Superconductivity and Jahn-Teller Polarons in Titanates

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The present work focuses on the superconductivity phenomenon in La-doped $SrTiO_3$ crystal, and the Jahn-Teller (JT) polarons in $BaTiO_3$ crystal. In the case of $SrTiO_3$ crystal this study shows the occurrence of free electrons in the conduction band of the crystal and explains a number of the experimental results obtained for the superconducting La-doped $SrTiO_3$ existing under 0.3K. Free electrons are found to be situated within the Ti-O planes similar as in the case of the high temperature superconducting (HTS) cuprates. Results obtained for the JT polarons in $BaTiO_3$ crystal explain a number of experimental observations and coincide with the other results obtained independently by the polaron theory. A phenomenological model explaining a bipolaron formation in titanates is suggested and analysed in the present work.

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1. INTRODUCTION

Until the middle of 1980s most of the superconducting compounds studied were elemental metals and their alloys. The breakthrough came in 1986, when Bednorz and Müller discovered superconductivity at 36 K in the $La_{2-x}M_xCuO_4$ compounds, with M = Ba, Sr, Ca.[1] Afterwards super-

conductivity was discovered in a number of oxides having the perovskite-type structure. It appears that some of the unusual properties of superconductivity are tied to the peculiar perovskite-type structure for which already the normal state properties are anomalous, like the normal state electrical conductivity. While most oxides are insulators, perovskites exhibit more metallic behaviour, with resistivity rising linearly with temperature. Such behaviour is not observed in conventional metals. The electrical conductivity of perovskites is controlled by adding charge carriers and it is well understood that the charge carriers in cuprates[2] and manganites[3–5] are strongly coupled to lattice vibrations. There is now a growing consensus that the dopant-induced charge carriers in high-T_c oxides exhibit a significant influence due to spin, charge and lattice fluctuations.[6] There is also growing experimental evidence that polarons and bipolarons are the charge carriers in high-T_c superconductors. In particular, studies of photoinduced carriers in dielectric parent compounds like La_2CuO_4 and $YBa_2Cu_3O_6$ confirm the formation of self-localised polarons.[7,8] A direct evidence for small polarons in doped copper oxides has been provided recently with infrared spectroscopy.[9]

Hitherto no serious analysis of polarons and bipolarons has been done for the titanates despite their fundamental and technological importance as well as their structural similarity to the HTS cuprates. It is well understood that charge carriers in perovskite-type titanates[10–14] are strongly related to the crystalline lattice and its point and space symmetries. That is why one can expect occurrence of hole and electron polarons in titanates. It is also known that a charge carrier in the titanates finds itself in a degenerate ground state; however, its energy is lowered by a spontaneous distortion of the surrounding lattice originated in the so-called Jahn-Teller (JT) effect.[15] In the case of an extra electron we have an electron polaron and it localises on the Ti atoms having a threefold, T_2, orbital degeneracy. This degeneracy is lifted by the $e \ x \ T_2$ JT effect breaking the crystal symmetry[16] by some asymmetric lattice relaxation and formation of a JT electron polaron. Similar effect occurs in the case of an extra hole, i.e. hole polaron, which is localised on the O atoms. In this case we have the so-called $e \ x \ E$ problem[16] and the atomic displacements promote the energy reduction and the lifting of twofold degenerate state, E, comprising atomic orbitals of the O atoms. It is important to state that both electron and hole polarons can condense into pairs, bipolarons.

In the present paper we describe the main features of these point defects in the $BaTiO_3$ and $SrTiO_3$ crystals and show that bipolarons in the La-doped $SrTiO_3$ crystal are supercarriers and as a result are responsible for the superconductivity in this material. We also propose a new mechanism of polaron pairing into bipolarons and creation of bosons. We suggest that not

only the electron-phonon and exchange interactions should be considered but also that a purely spatial correlation effect should be included in order to understand the nature of the pairing mechanism. It is worth to state that the correlation effects are known to be very strong and significant in any oxide crystal,[17] so it is in the titanates and cuprates. Additionally, the exchange interaction arising from the Pauli exclusion principle and the Coulomb repulsion results in a depletion of the probability of finding an electron near to a given electron. This depletion is called as the exchange-correlation hole[18] and can be responsible at least partially for the electron-electron bonding within a bipolaron and creation of a boson. It is worth to state that in titanates and perovskite-type crystals in general, there exist a strong electron-phonon correlation and a considerable spatial correlation between the local vibration modes. As a result just in these crystals one can expect the formation of a strong exchange-correlation hole leading to the creation of a bipolaron.

2. JT POLARONS IN TITANATES

There is direct electron paramagnetic resonance (EPR) evidence of JT electron polaron presence in the $BaTiO_3$ crystal.[19] Actually, Ti^{3+} electron polarons occur in different configurations in barium titanate depending on the locally fluctuating potentials. Theoretically, it has been suggested that the JT electron polarons occur in barium titanate due to the Nb-doping.[12,20] Asymmetric movements are obtained in the case of impurity-doped tetragonal phase of $BaTiO_3$ crystal. It is relevant to mention that an extra electron imposed by the donor impurity doping instead of occupying the local energy level within the band gap transfers to the conduction band. The electron transfer to the conduction band, i.e., the creation of the Ti^{3+} ion is in accordance with the experimental data,[19] where the conduction band electrons were identified by direct EPR measurements. Surprisingly similar results are also obtained in the Nb-doped orthorhombic phase of calcium titanate.[11,21] It is found that the conduction band electrons occur after the Nb-impurity doping and the lattice relaxation resembles the one due to the JT effect, so we can conclude that the JT electron polarons are present in barium and calcium titanates at low temperatures.

JT hole polarons in titanates, which have been studied theoretically in pure $SrTiO_3$[22,23] and $BaTiO_3$[10,14] crystals, are also of a primary importance. Additionally, these point defects have been investigated in the acceptor-doped $SrTiO_3$[22] and $BaTiO_3$[24] crystals. The most important result is the observed rotation of some O atoms in the defective region, especially in the case of the $BaTiO_3$ crystal.[24] This corresponds to the above-mentioned e

$x \, E$ problem for a strong linear coupling. In this case due to the JT effect some nuclei rotate freely around the distorted configuration of the system, avoiding the undisturbed configurations and carrying along the electronic states with the distortions. The JT hole polarons in barium titanate is of a special importance since they are obviously responsible for the non-linear photoconductivity[25] in this material and another light-induced charge-transfer processes. The formation energy of JT polarons in a pure $BaTiO_3$ tetragonal lattice obtained by the quantum-chemical computations[14] was found to be equal to 0.87 eV. This estimate is very close to the one obtained due to the Fröhlich electron-phonon interaction being equal to 0.842 eV.[26]

As a result, we can conclude that both electron and hole JT polarons are present in titanates and are responsible for a number of phenomena and some electronic properties in these materials. It is important to state that similar conclusions have been done for the polaronic charge carriers in the cuprates[2] and manganites.[26, 27] So, the JT polarons obviously are the most probable quasi-particles in oxides having a perovskite-type structure. Why oxides? Apparently, this is because of the fact that these crystals are highly polarisable materials having considerable correlation effects.

3. JT BIPOLARONS AND SUPERCONDUCTIVITY IN La-DOPED SrTiO$_3$

The JT polarons are common quasi-particles in titanates; then the question arises, if can they condense into pairs and form bipolarons? The answer to this question is affirmative and the evidence of bipolaron formation was demonstrated in the La-doped $SrTiO_3$ tetragonal structure.[13, 28] If two Sr atoms are substituted by two La atoms having higher valence number, then two extra electrons are automatically introduced into the system. Because of these two extra electrons the system might maintain in two different states, namely a singlet state and a triplet state. The singlet state corresponds to the case when two extra electrons have opposite spins and thus occupy the same energy level and the triplet state occurs when two extra electrons have equal spins occupying two different energy levels. Normally, the electrons (holes) occurring due to the impurity (defect) should occupy a local energy level within the band-gap of a given crystal. However, as it follows from the quantum-chemical calculations,[13] this is not the only possible case. It was observed that for some specific bi-impurity configurations, two extra electrons jump to the conduction band. This electron transfer is accompanied by an asymmetric lattice relaxation. Thus we observe the formation of Ti^{3+} JT bipolaron.

It is important to note that the creation of conduction band polarons

does not happen for all bi-impurity configurations, only if the lattice relaxation energy is sufficiently large the two extra electrons are transferred from their local energy levels within the band-gap to the conduction band. If the lattice relaxation energy is not sufficient the two electrons remain within the band-gap having wave functions composed mainly of the La 6s atomic orbitals.

The fact that the relaxation energy is not transferred to all electronic sub-system but just to the two extra electrons involved might be explained as follows. The energy transfer is a local effect occurring *within* the same quasi-particle, which consists of (i) two electrons, (ii) the local lattice deformation, i.e., the JT effect, and finally (iii) very strong electron-phonon coupling. These three constituent parts are necessary and required to form the conduction band bipolarons and are met in perovskite oxide crystals where a strong electron-phonon coupling is always present.

The crucial result in the La-doped $SrTiO_3$ crystal is that the conduction band bipolarons are triplet bipolarons.[13] Thus bipolarons described here are bosons having spin equal to 1, these quasi-particles (bosons) are supercarriers and originate superconductivity, which recently was discovered experimentally in the La-doped $SrTiO_3$ crystal at 0.3 K.[29]

An important question arises about the mechanism of bipolaron formation in titanates. It is well known that there exists a strong spatial correlation between ferroelectric (FE) vibration modes in a number of perovskites, e.g. $SrTiO_3$. It has been determined recently that the FE local modes in the cubic $SrTiO_3$ crystal are strongly correlated spatially,[30,31] i.e. the local FE vectors $f_z (R_i)$ correlate strongly only with $f_z (R_i \pm na_o \widehat{z})$, where n is a small integer number. According to Zhong and Vanderbilt,[30] the correlation distance is around 10 a_o, where a_o is the lattice constant. This means that approximately ten local vibration modes vectors are tied together in this crystal. Similar pattern is exhibited by the local antiferrodistortive (AFD) vibration modes, which, in the case of the $SrTiO_3$ crystal, includes rotation of oxygens forming an octahedron. The rigid nature of the oxygen octahedron also contributes into the strong spatial correlation. The correlation is known to be two-dimensional, 2D, i.e. $a_z (R_i)$ is coupled only with a_z $(R_i \pm na_o \widehat{x} +ma_o \widehat{y})$, where m is another small integer number. Considering the characteristic correlation longitude equal to 10 a_o in each direction, one obtains 100 vectors of the local vibration modes tied together. It is important to mention at this point that generally the intensity of quantum fluctuations are weaker for the case of the AFD modes compared to the case of the FE vibrations due to the larger effective mass of a bipolaron. The mathematical expression describing the system can be written using

the so-called Hubbard model:

$$H = -\sum_{ij\sigma} t_{ij} c_{i\sigma}^+ c_{j\sigma} + \frac{1}{2} \sum_{ijkl} \sum_{\sigma\sigma'} \langle ij \,|\nu|\, kl \rangle\, c_{i\sigma}^+ c_{j\sigma'}^+ c_{l\sigma'} c_{k\sigma} + \sum_{q,j} \hbar\omega_j (a_q^+ a_q + 1/2),$$

$$(1)$$

where
$$t_{ij} \equiv t(R_i - R_j) = -\int dr \phi_i^*(r) h(r) \phi_j(r) = t_{ij}^*, \tag{2}$$

$$\langle ij \,|\nu|\, kl \rangle = \int dr dr' \phi_i^*(r) \phi_j^*(r') \nu(r - r') \phi_k(r') \phi_l(r). \tag{3}$$

Here $h(r)$ is the part of Hamiltonian describing the kinetic energy and the interaction with some external potential, e.g. lattice potential, while ν considers electron-electron interaction. The energy is normalised in such a way that $t_{ii} = t(0) = 0$. It can be stated that the first two terms in equation (1) are obtained by applying the second quantization with respect to the following Hamiltonian:

$$H = \sum_i h(r_i) + \frac{1}{2} \sum_{i \neq j} \nu(r_i - r_j), \tag{4}$$

where $h(r)$ is the one-electron Hamiltonian and $\nu(r_i - r_j)$ describes electron-electron interaction. The third term in equation (1) describes interaction between the local modes, FE or AFD.

The following approximations could be used maintaining the physics of strong polaron-polaron correlation in order to simplify equation (1). One can take into account that in the La-doped SrTiO$_3$ tetragonal structure, the supercarriers (bipolarons) are found within the Ti-O planes, i.e., the phenomenon is basically two-dimensional. Thus, t_{ij} is considerably larger if i and j belong to the same plane compared to the case if they belong to the two different planes. As a result one can use the following simplification:

$$t_{ij} \approx \begin{cases} t, \text{ if } i \text{ and } j \text{ are adjacent belonging to the same plane} \\ rt, \text{ if } i \text{ and } j \text{ are adjacent in different planes} \\ 0, \text{ all other cases} \end{cases} \tag{5}$$

where $r \ll 1$. Considering that the electrons entering into bipolaron are screened effectively because of the exchange-correlation hole effect, the value of $\langle ij \,|\nu|\, kl \rangle$ will be significant only if $i = j = k = l$, i.e.:

$$\langle ij \,|\nu|\, kl \rangle \approx \begin{cases} U, \text{ if } i = j = k = l \\ 0, \text{ all other cases} \end{cases} \tag{6}$$

Additionally, due to the Pauli exclusion principle $\sigma' = -\sigma$, so the simplified Hubbard Hamiltonian is obtained for a bipolaron in a perovskite crystalline

lattice:

$$H = -\sum_{\langle ij \rangle \sigma} t_{ij} c_{i\sigma}^+ c_{j\sigma} + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} + \sum_{q,j} \hbar \omega_j (a_q^+ a_q + 1/2), \qquad (7)$$

where a_q^+ and a_q are the operators of creation and annihilation, ω_j are the frequencies of local vibration modes of the bipolaron. In equation (7) $\hat{n}_{i\sigma} = c_{i\sigma}^+ c_{i\sigma}$ and the summation is carried out over the closest neighbours only. In order to take into account the electron-phonon interaction, the function of $(R_i - R_j)$ is expanded in the lattice deviation functions, u_i and u_j, from the equilibrium position $t_o(R_i^o - R_j^o)$ as $t_{ij} \approx t_o - \alpha u_{ij}$, where α is the so-called Fröhlich coefficient[33] and the magnitude of u_{ij} is

$$u_{ij} = \frac{1}{\left| R_i^o - R_j^o \right|} (u_i - u_j)(R_i^o - R_j^o). \qquad (8)$$

The frequencies of local modes are calculated using the so-called dynamic matrix $D_{\mu\nu}$. Considering the SrTiO$_3$ crystal as an ionic material, the $D_{\mu\nu}$ might be written in the following form[33]

$$D_{\mu m, \nu n}^{LO}(q) = D_{\mu m, \nu n}^{TO}(q) + \frac{4\pi e^2}{\Omega} \frac{(Z_m^* \cdot \hat{q})_\mu (Z_n^* \cdot \hat{q})_\nu}{\varepsilon_\infty(q)}, \qquad (9)$$

where LO and TO stands for optical longitudinal and optical transversal vibration modes, respectively, e describes bipolaron charge, Ω is the unit cell volume of a given crystal, μ and ν are Cartesian indices, Z_m^* is the Born effective charge tensor, q is the wave vector and finally, $\varepsilon_\infty(q)$ is the optical macroscopic dielectric function for the crystal containing bipolarons. It is important to mention that the above described frequencies have been studied in detail for different perovskites. In particular, the existence of a huge separation between LO and TO frequencies in the ferroelectric perovskites was found[34] and the "chain" structure along the ferroelectric c axis for the instability in the KNbO$_3$ crystal was determined.[35]

We think that the above-depicted model can describe the occurrence of superconductivity in the La-doped SrTiO$_3$ crystal.[29] It is important to mention that both instabilities, FE and AFD usually are present in all perovskites due to their specific crystalline lattice structure. Therefore, the model might be applied to any perovskite crystal including the HTS cuprates. The important point to be discussed is the mutual interaction between these two modes due to the non-harmonic coupling as well as their mutual coupling to the elasticity.[35] These couplings could be rather different for different perovskites. If one takes as an example the BaTiO$_3$ crystal, then there is major intensity for the polar FE modes, which suppress the polar AFD modes in

this crystal.[35] Therefore, one can not expect the formation of bipolarons and furthermore the occurrence of superconductivity in the $BaTiO_3$ crystal. On the other hand, in the SrTiO3 crystal there exist a competition between two modes which could be resolved only if the Feynman path integrals are used. As a result, at some specific conditions the $SrTiO_3$ crystal turns to be a superconductor.

It is presumed that all HTS materials having perovskite-type structure are intrinsic to phonon instabilities, which in some manner are responsible for the high temperature superconductivity. That is why we think that the phonon instabilities, strong spatial correlation between the AFD modes as well as vigorous electron-phonon coupling lead in some specific perovskites under certain conditions to the formation of bipolarons. Thus our results are directly related to the HTS perovskites. If one considers the AFD modes as a factor leading to the superconductivity than it is worth to mention that these modes are rather improbable in $BaTiO_3$ crystal due to their considerably higher energy compared to the one of the FE modes. So, according to our model no superconductivity can occur in $BaTiO_3$ and this is consistent with the experimental data. On the other hand, it is well known that the FE modes are totally suppressed by purely quantum fluctuations in $SrTiO_3$ crystal below 40 K. These quantum fluctuations allow the AFD domination leading to the possibility of bipolaron formation in this material and thus the superconductivity phenomenon. Again, our model is consistent with the experimental data on La-doped $SrTiO_3$ crystal.[29] Taking into consideration the fact that the oxygen-deficient $SrTiO_3$ is an HTS material one can conclude that just bipolarons are responsible for the superconductivity phenomenon in this material and another HTS perovskites.

4. CONCLUSIONS

The formation of a quasi-particle known as polaron has been analysed in the present work demonstrating that these quasi-particles are one of the most probable charge carriers in titanate crystals having a perovskite-type crystalline structure. The polarons are thus responsible for a variety of different properties and phenomena in these crystals. Using the Hubbard model we show that these particles due to the AFD mode interaction can form bipolarons which in fact are triplet bosons and thus are responsible for the occurrence of superconductivity in the titanates. To our knowledge, the AFD vibrations are common for all perovskites, including the HTS cuprates; and in consequence our model might be applied as a first approximation to explain the origin of superconductivity in perovskites.

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