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Role of phonons in the mechanism of high-temperature superconductivity

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Abstract

While phonons are generally considered to be irrelevant to the mechanism of high-temperature superconductivity, a large number of experimental results indicate otherwise. We argue that the electron–phonon coupling in strongly correlated electron systems is unconventional, and results in a strong spin–charge–phonon coupling. It could contribute significantly to the superconductivity of the cuprates through the synergetic spin–phonon mechanism.
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1. Introduction

Currently the majority opinion in the field of high-temperature superconductivity (HTSC) is that it is a purely electronic phenomenon to be explained fully by an electronic model, such as the t–J Hamiltonian, and phonons are totally irrelevant. This view is largely based upon the observations of the near absence of the isotope effect and the apparent d-symmetry of the superconducting order parameter. However, the logic behind it is not as convincing as it may appear [1]. Indeed numerous experimental results suggest that the local lattice structure reflects the onset of HTSC in various ways, and phonons may play some meaningful role in the HTSC phenomenon [2]. The strong interaction between electrons and phonons was confirmed by recent ARPES studies [3,4]. In this paper we discuss how the Cu–O bond-stretching phonons can interact with charge and spin in an unconventional manner through spin-polar-

ized phonon-induced charge transfer, and could produce a synergetic effect by combining the magnetic and phononic mechanisms of pairing.

2. Phonon-induced charge transfer

The arguments against the phonon mechanism of HTSC are usually based on our knowledge of the electron–phonon (e–p) interaction in simple metals. However, the e–p coupling in the cuprates could be rather different, because of the ionicity, covalency and strong electron correlation. Even though the doped cuprates are metallic, it could be more instructive to compare them with insulating cousins, ferroelectric titanates. It has been known for some time that the ferroelectricity of transition metal oxides cannot be fully explained by the classical ionic model, and covalency of the bond has to be considered [5]. Recently significant advances have been made in this field, and we now fully understand the effect of covalency on ferroelectricity [6,7]. In titanates, such as $BaTiO_3$, Ti^{4+} is nominally in the d^0 state, but p–d hybridization with oxygen brings the charge density of Ti close to the d^1 state. If the Ti–O bond is strained and Ti moves to the right, closer to O (Fig. 1a), ionic polarization to the right is produced. But at the same time the p–d hybridization is increased, and electron is

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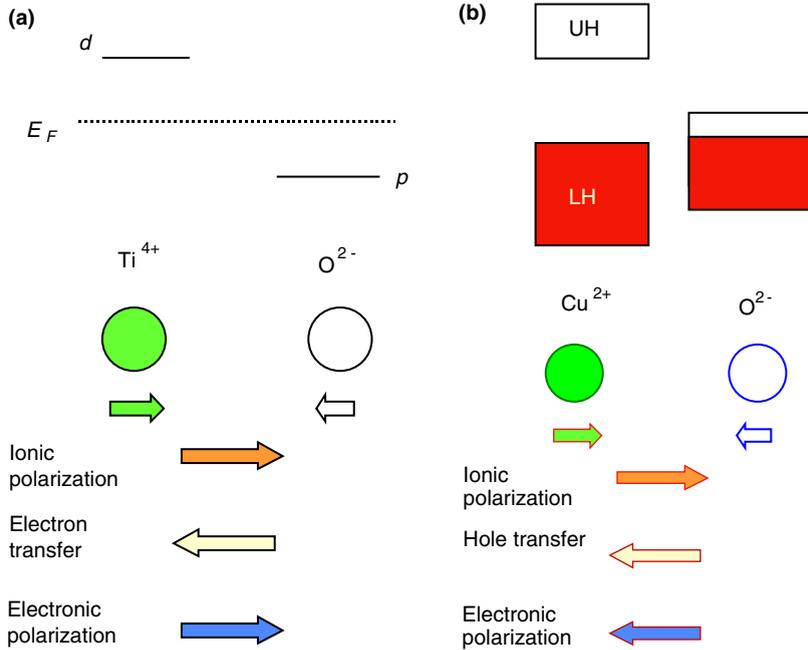*E-mail address:* egami@seas.upenn.edu (T. Egami).

Fig. 1. The electron energy bands for titanates (a) and for cuprates (b), directions of ionic displacements, currents and polarizations.

virtually transferred from O to Ti. This produces a virtual current from Ti to O, and thus polarization toward the right. It is now possible to calculate this polarization using the Berry phase method from single electron wavefunctions [6,7]. Thus in titanates LO phonons induce intersite, interband charge transfer that contributes to polarization. The strength of the electronic polarization can be expressed in terms of the Bron effective charge, Z^*,

$$Z^* = Z + \Delta Z \frac{a}{u} \tag{1}$$

where Z is the ionic charge, ΔZ is the amount of charge transfer, a is the interatomic distance and u is the ionic displacement. While the nominal valence of Ti is +4, the value of Z^* can be twice or more [6,7].

The undoped cuprates are charge transfer (CT) insulators with the CT gap between the oxygen p-band and the copper upper Hubbard states. Then the same should apply, and LO phonons should induce p–d charge transfer. The coupling, however, is not strong enough to induce ferroelectricity. Now, an interesting variation happens when the cuprates are doped with holes. Since holes enter mainly the oxygen band, a decrease in the Cu–O distance will move them to the Cu upper Hubbard band. If the density of holes is high enough, the hole current will surpass the electron current, and the direction of polarization will be reversed (Fig. 1b).

We calculated the Born effective charge of a doped cuprate as a function of the phonon momentum for the 1-dimensional two band Hubbard model using the exact diagonalization method [8]. The Hamiltonian is given by

$$H = \sum_{i,\sigma} (\varepsilon_i n_i + t c_{i,\sigma}^+ c_{j,\sigma} + U_i n_{i\uparrow} n_{i\downarrow} + V n_i n_{i+1}) \tag{2}$$

where $c_{i,\sigma}^+$ creates a hole with spin σ at the Cu or O site i, n_i is the local charge density operator, $c_i^+ c_i$, U_i is the
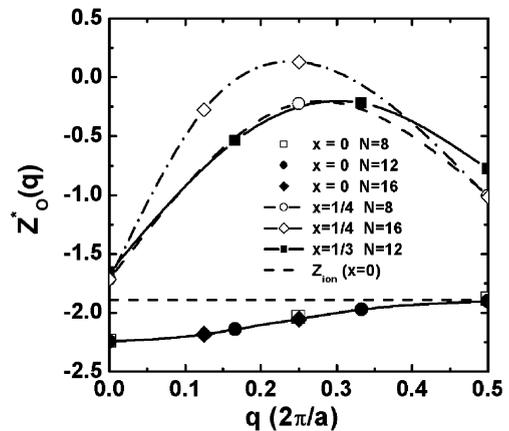

Fig. 2. The Born effective charge of oxygen for the LO phonon as a function of the phonon momentum in the unit of $2\pi/a$ for various sample sizes, N, and doping, x [8]. Note that the sign can reverse at the middle of the Brillouin zone.

on-site Coulomb repulsion, and V is the nearest neighbour Coulomb repulsion. The e–p coupling is included in the on-site energy and hopping, as $t = t_0 + \alpha u$ and $\varepsilon_i = \varepsilon_{i0} + \beta u$. The calculation was done for the system of $N = 12$ and 16 with 4 holes for the LO phonons with varying q. We used standard parameters fro the cuprates, $\Delta = 4$, $t = 1.3$, $U_d = 4$ and $V = 1.2$ in eV, and $\alpha = \beta = 1.2$ eV/Å. Since the system is metallic the Berry phase is invalid, and the value for $q = 0$ is only an approximation. For $q \neq 0$, we calculated the change in the local charge density by phonon displacement of the ith ion, $u_i(q)$, and deduced the local current, and expressed it in terms of the Born effective charge. As shown in Fig. 2 the Born effective charge of oxygen deviates strongly from the ionic value (dashed line), and in the middle of the Brillouin zone it becomes even positive.

Thus the e–p coupling in the doped curates at $q > 0$ is as strong as in the titanates, but the electronic and ionic polarizations are opposite in direction. It is not difficult to understand this q dependence. For small q holes are transferred from O to Cu. Since the lower Hubbard band is well below the oxygen band (by Δ) and the screening effect is strong, the amount of charge transfer will be small. On the other hand at large values of q the charge is transferred mainly from Cu to another Cu, easily tunneling through the oxygen states, resulting in strong response to the phonon. Note that the maximum of CT occurs near $q = n$, where n is the hole density per Cu ion, which corresponds to the wavevector of the stripe state.

3. Spin–phonon coupling

In strongly correlated electron systems such as the cuprates the phonon-induced charge transfer can be spin-dependent, producing a spin–phonon coupling. Indeed our calculation has shown that a strong spin–phonon coupling exists for the zone boundary, half-breathing phonon, as shown in Fig. 3. A part of this effect can be expressed by the t–J model as the dependence of the exchange interaction, $J = t^2/U$, on the phonon displacement of ions. But the effect is much stronger and more strongly q-dependent than expected for the t–J model. Furthermore phonons were found to soften the spin excitation greatly to the extent to stabilize incommensurate spin structure [9]. This spin–phonon coupling can explain the presence of the spin–charge stripe structure in this system [10]. If the spin–phonon coupling is not too strong to stabilize the stripe structure, it could collaborate with the phonons to create a synergetic effect of spin–phonon pairing mechanism. This unexpectedly strong spin–phonon coupling justifies to call the e–p coupling in the cuprates *unconventional*.
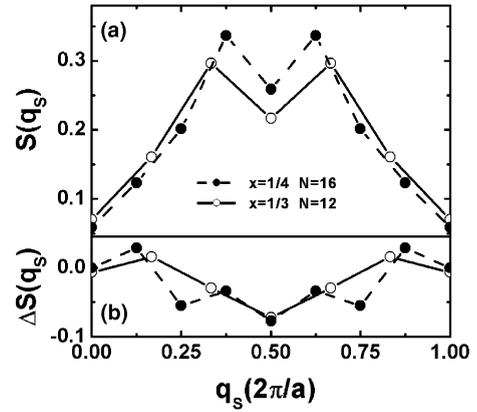

Fig. 3. Total spin structure factor (above) and changes induced by the zone-boundary phonon (below).

4. Experimental evidence

A strong evidence of the phonon-induced charge transfer shown in Fig. 2 is the softening of the LO phonons of the cuprates near the zone-boundary [11] (Fig. 4 [12]). While the LO modes soften strongly the
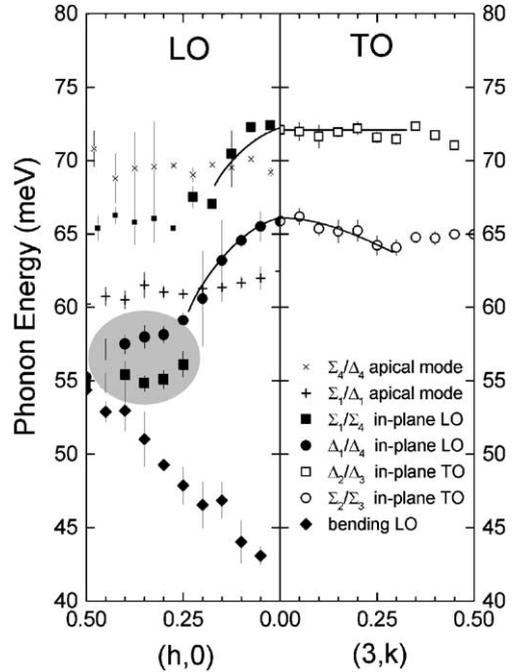

Fig. 4. Phonon dispersion of the Cu–O bond-stretching modes in $YBa_2Cu_3O_{6.95}$ determined by inelastic neutron scattering [12]. Small symbols describe weak peaks. Note that the in-plane LO modes soften towards the zone-boundary, while the TO modes remain nearly dispersionless. The LO phonons are most strongly softened in the shaded area where strong e–p coupling is expected.

corresponding TO modes remain dispersionless, which is rather counter-intuitive in the light of the Lyddane–Sachs–Teller relationships. To explain this softening with the regular lattice dynamics model very unnatural assumptions have to be made [13]. It is most natural to explain this as an electronic effect [14,15].

As a function of doping this softening occurs rather abruptly right after the metal-insulator transition [16], and disappears again at overdoping [17]. This anomalous behavior is best explained by the present mechanism. In an insulator charges are immobile because of strong spin correlation, so that the CT mechanism does not operate. At high doping screening also kills the CT effect. Thus in the intermediate doping levels where screening is weak and yet holes are mobile the CT effect is most pronounced. The transfer of holes from O to Cu enhances ionicity and allows holes to delocalize more, thus reduces the electron energy, which softens the phonon.

We have recently initiated a study of the spin–phonon coupling with spin-polarized neutron inelastic scattering. A preliminary measurement carried out for a single crystal of $YBa_2Cu_3O_{6.95}$ at $T = 110$ K at the IN20 of the ILL showed some spin excitation intensity around (π, π) and $\hbar\omega = 55$ meV, which may be associated with the $(\pi, 0)$ LO phonon [18]. This peak is absent below T_C where only the resonance peak at 41 meV is observed.

5. Relevance to HTSC

The strong unconventional coupling of the zone-boundary LO phonons to charge and spin degrees of freedom suggests that they may significantly contribute to the hole pairing. Since the strong coupling is limited to the LO phonons in the vicinity of the $(\pi, 0)$ points coupling is very anisotropic. In fact a phenomenological Eliashberg theory calculation carried out with the model electron and phonon dispersions fitted to experimental data (electron to the ARPES data and phonon to the neutron data) using the negative dielectric theory of Tachiki and Takahashi [15] has demonstrated that such a coupling can result in the d-wave superconductivity with the critical temperature over 100 K [19].

It should be noted that because of the strong anisotropy in coupling this phonon mechanism is compatible with the d-symmetry and does not necessarily compete against the repulsive spin mechanism. In addition the spin excitations created by the phonon [9] themselves contribute to coupling. It is also interesting to note that in the ferroelectric oxides such as titanates the phonon-induced charge transfer softens the TO phonons leading to the structural transition. In the cuprates it softens the LO phonons, since the electronic polarization is anti-parallel to the ionic polarization, and thus less likely to induce structural instability, allowing high values of T_C to be achieved.

In conclusion, while the conventional BCS phonon mechanism fails to account for the HTSC phenomenon, the e–p coupling in the cuprates is rather unconventional, and has a possibility to orchestrate a synergetic effect of pairing by spin and phonon, and to contribute significantly to the HTSC mechanism. It is most likely that the relative strengths of the spin vs. phonon mechanisms depend upon the hole concentration; our conjecture at present is that the underdoped systems are dominated by a spin mechanism, while the phonon mechanism is more important for the optimum to overdoped systems. It is definitely too early to dismiss the role of phonons in the mechanism of high-temperature superconductivity.

Acknowledgements

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