Universal non-Landau, self-organized, lattice disordering percolative dopant network sub- T_c phase transition in ceramic superconductors

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Ceramic superconductors (cuprates, pnictides, etc.) exhibit universal features in both $T_c^{\max}$ and in their planar lattice disordering measured by EXAFS, as reflected by three phase transitions. The two highest temperature transitions are known to be associated with formation of Jahn–Teller pseudogaps and superconductive gaps, with corresponding Landau order parameters, but no new gap is associated with the third transition below T_c , and its origin is mysterious. It is argued that the third sub T_c transition is a dopant glass transition, which is remarkably similar to topological transitions previously observed in chalcogenide and oxide alloy network glasses (like window glass).

EXAFS | superconductivity | topological

Conventional metals achieve high superconductive transition temperatures by means of strong electron-phonon interactions, which provide an attractive interaction for Cooper pairs that overcomes Coulomb repulsion. In ceramic materials (oxides, halides, pnictides), one would expect to find strong ionic charges, little screening, and correspondingly strong Coulomb interactions, which would make superconductivity unlikely. Moreover, enhancing the electron-phonon interactions usually leads to large Jahn–Teller lattice distortions, which convert metals into semiconductors or insulators. Yet in certain ceramic materials, nature has found a way to circumvent both of these unfavorable mechanisms and to produce not only superconductivity but even superconductivity at temperatures far higher than are usually found in metals, thus posing the greatest scientific paradox discovered in recent decades (1), with over 7000 research citations.

Several theoretical mechanisms propose to resolve this paradox by invoking interactions other than the traditional attractive electron-phonon interactions, but so far there has been little evidence to support such models, apart from the fact that magnetic nanophases often coexist with superconductive nanophases in samples with Meissner filling factors that are never close to unity (and seldom reported). The simplest idea, which recommends itself as minimally complex, is that certain special ceramics (like the layered cuprates, with layered crystal structures chemically similar to ferroelastic perovskites) have very strong electron-phonon interactions, and that upon being doped, the resulting structures lose most of their magnetic nanophases and instead phase-separate into pseudogapped (charge density wave, CDW, or Jahn–Teller distorted) and metallic superconductive nanophases (2). These superlattice phases have long been described as “stripes” (dynamical or otherwise), but it is noteworthy that in the rare materials (such as $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ near $x = 1/8$) where stripes have been observed by diffraction, T_c has been either strongly depressed or reduced to zero. It appears that ordering of nanophases into superlattices describable by Landau order parameters is extremely unfavorable for superconductivity.

The opposite of “stripes” (superlattice ordering) would be the very strong disordering found in network glasses, such as window glass. Doped ceramics still have a host lattice structure, but if the

dopants themselves do not order, then they can be regarded as forming a glassy carrier network embedded in the host crystal. The average properties of substitutional dopants can be studied by EXAFS, and the average strain fields induced by them in planar Cu–O bonds studied in detail as a function of temperature T . These strain fields exhibit breaks in slope both at the pseudogap T^* and superconductive T_c transition temperatures in ceramic superconductors based on both CuO_2 planes (3) and FeAs planes (4). Since the magnetic properties of Cu and Fe are quite different, this suggests that the minimal model based on dopant-centered strong electron-phonon interactions alone (5) may be a good starting point for building a universal theoretical model for high temperature superconductivity (HTSC) in layered ceramics. This model has recently provided the only known strong least upper bounds on T_c in all ceramic superconductors (6). Its physical motivation is described in detail in reference 6 (especially the role played by network self-organization). It provides detailed models for many other effects as well [isotope effect, precursive diamagnetic effects at high T , normal-state transport anomalies at even higher T 's, etc. (6)]. The EXAFS data will enable us to separate the pseudogap (or large Jahn–Teller lattice distortion) and superconductive effects, a separation that has proved difficult both in angle-resolved spectroscopy (ARPES) (7) and large scale scanning tunneling microscope (STM) experiments (8).

Experiments. The EXAFs experiments (3, 4) were done on optimally doped (highest T_c) $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x = 0.15$), where the Jahn–Teller pseudogap, metallic, and superconductive effects are closely balanced (6). The samples were single crystals, and the EXAFS analysis focused on fluctuations of the most accurately measurable length, the planar Cu–O bond length. Also studied were the effects of replacing the Cu with a small percentage of Ni, Co, or Mn. The width of the distribution of planar Cu–O bond lengths was measured by the mean-square relative displacement $\sigma^2(\text{Cu–O})$, which may reflect local orthorhombic (double-well) splittings. Importantly, because of the small spin-orbit Cu 3d and O2p splitting, magnetic nanodomains (if present) contribute only to the background $\sigma^2(\text{Cu–O})$ and have no effect on the sharp peaks and dips associated with structural phase transitions.

The most striking features of the experimental data (Fig. 1) were the breaks in slope of $\sigma^2(T)$ at two temperatures, corresponding to the opening of a pseudogap (at $T = T^*$) and the opening of the superconductive gap (at $T = T_c$). These features were common to all samples and varied only in magnitude. For T above T^* , σ^2 decreased with decreasing T , but between T^* and T_c , σ^2 increased with decreasing T . Below T_c , σ^2 at first decreased, but near $T_{OP} = 0.8T_c$, σ^2 unexpectedly reversed and

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Fig. 1. This is the inset of Fig. 3 of reference 4, annotated to emphasize the third phase transition at $T = T_{OP}$.

began to increase. The origin of this sharp reversal, which is not associated with a conventional transition temperature or an easily identified order parameter, is mysterious, especially as increasing lattice disorder with T decreasing toward zero seems to violate the third law of thermodynamics.

As is well-known, substitutions of Cu by Ni or Co decrease T_c , but surprisingly Mn substitution seems to have little effect on T_c . Substitution of Ni or Co at 3% reduces the amplitude of the oscillations above and below T_c , while 5% virtually erases them completely. The situation for Mn is quite different, as Mn gradually reduces the amplitude of the oscillations, which are still present at 5% concentrations. Qualitatively, Mn is expected to give rise to different behavior, as it is $\approx 10\%$ larger than Co, Ni, or Cu (from MnO and NiO lattice constants, for example). Some of these differences can also arise from crystal field splittings of the d electrons on Co and Ni, while Mn^{2+} is expected to have a half-filled magnetically polarized d shell with no associated Jahn–Teller distortions. A more detailed discussion of these chemical effects is given in references (3 and 4).

Theory. The most important features of Fig. 1 are the three abrupt changes in slope of σ^2 that occur around T^* , T_c , and $T_{OP} < (0.6-0.8)T_c$. The increase of σ^2 as T decreases below T^* is easily understood, as the area associated with the formation of pseudogapped nanodomains with local orthorhombic symmetry will grow with decreasing T , as previously discussed (3, 4). These nanodomains are apparent at low temperatures in STM studies (8), and the onset of their formation at T^* coincides with a sign reversal in $d^2\rho_{ab}/dT^2$, where ρ_{ab} is the planar resistivity (9). An alternative interpretation of the increase in σ^2 as T decreases below T^* is that it is caused by the decrease in LO (100) zone boundary phonon frequencies (the “half-breathing” mode shift), which correlates very well with T_c (Fig. 2B of reference 6). This decrease itself is associated either with the formation of pseudogapped nanodomains with local orthorhombic symmetry, or with the growth of conductive filaments. When the latter are large enough (compared to vortex dimensions), superconductivity sets in. The rapid increase of σ^2 (Cu–O) as T decreases below T^* is closer to what one would expect from $d = 1$ dimensional (filamentary) density of states threshold at T_c than from a $d = 2$ threshold.

Below T_c , as T decreases σ^2 drops sharply (see Fig. 2) to a level corresponding to the extrapolation of the data above T^* ; in other words, the superconductive filaments almost completely disrupt the pseudogapped nanodomains and erase the disorder induced by pseudogap lattice distortions. The filaments are still separated by pseudogap walls, but these walls are thin and in them σ^2 is small.

Fig. 2. The extrapolation of the high-temperature data [smooth curve, (4)] through the T_c peak shows that the superconductive ordering below T_c nearly completely erases the pseudogap disorder before the turbulent disorder associated with the third (glassy) phase transition sets in at $T = T_{OP}$.

One can suppose that the strain and σ^2 decrease in thin walls (misfit strain energies increase at least harmonically with length).

The 1989 zigzag interlayer percolation (ZZIP) model (10) enables us to understand the reversal of $d\sigma^2/dT$ below T_{OP} . As T decreases below T_c , the density of filaments increases until at $T = T_{OP}$ the filaments have filled the available volume and begin to overlap. Current flow in these filaments has many hydrodynamic properties, which are useful in explaining diamagnetic “precursive” effects that occur in underdoped samples between T_c and T^* (6). Flow is always turbulent at the junction or contact of two hydrodynamic channels, and current fluctuations associated with this turbulence can explain the increase in σ^2 below T_{OP} . Another way of saying this is that the energy gained from long-range electronic filamentary coherence can be large enough to increase short-range lattice disorder (incoherence). See Fig. 3 for examples and discussion.

Prediction. The explanation for the abrupt sign reversal of $d\sigma^2/dT$ at $T = T_{OP}$ given above describes a kind of non-Landau topological phase transition associated with filamentary space filling. Because filamentary junctions depend on pair spacing, one can expect that near the metal-insulator transition (which occurs near $x = x_0 = 0.06$ in $La_{2-x}Sr_xCuO_4$), one should find $T_c \approx x - x_0$ and $T_{OP} \approx (x - x_0)^2$, or $T_{OP}/T_c \approx x - x_0$. In $La_{2-x}Sr_xCuO_4$, this relation could hold between $x = 0.07$ and $x = 0.10$.

FeAs Ceramic Superconductors. There are many similarities between ceramic superconductors based on both CuO_2 planes and FeAs planes, and percolative theory is equally successful in predicting $T_c^{max}(<R>)$ as a function of the all-atom, equally weighted average number $<R>$ of Pauling resonating chemical bonds in cuprates (6) and pnictides (11). One would therefore

Fig. 3. Superconductive turbulence occurs at the contacts or junctions of superconductive filaments, whose density increases with increasing T . (A) This is Fig. 7D of reference 6, annotated to identify a region (circled) of possible turbulence. This figure was constructed for ref. 6 to show how two kinds of dopants could segregate to define metallic channels embedded in a pseudogapped matrix. (B) The simplest possible turbulent region (here a dark circle) arises at a junction where two metallic channels flow together.

expect to find many similarities in the disorder σ^2 in the two (chemically quite different) families. As shown in Fig. 1, all of the main features of σ^2 found in the cuprates (not only T^* and T_c , but also even T_{OP} !) are also found in FeAs disorder (4). According to the glassy network model ([12], the main difference between the two families is that the FeAs materials have $T_c^{\max}(\langle R \rangle)$ centered near the top of the covalent range, $\langle R \rangle = 2.5$, while the cuprate center is much lower, at $\langle R \rangle = 2.0$ (6, 11). This shift in $\langle R \rangle$ may be related to a shift in T_{OP}/T_c from 0.8 (cuprates) to 0.65 (FeAs), as shown in Fig. 1.

A Third Phase Transition? The lattice phase transitions discussed occur in the context of strong lattice disorder, which is pervasive in ceramic HTSC and strongly suggestive of dopant-centered bipolaronic interactions (12). There is little doubt that T^* and T_c mark lattice phase transitions, but does T_{OP} also mark a phase transition, and if so, what kind of lattice transition could occur in zero magnetic field below T_c ? According to the network model (6, 9, 11), T_{OP} is the temperature where filaments begin to intersect or cross-link, which will rigidify the filamentary array. Thus, we may think of this transition as a kind of topological glass transition and look to glass phenomenology for an estimate of T_{OP}/T_c at optimal doping. Indeed glass scientists do estimate that T_g/T_m is about 2/3 in many cases, where T_g is the glass transition temperature and T_m is the crystalline melting point (13, 14).

If one wants specific examples of such glasses, one could consider the system of chalcogenide alloys (As,Ge)Se, where Se chains can be cross-linked by As or Ge (15) or the metallic glasses formed by (Zr,Pt) alloys (16). Probably Urbach tails provide the best example of filamentary internal ordering of electronic states near a band gap (17). In all theoretical studies of glasses, the glass transition occurs with decreasing T as the result of increasing stiffness of a space-filling, deeply supercooled liquid. The role of network stiffening is particularly clear in the case of the network glasses, where an intermediate phase has been identified, which has many similarities to ceramic superconductive phases (15). Such comparisons might have seemed remote in 2005, except that now we have identified similar universal features of ceramic superconductors in terms of both a universal master curve for $T_c^{\max}$, and here three characteristic transitions, T^* , T_c , and T_{OP} , where only T_c has ever been seen in traditional metallic superconductors. Of course, the best example of such intrafilamentary contacts may be Cys-Cys disulfide protein bonds; the most studied X-rich proteins are indeed those with $X = \text{Cys}$.

Interesting Analogies. The formation of filaments even in the HTSC ceramic normal state occurs universally to gain dielectric energy through screening of fluctuating internal electric fields (6). Here we have proposed that such filaments also universally engender inhomogeneous lattice disorder for $T < T_{OP} < T_c$ because of turbulent filamentary contacts. (Of course, the appearance of such lattice disorder with decreasing T at low temperatures would appear to violate the third law of thermodynamics. It does not, because of the energy of the electrons near E_F , with specific heat proportional to T , whereas the lattice specific heat is proportional to T^3 .) It is interesting to note that there has been theoretical speculation concerning Cooper pair inhomogeneities (turbulence) in a uniform magnetic field quench of a superfluid atomic Fermi gas (18). Field-free inhomogeneities are well-known to exist in some molecular glasses

such as OrthoTerPhenyl [planar, quasi-orthorhombic symmetry], but not in others (19). Their identification in OTP (where T_g is close to room temperature) has taken decades, and similar identification in an atomic Fermi gas (not condensed on diatomic molecules) may not be easy. By contrast, the Boson peak and the First Sharp Diffraction Peak are nearly universal features of network glasses (19), which reinforces their similarities to the filamentary network model of ceramic HTSC.

Random Boolean constraints (the K-SAT problem, one of the prototypical computational complexity problems, with a complexity parameter α) provide a much more instructive analogy (20). There two transitions are found. The first transition, from linear to exponential solution times (analogous to the superconductive transition at $T = T_c$ from one-electron basis states to exponentially correlated Cooper pairs) occurs at $\alpha_1 = 2.7$, while the second transition, which involves solution clustering (analogous to the turbulent lattice disordering interactions at $T = T_{OP}$ here), occurs at $\alpha_2 = 3.86$. Such similarities are a striking feature of the phase transitions of many exponentially complex systems. Unlike polynomially complex systems, where exact solutions are sometimes possible (the BCS theory itself is exact in the weak-coupling limit), exponentially complex systems cannot be solved exactly, so this kind of commonality is doubly useful.

Conclusions

When it was first discovered (1), ceramic HTSC appeared to be almost a freak of nature, so different was it from conventional metallic superconductivity. The latter appeals to theorists in many ways: by taking full advantage of modern computational methods (such as pseudopotential theory), it is possible to exploit calculable complete sets of electronic and vibrational states, and predict T_c with only one slowly varying adjustable parameter. The most successful predated prediction of T_c for conventional superconductors was for the high-pressure metallic phase of Si (21), where the experimental maximum T_c is 8.2 K, and estimation of T_c using the most popular rules gave $T_c = 5$ K. However, crystalline periodicity has prevented the identification of chemical trends in the factors which determine T_c , and the discovery of conventional metallic superconductivity in MgB_2 with $T_c \approx 40$ K was completely unexpected by theory; although since its discovery, many successful post hoc calculations of its T_c have been reported (22).

With the modern database, embracing both layered cuprates and layered pnictides (all “bad” metals with low normal-state conductivities), ceramic HTSC has by contrast assumed universal characteristics, which apparently contradict the Bloch-Sommerfeld theory of metals (which goes back to the 1920s; 6), but allow the identification of chemical trends in the factors that have successfully predicted (11) the highest possible T_c . Quite early it was proposed that these peculiar materials merely exhibit self-organized filamentary characteristics (the ZZIP model; 10). The discovery of a third sub T_c lattice transition, which itself exhibits universal features, provides strong support for the self-organized ZZIP model and raises the interesting question of whether or not an alternative non-percolative, non-self-organized Bloch-Sommerfeld model can exist that would explain the data equally well.

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