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Superionic behavior of high-temperature superconductors

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Ionic transport, a characteristic feature of superionic conductors, is analyzed microscopically for the $R\mathrm{Ba}_2\mathrm{Cu}_3\mathrm{O}_{7-\delta}$ (R=rare earth) high-temperature superconductors. The electronic correlation effects are considered to be responsible for the formation of a local double-well potential for apical oxygen, which, in turn, results in a decrease of the activation energy for interstitial chain oxygen defects. [S0163-1829(97)05302-2]

I. INTRODUCTION

Intensive experimental investigations of oxide high-temperature superconductors (HTSC's) during the past decade provide an extensive database on structural as well as dynamical properties of these compounds. We concentrate our attention on the phenomenon of oxygen transport in the superconductors of the $R\mathrm{Ba}_2\mathrm{Cu}_3\mathrm{O}_{7-\delta}$ (R123) family.[1,2] Oxygen ions exhibit pronounced mobility even at room temperature (i.e., far below the melting point) and the effect of oxygen ordering has been studied experimentally by neutron and x-ray diffraction[3] as well as by spectroscopic techniques.[4,5] The binding energy of oxygen is known to vary strongly for different lattice sites, which allows, e.g., realizing the site-selective oxygen-isotope substitution within the R123 structure.[6,7] At a temperature about 1000 K oxygen moves easily away from the O(1) chain sites toward the vacancy sites O(5) in a basal plane.[8] At still higher temperatures oxygen is removed from the structure.[3] As oxygen is removed from the Cu-O(1) chains and the occupancies of the O(1) and O(5) sites become equal, the orthorhombic structure transforms into the tetragonal modification with no crucial change of lattice parameters[9] but with *disorder* of oxygen ions in the plain.[3] Pressure above 70 kbar is known to stabilize the tetragonal modification.[10]

There is some experimental evidence supported by theoretical treatment[11–13] that bulk R123 materials exhibit ferroelectric properties, with the apical oxygen atoms, O(4), playing the key role. Ferroelectric models,[11,12] in which the O(4) atom is moving along the c axis in a double-well potential, have been proposed with the origin ascribed to the *polaron tunneling*.[14]

In what follows we consider the oxygen transport phenomenon in oxide HTSC materials from the "superionic point of view." Given a small concentration of defects in a crystal, it is possible to examine their contribution to the crystal properties through an expansion in a perturbation series. However, the relevant small parameter fails as the number of defects increases, i.e., the system becomes qualitatively different. A regime where the number of allowable sites is much greater than the number of particles and, besides, the activation energy essentially decreases, may take place long before the crystal melting temperature is approached. The transition of a crystal into such a superionic (from the ionic conductivity standpoint) state happens due to the stepwise growth in the concentration of Frenkel (or Schottky) defects which is promoted by their interaction through the mediation of the lattice distortion[15] and the direct Coulomb interaction.[16]

$A^N B^{8-N}$ compounds, which exhibit variation of the chemical bond from the ionic to the covalent type upon N increasing from 1 to 4, probably represent the best studied family of materials.[17] If the materials were arranged so that their chemical bond progressively changed from the former type to the latter one, superionic conductors (SIC's) would occupy the borderline position. As it is generally accepted,[17] this borderline corresponds to the ionicity coefficient $F_i=0.785$ and separates materials of predominantly the covalent zinc-blende or wurzite structure (fourfold coordinated) from the materials of the ionic rocksalt structure (sixfold coordinated). As a consequence, SIC's exhibit the ability to vary the coordination number under the pressure easily. For example, such a popularly known superionic conductor as AgI can be transformed into the NaCl structure under the pressure of only a few thousand atmospheres.

The electronic structure of AgI and other silver halides has been investigated experimentally by means of x-ray and UV photoemission spectroscopies[18,19] and an appreciable overlap of $4d$-silver and $5p$-halogen orbitals was found. The Brillouin-zone symmetry of both the wurzite and the zinc-blende (covalent bond) structures allows the p-d mixing throughout the zone, whereas the rocksalt (ionic bond) structure would forbid p and d orbitals mixing at $k=0$.[19] It seems plausible to conclude that, in accordance with a degree of the p-d mixing, crystals exhibit (AgI), or, alternatively, do not exhibit (AgCl and AgBr) the superionic properties.

It is important to note that ferroelectric properties of the perovskite-structure oxides (e.g., BaTiO_3 and PbTiO_3) have been recently discussed with the origin attributed to the hybridization between the titanium $3d$ and oxygen $2p$ states.[20] Strong correlation between the Cu ($3d$) and O ($2p$) electronic states is the generally recognized property of HTSC's. Considering the existence of oxygen transport as well, we analyze the ionic transport properties of R123 superconductors from the standpoint of superionic conductivity.

We have recently developed a microscopic model for es-

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tablishing a relationship between the superionic properties of a material and the electronic subsystem features.[21] The approach places primary emphasis upon the possibility of local double-well potential formation for one type of crystal constituent ions as a consequence of the appearance of specific electronic excitations, namely, the electron-hole pairs that originate from the p and d states and are dressed with the transverse optical phonon cloud.

It is worth noticing that p-d correlation is not the only possible source of formation of a double-well carrying the dipole moment. A similar conclusion could be reached within independent models,[11,22] with some reservations about the polarization (transverse rather than longitudinal) and statistics (Bose rather than Fermi) of involved excitations.[23] In general, suppression of the oxygen activation energy is independent of the mechanism of double-well potential formation provided that the resultant dipole magnitude is the same [see Eq. (3) and the discussion below]. But when treating the problem of ''fast ionic transport,'' it is natural to try first to apply the microscopic model[21] which seems to be adequate for superionic conductivity.

II. MICROSCOPIC MODEL AND DISCUSSION

As it is shown in Ref. 21, the local potential for some ions may exhibit the double-well shape, nonsymmetrical with respect to the original lattice site, even at a temperature far below the superionic transition point. The spacing of potential minima δ was found to be

$$\delta \simeq f_{\mathrm{exc}}\left[\frac{2}{M_i\overline{\omega}^2}A\right]^{1/2}, \tag{1}$$

where

$$A=\frac{1}{N}\sum_q |\gamma_q|^2\omega_q, \tag{2}$$

M_i is the effective ionic mass (we take $M_i \simeq M_{\mathrm{O}}$ below, considering $M_{\mathrm{Cu}} \gg M_{\mathrm{O}}$), N is the total number of ions, $\overline{\omega}$ is the characteristic phonon frequency ($\hbar = 1$), γ_q is the electron-hole pair–transverse-optical phonon coupling constant, and f_{exc} is the expectation value for the operator of a number of electron-hole excitations. In the case under consideration the electron-hole excitations are of a nonzero chemical potential (unlike Ref. 21), which is due to the finite concentration of holes fixed by oxygen content even at low temperatures.

As a result of the Coulomb interaction of a stable Frenkel defect with the ionic dipoles D, originating from O(4) sites (Fig. 1), the defect activation energy decreases. Disregarding anisotropy within the range of integration (see discussion below), the gain in activation energy can be estimated as ($k_B = 1$) (Ref. 24)

$$\Delta E_a \simeq -4\pi N_D T\int dR R^2(\varepsilon_0 - 2\langle U_{\mathrm{int}}\rangle), \tag{3}$$

where

$$\langle U_{\mathrm{int}}\rangle = 1 - x\frac{I_1(x)}{I_0(x)} - 2\frac{\sinh(x)\cosh(y)}{\mathrm{Shi}(x-y)+\mathrm{Shi}(x+y)} \tag{4}$$

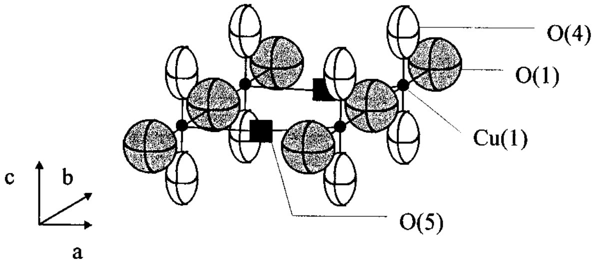

FIG. 1. A schematic figure illustrating the arrangement of oxygen at different sites.

is the averaged energy of the dipole D in the field of a charged particle (see Ref. 24, Fig. 1), with the factor 2 in front of $\langle U_{\mathrm{int}}\rangle$ in Eq. (3) being due to necessity of considering contributions from both ions at interstitial sites and vacancies, which remain at lattice sites,

$$x = e_i D/\epsilon_1 R^2 T, \quad y = DE_{NS}/T, \quad D \simeq e_i\delta,$$

I_l is the lth-order Bessel function with an imaginary argument, and Shi is the integral hyperbolic sine function. N_D is the concentration of dipoles, ε_0 is the reduced energy of a dipole in the absence of Frenkel defects given by

$$\varepsilon_0 = 1 - y\coth y, \tag{5}$$

E_{NS} is the intensity of an external electric field which is due to the presence of a charged double layer, if any, near the crystal surface, e_i is the charge of the ion, and ϵ_1 is the background dielectric constant. The integral in Eq. (3) is taken over $R < R_s$, where R_s is the screening length, as the Coulomb interaction is essentially suppressed at larger distances. The electric field E_{NS} can be roughly approximated by a steplike function, which takes the approximately constant value[25] of $E_{NS} \simeq T/eR_s$ in the vicinity of the surface and abruptly decays at distances larger than R_s. The screening length is taken hereafter as $R_s \sim 10^{-7}$ cm which provides a feasible analysis when the influence of the surface is totally neglected.

Following Eq. (2), it is possible to evaluate the eigenenergy shift due to the electron-hole–phonon coupling,[21] as $A \sim M^2/\overline{\omega}$, where M is the characteristic matrix element of the proper dipole-dipole interaction. In accordance with the form of the Hamiltonian for this interaction, $M \simeq (u/a)V$, where u is the ion displacement, a is the O(4)-Cu(1) spacing, and V is the total self-consistent potential[26] felt by an electron-hole pair. Thus we finally obtain

$$A \sim \frac{V^2}{M_i\overline{\omega}^2 a^2} \tag{6}$$

at low ($T \ll T_D$) and

$$A \sim 2\frac{V^2}{\overline{\omega}}\frac{T}{M_i\overline{\omega}^2 a^2} \tag{7}$$

at high ($T \gg T_D$) temperatures. Here T_D is the Debye temperature,

$$V \sim |\overline{\varepsilon_p} + \overline{\varepsilon_d} - \Delta W|, \tag{8}$$

and

$$\overline{\varepsilon_p}+\overline{\varepsilon_d}=\varepsilon_p+\varepsilon_d+\sum_{l'} W\begin{pmatrix} l' & l & l & l' \\ 1 & 2 & 2 & 1 \end{pmatrix} - W\begin{pmatrix} l & l & l & l \\ 1 & 2 & 1 & 2 \end{pmatrix} \qquad (9)$$

is the sum of p- and d-electron energies renormalized with regard to the Coulomb interaction between full levels.[27]

$$\Delta W = W\begin{pmatrix} l & l & l & l \\ 1 & 2 & 2 & 1 \end{pmatrix} - W\begin{pmatrix} l & l & l & l \\ 1 & 2 & 1 & 2 \end{pmatrix}$$

is the difference between the direct and exchange Coulomb interaction terms, where W is

$$W\begin{pmatrix} l_1 & l_2 & l_3 & l_4 \\ j_1 & j_2 & j_3 & j_4 \end{pmatrix} = \int\int \phi_{j_1}^*(x-R_{l_1}^0)\phi_{j_2}^*(x'-R_{l_2}^0) \times \frac{e^2}{\epsilon_\infty(x,x')|x-x'|}\phi_{j_3}(x'-R_{l_3}^0) \times \phi_{j_4}(x-R_{l_4}^0)dx\, dx',$$

with ϕ_j being the Wannier functions. In deducing Eq. (8) we did not explicitly consider the processes where an electron leaves out the hole destroying the pair.[21,27] It is easy to show that we can implicitly include into consideration the appropriate effects with no change of formal procedure. All one has to do is to transform to wave functions of the form:

$$\tilde{\phi}_j(x-R_l^0)=\phi_j(x-R_l^0)-\frac{1}{2}\sum_{i\neq j,l'\neq l}\phi_i(x-R_{l'}^0)\Gamma_{ll'}^{ij},$$

where $\Gamma_{ll'}^{ij}=\int d^3x\ \phi_i^*(x-R_{l'}^0)\phi_j(x-R_l^0)$ is the overlap integral. The set of new functions, once orthogonal [to an accuracy of $O(\Gamma^3)$] and normalized [to an accuracy of $O(\Gamma^2)$], enables one to take into consideration transitions similar to $(l,p)\rightarrow(l',d)$ through a simple modification of the available matrix elements. For example, the p-level energy ε_p is changed to $\tilde{\varepsilon}_p=\varepsilon_p-\Gamma Q$, where

$$Q\simeq\sum_{l'} W\begin{pmatrix} l' & l & l & l' \\ 1 & 2 & 2 & 1 \end{pmatrix} - W\begin{pmatrix} l & l & l & l \\ 1 & 2 & 1 & 2 \end{pmatrix},$$

and so on.

In order to proceed further we consider the following set of the parameters. The characteristic energy of a pair is estimated at $V\simeq 2$ eV ($\epsilon_\infty\simeq 4$, $\Gamma\simeq 0.2$),[28–30] $f_{\rm exc}\sim 1$, that is to say that the number of holes is only weakly temperature dependent, which is a good approximation[3] for temperatures below the orthogonal-tetragonal phase transition. Taking into account that the frequency of the highest energy long-wavelength optical phonon for $R123$ is $\overline{\omega}\simeq 1.1\times 10^{14}$ s^{-1} (570 cm^{-1}) and the Cu(1)-O(4) distance is $a\simeq 2$ Å, we immediately get the value of the O(4) ion displacement $\delta\simeq 0.14$ Å at low temperatures and $\delta\simeq 0.21$ Å at $T=10^3$ K.

If we take the background dielectric constant as $\epsilon_1\simeq 10$ ($\epsilon_1\approx\epsilon_0\|c$ axis),[29,31] and consider that the concentration of dipoles $N_D\simeq N_{\rm O}$, where $N_{\rm O}$ is the concentration of apical O(4) oxygen ions, Eq. (3) yields the estimation of the energy gain ($e_iD/R^2T\gg 1$) (Ref. 24):

$$\Delta E_a\simeq -16\pi\overline{R}N_{\rm O}\frac{e_i'D}{\epsilon_1}. \qquad (10)$$

In accordance with the cutoff procedure used to approximate the integral in Eq. (3), $\overline{R}$ is to be of the order of R_s, but at the same time, it is physically clear that $\overline{R}$ is within the interval $R_0<\overline{R}<R_s$, where $R_0\simeq 2.6$ Å is the characteristic O(1)-O(4) distance. The upper limit to the energy for displacement of the chain oxygen into interstitial position has been recently determined as $E_a\simeq 2.8$ eV, with the energy for plain oxygen (displacement along the c axis) being about $E_a\simeq 8.4$ eV.[32] Taking into account the anisotropy correction factor of 2/3 and the effective charges of oxygen[33] $e_i=-2.6$ at the O(4) site and $e_i'=-1.8$ at the O(1) site, we estimate the gain in activation energy according to Eq. (10) at -1.4 eV$>\Delta E_a>-5.4$ eV at $T\simeq 10^3$ K. It means that promotion of oxygen transport due to the interaction in question is expected to be really pronounced.

Let us briefly consider the case of oxygen-depleted RBa$_2$Cu$_3$O$_{7-\delta}$ superconductors. As it is known, increase in δ is accompanied by a reduction of the in-plane hole concentration as well as by the appearance of chain-oxygen vacancies. Because of the proper increase of the screening length, the parameter V grows

$$V\sim\left|\varepsilon_p+\varepsilon_d+\sum_{l'\neq l} W\begin{pmatrix} l' & l & l & l' \\ 1 & 2 & 2 & 1 \end{pmatrix}\right| \approx \left|\varepsilon_p+\varepsilon_d+\frac{e^2}{R_s}\right|,$$

which results in the double-well spacing δ increase [Eqs. (1), (6)–(9)]. Besides, the difference in depth of the double-well potential minima becomes negative,[21] i.e., the ion occupation of the shifted minimum becomes preferable, which means that the characteristic O(4)-Cu(1) distance a decreases.[34] We expect that increase in the IR phonon frequency $\overline{\omega}$ upon oxygen depletion from the chains[33] may compensate the contribution of the potential V and spacing a variation and in this way stabilizes the spacing δ. Another important factor is the appearance of chain-oxygen vacancies, which in itself promotes the formation of oxygen defects through the mediation of lattice distortion in complete agreement with the scenario for superionic transition.[15] To summarize, the oxygen deficiency increase promotes the ionic transport both through the increase in the apical double-well spacing and through additional lattice distortion.

In conclusion, we have found that RBa$_2$Cu$_3$O$_{7-\delta}$ high-temperature superconductors exhibit remarkable similarity to superionic conductors in electronic structure and existence of a double-well potential for O(4) apex-oxygen ions. According to the developed microscopic model, this potential is responsible for the pronounced oxygen transport in $R123$ materials in the normal state.

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