Multicritical Phase Diagram and Random Field Effects in Superconducting Bismuthates

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The temperature-concentration phase diagram of doped bismuthate superconductors is described using a coarse grained anisotropic Heisenberg model. In contrast to previous treatments, we find a robust region of coexistence between the charge density wave (CDW) and the superconducting phases. Random fields break the CDW phase into metastable domains, which may explain various recent experiments. A partial Meissner effect without bulk superconductivity is predicted at low doping concentrations and at low temperatures.

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The observation of superconductivity [1] in the perovskite oxide $BaPb_xBi_{1-x}O_3$ may have been the precursor for the discovery of high temperature superconductivity in the copper oxides [2]. The latter are characterized by the existence of a semiconducting antiferromagnetic phase close to the superconductivity, and the full understanding of their temperature-concentration (T-x) phase diagrams remains one of the intriguing challenges of the field. Similarly, pure $BaBiO_3$ is a semiconductor, characterized by a commensurate charge density wave (CDW) associated with the disproportionation of Bi^{5+} and Bi^{3+} ions on two interpenetrating sublattices, combined with an oxygen breathing mode optical phonon [3, 4]. This charge density wave phase is depressed as the concentration of charge carriers is increased, either by replacing Bi by Pb, as in $BaPb_xBi_{1-x}O_3$, or by replacing Ba by K as in $Ba_{1-x}K_xBiO_3$ [5]. In both systems, the semiconducting phase turns into a superconductor (SC) as x increases. The present Letter addresses the theoretical understanding of the common features of their phase diagram.

Both the CDW and the SC are natural variational candidates for the ground state of the negative-U Hubbard model [6–9]. A microscopic derivation of an effective negative interaction has been given by Rice and Sneddon using a bipolaron (strong electron phonon) mechanism. The charge disproportionation observed in $BaBiO_3$ [4] can be viewed as a signature of the pairing attraction on the Bi sites, preferring Bi^{5+} and Bi^{3+} over Bi^{4+}. The same attraction can produce superconductivity when the conduction band is doped away from the half filled limit. A local attraction mechanism seems also to underly superconductivity in the newly discovered alkali-fullerenes [10, 11].

As we shall discuss later, the low energy excitations of bismuthates at different levels of doping can be described by an anisotropic Ising-Heisenberg model [8, 9]

$$\mathcal{H} = \frac{1}{2z}\sum_{ij}^{nn}\left[J_{ij}^z S_i^z S_j^z - J_{ij}^x\left(S_i^x S_j^x + S_i^y S_j^y\right)\right] + \mathcal{H}' - \sum_i h_i S_i^z , \quad (1)$$

$$\mathcal{H}' = \frac{1}{2z'}\sum_{ik}^{nnn}\left[K_{ik}^z S_i^z S_k^z - K_{ik}^x\left(S_i^x S_k^x + S_i^y S_k^y\right)\right] ,$$

where z and z' are the numbers of first (nn) and second (nnn) nearest neighbors, respectively. The pseudo spin-$\frac{1}{2}$ operators represent the carrier density $S_i^z = (n_i - 1)/2$, and the superconducting pairing operator $S_i^+ = S_i^x + iS_i^y = c_{i\uparrow}^\dagger c_{i\downarrow}^\dagger$.

Equation (1) should be regarded as an *effective* model for the low lying excitations. The pseudo spins are coarse grained over a microscopic correlation length which can be determined experimentally. The "exchange" coefficients $J_{ij}^\alpha, K_{ik}^\alpha, \alpha = x, z$, depend on the conduction bandwidth and the bipolaron interactions as shown below. The "fields" h_i are local chemical potentials due to the dopant ions. Experiments are consistent with $J^z > J^x > 0$, since for the half-filled $BaBiO_3$ system (no external fields) the pseudo spins order antiferromagnetically (AFM) in the z direction, implying a CDW.

For fixed nonrandom values $J_{ij}^\alpha = J^\alpha, K_{ik}^\alpha = K^\alpha$, and $h_i = h$, the Hamiltonian (1) has been studied extensively, both in the context of superfluid ^{4}He [12, 13], and in the context of spin-flop phase diagrams in antiferromagnets [14]. Except for a narrow range of parameters, one found a bicritical phase diagram, with a longitudinal AFM long-range order ($\langle S_i^z\rangle = m, -m$ on the two sublattices) for small h, and a first-order spin-flop transition into a phase with transverse ordering ($\langle S_i^x\rangle, \langle S_i^y\rangle \neq 0$) [14]. Here, the longitudinal and transverse ordering correspond to the CDW and SC phases, respectively.

For the bismuthates, the experiments are performed at constant "magnetization" (i.e., constant density x).

Imposing this additional constraint and assuming homogeneity, Robaszkiewitz, Micnas, and Chao [15] used mean field theory to determine the phase diagram. In addition to the CDW and SC phases, they found a homogeneous mixed (M) phase in which both order parameters are nonzero everywhere in the sample. This calculation seems to represent the current theoretical description of the bismuthates [8, 9].

The predictions of Ref. [15] encounter several problems: First, no bulk superconductivity has been detected at low temperatures in the low doping regime $0 < x < 0.35$, as would be expected if an M phase existed. Second, susceptibility measurements found precursor Meissner effects without zero resistance, and magnetoresistance data are suggestive of granular superconductivity even in samples with high chemical homogeneity [16]. Third, the experiments [5] have difficulties identifying the CDW ordering in most of that regime, except at very small x. Instead, there are some possible indications of an incommensurate modulation. The semiconducting behavior was thus attributed to either phase separation, or a "local" charge density wave [6].

In this Letter we overcome these difficulties. First, we note that the calculations of Ref. [15] have assumed only homogeneous phases. Once *phase separation* is allowed, the phase boundary of the SC phase plotted at constant "magnetization," is replaced by a *coexistence region* [14]. As one cools into the CDW phase, one reaches the coexistence curve, below which the system breaks into domains of pure CDW and SC phases. When the SC domains do not percolate, one should not observe zero resistance. However, there would be a finite Meissner effect. Without long-range Coulomb interactions, the true phases could separate completely, into low and high concentration macroscopic regimes. Long-range repulsion prevents this separation, and determines the sizes of the domains. For oxide perovskites, the large dielectric constant weakens this repulsion and allows relatively large domains [17].

Second, we emphasize that for the real system the coefficients in Eq. (1) are not uniform. The system has quenched randomness due to the positional disorder of the dopant ions, influencing both the "exchange" coefficients and the "fields" h_i. Thus, the phase diagram should resemble that of random AFMs in a field [18–20]. In three dimensions, true equilibrium should yield the same bicritical phase diagram as discussed above, although with largely modified critical exponents [19]. However, irreversibility and metastability effects [20] cause the breakup of the longitudinal AFM phase into domains, with no net long-range order. In analogy we predict that upon cooling, at concentrations below the bicritical concentration x_{bc}, the system should freeze into domains of CDW with random local ordering of the two sublattices. On further cooling, small SC domains should appear between the CDW domains even at small values of x, reflecting the coexistence. At low temperatures and doping concentrations, we expect the superconducting volume fraction to be proportional to x. Since the randomness is relatively strong, it is expected to determine the sizes of the domains, overcoming the long-range Coulomb interaction effects mentioned above.

To obtain more quantitative information, we start by following Rice and Sneddon in considering the strongly coupled electrons and breathing mode optical phonons [6]. The phonons can be eliminated to obtain an on-site attraction between the electrons in the form of a negative-U Hubbard model, which includes an on-site attractive interaction on the Bi sites $-\frac{U}{2}\sum_i (n_i - 1)^2$. It is also important to include nearest-neighbor and next-nearest-neighbor interactions *between bipolarons*, which we parametrize by V_{nn} and V_{nnn}, respectively. The negative-U model transforms to a positive-U model by the particle-hole transformation of the downspin electron [21]: $c_{i\downarrow} \rightarrow c^{\dagger}_{i\downarrow}$ and $c_{i\uparrow} \rightarrow c_{i\uparrow}$. An important simplifying feature is that on a bipartite (e.g., cubic) lattice, the positive-U model is at exactly half filling. This model simplifies further at large values of $U/t >> 1$, where it directly maps onto the Ising-Heisenberg model of Eq. (1).

$Ba_{1-x}K_xBiO_3$, however, appears to be in the weak coupling regime as deduced from the observed ratio between the highest superconducting transition temperature T_c and the gap 2Δ in the optical absorption $2\Delta/T_c \approx 3.5$ [22]. The relations between the microscopic interactions t, U, V_{nn}, V_{nnn}, and the parameters of Eq. (1) are hard to quantify in this regime [23], and therefore we determine them from experiments. By fitting the highest observed transition temperatures to the mean field theory of Eq. (1) we obtain $J^z = 4T_c^{cdw}$, $J^x = 4T_c^{sc}$.

The next-nearest-neighbor (nnn) parameters, K^α, are harder to relate directly to experiments. In the strong coupling limit K^x describes the coherent direct hopping of bipolarons between nnn sites, and is of the same order as J^x. Since bipolarons on nnn sites share the relatively large lattice energy associated with the breathing mode of the intermediary oxygens, we expect $K^z = 4V_{nnn} < 0$, and $|K^z| > K^x$. We also expect (without rigorous justification) that the inequality $K^z + K^x = K < 0$ holds under renormalization to the weak coupling regime. In reality, this expectation seems to be confirmed by the apparent absence of a mixed phase, as will be explained shortly.

The "spin size" m_0 is renormalized by coarse graining the spin operators over the correlation volume ξ^3, where $\xi = \hbar v_F/\Delta$ and v_F is the Fermi velocity. At low concentrations, we define the renormalized concentration (magnetization) of Eq. (1) as $x \rightarrow \bar{x} = x/2m_0$. By pushing the effective model to $\bar{x} \approx 1$, we obtain a crude estimate for the upper critical concentration $x_{\max} \approx 2m_0$. This estimate is crude since for $x \approx x_{\max}$ we expect the magnitude of the order parameter to diminish by pair-breaking effects, thus invalidating Eq. (1).

The renormalized parameters (m_0, J^α, K^α) depend on temperature and doping concentration. We can ig-

nore their variation in the vicinity of the phase transition which is driven by *orientations* of the order parameter. We can also appeal to the universality of critical properties near the phase transition lines. The effects of random fields on Heisenberg bicritical points are therefore relevant to the bismuthates. Furthermore, universality also allows us to ignore quantum fluctuations which modify the effective couplings and spin sizes at finite T transitions.

The *homogeneous* ground states of (1), without randomness and at fixed magnetization, can be determined variationally using two independent unit vectors to parametrize the magnetization on the two sublattices. By minimizing (1) with respect to these order parameters we obtain

$$\begin{aligned} E(\bar{x}) &= \min\left[E_M, E_{SC}\right] , \\ E_M &= \sqrt{\frac{(J^z-K)^2-J^x}{4}}\,\bar{x} + \frac{K}{4}\bar{x}^2 - \frac{J^z-K}{8} , \\ E_{SC} &= \frac{J^x+J^z+K}{8}\bar{x}^2 - \frac{J^x+K^x}{8} , \end{aligned} \tag{2}$$

where $K = K^x + K^z$. For $0 < \bar{x} < \bar{x}_{\tan}$ the spins have a finite component in the x-y plane, and a staggered component in the z direction. This is the mixed (M) phase. Above $\bar{x}_{\tan}$ the staggered magnetization in the z direction vanishes, and the negative-U system is a pure superconductor with no charge ordering. $\bar{x}_{\tan}$ is the point where $E_M = E_{SC}$. It is given by $\bar{x}_{\tan} = \sqrt{(J^z-K-J^x)/(J^z-K+J^x)}$. By (2), using a tangential Maxwell construction, it is clear that for $K \leq 0$ one has phase separation between the $\bar{x} = 0$ CDW state, and a pure SC state at some $\bar{x} > \bar{x}_{\tan}$. This implies the absence of the M phase at low temperatures. This condition was first derived by Matsuda and Tsuneto [24] in the context of ^{4}He. Our M phase is analogous to their supersolid phase. Experimentally, the absence of superconductivity at low temperatures and doping in $Ba_{1-x}K_xBiO_3$ and $BaPb_xBi_{1-x}O_3$ is indicative that $K < 0$. This in turn implies that the intersite parameters obey $V_{nnn} < 0$ and $|V_{nnn}| > K^x$. This could be understood as an attractive interaction between bipolarons on next-nearest-neighbor sites due to the shared oxygen breathing mode distortion. For large negative couplings $K \leq -J^x - K^x/2$, the phase separation will occur between $\bar{x} = 0$ and $\bar{x} = 1$, i.e., there will be no superconducting phase at $T = 0$.

At finite temperatures, the interactions can be decoupled by standard mean field theory. The mean field free energy (at fixed $\bar{x}$) is

$$\begin{aligned} F(\bar{x},T) = &-\frac{T}{2}\sum_{i=1}^{2} \ln\cosh\left(\frac{h_i}{2T}\right) \\ &+\frac{2h_1^x h_2^x - (K^x/J^x)[(h_1^x)^2+(h_2^x)^2]}{4J^z[1-(K^x/J^x)^2]} \\ &-\frac{2h_1^z h_2^z - (K^z/J^z)[(h_1^z)^2+(h_2^z)^2]}{4J^z[1-(K^z/J^z)^2]} - B\bar{x}, \end{aligned} \tag{3}$$

where $h_i = \sqrt{(h_i^x)^2 + (h_i^z + 2B)^2}$. (h_i^x, h_i^z) (i=1, 2 represents the two sublattices) and the magnetic field B are five independent variational parameters. By minimizing F, we obtain five mean field equations. Solving the mean field equations yields the explicit dependence of the order parameters on x, T, and the phase diagram.

The upper transition lines are obtained by expanding the mean field equations to lowest order in $h_1^z - h_2^z$, and in h^x, yielding

$$\begin{aligned} T_c^{CDW}(\bar{x}) &= \tfrac{1}{4}(J^z - K^z)\,(1-\bar{x}^2) , \\ T_c^{SC}(\bar{x}) &= \frac{J^x\,[1+(K^x/J^x)]\;\bar{x}}{4\,\mathrm{arctanh}(\bar{x})} . \end{aligned} \tag{4}$$

The bicritical point is given by $T_{bc} = T_c^{SC}(\bar{x}_{bc}) = T_c^{CDW}(\bar{x}_{bc})$. By expanding the free energy (as a function of magnetic field) at $\bar{x}_{bc}$, we found that there is a *first-order* transition between the SC and CDW phases, throughout the regime of physically sensible exchange parameters [25]. This includes the regime of $K > 0$ where an M phase (and a second-order transition) exists at low temperatures.

Figure 1 shows a mean field phase diagram where the parameters have been chosen to imitate the phase diagram of $Ba_{1-x}K_xBiO_3$. We use $J^z/J^x = 10$, and a small negative nnn interaction $K = -0.5J^x$. This yields a factor of ~ 25 between the CDW and the highest SC transition temperatures at the bicritical point T_{bc}, which agrees with the experimental values. The SC upper critical concentration for $Ba_{1-x}K_xBiO_3$ is $x_{\max} = 0.5$ [5], which yields an estimate of $m_0 \approx 0.25$.

The mean field phase diagram is modified by thermal and quantum fluctuations. The critical fluctuations reduce the upper transition temperatures and modify their shape near the bicritical point [see inset Fig. 1(b)]. Quantum fluctuations are expected to reduce slightly the size of m_0 [26].

The random fields h_i couple linearly only to S_i^z, and not to the SC order parameter. The latter suffers only from the weaker effects of random exchanges. Thus, for

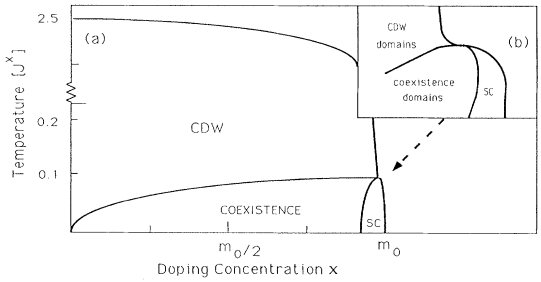

FIG. 1. (a) Mean field phase diagram of $Ba_{1-x}K_xBiO_3$. Solid lines are given by the mean field theory of Eq. (3). The parameters $J^z/J^x = 10$, $K/J^x = -0.5$, and $m_0 = 0.25$ are chosen to describe the experimental phase diagram of Ref. [5]. (b) Schematic effects of random fields and critical fluctuations near the bicritical point. The CDW and the coexistence regimes are replaced by metastable domains.

$x > x_{bc}$, we still expect SC long-range order, with zero resistance, as indeed observed experimentally. However, the random field will lower $T^{CDW}(x)$, and therefore also T_{bc}. The randomness in $BaPb_xBi_{1-x}O_3$ is stronger than in $Ba_{1-x}K_xBiO_3$ since the former involves substitution of Bi atoms which participate in the conduction band. This explains the lower value of T_{bc} in the Pb doped system.

Note the shape of the coexistance curve in the inset Fig. 1(b). Since it is tangential to the SC phase boundary, as predicted by the renormalization group [14], one may encounter some CDW domains upon cooling at $x \geq x_{bc}$. The random fields of the dopant ions turn the CDW phase (and thus also the coexistence region) into a metastable domains phase. They also lower the bicritical temperature, reduce the tendency for coexistence [27], and modify the critical properties [19].

Quantitative experimental studies of the Meissner effect as a function of T and x, a search for metastability and hysteresis effects near the boundary of the semiconducting phase and for local CDW ordering in domains, as well as detailed studies of the phase diagram near the bicritical point, would help to test our predictions and to confirm the description of these medium temperature superconductors by this simple pseudomagnetic theory.

In summary, we have shown that it is possible to understand the gross features of the bismuthates CDW-SC phases using a renormalized pseudospin Hamiltonian. We found a robust tendency of this system to produce coexisting domains of the two phases at low concentrations and temperatures. We also explained the failure of experiments to observe CDW order as a consequence of the random field effects. Finally, we draw attention to the effects of fluctuations on the shape of the phase diagram near the bicritical point.

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