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Anomalous properties and microstructural model of superconductivity in $La_{2-x}(Ba,Sr)_xCuO_4$

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A specific microstructural model involving short- or long-range order of $(Ba,Sr)_{[La]}$ dopant substituents explains the composition $x_0=0.125$ most favorable for the formation of the low-temperature $Ba_{[La]}$ tetragonal phase. The microstructural model shows that the normal state of these alloys can be described as a two-component Fermi liquid in order to explain the acoustic, magnetic, and thermal anomalies centered on x_0 as well as the related drastic reduction in T_c over a narrow range of x.

Following the discovery by Moodenbaugh *et al.*[1] that the superconductive transition temperature in $La_{2-x}Ba_xCuO_4$ is a sensitive function of x, with not only a maximum near $x=0.16$, as in $La_{2-x}Sr_xCuO_4$, but also with an additional deep and narrow minimum near $x=x_0=0.123(3)$, many experimentalists have studied other properties of carefully prepared samples of these alloys. A number of drastic anomalies appear near x_0 with Ba substitution that are weaker or absent with Sr substitution, as shown by the phase diagrams of Figs. 1(a) and 1(b). The studied properties include electronic specific heat,[2] ultrasonic velocity and attenuation,[3] and nuclear heat capacities.[4] Broadly speaking, all these anomalies arise from the formation of a low-temperature tetragonal (LTT) phase,[5] whose relation to the higher-temperature tetragonal (T) and orthorhombic (O) phases has been discussed by Landau theory.[6]

In this paper we propose a microstructural model for the origin of the LTT phase. With this model and an electronic theory based on a two-component Fermi-liquid (FLII) theory,[7] we discuss all the experimental anomalies in both the Ba and Sr alloys and their alloys.[8]

First we note that any electronic model of the (x_0,Ba) anomalies based solely on doping of the CuO_2 planes by Sr or Ba cannot explain the narrow (x_0,Ba) dip in T_c or the other Ba anomalies which are nearly symmetric about x_0. This is because doping with Ba or Sr should be virtually indistinguishable, and with increasing x should yield monotonic behavior in T_c and $N(E_F)$, as observed with Sr doping. (The decrease in T_c beyond $x=0.2$ is due to self-compensation through the formation of $Sr_2O^{\square}$ complexes, where $O^{\square}$ is an oxygen vacancy.[9,10]) This remark also applies to electronic models[11] of the LTT structure which attribute the stabilization of that phase to O-O charge fluctuations, while the O phase is supposed to be stabilized by Cu-O charge fluctuations. Instead, the x dependence of the O-T transformation can be explained simply by the rotation of oxygen octahedra[12] induced by

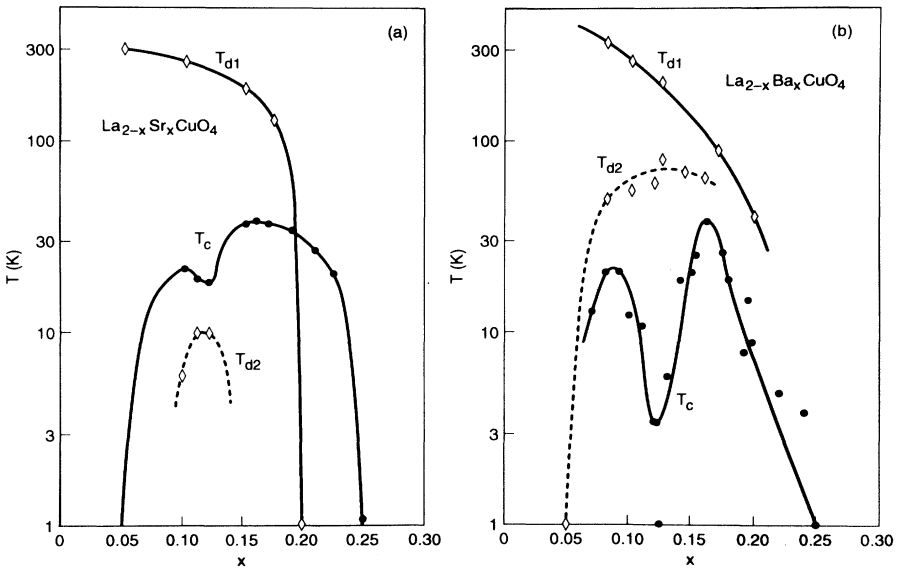

FIG. 1. Superconductive transition temperature T_c and (T-O), (O-LTT) transition temperatures, respectively T_{d1} and T_{d2}, for (a) $La_{2-x}Sr_xCuO_4$ and (b) $La_{2-x}Ba_xCuO_4$, from Refs. 1, 3, 5, and 7.

interplanar (La,Ba or Sr)$_2O_2$-CuO_2 misfit.[13]

A microstructural model which does explain the symmetric (x_0,Ba) dip assumes that the effective interaction between the A=Ba (or Sr) dopant substituents is repulsive, leading to 4×4 tetragonal supercell long- or short-range ordering of the $A_{[La]}$ dopants. The A-A effective interaction contains two components due to Coulomb repulsion and strain misfit. The Coulomb repulsion term is similar for A=Ba or Sr, but the strain misfit term is larger for Ba than for Sr. [The Pauling radii in Å are $R(La^{3+})=1.15$, $R(Sr^{2+})=1.13$, and $R(Ba^{2+})=1.35$.] This explains qualitatively why Ba(Sr) substitution affects long-range (short-range) order.

The space-group symmetry, O, T, or LTT, is determined by the competition between interplanar misfit (which favors O) and A supercell forces (which favor T or LTT). Each of these is temperature dependent, and this dependence is described by an appropriate Debye-Waller factor. The key simplification now is that because the Ba mass is much larger than the Cu and O masses, its Debye-Waller factor is much larger, so that the A=Ba LTT-favoring supercell forces can dominate the interplanar misfit forces at low T. For A=Sr this dominance is much less pronounced, and so apparently only residual short-range tetragonal order is observable[3] near 10 K (see Fig. 1), with a shallow dip in T_c. Because the balance between these competing forces is so delicate, the supercell ordering is destroyed for $|x-x_0|\gtrsim 0.01$.

Given the supercell microstructural model, we can now explain the electronic anomalies in the context of FLII theory.[7] In doped semiconductors (such as Si:P), the dopant electron at $\mathbf{r}_d$ is separated from the valence electrons of the host lattice by the model wave function

$$\Psi=\phi(\mathbf{R}_d-\mathbf{R}_0)\psi_{\mathbf{k}_0}(\mathbf{r}_d)\chi\,, \tag{1}$$

where χ is the wave function of the host valence electrons, $\psi_{\mathbf{k}_0}(\mathbf{r}_d)$ is the Bloch valence- or conduction-band-edge wave function, and ϕ is a cellular envelope function for the dopant state with the impurity centered in the cell $\mathbf{R}_0$. A similar separation is made for FLII, with respect in this case to all the dopant holes associated with the A=Ba or Sr dopants, so that χ now refers to the remaining valence electrons of La, Cu, and O. In both cases, the separation is necessary to describe the correlations between the host valence electrons and the dopant carriers. For Si:P this modifies the kinetic energy ($m\rightarrow m^*$) and yields correlated dielectric screening of the impurity potential. For heavily doped Si:P, a second separation into localized and extended states explains *completely* the impurity band metal-insulator transition.[14]

We now describe the $La_{2-x}A_xCuO_4$ valence wave function by

$$\Psi=\phi\chi\,, \tag{2}$$

where χ refers to the host Fermi liquid and ϕ to the dopant Fermi liquid. The basis functions describing the dopant carriers, or dopons, should be generalizations of $\phi(\mathbf{R}_d-\mathbf{R}_0)\psi_{\mathbf{k}_0}(\mathbf{r}_d)$ from (1). If we let $\{\mathbf{R}_0\}$ label the dopant sites, each two-dimensional dopon wave function again can be a product of an envelope function $\phi(\mathbf{R}_d-\mathbf{R}_0)$ and a weighted average of states near the Fermi line in the original lumped (not separated) energy bands represented by ψ_d. Thus ψ_d plays a role analogous to $\psi_{\mathbf{k}_0}$ in (1),

$$\psi_d(\mathbf{r})=\sum_{\mathbf{k}}\{1-[E_F-E(\mathbf{k})]/E_0\}u_{\mathbf{k}}(\mathbf{r}-\mathbf{r}_d)\,, \tag{3}$$

where $u_{\mathbf{k}}(\mathbf{r})$ is the real part of the Bloch function $\psi_{\mathbf{k}}(\mathbf{r})$ with $u_{\mathbf{k}}(0)>0$. The linear weighting factor[15] in (3) with the cutoff at $E_0\sim 0.05$ eV explains[7] the linear temperature dependence of the normal-state resistivity. It is beyond the scope of this paper to expand the discussion to include the connection of the dopon states to interlayer coupling, but if the marginal conductivity hypothesis[9] is correct, they play an essential role. Charge fluctuations of the dopant states may be large and this can explain the observed reductions in T_c with decreasing superconductive layer thickness.[16]

The dopons described by ϕ contribute a narrow band of states $N_\phi(E)$ to the total density of states,

$$N(E)=N_\chi(E)+N_\phi(E)\,, \tag{4}$$

which pins E_F close to the center of the ϕ band, just as defects typically pin E_F at Schottky metal-semiconductor interfaces. When the A atoms order in the A=Ba LTT phase, a separate two-dimensional energy band $E_d(\mathbf{k}_d)$ for dopons can develop. Because the Ba supercell atoms are far apart, this band will be nearly flat ($m^*\sim 10$ m) and can be described by nearest-neighbor interactions only. Then $E_d(\mathbf{k}_d)$ will have extrema at the two-dimensional reduced zone center and corner, and saddle points at the centers of the zone edges. The Ba band is half full and the Fermi line is a square which passes through the saddle-point zone-edge centers. This nested Fermi line should produce antiferromagnetic spin-density waves (SDW), and the energy associated with these waves may help to stabilize the supercell phase.

A corollary of dopon SDW is that the development of SDW in ϕ implies that the χ valence band is also nearly half full, which means that SDW might develop in this band as well, because the states in the χ band are just those of La_2CuO_4 with the La atoms at the Ba supercell sites removed. This modified La_2CuO_4 already would be partially orbitally insulating because of the supercell potential, which produces small energy gaps at the La_2CuO_4 two-dimensional half-full energy line. These gaps might be incomplete over the full three-dimensional Fermi surface. If the SDW energy gain were larger than the supercell orbital gain, SDW's could then form in the χ band, leading to $N(E_F)=0$ for $x=x_0$.

To compare this electronic model with experiment we first note that the model just described is idealized in the sense that we have assumed that all of the Ba atoms order to form a perfectly homogeneous superlattice. In practice this is very unlikely. Great care has been taken experimentally, through repeated powdering and sintering,[1] to produce homogeneity, but it seems very unlikely that perfect homogeneity was achieved. Convergent beam electron-diffraction studies show[17] the processing was sufficient only to produce partial homogeneity and partial supercell ordering, with a domain size in the LTT phase of ~300 A; in other words, the actual electronic structure is a mixture of that of ordered and disordered structures.

The value of $\bar{S}(x_0)=[\overline{S^2(x_0)}]^{1/2}$ measured from the nuclear specific heat,[4] shown in Fig. 2, is about half that of $x=0$, which suggests that about half of the Ba atoms have ordered to form the supercell phase. One would then expect to find that the electronic specific-heat coefficient γ was reduced also by about a factor of 2, and this expectation is consistent with experiment.[2] (In units of $\mathrm{mJ\,mol^{-1}K^{-2}}$, γ is reduced[2] from about 4.5 to about 2.2, as also shown in Fig. 2.)

The foregoing model has some far-reaching implications. By separating the dopons from the host valence electrons the product wave functions (1) and (2) permit an improved treatment (compared, for instance, to a local-density approximation on the lumped charge density) of the correlation energies which are crucial to phase transitions of particles with energies E near E_F. This separability is the essence of the quantum percolation method.[7] When the dopant impurities are disordered, because of marginal dimensionality the separation may still be possible[18] even though the sharp Fermi edge in $\mathbf{k}_d$ space is reduced. The separation is important because electron-phonon interactions of dopons can be much stronger than those of the host valence electrons.[19] This can explain why estimates of T_c based on electron-phonon coupling of the latter yield values which are too low.[20]

In conclusion, we have constructed a microstructural model which explains the electronic anomalies which are present in $La_{2-x}Ba_xCuO_4$ alloys but are largely absent from $La_{2-x}Sr_xCuO_4$, even though both alloys are chemically very similar. Our model requires that dopons be separated from the host valence electrons, as described by a two-component Fermi-liquid model.[7] The model shows that dopon-magnon interactions, and presumably dopon-phonon interactions, can be anomalously large. The present discussion provides strong support for this FLII model, and apparently rules out all the many one-component Fermi-liquid models in which exotic dynamical correlations of carriers confined to CuO_2 planes but independent of dopant coordinates are the basis for high-temperature superconductivity. Our model shows that at $x_0=0.125$ the electronic[2] and Cu nuclear[4] specific heats are both internally consistent with a supercell structure. Because of the complexity of the crystal structure of $La_{2-x}(Sr,Ba)_xCuO_4$ and the difficulty of obtaining truly homogeneous samples, more detailed quantitative modeling seems inappropriate. It is worth noting that compositionally dependent short-range order in $La_{2-x}Sr_xCuO_{4-y}$ may be correlated with an isotopic dependence of y because both contribute to internal stress fields. This provides a model for the anomalous isotope shift observed at $x=0.12$ in agreement with the structural conjecture given with the original data,[21] but in disagreement with the claims of uniqueness for a recent band model.[22] Our model also explains the dramatic observation[23] of a 10% reduction below T_c in the planar Cu-O peak height in the pair distribution function at $x=0.12$ as inhomogeneous broadening due to competition between anharmonic superconductivity and antiferromagnetic spin-density waves, both centered on Sr dopants.

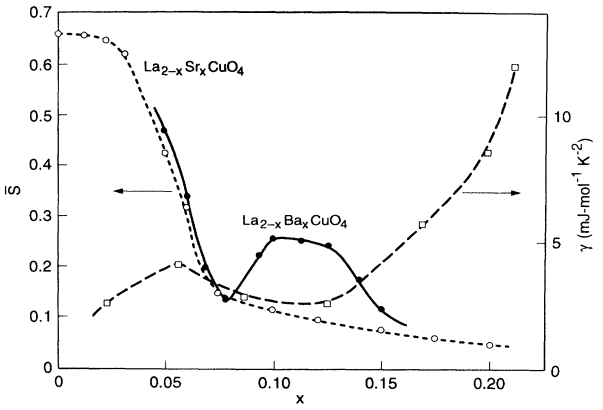

FIG. 2. Values of $\bar{S}(x)$ and electronic specific-heat coefficient $\gamma(x)$ for $La_{2-x}Ba_xCuO_4$, from Refs. 2 and 4. Also shown is $\bar{S}(x)$ for $La_{2-x}Sr_xCuO_4$.

Note added. After this paper was completed we were informed[24] that band calculations based on a 2×2 virtual crystal model of the Ba-La sublattice in the LTT phase (with atomic distortions in a supercell estimated by analogy with those known for the O phase) yield a large depression in $N(E_F)$. This result provides a mechanism which enhances the tendency towards 4×4 supercell structure we have discussed. Of course, a full self-consistent calculation of the atomic distortions of either the 2×2 virtual crystal or the more realistic 4×4 superlattice (~100 atoms per unit cell) is not within the realm of feasibility of current electronic calculations.

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