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HTC oxides: a collusion of spin, charge and lattice

A R Bishop
Los Alamos National Laboratory, Los Alamos, NM 87545, USA
E-mail: arb@lanl.gov

Abstract. We briefly summarize a perspective on high-temperature oxide superconductors (HTC) as systems of intrinsic, functional, and connected spatial scales, with an associated set of temporal scales. We emphasize the importance of local bonding constraints, leading to a framework of coexisting short- and long-range fields, as the source of multiscale systems in HTC and many other strongly correlated materials.

1. Introduction
We propose that HTC materials should be viewed as particularly visible members of broad classes of intrinsically multiscale materials, where the multiscale complexity is both intrinsic and essential to key functionalities. This perspective now spans large classes of hard, soft, and biological matter. It is driven by remarkable advances in experimental and synthesis precision, as well as in simulation and modeling capacity, and requires substantially new conceptual frameworks that incorporate details of the origins, signatures, and consequences of the multiscale complexity. The transition metal oxides (TMOs), and many related “strongly correlated” electronic materials, inherit manifestations of this complexity through fascinating collusions of coupled spin, charge, and lattice degrees-of-freedom [1]. Here we emphasize [2] the importance of local bonding constraints and their long-range consequences of strongly anisotropic elasticity, leading to coexisting short- and long-range forces which result in specific systems (networks) of multiple, connected scales [3]. The bonding constraints are important in d- and f-shell materials because of the high bonding directionality and the localized orbitals, which allow secondary fields (lattice, impurity, etc.) to localize charge on a long timescale, limiting dynamic screening. The bonding constraints and their long-range elastic consequences then follow in a bootstrap fashion, and the material functions result from the lattice, spin, and charge consequences of the structural multiscales. In particular, in doped TMOs small polaron formation occurs below a characteristic temperature(s) T* and the multiscale system formation – a self-assembly of polaron patterns into filaments, checkerboards and clumps – then occurs. At lower temperatures, collective electronic or magnetic behaviors stabilize, built on the excitations supported by the multiscale structural templates. This scenario is captured schematically in Fig. 1.

2. Coexisting short-and-long-range forces
Multiscale complexity is inherent to systems with coexisting short- and long-range forces, including surfactants [4], filamentary flux flow in superconductors [5], polyelectrolytes [6], dislocation ordering and flow in metals, etc. As an example characteristic of the doped transition metal oxides, consider a 2D (analog of a layer in layered TMOs) antiferromagnet doped with a finite density of holes. In a semi-classical calculation [7], this results in a system of particles (“spin polarons”) coupled through a dipolar potential with additional Coulomb forces introduced phenomenologically. Solving this
problem with a highly efficient numerical algorithm [7] results in the rich phase diagram as a function of hole (polaron) density and temperature shown in Fig. 2. Note the polaron clustering below a “correlated percolation” density $n_l \approx 5$ percent (using parameters characteristic of cuprate TMOs) and the tendency toward Wigner crystal patterns above a second density $n_u \approx 15$ percent (quantum polaron melting is not included here). The intermediate phase between $n_l$ and $n_u$ is a self-adaptive phase which exhibits (geometric) percolation for a small fraction of the total polaron population. Strikingly, the polaron patterns are very robust for $n < n_l$ or $n > n_u$ – the melting temperature $T_m$ is very high (~$10^4$ K in the model calculation, i.e. $>> T^\ast$). However, in the soft intermediate percolative phase, $T_m$ is very low (~$10^2$ K), characterized by transverse fluctuations of the percolative filaments. In this intermediate density regime the dynamically averaged polaron patterns form a checkerboard for $T > T_m$, reminiscent of recent scanning tunneling spectroscopy data [8]. This intermediate regime is also characterized by distinct hysteresis and noise [9], again reminiscent of recent data in HTC [10] and CMR [11] TMOs. Finally, we note that physically relevant (attractive or repulsive) impurities tend to pin or orient the collective patterns [7] but not destroy them, since they are the result of global force balances.

3. Polarizability and elasticity in transition metal oxides

Although the doped antiferromagnet scenario considered in Section 2 captures many of the features relevant to the HTC phase diagram, it does not explicitly include the lattice degrees-of-freedom which are fundamental to TMO physics and to understanding many of the experimental data available in recent years. In fact, the research history over the last 60 years or so clearly demonstrates rich signatures of TMOs as both “polarizable” materials (emphasizing their metal-oxygen charge-transfer and covalency and magneto-elastic polaron formation), and as structurally soft materials (because of proximity to solid-solid/martensitic phase boundaries). These two characteristics of TMOs have frequently been pursued independently in solid state/chemistry and materials science research, and therefore probed on distinct scales, from Angstrom to micron to continuum. It is now clear [12] that these views of TMOs are intimately coupled and must be studied together if predictive understanding and control is to be achieved. Indeed, the sensitivity to strain and pressure of TMOs (including HTC,
CMR, Ferroelectrics) has long been evident [13], and striking examples of cross-coupling between structural and electronic/magnetic/ferroelectric properties are now apparent from recent experimental studies [14].

A mathematical and computational framework to describe the elasticity in TMOs has been initiated in refs [2,3]. While this work is too extensive to reproduce here, we note that it is characterized by systematic multiscale complexity resulting from (a) local bonding constraints, and (b) proximity to a first order (solid-solid) phase transition. If spin and charge degrees-of-freedom are then coupled to the lattice in symmetry-allowed ways, the consequences are rich and diverse, including: entropy-driven transitions; extended precursor regimes (in temperature, pressure, doping, magnetization) and “giant” precursor effects; coexistence “landscapes” with distinctive filamentary, percolative, and “glassy” properties; strong global pattern sensitivity to local perturbations and, reciprocally, strong local sensitivity to global perturbations (e.g. pressure). These are all manifestations of the coexisting short- and long-range forces arising from local constraints and their long-range elastic consequences. Of course, elastic forces originate in Coulomb fields but, crucially, include symmetry-allowed self-consistent lattice deformations.

In particular, with small polarons producing strong local lattice distortions, the elasticity self-consistently orders the polarons into patterns of filaments and clumps. The strength of the local distortion (“micro-strain”) [15] versus the bulk modulus elasticity (from the bonding directionality strength) determines the scales of structural patterns from nano to micron [3], and naturally explains much data in HTC, CMR and FE materials – e.g., coexisting metallic and insulating or FE and paraelectric phases with sharp (atomic scale) interfaces; precursor short-range order and quasi-elastic scattering; hysteretic, glassy dynamics, and metastability; photo-, thermal-, magnetic-, electric-field induced metal-insulator transitions.

An example of this modeling framework is shown in Fig. 3 based on the minimal spin-charge-lattice coupling used in ref [3a]. Notice the distinctive long-range “butterfly” strain pattern produced by very local holes, consistent with diffuse x-ray scattering data in both HTC and CMR materials [16].

**Figure 2.** Fibrillar templates and soft intermediate phases in systems with short-range dipolar and long-range interactions [7]
At sufficient doping levels, polaron percolation patterns are predicted, much as in the simplified model of coexisting short- and long-range forces in Fig.1.

4. Electronic consequences of intrinsic heterogeneity

While much research remains to fully characterize, understand, and exploit the intrinsic systems of multiscale complexity outlined above, some results are known. For instance, coupling generic Bogliubov-de Gennes pairing for superconductivity on the elastic templates leads [17] to (a) superconductivity (and transport) “propagated” anisotropically over long distances, and (b) texture-induces pairing symmetry. The former result is interesting in view of “giant proximity” effects reported in HTC multilayers and SNS junctions [18]. The latter result should be included in the continuing debate [19] on experimental signatures of the superconducting pairing symmetry in HTC materials.

We emphasize that doping into broken-symmetry ground states, such as those in TMOs (antiferromagnet, charge-density-wave, etc.), result in sharp (atomic scale) interfaces between structurally/charge-density/spin-density distinct domains. These sharply defined patterns then directly produce local modes at the interfaces in lattice, charge (dielectric), and spin degrees-of-freedom. These local modes have been calculated at the level of Hartree-Fock and real-space RPA in ref. [20]. For single polarons/bipolarons these modes are the “shape modes” found in many small polaron situations, e.g., doped charge-transfer salts and conjugated polymers [21]. For the filamentary/cluster patterns of multi-polaron situations, the local modes are very distinct signatures of those patterns. For instance, the local (edge) modes around stripes or checkerboards are predicted [20] to be in the 30-50 meV range for longitudinal oxygen vibrations along stripes, but ~ 70 meV for oxygen vibrations transverse to charge rich-poor interfaces. Phonon frequencies in undoped TMOs are higher (e.g., ~ 85 meV for the cuprates) and magnetic energy scales for the undoped AF are in the ~eV range. The longitudinal edge modes are only present for vertical stripe segments and thus distinguish vertical from diagonal filaments [20]. The correlations among the meV-scale local spin, charge and lattice modes are specific, as is the correlation to eV scale electronic transitions (e.g., optical absorption) associated with polarons or polaron filaments [20]. Measuring these correlations should provide clear experimental signatures of the various magnet elastic patterns. Certainly the 30-70 meV range is where much new experimental data is finding signatures: $S(q,\omega)$ [22], XAFS [23], EPR [24], NQR,
Figure 4. A scenario for filamentary superconductivity in cuprate oxides.

\[ \sigma(\omega), \rho(T) \] (25), ARPES (26), STS (27), ultrafast pump-probe spectroscopy (28), etc. We also note that while impurities tend to pin or orient polarons and polaron patterns, they have only modest effects on the local mode frequencies.

Fully non-adiabatic quantum mechanical calculations are required to completely describe small polarons—the coupling of charge oscillations to (oxygen) lattice dynamics. Such calculations are computationally limited to small metal-oxygen clusters (29). However, given the expectation of filamentary patterns, these small cluster calculations are especially relevant and again show notably strong relationships to available data, as described here in the report of Mustre de Leon, et al. In particular, the internal small polaron shape oscillations are in the same ~ 50 meV range and yield distinct isotope effects and similarity with XAFS, \( S(\mathbf{q},\omega) \), STS, etc., data below \( T^* \) (the polaron formation temperature(s)); see Fig. 4.

The functional consequences of the heterogeneity we have described (1,3,30) for HTC and CMR and FE materials remains a subject of considerable debate. Regarding HTC materials, there is now compelling evidence for the break-down of purely electronic models, as reviewed in, e.g., the articles of Bussmann-Holder and Keller in this volume. It is possible that heterogeneity degrades HTC, interfering with pairing mechanisms based on a homogeneous material. However, we take the opposite view that strong-pairing may be a natural consequence of the confinement induced by the intrinsic heterogeneity scales. In this regard, several mechanisms have been proposed, all of which are enhanced by or explicitly dependent on the heterogeneity. These include: multi-band (orbital) coupling (31) via oxygen (e.g., buckling) distortions or spin-orbit coupling; Josephson coupling (32); percolation (33). As described in ref. (32), magnetic stripes which locally enhance \( t\)-\( J\) coupling result in strongly enhanced local pairing as compared with the same coupling homogeneously: such Ising-like local enhancement is natural from local oxygen distortions implied at stripes (23). The charge of stripes is an outstanding issue. An exotic speculation regarding percolative fully-charged filaments is that these provide the ideal environment for resonant, lattice-assisted charge-transfer, see
Fig. 4. This corresponds to a quantum Fröhlich sliding CDW, a situation usually not possible because quasi-1D materials are disordered or unstable at low T. However, here the self-assembled filament of polarons is – because of the strong elastic forces – highly coherent even at elevated T, and oxygens are shared by neighboring polarons, providing an ideal environment for a sliding CDW on the small fraction of polarons involved in percolation channels. This scenario is consistent with the same activation energy ( ~ 500 K) being evident in both local (EPR) [24] and global (resistivity) [25] measurements in HTC materials. In the spirit of Fig.1., transverse oxygen vibration on filaments will destroy the macroscopic percolation.

5. Discussion

The intrinsically multiscale scenario of doped TMOs which we have very briefly summarized here leads [1,34] to “phase diagrams” which are rather different from those constructed on the basis of regular period structures, the Bloch theorem, extended fluctuation modes, etc. Indeed if essential functions occur at specific scales, and networks of coupled scales are fundamental to supporting those scales, then conventional averaging or RG methodologies are of limited value. Rather, we must learn how to measure and formulate descriptive frameworks for networks of local and mesoscopic patterns and face crucial issues of non-averaging, non-thermal, non-linear, non-adiabatic, non-equilibrium, and even non-ergodic properties. A great deal of research remains to achieve predictive capabilities faced with these challenges, but that research is unavoidable if we are to understand the origins, measures, and consequences of the intrinsic complexity in TMOs.

The theme of bonding constraints and long-range consequences, including soft, self-adaptive intermediate phases [35], has fascinating interdisciplinary relations, as has been emphasized by, e.g., Phillips and co-workers [36]. The context for intermediate phases extends from biological matter to spin glasses to computability algorithms, and has a common characteristic. Namely, that depending on the bonding connectivity and strength, there are distinct phases – hard and stressed, soft and unstressed, and an intermediate phase which self-organizes to be unstressed but with local “hot spots” organizing into (typically filamentary) patterns. Remarkably, many organic, inorganic and biological materials seem to lie in the tunable intermediate phase regimes for their most interesting and technologically important functionalities. Certainly, the notion here that strong local, dynamic deviations from average structures are essential for some key functions is now a major topic of research. In a biological context, for example, adapting the same global structure of a protein for distinct functions through specific local distortions is appealingly efficient from an evolutionary perspective.

It is important to note that these hotspots and network and adaptive phase properties do not require different force fields for hot spots. They are the local and mesoscopic consequences of local constraints and their nonlinear and long-range consequences. In the context of materials science, this framework now appears directly relevant not only to the TMOs of these proceedings but to many other so-termed “strongly correlated” materials, including bismuthate oxide superconductors, Laves phase materials, VO₂, WOₓ, many multi-ferroics, CDW dicalcogenides, conjugated organics, charge-transfer salts, and many bio-macromolecules.

In all these materials, we suggest that there is a common system or network framework that provides the most appropriate conceptual approach for modeling and for choosing and interpreting experiments, namely in situations where potential energy > kinetic energy, structure drives function on multiple scales, and function reciprocally modifies structure; in these situations strong localization tendencies and weak dynamic screening result in locally strong effects of globally weak fields [20] – e.g., weak average electron-lattice coupling producing strong local electron-lattice coupling and the local shape modes at polarons discussed in Section 4. In these situations, strong directional bonding constraints lead to coexisting short- and long-range fields, resulting in self-assembled multiscale, glassy landscapes; these landscapes or networks are frequently filamentary in nature and provide templates for low-D lattice, electronic, magnetic, optical properties from which novel functionalities follow. An important issue here is that as “kinetic energy” increases, dynamical screening destroys the above scenario – screening away the long-range consequences of local constraints [38]. Understanding
this crossover from local to extended physics is a major challenge for the next phase of research in this field. From a pragmatic experimental perspective, it is clear that no single experiment is sufficient to understand networks and their coupled scales and functions. Measurements on multiple scales are needed and they need to be considered together in suites. The remarkable advances in measurement techniques using high intensity neutrons, light sources, high-resolution scanning tunneling and time-resolved spectroscopies, etc., give hope that we can begin to discriminate relevant spatial and temporal scales and probe the correlations between distinct scales.

Finally, returning to HTC oxides, we note that in the larger context discussed above they are one example among many materials to be studied. However, given their huge technological importance and the vast data accumulated for them over the last two decades, they are prototypes that must be understood. We suggest that their “phase diagram” be viewed along the lines of the schematic in Fig. 5. This view follows the logic discussed here – that the cuprate oxides are indeed a collusion of spin, charge, and lattice, leading intrinsically to a network of connected, functional scales. From this perspective, the actual superconductivity is very much the “flea on the hair of the dog”. It is therefore not surprising that it has taken many years and many experiments to begin to isolate this key functionality amongst the whole essential network which supports it.

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