe the changes in the temperature dependence of $C(T)/T$ after the switching-on of the magnetic field and to overcome the difficulties arising earlier in the interpretation of the observed anomalies in the framework of the two-level model [6]. Satisfactory results were obtained under the conditions

$$\lambda \sim K > 0; \quad \lambda, K \gg \Delta, \mu_B H.$$

Let us emphasize that in the intermediate field range, the experimental points were put onto the curves obtained without any additional fitting, that is, using the same model parameters found for $H = 0$ and 9 T.

The molar specific heat for the set of Schottky centers formed by solitary copper ions was calculated using the expression

$$C_1 = \frac{n_1 N_A}{k_B T^2}\left\{\overline{E^2} - (\overline{E})^2\right\}, \quad (3)$$

where n_1 is the concentration of Cu^{2+} ions surrounded by copper vacancies (see Fig. 3). The averages appearing in Eq. (3) were determined using the Gibbs distribution ($q = 1, 2$)

$$\overline{E^q} = \sum_n (E_n)^q \exp(-E_n/T) / \sum_m \exp(-E_m/T),$$

where E_n are the eigenvalues of Hamiltonian (1).

[1] We are grateful to a referee, who drew our attention to this fact significant for the further analysis.

In a similar way, we calculated the specific heat of the five-ion complexes C_5 with the concentration per unit cell $n_5 = px^2(1-x)^2/3$, where p is the correction factor related to the possibility for a hole to be located at the five-ion complexes (see above):

$$C_5 = \frac{n_5 N_A}{k_B T^2}\left\{\overline{E^2} - (\overline{E})^2\right\}. \quad (4)$$

The corresponding Gibbs distribution was determined using 1000 eigenvalues of Hamiltonian (2).

4. To calculate the contribution to the specific heat from the charge carriers in CuO_2 planes, we should take into account the well-known concept concerning the existence of strong electron correlations in the Fermi subsystem. These correlations depend both on the temperature and applied magnetic field. Thus, their variations can lead to additional changes in the specific heat of the charge carriers under the effect of the magnetic field.

The main features of the electron structure of the CuO_2 plane are reproduced quite well by the t–J model described by the Hamiltonian

$$H_{t-J} = \sum_{f\sigma}(\varepsilon - 2\mu_B H\sigma - \mu)X_f^{\sigma\sigma} + \sum_{fm\sigma} t_{fm} X_f^{\sigma 0} X_m^{0\sigma}$$

$$+ \frac{1}{2}\sum_{fm\sigma} J_{fm}(X_f^{\sigma\bar{\sigma}} X_m^{\bar{\sigma}\sigma} - X_f^{\sigma\sigma} X_m^{\bar{\sigma}\bar{\sigma}}),$$

where μ is the chemical potential, t_{fm} is the hopping integral, J_{fm} is the exchange coupling constant, ε is the electron self-energy, and $-2\mu_B H\sigma$ is the energy of the interaction of the magnetic field with an electron having spin projection σ onto the direction of the magnetic field.

The Hamiltonian H_{t-J} describes an ensemble of the Hubbard fermions, a pair of which cannot occupy the same site. In addition to the kinetic energy of fermions, this Hamiltonian includes the exchange coupling between their spin moments. This coupling affects the value of the magnetic correlation functions, thus leading to additional changes in the specific heat under the effect of the applied magnetic field.

Further on, to calculate the electronic specific heat of the itinerant subsystem, we will use the Hubbard-I approximation and consider only the case of the nearest-neighbor hopping. In this case, the spectrum of fermionic excitations has the form [7]

$$\varepsilon_k = 2c_n t_1(\cos k_x + \cos k_y), \quad (5)$$

where t_1 is the in-plane nearest-neighbor hopping integral, $c_n = 1 - n/2$, and n is the number of electrons per oxygen ion in the plane. Note that $YBa_2Cu_3O_{6+x}$ contains four oxygen atoms located in a CuO_2 plane per each unit cell of $YBa_2Cu_3O_{6+x}$. Hence, the electron density n introduced above is given by the expression

$$n = 1 - h/4.$$

Here, h is the number of holes per unit cell in the $YBa_2Cu_3O_{6+x}$ compound.

In the system of Hubbard fermions, the internal energy per unit cell can be written in the form (if we neglect the terms unimportant for the problem under study)

$$U = \frac{1}{N}\sum_{k\sigma}\varepsilon_{k\sigma}\langle X_{k\sigma}^{+} X_{k\sigma}\rangle + \sum_{\delta} J_\delta \langle \mathbf{S}_f \mathbf{S}_{f+\delta}\rangle.$$

Here, the second term corresponds to the exchange interaction energy, which depends on the spin correlation function $\langle \mathbf{S}_f \mathbf{S}_{f+\delta}\rangle$. While considering the exchange interaction, we take into account the existence of two CuO_2 planes within each unit cell and use the nearest-neighbor approximation. In this case, the parameter δ corresponds either to the vector connecting the nearest neighbors in the CuO_2 plane (δ_{xy}) or to each of the two vectors connecting spin moments in the perpendicular direction. One of them, $\delta_\perp$, connects the spin moments lying in those two planes, which are located in one unit cell and are separated only by yttrium ions. The second vector, $\delta'_\perp$, connects the spin moments lying in CuO_2 planes located within the neighboring unit cells in the direction of the c axis and separated by the charge reservoir [4]. The exchange coupling constants for these pairs should be different, $J_{\delta_\perp}$ and $J_{\delta'_\perp}$, respectively.

Note that the distance between the CuO_2 planes separated by the charge reservoir is three times longer than the distance between the planes separated by yttrium ions. Consequently, we can neglect the contribution of correlation functions $\langle \mathbf{S}_f \mathbf{S}_{f+\delta'_\perp}\rangle$ for the distant spins.

It is important that the in-plane exchange coupling constant $J_{\delta_{xy}} \sim 300$ K and, hence, the in-plane magnetic correlation function $\langle \mathbf{S}_f \mathbf{S}_{f+\delta_{xy}}\rangle$ vary only slightly in the low-temperature range. Therefore, the corresponding contribution to the specific heat is small and neglected below.

The interplane interaction $J_{\delta_\perp}$ is relatively weak and, consequently, the interplane correlation function $\langle \mathbf{S}_f \mathbf{S}_{f+\delta_\perp}\rangle$ will be significantly modified in the considered temperature range due to both the temperature and applied magnetic field. When the exchange interaction tends to establish an antiferromagnetic ordering, which corresponds to a negative value of the correlation function $\langle \mathbf{S}_f \mathbf{S}_{f+\delta_\perp}\rangle_0$ in zero magnetic field,

Parameters of the samples for various oxygen content, h is the hole density per unit cell in the planes

x	h	β, 10^{-4} J/mol K^4
0.28	0.05	6.0
0.32	0.06	5.8
0.34	0.07	5.2

this modification can be described by the relationship [8]

$$\langle \mathbf{S}_f \mathbf{S}_{f+\delta_\perp} \rangle = \langle \mathbf{S}_f \mathbf{S}_{f+\delta_\perp} \rangle_0 \left(1 - \left(\frac{H}{H^*}\right)^2\right)\left(1 - \left(\frac{T}{T^*}\right)^3\right)$$

at $H \ll H^*$ and $T \ll T^*$, where H^* and T^* are the characteristic values of the magnetic field and the temperature corresponding to significant changes in the spin correlation function. These characteristic values will be determined by the comparison of the calculations and the experimental data.

The previous discussion suggests that the part of the exchange energy significantly contributing to the specific heat (per lattice site) of the system under study can be written as

$$U_J = J_{\delta_\perp} \langle \mathbf{S}_f \mathbf{S}_{f+\delta_\perp} \rangle.$$

The kinetic energy of itinerant electrons per oxygen ion is given by the expression

$$U_t = 2\int \frac{c_n g(\omega)\omega}{1 + \exp\{(\omega - \mu)/T\}} d\omega,$$

in which the chemical potential μ as a function of the temperature and charge carrier density is found from the equation

$$\frac{n}{2} = \int \frac{c_n g(\omega) d\omega}{1 + \exp\{(\omega - \mu)/T\}},$$

where $g(\omega)$ is the density of states

$$g(\omega) = \frac{1}{N}\sum_k \delta(\omega - \varepsilon_k).$$

The molar specific heat of the system consisting of the Hubbard fermions is given by the formula

$$C_{t-J} = 4N_A \frac{dU}{dT}.$$

The total molar specific heat is expressed as a sum of the electronic specific heat, the specific heat due to the complexes in the chains, and the lattice specific heat

$$C = C_{t-J} + C_1 + C_5 + \beta T^3.$$

Note that the factor β can depend on the annealing temperature owing to the difference in the structure of the samples.

Comparing the calculated plots of the specific heat with the experimental data, we found the following parameters: $t_1 = -2.0$ eV, $H^* = 11$ T, $K = 600$ K, $\lambda = 1000$ K, $\Delta = 0.6$ K, $I_{ex} = 500$ K, $n_1 = 0.01$, $p = 1/4$, and $\langle \mathbf{S}_f \mathbf{S}_{f+\delta_\perp} \rangle_0 J_{\delta_\perp} (T^*)^{-3} = 2.4 \times 10^{-8}$ eV/K^3. These parameters are the same for different annealing temperatures. The parameters depending on the oxygen content x in the chains are presented in the table.

In all of the samples under study, the hole density is low and the Fermi energy lies near the upper bound of the energy spectrum, where the density of states in the two-dimensional case varies rather slowly. It leads to a weak dependence of the density of states at the Fermi level on the hole density in CuO_2 planes and, hence, on the oxygen content. This accounts for the fact that the Sommerfeld constant $\gamma = 1.5$ mJ/(mol K^2) remains the same for different samples.

5. The agreement of the theoretical and experimental curves demonstrates that the suggested model provides a qualitatively correct description for the low-temperature features experimentally observed in the heat capacity of underdoped $YBa_2Cu_3O_{6+x}$ compounds. Let us emphasize that for the description of such subtle features of the Schottky anomalies varying under the effect of the applied magnetic field, the introduced structure of the chain complexes turned out to be quite significant. The different dependences of the interplane and in-plane spin correlation functions on the external parameters also appeared to be important.

In conclusion, note that the performed experimental studies of the underdoped $YBa_2Cu_3O_{6+x}$ copper oxides and the analysis of the obtained anomalies have allowed us to specify the nature of the Schottky-type centers and their energy structure. The parameters of the energy structure and the characteristic values of the temperature and magnetic field corresponding to the ranges of steep changes in magnetic correlation functions, which we determined during the course of this study, agree well with the existing data. An important role in fitting the theory and experiment was assigned to the factors determining the magnitude of the Schottky anomalies. One of such factors is the number of the Schottky-type centers. The mechanism underlying the formation of such centers, which was discussed in this paper, provided an opportunity to relate the concentration of the Schottky-type centers to the concentration of oxygen ions and to determine the parameters necessary for the experiment.

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