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Quantum percolation in electron cuprate superconductors $Nd_{2-x}Ce_xCuO_{4-y}$

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Chemical trends in metallic and superconductive properties of these materials are incompatible with theoretical models based on formal carrier density alone. Defect-assisted quantum percolation explains these trends and identifies the specific defect complex responsible for interlayer electrical currents.

I. INTRODUCTION

Square-planar CuO_2 complexes can occur in several ways in ternary compounds, as shown in Fig. 1. After the discovery of metallic normal state and high-T_c superconductive states in $(La,Sr)_2CuO_4$ and in $YBa_2Cu_3O_7$, however, it seemed that parent compounds containing these complexes alone (as in Sr_2CuO_3, Fig. 1), or polymerized as CuO_2 planes (as in Nd_2CuO_4, Fig. 1) could not be doped to become superconductive. This led many workers to conclude that additional apical-oxygen sites are necessary, as in La_2CuO_4 or $YBa_2Cu_3O_7$, to produce metallic and superconductive behavior.

The discovery by Tokura and co-workers[1,2] of metallic behavior with $T_c \gtrsim 20$ K in $Nd_{2-x}Ce_xCuO_{4-y}$ has shown, however, that the T' structure containing only CuO_2 planes without apical-oxygen coordination can be superconductive in analogy with other cuprates. There are, however, two additional differences between this material and those studied previously (including the bismates and thallates). The first difference is electronic, and as we shall see, is of secondary importance, although it is the only one which has been extensively discussed so far. The second difference is a special feature of the atomic structure of the T' phase which has been ignored because it apparently has no connection with the CuO_2 planes. In all theories (other than quantum percolation) these planes play the dominant role, with the interlayer atomic structure being largely neglected.

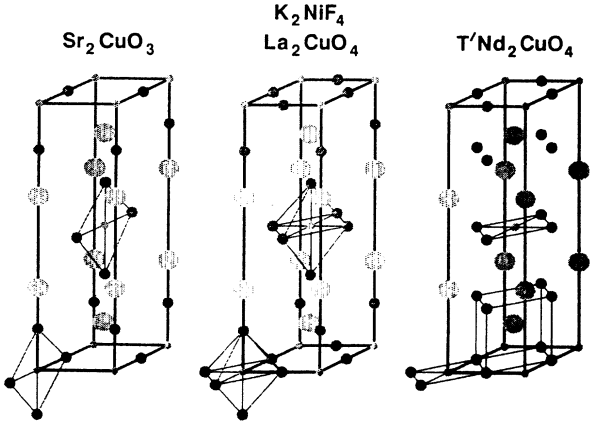

FIG. 1. Comparison of CuO_2 complexes and unit cells of $SrCuO_3$, La_2CuO_4 (K_2NiF_4 structure), and Nd_2CuO_4 (T' structure).

The electronic difference concerns *n*-type vs *p*-type carriers, as determined by Hall and Seebeck effect data. In $(La,Sr)_2CuO_4$, $YBa_2Cu_3O_7$, and the bismates and thallates, the carriers are holes, whereas for the T' phase to be metallic and superconductive the carriers must be electrons. However, most theories agree that the sign of the charge carriers is irrelevant to Cooper pair formation, and only in some exotic theories is this common-sense notion challenged.[3] This electronic distinction is indeed of no significance in quantum percolation theory.

The difference in atomic structure between the doped T' phase and the other superconductors is quite subtle and has, so far, been overlooked by experimentalists who have focused on doping CuO_2 planes and by theorists quibbing over Hamiltonians. The difference is a topological one and it arises quite naturally in quantum percolation theory as a result of marginal conductivity.[4] This theory has already been dramatically successful in explaining why phonon anomalies occur not only for intralayer CuO_2 modes but for interlayer modes as well.[5] Quantum percolation also explains in detail the preparative chemistry of metallic and superconductive $Nd_{2-x}Ce_xCuO_{4-y}$ as we shall now see.

II. QUANTUM PERCOLATION AND FORMAL CARRIER DENSITIES

The basic idea in the quantum percolation model[4] is that because of disorder, the two-dimensional CuO_2 planes do not contain extended metallic states unless there is interlayer defect-assisted coupling through the semiconductive layers. When such coupling exists the number of extended metallic states is limited by the number of interlayer metallic bridges. Strong electron-phonon coupling can, and probably does, occur not only in the CuO_2 planes but also in the bridges themselves.[5] Electrons in extended percolative states themselves are not ballistic and cannot be associated with the conventional one-electron Fermi surface and cannot be labeled by the usual Bloch indices. They do, however, still form a Fermi liquid in the Landau sense.

Because the number of percolative extended states can be much smaller than the number of Bloch-like valence states, their electron-phonon coupling strength λ can be much larger (especially at bridges) than in normal metals.

This increased upper limit for λ is what makes possible high-T_c superconductivity without lattice instabilities. This point is discussed further elsewhere.[6] The defect model can also be used to explain why the normal-state resistivity is linear in temperature over a wide range.[7]

Most experimentalists have tried to establish correlations between T_c and the formal carrier density n measured relative to $n=0$ at half-filling in La_2CuO_4, and some workers have even claimed that these correlations are "universal" for all p-type cuprates including $YBa_2Cu_3O_{7-x}$, the bismates, and the thallates.[8] Actually these correlations require several assumptions about filling factors which may not hold with perfect accuracy in electronically heterophase samples,[9] but nevertheless the general trends which are reported for these materials[8] are probably qualitatively correct. As we shall see, these trends fail for the new n-type materials such as $Nd_{2-x}Ce_xCuO_{4-y}$ because T_c does not scale with $x+2y$. However, all the "anomalies" observed so far are what would be expected from quantum percolation.

III. DISTINCTIVE *n*-TYPE ANOMALIES

Apart from the change in sign of carriers, which means that n-type cuprates contain a mixture of Cu^{2+} and Cu^{1+}, while p-type contain Cu^{2+} and Cu^{3+}, there is an important structural difference between the semiconductive layers that separate the CuO_2 planes. This difference is apparent from Fig. 1 when we compare T' structure of Nd_2CuO_4 with the K_2NiF_4 structure of La_2CuO_4. In the latter the semiconductive layer consists of two LaO planes; similarly, in $YBa_2Cu_3O_7$, the semiconductive layer separating CuO_2 planes and CuO chains is a single BaO plane. However, in Nd_2CuO_4 the CuO_2 planes are separated by *three* planes: Nd, O_2, and Nd.

If we were interested only in the properties of CuO_2 planes, these distinctions would seem minor, which may explain why so far they have been so little discussed. However, according to quantum percolation theory, the CuO_2 planes in the absence of interplanar electrical bridges contain only localized valence states.[4] To obtain extended metallic states one needs chains of electrically active atomic defects across each semiconductive atomic layer. Thus in $La_{2-x}Sr_xCuO_4$, Sr plays a dual role: (i), it makes the carrier concentration $n\neq0$, which suppresses antiferromagnetism, and (ii), it provides an electrical bridge between CuO_2 layers. Several exotic theories of cuprate superconductivity are based on (i) alone, but as pointed out already in Ref. 4, p. 151, it is (ii) that explains the well-known gap between the disappearance of antiferromagnetism near $x=0.03$ and the sharp peak in $T_c(x)$ near $x=0.15$. Point (ii) is concealed by the crystal structure of La_2CuO_4, which utilizes apical oxygens to complete the bridge. It is worth noting that this bridge has nothing to do with excitons.[10] A similar bridge in $YBa_2Cu_3O_7$ probably involves the Ba site,[5] possibly through Y_{Ba}.

In $Nd_{2-x}Ce_xCuO_{4-y}$ the relevant bridge is Ce-$O^{\square}$-Ce where $O^{\square}$ denotes an oxygen vacancy in the semiconductive O_2 plane sandwiched between Nd planes. If the Ce_{Nd} atoms are spatially uncorrelated, the concentration of these bridges will be maximized when $y\geq x^2$. Recent data apparently indicate that[11] the optimal values of x and y are $x_0=0.16$ and $y_0=0.02\pm0.01$, in good agreement with the lower limit of this relation. In addition, if the $O^{\square}$ are strongly attracted by Ce pairs, the concentration of this series bridge scales with the lesser of x^2 and y, so that if $y=0$, $T_c=0$, and not with $x+2y$. Although there are small variations in estimates of x_0 and y_0 from laboratory to laboratory,[11] all agree that for samples to be superconductive they must contain regions with $y_0>0$ and x_0 is an order of magnitude larger than y_0. This is the essential prediction of the present model.

The question now arises as to whether a charged complex such as $(Ce_{Nd})_2O^{\square}$ is stable. In normal ionic crystals such charged complexes would probably dissociate. However, the layered cuprates have many anomalous physical properties (such as high oxygen diffusivity) which are suggestive of uncommonly large internal atomic relaxation around defects. Also electron cuprate superconductors are much more difficult to prepare than hole cuprate superconductors.[3] Especially in the T' structure, where Nd, O_2, and Nd planes are separated already, it is clear that conventional rules of stability (which would apply to the LaO planes in La_2CuO_4) are broken. Therefore at present it seems that such a charged complex may be stable, although it should cause considerable local buckling of the interlayer Nd and O planes. Stated more formally, the internal local coordinates associated with the interlayer interplanar z spacing may be strongly coupled to the charge state of the defect, which may be stabilized by relaxation of these coordinates.

A number of workers have commented that $T_c(x)$ is sharply peaked[11,12] near $x_0=0.16$, while the T' phase is unstable above $x_1=0.20$. This strongly suggests short-range ordering of the $Ce_2O^{\square}$ chains with T_c increasing with the concentration of these chains until they destabilize the T' phase. Such strong short-range ordering, with $|x_1-x_0|/x_1\ll1$, suggest an exceptionally homogeneous defect array which forms superlattice domains. This is not surprising, for the strain-ordering energy for a triatomic $Ce_2O^{\square}$ interlayer defect in $Nd_{2-x}Ce_xCuO_{3-y}$ must be much larger[13] than for a Sr monatomic defect in $La_{2-x}Sr_xCuO_4$.

Electrical bridges based on interstitial O explain $T_c=37$ K in p-type $La_2CuO_{4.03}$. The interstitial O is located[14] between two LaO planes and forms a triatomic bridge including two apical oxygens between CuO_2 layers. Note that the concentrations of oxygen interstitials (vacancies) are comparable in La_2CuO_{4+y} ($Nd_{2-x}Ce_xCuO_{4-y}$) for highest T_c, which suggests similar strain energies for interlayer oxygen vacancies and interstitials.

Several groups[15,16] have reported diffraction evidence for apical interstitial oxygen in $Nd_{2-x}Ce_xCuO_{4-y}$, while electron diffraction and microscopy[17] show phase separation and superlattice formation. This suggests oxygen disproportionation with excess oxygen in insulating regions and oxygen vacancies in superconductive regions. Just as oxygen vacancies compensate Sr acceptors in $La_{2-x}Sr_xCuO_{4-y}$ for $x>0.2$, so we expect here that excess oxygen will compensate Ce donors.

In conclusion, I have shown that with only the assumptions of oxygen vacancy ordering and association with Ce paris that all the novel properties of $Nd_{2-x}Ce_xCuO_{4-y}$ can be understood by quantum percolation theory.[4,5] This theory finds no need for exotic unconventional interactions (such as magnons or excitons) to explain high-T_c superconductivity. Instead the novel properties are the result of strong electron-phonon interactions at interlayer defects by electrons in percolative extended states. Implementation of this theory requires close attention to crystal chemistry[4] to identify the relevant defects, as illustrated here by the example of $Nd_{2-x}Ce_xCuO_{4-y}$. Together with the previous analysis of phonon anomalies,[5] this is the first time a general theoretical model, based entirely on preexisting concepts,[4] has been able to explain chemical trends in specific microscopic terms.

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[13] A simple way of measuring this strain energy is to calculate $\Sigma(\Delta R_i)^2$, where $\Sigma\Delta R_i^2$ is the ionic radius difference $[R(\mathrm{La})-R(\mathrm{Sr})]^2$ in $(La,Sr)_2CuO_4$, and for the $Ce_2O^{\square}$ complex is $2[R(\mathrm{Nd})^2-R(\mathrm{Ce})]^2+R^2(O^{2-})$. The latter is 25 times the former.

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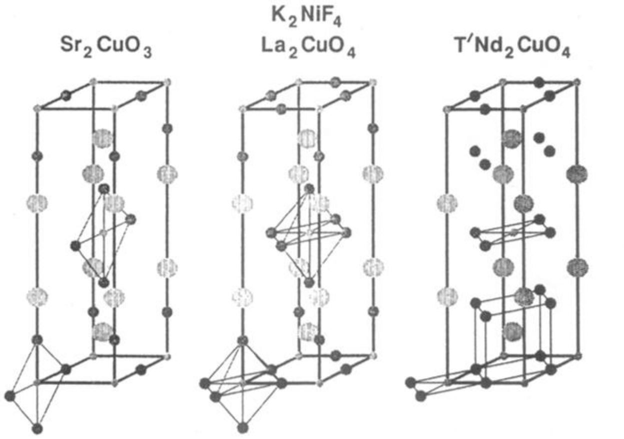

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