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Structural phase transitions and superconductivity in $La_{2-x}A_xCuO_4$, A = Sr, Ba

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Abstract. A low temperature structural phase transition in $La_{2-x}Ba_xCuO_4$ was recently discovered, and has been shown to severely depress the superconducting transition temperature. It is suggested that this structural transition is associated with a charge density wave in the CuO_2 planes which was predicted to play a major role in high-T_c oxide superconductivity.

The superconductivity in the new high-T_c oxide superconductors [1] is generally agreed to be of a BCS pairing form, but the extremely high T_c values and weak isotope effect [2] argue against virtual phonons as the cause of the pairing. A number of theories have arisen, based on more exotic pairing, generally related to exchange [3] or excitonic [4, 5] effects. An exchange related mechanism is suggested by the proximity of the superconducting phase to an antiferromagnetic insulator, as in La_2CuO_4 and $YBa_2Cu_3O_6$. The excitonic models generally require the presence of two bands near the Fermi level—either the antibonding and non-bonding bands of the CuO_2 planes [4], or planes versus chains [4] in $YBa_2Cu_3O_7$. In a recent series of papers [6–8], I have shown that an excitonic transition can arise in the single CuO_2-antibonding band, thanks to the van Hove singularity of that band.

When the Fermi level is precisely at the van Hove singularity, the Fermi surface is an exact two-dimensional analog of the Bilbro–McMillan model [9] of the A15 compounds. There is a competition between superconductivity and charge density wave (CDW) formation, both driven by the high density of states associated with the van Hove singularity. When the CDW forms, it will have the smallest electronic gap in the material, and hence should be an excellent candidate for excitonic pairing. However, in the A15 compounds, superconductivity is depressed when long-range CDW order sets in. Hence in the high-T_c oxides I postulated that the pairing is associated with short-range CDW order. Short-range order should be present over a broad temperature range, due to the nearly two-dimensional nature of these compounds.

It has been suggested [10] that this long-range CDW order is associated with the tetragonal-orthorhombic (TO) transition in these materials. However, this is unlikely, since $T_{TO} > T_C$, and the TO transition has very little effect on electronic structure in these materials. The transition is more likely to be an antiferrodistortive transition of the form common to many perovskites [11, 12]. Thus, while the TO transition in La_2CuO_4 involves

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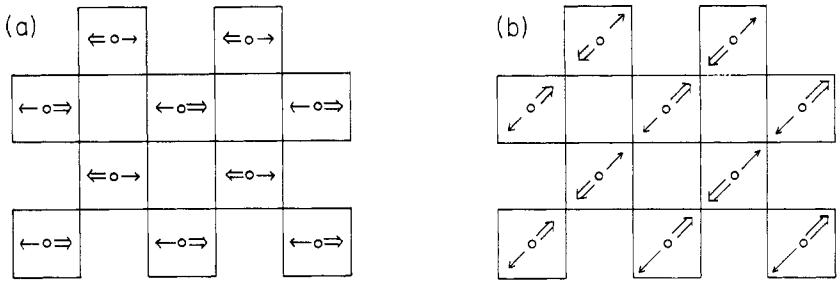

Figure 1. Tilt distortion in the low-temperature phases of $La_{2-x}A_xCuO_4$, A = Sr, Ba. Open circles represent Cu atoms; in-plane oxygens are at corners of squares. The distortions are represented by the motion of the apical oxygens, represented by arrows (single arrow: oxygen below the CuO_2 plane; double arrow: above). (*a*) Low temperature orthorhombic phase; (*b*) low temperature tetragonal phase.

a rotation of CuO_6 octahedra about (110)-axes (figure 1(*a*)), the similar transition in $SrTiO_3$ involves rotation of TiO_6 octahedra about cubic (100) axes.

Recently, a low-temperature tetragonal (LTT) phase transition has been found [13–16] in $La_{2-x}Ba_xCuO_4$, and this transition does significantly modify the electronic structure, and reduce T_c. This LTT transition may be identical to the CDW state postulated above [6–8].

At first glance, the tilting distortion in the LTT phase (figure 1(*b*)) looks similar to that in the orthorhombic phase (figure 1(*a*)) except that the octahedra are rotated about a (100) axis. (The tetragonal symmetry arises from the stacking order of successive layers.) This change of tilt axes is important, however. In the orthorhombic phase, the two oxygen atoms in the CuO_2 plane are in symmetrical positions, while the LTT deformation breaks this symmetry. This symmetry breaking splits the van Hove singularity, driving one density-of-states peak below the Fermi level, the other above it. Changes in normal state transport properties [14] confirm that a large part of the Fermi surface is gapped by the LTT transition.

This then is the CDW transition postulated in [6–8], with the tilting of the octahedra providing the accompanying Peierls distortion. As shown in figure 1(*b*), the tilting is associated with a partial *dimerisation* of the apical (out-of-plane) oxygens, with a corresponding charge pile-up between them. This will induce a build-up of the opposite charge of the in-plane oxygen below the dimer—the CDW. It is similar in form to figure 10(*c*) of [6]. Note that in this layered compound the positive and negative charges are displaced along the *c* axis.

To model the CDW transition, the calculation of [6] must be modified to account for the proximity of the TO transition. Following Axe *et al* [15], the Landau free energy of the soft phonon modes associated with the TO transition is

$$F = \tfrac{1}{2}a(T - T_0)(Q_1^2 + Q_2^2) + u(Q_1^2 + Q_2^2)^2 + v(Q_1^4 + Q_2^4) \qquad (1)$$

where Q_1, Q_2 are the amplitudes associated with the degenerate soft modes at wave vectors $q_1, q_2 = \frac{1}{2}(1, \pm 1, 0)$ and a, u and v are Landau parameters. If $(u + v) > 0$, $v < 0$, then in the mean field the TO transition takes place at $T = T_0$, with $Q_1 \neq 0$, $Q_2 = 0$ or $Q_2 \neq 0$, $Q_1 = 0$ for $T < T_0$, $Q_1 = Q_2 = 0$ for $T > T_0$. Axe *et al* [15] showed that if v changed sign at $T_1 < T_0$, then a transition at T_1 from orthorhombic to the LTT phase would be found experimentally. In this LTT phase, $Q_1 = Q_2 \neq 0$. Now the TO transition,

in common with many other perovskites, depends on the non-linear O^{2-} polarisability [17]. Hence the TO transition will be sensitive to Cu–O charge transfer, making T_0 a strong function of x, as observed.

In modifying (1), I assume that v is T-independent, and include an electronic contribution, due to the opening of a CDW gap W [6, 9]

$$\Delta F = -N(0)W^2 \int_0^{E_B} \frac{d\varepsilon}{\Omega} \tanh\left(\frac{\Omega}{2kT}\right) \tag{2}$$

where $N(0)$ is the electronic density of states, $\Omega = \sqrt{\varepsilon^2 + W^2}$ and E_B is half the electronic band width. Now W only couples to phonon modes which split the degeneracy of the oxygen nearest neighbours of the Cu atoms, i.e. for $q_x = (100)$ or $q_y = (010)$, but not for q_1, q_2. Hence W is zero in the orthorhombic phase. However W does couple to the coherent combination $Q_\pm = Q_1 \pm Q_2$, and hence is non-vanishing in the LTT phase. The simplest analytic functional relationship is that $W \sim Q_+^2 - Q_-^2$, or

$$W^2 = \gamma Q_1^2 Q_2^2 \tag{3}$$

where γ is a constant. Equations (1–3) then describe the double transition $T \rightarrow 0 \rightarrow$ LTT.

For instance, suppose that $T_0 \gg T_1$. Near T_1, assume $Q_1 \simeq Q_{10} =$ constant, $Q_2 \simeq 0$. Then the free energy can be written as a constant plus terms involving Q_2:

$$F = -Q_{10}^2 Q_2^2 \left[2v + \gamma N(0) \int_0^{E_B} \frac{d\varepsilon}{\Omega} \tanh\left(\frac{\Omega}{2kT}\right)\right] + (u + v)Q_2^4. \tag{4}$$

Defining the electron–phonon coupling constant as $V_p = -\gamma/2v$ (recall that $v < 0$), the term in brackets becomes the usual expression for CDWs, with

$$kT_1 = 1.13E_B \, e^{-1/N(0)V_p}$$

The last term in (4), being $\sim Q_2^4$, does not affect T_1, but modifies growth of $Q_2(T)$ for $T < T_1$. In principle, the CDW can couple to other phonon modes with displacements along q_x or q_y. Presumably, the mode analysed above is the softest such mode because of its proximity to the TO transition.

The expression, (2), is strictly speaking true for one-dimensional, nesting Fermi surfaces, but a similar result is valid at the van Hove singularity. This will be discussed further in a forthcoming publication. Superconductivity may be incorporated into the model as in [6, 9].

This CDW transition is very similar to that found in the A15 compounds, or in $BaPb_{1-x}Bi_xO_3$. Just as in these materials, the presence of long-range CDW order in $La_{2-x}Ba_xCuO_4$ (the LTT phase) depresses T_c virtually to zero. In $La_{2-x}Sr_xCuO_4$, there is no long range CDW order, but the model of [6] predicts a strong short-range order, and Axe has observed [15] that the relevant phonon mode does soften significantly, but never to zero frequency in the high-T_c material. The recent observation that superconductivity is associated with a peak in the density-of-states [18], along with the present finding that gapping of this peak destroys superconductivity, provide considerable evidence of the important role of the van Hove singularity (VHS) in high-T_c superconductivity.

The VHS arises in the one-electron band structure calculation, and it has been questioned whether such Fermi surface features survive in the presence of strong correlations. In [8], the effect of these correlations was incorporated into a band structure

calculation by means of the slave boson technique. It was found that, whereas correlations drive a Mott transition near half-filling, a Fermi liquid picture is more appropriate away from half-filling (e.g., $x > 0.03$ in $La_{2-x}Sr_xCuO_4$), and the high density-of-states associated with the VHS is still found at nearly the same filling factor.

It should be noted that the suggestion of a CDW transition in these materials is not new. Prior to the discovery of the LTT phases a CDW model was applied to the TO transition [10], and to what is now known to be the transition to an antiferromagnetic insulator [19]. In addition to differing on the identification of the CDW phase, these earlier models differ from the present in one important aspect. By using simplified energy bands, these models shifted the VHS to the position of the half-filled band—i.e., to undoped La_2CuO_4. This would make the CDW transition temperature largest at half filling, and monotonically decreasing as the material is doped, in contrast to experiment. In the present model, the VHS occurs at the doping which would correspond to the highest T_c, and hence coincides with the optimum doping for the observed LTT phase.

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