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DYNAMIC JAHN-TELLER COUPLING AND HIGH T_C SUPERCONDUCTIVITY

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Based on the cooperative dynamic Jahn-Teller effect, a universal model of superconductivity is sketched which accounts for many aspects of conventional BCS and high T_c superconductors. Within the quasi-molecular approximation, a real space vibronic coupling of degenerate (or nearly degenerate) electronic states to anharmonically mixed nuclear distortions is shown to lead to electron pairing. The crossover from electron-phonon behavior to electronic behavior as a function of Jahn-Teller coupling and anharmonic mixing is illustrated for the case of a CuO_4 cluster having D_{4h} symmetry.

1. INTRODUCTION

The recurrent observation of degenerate or nearly degenerate bonding electronic states at E_F in all types of superconductors provides a strong clue for a unifying pairing mechanism of superconductivity. Specifically in the case of $La_{2-x}Sr_xCuO_4$, electronic structure calculations[1,2] reveal $O(p_z\pi)$-$O(p_z\pi)$ two fold degenerate bonding molecular orbitals at E_F. This O-O bonding is promoted by $Cu(d_{xz,yz}\pi^*)$-$O(p_z\pi)$ antibonding which squeezes the $O(p_z\pi)$-$O(p_z\pi)$ overlap. The predominantly oxygen p character of this state has been confirmed spectroscopically[3,4]

Consideration of a simple CuO_4 cluster gives insight into the pertinent electronic states. Within the D_{4h} point group, this predominantly oxygen p_z state transforms as an e_g representation. In the ground state, these $O(p_z\pi)$-$O(p_z\pi)$ bonding e_g orbitals are nearly degenerate at E_F with $O(p_{x,y}\pi)$ non-bonding e_u orbitals in the Cu-O plane. Some confusion has resulted from the fact that EELS measurements[4] of $La_{2-x}Sr_xCuO_4$ which produce O(1s) and O(2p) core holes mistakenly conclude[4] that O(p) holes at E_F are associated with the non-bonding in plane e_u orbitals. Core excitations resulting from measurement are sufficient to excitonically depress the e_g states below the e_u.[5]

This degeneracy of bonding orbitals with delocalized topology at E_F can lead to electron pairing through cooperative nuclear distortions driven by the dynamic Jahn-Teller (DJT) effect. In this model, a real-space view of pairing is a necessity, given that degeneracy and quasi-local distortions are difficult to treat in a field-theoretical manner.

2. D_{4h} VIBRONIC MODEL: $E_g \otimes \beta_{2g}$

The JT theorem states that for a degenerate or nearly degenerate system, a spontaneous distortion will lower the energy of the system if a vibrational mode exists which is included in the decomposition of the non symmetric square of the electronically degenerate representation. Given a two fold degenerate electronic state whose orbitals $|u>$ and $|v>$ transform as the partners of the E irreducible representation (IR), vibrational modes which are included in the non symmetric square $[E^2]$ will split the degeneracy. In D_{4h}, $[E^2] = A_{1g} \oplus B_{1g} \oplus B_{2g}$. The α_{1g} mode is recognized as the symmetric breathing mode. The β_{1g} and β_{2g} modes are non symmetric (Fig. 1) and will therefore split the electronic degeneracy.

Using the Wigner-Eckart theorem, the vibronic interaction term[6] is found to be of the form:

$$H_{vib} = \begin{pmatrix} AQ_2 & -BQ_3 \\ -BQ_3 & -AQ_2 \end{pmatrix}$$

where Q_2 and Q_3 are normal coordinates of the two non symmetric JT modes, β_{1g} and β_{2g}, and A and B are their reduced matrix elements.

A nuclear potential surface can be calculated by diagonalizing $H_{vib} + H_{nuc}$

$$V_n(Q_2, Q_3) = \frac{1}{2}M\omega_2^2Q_2^2 + \frac{1}{2}M\omega_3^2Q_3^2 \pm \sqrt{A^2Q_2^2 + B^2Q_3^2}$$

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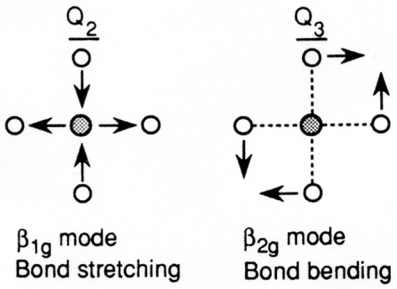

FIGURE 1

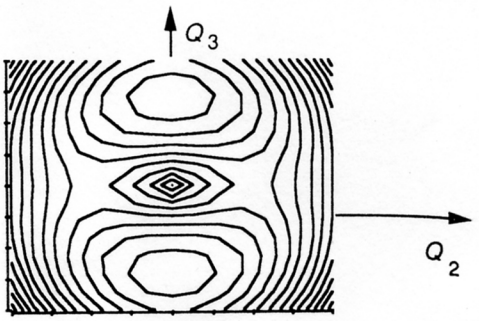

FIGURE 2 (After Herzberg)
$V_{nuc}(Q_2, Q_3)$ with slight anharmonicity

O(2) group symmetry exists on the potential surface if $\omega_2 = \omega_3$ and $A = B$. Rotational modes exist in this Q_2-Q_3 space, which correspond in real space to ligand vibrational modes. In the case of oxide superconductors, O-O vibrational modes (LO) have been detected spectroscopically.[7] A small degree of asymmetry in the parameters will cause the formation of small potential wells about non zero values of nuclear distortions, and the symmetry of the potential drops to D_{2h} (Fig. 2). If the wells become too deep, a static JT distortion results, and decoupled harmonic oscillations occur about the minimum. For shallow wells, resonant tunneling between nuclear configurations is possible. The characteristic frequency, ω_{tun}, of such an event is determined by JT electronic energy scales.

3. PHENOMENOLOGY

With increasing bond overlap between ligands, the amount of anharmonic mixing of β_{1g} and β_{2g} modes increases. The height of the saddle points in Q_2-Q_3 space decreases. The time averaged length of the nuclear excursions, δ, is consequently decreasing, while the effective frequency, dominated by the tunneling process for large mode mixing, is increasing. By expanding vibrational modes in terms of a harmonic oscillator basis set centered about the potential minima, ω_{tun} and δ as a function of anharmonic mixing can be obtained.[8] The time dependent polarization resulting from nuclear displacements yields an attractive real space pairing potential which has been effectively modeled by Johnson et al.[1] The mixture of tunneling to phononic events is parameterized by a general DJT exponent, β, which can be calculated from ligand bond overlap ($0 < \beta \leq \frac{1}{2}$). The limit of $\beta \rightarrow \frac{1}{2}$ corresponds to the BCS limit of phonon mediated weak coupling, while decreasing β mixes in more electronic effects. β, together with the Coulomb screening length, d, determines the form of the real space pairing potential.

Thermodynamic critical fields, isotope shifts, T_cs, Debye frequencies for a variety of both high T_c and conventional superconductors have been successfully calculated using this phenomenological model.[1,9] Critical behavior with magnetic fields can be thought of in the context of this model as lifting the orbital degeneracy to the point where vibronic states no longer couple, thus precluding the DJT interactions.

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REFERENCES

1. K.H. Johnson et al., Novel Superconductivity (Plenum, New York, 1987) p. 563
2. A.J. Freeman, J. Yu, C.L. Fu, Phys. Rev. B 36, 7111 (1987).
3. Z.-X. Shen et al., Phys. Rev. B 39 (1989) 823.
4. N. Nücker et al., Phys. Rev. B 39 (1989) 6619.
5. K.H. Johnson, D.P. Clougherty, and M.E. McHenry, Mod. Phys. Lett. B (in print).
6. G. Herzberg, Electronic Spectra and Electronic Structure of Polyatomic Molecules (Van Nostrand, New York, 1966).
7. I. Ohana et al., Phys. Rev. 39 (1989) 2293.
8. D.P. Clougherty, unpublished.
9. D.P. Clougherty and K.H. Johnson, Physica C 153-155 (1988) 699.