

Polaron Effects on Superexchange Interaction: Isotope Shifts of T_N , T_c , and T^* in Layered Copper Oxides

M. V. Eremin*, I. M. Eremin, I. A. Larionov, and A. V. Terzi

Kazan State University, Kazan, 420008 Tatarstan, Russia

*Mikhail.Eremin@ksu.ru

Received February 21, 2002; in final form, March 14, 2002

A compact expression has been obtained for the superexchange coupling of magnetic ions via intermediate anions with regard to polaron effects on both magnetic ions and intermediate anions. This expression is used to analyze the main features of the behavior of isotope shifts for temperatures of three types in layered cuprates: the Neel temperatures (T_N), critical temperatures of transitions to a superconducting state (T_c), and characteristic temperatures of the pseudogap state of normal phases (T^*). © 2002 MAIK "Nauka/Interperiodica".

PACS numbers: 74.25.-q; 74.72.-h

Elucidating the nature of an unusual isotope effect in copper–oxygen superconductors is one of the most important problems on the way to ascertaining the mechanism of the pairing of charge carriers in these compounds. It is known that it was the observation of an isotope shift of the superconducting transition temperature (T_c) that was of crucial importance in ascertaining the phonon mechanism of pairing in conventional (low-temperature) superconductors. The fact that an isotope effect exists in high-temperature superconductors built of copper–oxygen planes has long been beyond question; however, the relative smallness of the coefficient (for example, $\alpha_{T_c} \sim 0.056$ for $\text{YBa}_2\text{Cu}_4\text{O}_8$ upon replacing ^{16}O with ^{18}O , instead of the standard value 0.5) and the specific features of its behavior in other compounds upon changing the number of holes in copper–oxygen planes do not fit the Bardeen–Cooper–Schrieffer (BCS) scenario. At the same time, the majority of authors of articles related to the isotope effect (see the recent review [1]) correctly point out that, nevertheless, phonon modes, in some mysterious way, affect the superconducting transition temperature. In this context, we believe that the facts of observing an isotope effect for the characteristic temperature of the pseudogap state of underdoped cuprates (so-called pseudogap onset temperature T^*) gain great importance. Thus, according to [2], the isotope exponent upon replacing ^{16}O with ^{18}O corresponding to T^* is $\alpha_{T^*} = 0.061$. It was natural that this fact suggested a common origin of α_{T_c} and α_{T^*} [2].

We believe that another and even more important similarity in the dependence of the order parameters of the superconducting and pseudogap phases on the d -type wave vector (that is, $\cos q_x - \cos q_y$) explained had been under the assumption that the transitions to

both these phases are associated with short-range potentials [3]. It seems that superexchange interaction, screened Coulomb repulsion, and interaction of holes mediated by optical phonons are the most significant of these. The isotope shift of T_c and T^* due to interaction mediated by optical phonons was discussed in a few works (see, for example, [4, 5]), and that for T^* was considered in [6]. Below, we will focus our attention on polaron corrections to the superexchange coupling of copper spins (J) and demonstrate that a number of features in the behavior of the isotope shift of T_c upon changing the number of holes in the CuO_2 plane can be quite reasonably explained even within the framework of the purely superexchange mechanism of pairing.

First, we emphasize the following important fact. Within the scenario [3], the superconducting transition temperature $T_c \sim 2J - G$, whereas the characteristic temperature of the pseudogap phase $T^* \sim J + G$ [3, 7]. Here, G is the parameter of the screened Coulomb interaction of holes on the nearest copper sites, which partially includes the correction due to interaction mediated by optical phonon modes. If it is granted that the isotope shift is associated with the phonon renormalization of G , the shifts of T_c and T^* would be of opposite sign, which is in contradiction with the experimental results [2]. In this connection, it is believed that the scenario of phonon renormalization of the parameter J is more reasonable to suggest as the source of positive isotope shifts of T_c and T^* .

The renormalization of J within the Hubbard model was investigated in detail by Kugel' and Khomskii [8]. It is evident from the above estimates $T_c \sim 2J - G$ and $T^* \sim J + G$ that the small increase in J proportional to the phonon frequency found in this work gives the correct sign of the isotope shifts but does not provide the required magnitude of the shifts. This can be most sim-

ply demonstrated with the example of the isotope shift of the Neel temperature in related high- T_c compounds. As was already indicated in [1], the Kugel' and Khomskii correction gives the correct sign of the isotope shift of the Neel temperature (T_N) in La_2CuO_4 upon replacing ^{16}O with ^{18}O ; however, even the most overrated estimates give a value that is six times lower than the experimental one.

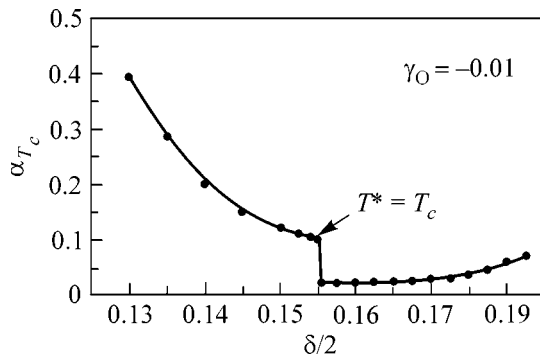
We believe that the main reason for the quantitative disagreement between the theory [8] and the experiment [1] is in the fact that the Hubbard model is not suitable for the compounds we are interested in. As was already stressed in [9], the energies of electron transfer from oxygen to a magnetic ion (Δ_c) in the majority of copper oxides are smaller than the energy of electron transfer from copper to copper (Δ_a). However, the Hubbard model gives correct estimates only when $\Delta_a \geq \Delta_c$.

The Hamiltonian in the form

$$\hat{H} = \sum \varepsilon_a a_\sigma^+ a_\sigma + \sum \varepsilon_c c_\sigma^+ c_\sigma + \sum U_a n_\uparrow^a n_\downarrow^a + \sum U_c n_\uparrow^c n_\downarrow^c + \sum t_{ac} (a_\sigma^+ c_\sigma + c_\sigma^+ a_\sigma) \quad (1)$$

is best suited to the description of superexchange interaction explicitly taking into account the cascade hopping of electrons over oxygen. As applied to high- T_c superconductors, it is rather frequently named the Emery Hamiltonian. Here, t_{ac} is the hopping integral between neighboring copper and oxygen sites, and U_a and U_c are the parameters of electron Coulomb repulsion. We will estimate the corrections to the superexchange parameter J due to polaron effects at copper (a) and oxygen (c) sites in the fashion of [8], supplementing Eq. (1) with the electron-phonon coupling operator

$$\hat{H}_{ep} = \sum_{a,b,c} g_i n_i (p_q + p_{-q}^+). \quad (2)$$



Exponent of the isotope shift of T_c upon replacing ^{16}O with ^{18}O as a function of the number of holes per one copper site. The symbols in the curve correspond to the points at which T_c and T^* were calculated.

Here, p_q and p_{-q}^+ are phonon annihilation and creation operators, and g_i is the coupling parameter connected with the polaron stabilization energy (E_i) at site i by the equation $E_i = g_i^2 / \hbar \omega_i$, where ω_i are local vibrational frequencies.

In the physical context, this calculation corresponds to a simplified Holstein model, where the migrating charge locally interacts with breathing modes, forming electron-vibrational states with dispersionless optical phonons. In this connection, it is pertinent to note that conduction in the compounds under consideration is exactly of the polaron type and is accomplished mainly via oxygen ion sites [10].

This calculation is performed most simply by the method of canonical transformations. The matrix of the unitary transformation of the initial Hamiltonian is found by excluding the odd terms with respect to hopping integrals with an accuracy up to sixth-order perturbation theory. The calculation, whose mathematical details will be given in a more detailed article, gives the following result:

$$J = J_0 \left\{ 1 + \frac{3\hbar}{(\Delta_{ca})^2} \left[E_a \omega_a \coth\left(\frac{\hbar \omega_a}{2k_B T}\right) + E_c \omega_c \coth\left(\frac{\hbar \omega_c}{2k_B T}\right) \right] \right\}, \quad (3)$$

where $\Delta_{ac} = \varepsilon_a - \varepsilon_c + U_a - U_c$ means the energy of transfer from oxygen to copper, and the corrections proportional to $E_a \hbar \omega_a / \Delta_{ac} U_a^2$ and $E_c \hbar \omega_c / U_a^3$ are not given because of their smallness for the compounds under consideration. J_0 is the parameter of superexchange interaction of copper spins via the intermediate oxygen atom in the absence of phonons [9, 11]. Note that the appearance of temperature factors in our equation is generally characteristic of the problems on transitions in transition metal compounds with the participation of quasilocal vibrations [12]. At the same time, it should be born in mind that polaron effects break down at $T \sim \omega$ and the concepts used here become inapplicable.

The results of our calculations are given in the figure. The system of integral equations for the mean field parameters corresponding to the transition to the pseudogap phase was solved self-consistently. We identify the pseudogap phase with the phase of sliding charge-density waves. This system was written in detail in [3] and is not given here.

For the description of the superexchange coupling parameter upon replacing some isotopes for other ones at $\hbar \omega \gg k_B T$, it is convenient to introduce parameters γ_{Cu} and γ_{O} by writing

$$J = J_0 \left[1 + \gamma_{\text{Cu}} \left(\frac{\Delta M_{\text{Cu}}}{M_{\text{Cu}}} \right) + \gamma_{\text{O}} \left(\frac{\Delta M_{\text{O}}}{M_{\text{O}}} \right) \right]. \quad (4)$$

It follows from Eq. (3) that, upon replacing ^{16}O with ^{18}O ,

$$\gamma_{\text{O}} \approx -\frac{3}{2} \left(\frac{E_a \hbar \omega_a}{\Delta_{\text{Cu-O}}^2} \right), \quad (5)$$

whereas, upon replacing ^{63}Cu with ^{65}Cu ,

$$\gamma_{\text{Cu}} \approx -\frac{3}{2} \left(\frac{E_c \hbar \omega_c}{\Delta_{\text{Cu-O}}^2} \right). \quad (6)$$

Substituting here (in electronvolts) $\Delta_{\text{Cu-O}} = 1.5$ [13] and standard values $\hbar \omega_a = 0.05$, $E_a = 0.4$ [10, 14], and using the relationship $\Delta T_N/T_N \approx \Delta J/J$ characteristic of layered cuprates (see [1]), we find that the Neel temperature should decrease by 0.2% upon replacing ^{16}O with ^{18}O in $\text{YBa}_2\text{Cu}_3\text{O}_{6.383}$. According to measurements in La_2CuO_4 [15], the shift $\approx 0.6\%$. If, however, it is assumed, following [1], that $E_a = 1.2$ eV, our estimate will coincide with the experimental value. We hope that this explanation of the isotope shift of T_N will stimulate further experimental investigations of this important problem. Our estimated value $\gamma_{\text{O}} \approx -0.014$ is overrated. The value $\gamma_{\text{O}} \approx -0.01$ is better suited for comparison of the calculated α_{T_c} with experiment; see the figure.

It is relevant to note that, generally speaking, there is another possibility of changing J , which is given by Eq. (4). This possibility is associated with the change in the distance between copper ions upon replacing some isotopes with other ones. It is known that the superexchange parameters very strongly depend on the distance between the interacting ions. This mechanism explains well the increase in T_c under the action of an external pressure on a high- T_c crystal [16, 17]. The question naturally arises in this case as to what occurs with the lattice parameters upon substituting some isotopes for other ones. Recent precision measurements in a $\text{YBa}_2\text{Cu}_4\text{O}_8$ crystal showed [18] that the lattice parameters a , b , and c in the case of ^{16}O equal (A) 3.8411(1), 3.8717(1), and 27.2372(8), respectively, whereas these are equal to 3.8408(1), 3.8718(1), and 27.2366(8), respectively, for ^{18}O ; that is, these parameters are somewhat smaller in the latter case. The positive isotope shift of the nuclear quadrupole resonance frequency of plane copper nuclei [18] is another important experimental fact, which indicates that interatomic copper–oxygen distances are smaller in the case of ^{18}O . Based on these data, one may only conclude that the change of interatomic distances upon replacing some isotopes with other ones must lead to negative shifts of T_c and T^* and will, probably, be relatively small. From the theoretical point of view, this fact seems quite understandable, because changes in interatomic distances upon substituting some isotopes with other ones are due to the lattice anharmonicity, and its effect is naturally of less importance than the effect of harmonic vibrations.

In the figure, the values of the coefficient $\alpha_{T_c} = -d \ln(T_c)/d \ln(M)$ for the replacement of ^{16}O with ^{18}O are plotted as abscissas and the numbers of holes per one copper site are plotted as ordinates. The symbols in the curve correspond to the points at which the system of self-consistent equations from [3] was solved. Because only the order of magnitude is known for the polaron energies E_a and E_c , the parameter γ_{O} was normalized in such a way that α_{T_c} was equal to 0.1 at the optimal level of doping. The calculated behavior of α_{T_c} is not symmetric with respect to the point of optimal doping. The physical nature of this asymmetry is associated with strong competition between d -SC and id -CDW phases in the underdoped state. On the left of this point, the isotope shift exponent increases with decreasing number of holes, approaching 0.5, whereas the value of α_{T_c} remains virtually constant, as it also does at $\delta/2$ greater than 0.16 (the so-called overdoped regime). It is this kind of asymmetry (but without a step!) in the behavior of α_{T_c} as a function of the number of holes that was found recently in measurements [19]. The authors of this work mentioned already that, if only conventional interaction via the phonon field were responsible for the isotope effect and the unusual drop of α_{T_c} in the optimal doping region and were related to a peak in the density of states, the curve would have been approximately symmetric with respect to the point of optimal doping. At $\delta/2$ larger than 0.16, the value of α_{T_c} would strongly increase; however, this was not found [19].

As to the isotope shift of T_c upon replacing the copper ^{63}Cu isotope with ^{65}Cu or ^{66}Cu , the fact noted in [20] that the ratio $\alpha_{T_c}(\text{Cu})/\alpha_{T_c}(\text{O}) \approx 0.75 \pm 0.1$ does not depend on the type of the compound and on the doping level is naturally explained based on Eq. (3). The stabilization energy of a small-radius polaron (hole) at a copper site is higher than that at an oxygen site. The nearest environment of a hole at an oxygen site comprises positive copper ions, whereas the nearest environment of copper comprises negative oxygen ions. It is this fact that is the reason for the difference between γ_{O} and γ_{Cu} .

The value of α_{T^*} calculated in this work in the region $0.1 < \delta/2 < 0.16$ turned out to be approximately constant: $\alpha_{T^*} \approx 0.01$. This is smaller than the value estimated in experiments (0.061) [2]; therefore, the effect of interaction via optical phonons on α_{T^*} discussed in [6] cannot be excluded. This is also corroborated by a number of experimental points in Fig. 2 from [19] on the right of the point of optimal doping. It is hoped that this problem will be described in a more detailed work.

Thus, the renormalization of the superexchange interaction of copper spins due to polaron effects noted in this work explains the main regularities of the isotope shift of the superconducting transition temperature

in layered cuprates both in the order of magnitude and in the sign and the character of the dependence on the number of holes. The starting equation for the renormalization of the superexchange parameter was verified using the isotope shifts of the Neel temperature of the parent compounds as an example. Our calculations were based on the scenario of competition between the superconducting phase and the charge-density-wave phase. Agreement between the calculations and experiment confirms this scenario. At the same time, our calculation predicts a rather sharp jump of the isotope exponent α_{T_c} on passing through the point of optimal doping. This effect is relatively small; however, we believe that the experimental observation of this effect will be of principal importance.

This work was supported by the Russian Program "Superconductivity," project no. 98014-1, INTAS, project no. YSF 2001/2-45, and the partially supported by Swiss National Scientific Foundation, project no. 7SUPJ062258.

REFERENCES

1. Guo-meng Zhao, H. Keller, and K. Conder, *J. Phys.: Condens. Matter* **13**, R569 (2001).
2. F. Raffa, T. Ohno, M. Mali, *et al.*, *Phys. Rev. Lett.* **81**, 5912 (1998).
3. M. V. Eremin and I. A. Larionov, *Pis'ma Zh. Éksp. Teor. Fiz.* **68**, 583 (1998) [*JETP Lett.* **68**, 611 (1998)]; M. V. Eremin, I. A. Larionov, and S. V. Varlamov, *Physica B (Amsterdam)* **259-261**, 456 (1999).
4. A. Nazarenko and E. Dagotto, *Phys. Rev. B* **53**, 2987 (1996).
5. A. Bill, V. Z. Kresin, and S. A. Wolf, *Z. Phys.* **104**, 759 (1997).
6. I. Eremin, M. Eremin, S. Varlamov, *et al.*, *Phys. Rev. B* **56**, 11305 (1997).
7. S. V. Varlamov, M. V. Eremin, and I. M. Eremin, *Pis'ma Zh. Éksp. Teor. Fiz.* **66**, 726 (1997) [*JETP Lett.* **66**, 569 (1997)].
8. K. I. Kugel' and D. I. Khomskii, *Zh. Éksp. Teor. Fiz.* **3**, 987 (1980) [*Sov. Phys. JETP* **52**, 501 (1980)].
9. M. V. Eremin, *Fiz. Tverd. Tela (Leningrad)* **24**, 423 (1982) [*Sov. Phys. Solid State* **24**, 239 (1982)].
10. X.-X. Bi and P. C. Eklund, *Phys. Rev. Lett.* **70**, 2625 (1993); K. A. Müller, G.-M. Zhao, K. Conder, and H. Keller, *J. Phys.: Condens. Matter* **10**, L291 (1998); O. V. Dolgov, H. J. Kaufmann, E. K. H. Salje, and Y. Yagil, *Physica C (Amsterdam)* **279**, 113 (1997).
11. P. W. Anderson, *Phys. Rev.* **115**, 2 (1959).
12. S. Sugano, Y. Tanabe, and H. Kamimura, in *Multiplets of Transition-Metal Ions in Crystals* (Academic, New York, 1970).
13. H. Eskes, L. H. Tjeng, and G. A. Sawatzky, *Phys. Rev. B* **41**, 288 (1990).
14. A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Metal Ions* (Clarendon, Oxford, 1970; Mir, Moscow, 1972), Vol. 2.
15. G. M. Zhao, K. K. Singh, and D. E. Morris, *Phys. Rev. B* **50**, 4112 (1994).
16. L. Jansen and R. Block, *Physica A (Amsterdam)* **262**, 455 (1999); **247**, 265 (1997).
17. N. M. Plakida, *Pis'ma Zh. Éksp. Teor. Fiz.* **74**, 38 (2001) [*JETP Lett.* **74**, 36 (2001)].
18. M. Mali, J. Roos, H. Keller, *et al.*, cond-mat/0112212.
19. D. J. Pringle, G. V. M. Williams, and J. L. Tallon, *Phys. Rev. B* **62**, 12527 (2000).
20. D. E. Morris, A. P. B. Sinha, V. Kirtikar, *et al.*, *Physica C (Amsterdam)* **298**, 203 (1998).

Translated by A. Bagatur'yants