Charging effects and the phase-ordering transition in granular superconductors

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We examine the influence of the charging energy on the phase-ordering transition in a lattice of superconducting grains connected by Josephson coupling. We use a finite-temperature self-consistent phonon procedure which is a generalization of the $T=0$ method of Simanek. The transition temperature $T_c$ is found to be monotonically reduced as the ratio of charging energy to Josephson coupling energy is increased. No evidence of reentrant normal behavior is seen. The specific heat for the phase degrees of freedom is seen to be phononlike ($\sim T^3$) at sufficiently low temperatures, diverging at $T_c$. The $T^3$ behavior persists to very small charging energies. Effects of site-dilution disorder are considered qualitatively using an estimate of "phase-phonon" softening derived from spin-wave-stiffness results of Harris and Kirkpatrick. For a given nonzero charging energy, the critical concentration for onset of phase coherence always exceeds the site-percolation threshold because of zero-point phase fluctuations. Criteria for possible experimental observation of "phase-phonon" effects are discussed, and a simple experiment is proposed.

I. INTRODUCTION

Three-dimensional granular superconductors differ considerably from corresponding bulk metal samples.\textsuperscript{1–3} In general, for systems whose constituent grains are not in direct electrical contact with one another, there are expected to be two ordering phenomena in, for example, the resistivity of the sample. The first (at the single-grain ordering temperature $T_c^0$) corresponds to the onset of a superconducting gap in the electronic states of an individual grain; because of the finite size of a grain, however, this feature is not a true phase transition with associated long-range order (but, instead, is broadened because of finite-size effects and enhanced fluctuations).\textsuperscript{4} At a lower temperature $T_c$, intergrain Josephson coupling causes a locking of the phases of the order parameters on different grains and hence a true phase transition with long-range phase coherence and the onset of zero resistivity. Such phenomena have apparently been observed in systems as diverse as granular Al films and HgXe and (Nb$_2$Sn)In composites.

Attention has recently focused on the possible importance of charging effects for the phase-ordering transition in such granular metal-insulator composites. Such Coulomb effects arise from Cooper-pair exchange between grains, which causes departure of a single metal grain from charge neutrality.\textsuperscript{5–10} The possibility of reentrance into the normal state at very low temperatures because of Coulomb-induced zero-point phase fluctuations has been raised within mean-field theory by Simanek,\textsuperscript{7,10} Efetov,\textsuperscript{3} and Mae-kawa et al.\textsuperscript{9} These workers have all used an effective Hamiltonian which is believed to embody the essential features of the phase-ordering transition, provided $T_c$ is well separated from $T_c^0$. It is

$$H = \frac{U}{2} \sum_i \hat{n}_i^2 + \sum_{\langle ij \rangle} E_{ij} [1 - \cos(\phi_i - \phi_j)],$$

(1)

where in the first term (the charging energy) $\hat{n}_i$ is the number operator for excess Cooper pairs on the $i$th grain and $U$ is, in general, related to the inverse of the capacitance of the assembly of grains. The second term is specified by the Josephson coupling energy $E_{ij}$, here assumed the same for all nearest-neighbor pairs of grains $\langle ij \rangle$. In the absence of a magnetic field it is of an explicitly "ferromagnetic" form favoring alignment of the phases of the order parameter on neighboring grains. The Hamiltonian (1) is thus, when $U = 0$, in the universality class of the $d=2$ XY ($n=2$) model,\textsuperscript{11} which has a second-order phase transition, at least for an ordered lattice of grains. The amplitude of the superconducting order parameter $|\phi_i|$ (i.e., the energy gap) on each grain is assumed constant in (1) (and identical for all grains assuming all are small on the scale of the bulk metal coherence length), and possible temperature dependence of the parameters $U$ and $E_{ij}$ has been neglected.\textsuperscript{12} Many possible objections might be raised to this particular choice of Hamiltonian, e.g., the restriction to a site-diagonal approximation for the charging energy\textsuperscript{13} and the neglect of possible temperature dependence of the parameters. But real granular metal-insulator composites are so complex that a simple parametrization of anticipated effects is
of considerable value. Moreover, the Hamiltonian (1) has been widely used in the literature, and a clear understanding of its predictions is therefore useful.

The purpose of this paper is to analyze the thermodynamics of (1) within a simple finite-temperature self-consistent phonon approximation. This procedure is a generalization of the zero temperature work of Simanek,\(^8\) and leads to qualitatively new predictions about the behavior of several properties. In particular we find that the reentrance phenomenon found by others is absent in our approximation.

The paper is organized in the following way. The mean-field approximation and its predictions are discussed qualitatively in Sec. II. The self-consistent phonon approximation is then introduced in Sec. III and the numerical predictions for the transition temperature and phase-order parameter are displayed. Section IV gives numerical results for one readily measurable quantity, the specific heat. In Sec. V, we present some rough estimates of the way in which the critical temperature is reduced by structural disorder within the framework of percolation theory. Possible experimental consequences and criteria for their observation follow in Sec. VI.

II. DISCUSSION OF THE MODEL

HAMILTONIAN: MEAN-FIELD THEORY

In the absence of the charging energy term, the usual Weiss molecular field arguments\(^7\) give the phase-ordering transition of (1) at a temperature \(k_B T_{c} = z E_J / 2\), where \(z\) is the number of nearest neighbors of a given grain. The charging term makes a mean-field argument more complex because the two terms of the Hamiltonian do not commute. This feature is made apparent by rewriting (1) as

\[
H = \frac{U}{2} \sum_{\langle i, j \rangle} \left( \frac{\mathbf{\hat{r}}_i \cdot \mathbf{\hat{r}}_j}{2 U} \right)^2 \phi_i^2 + E_J \sum_{\langle i \rangle} \left( 1 - \cos(\phi_i - \phi_j) \right),
\]

where we have used the conjugate relation between the number operator and the phase,\(^14\)

\(\mathbf{\hat{r}}_i = -2i(\partial / \partial \phi_i)\) and we have also used the equation of motion for \(\phi_i\), i.e., \(i \hbar \dot{\phi}_i = [H, \phi_i] = -2iU \mathbf{\hat{r}}_i\). The Hamiltonian (2) resembles that for an array of coupled anharmonic oscillators. In the limit of small amplitude, the long-wavelength, low-frequency modes of (2) have the dispersion relation \(\omega_k = 2 \sqrt{UE_J} k a\), where \(a\) is the lattice constant and \(k\) the wave number. The excitations corresponding to the modes \(\omega_k\) we shall term phase phonons; these may be regarded as Goldstone modes of the Hamiltonian (1), whose existence is guaranteed by the small-amplitude limit of (1).\(^15\)

The mean-field approximation as applied to the Hamiltonian (2) consists of replacing the Josephson coupling term in (2) according to the prescription

\[
E_J \sum_{\langle i, j \rangle} \left( 1 - \cos(\phi_i - \phi_j) \right) \rightarrow -2zE_J \langle \cos \phi \rangle \sum_i \cos \phi_i.
\]

(3)

This procedure destroys the symmetry of the Hamiltonian which gives rise to long-wavelength, low-energy excitations,\(^16\) replacing the true phase-phonon spectrum with a set of Einstein oscillators. The effective Hamiltonian corresponding to (3) becomes, on using \(\mathbf{\hat{r}}_i = -2i(\partial / \partial \phi_i)\), an effective Schrödinger equation of the form of Mathieu’s equation:

\[
\left[ 2U \frac{d^2}{d\phi^2} + 2zE_J \langle \cos \phi \rangle \dot{\phi} \right] \phi_n(\phi) = -E_n \phi_n(\phi).
\]

(4)

The mean-field theory is defined by the self-consistency requirement on \(\langle \cos \phi \rangle\):

\[
\mu = \langle \cos \phi \rangle
\]

\[-\sum_n \exp \left( -\frac{E_n}{k_B T} \right) \langle \psi_n | \cos \phi | \psi_n \rangle \sum_n \exp \left( -\frac{E_n}{k_B T} \right) \].

(5)

Equation (5) may be solved for \(\mu(T)\); \(T_c\) is the temperature where \(\mu(T) = 0\). Numerical solution of this equation gives rise to a phase diagram exhibiting reentrant superconductivity: For values of the parameter \(\alpha = zE_J / U\) between about 0.8 and 1.0, the superconducting state is bounded by lower and upper critical temperatures outside of which the system is normal.\(^7\)\(^10\) For \(\alpha \leq 0.8\) no superconducting order is possible because of the disruptive effects of particle charging. For \(\alpha > 1\), superconductivity persists from \(T_c\) down to zero temperature.

Because of the neglect of the Goldstone modes in this approximation, the reentrant feature of the predictions deserves closer examination. In Sec. III we study the Hamiltonian (1) via a finite-temperature generalization of a self-consistent phonon approximation, used by Simanek for \(T = 0\),\(^8\) which retains the Goldstone modes, and we find no reentrance.

III. FINITE-TEMPERATURE SELF-CONSISTENT PHONON APPROXIMATION

The Gibbs-Bogoliubov inequality\(^11\) states that for a system described by a Hamiltonian \(H\) the Helmholtz free-energy \(F\) satisfies the inequality

\[
F \leq F = F_{\text{ref}} + (U - U_{\text{ref}})_{\text{ref}}
\]

(6)
where $F_{\text{ref}}$ is the free energy of a system described by a reference Hamiltonian $H_{\text{ref}}$ selected for convenience and $(U - U_{\text{ref}})$ is the thermal average of the difference between the true potential energy $U$ and the corresponding quantity $U_{\text{ref}}$ for the reference system, evaluated in an ensemble defined by $H_{\text{ref}}$.

The self-consistent phonon approximation (henceforth denoted SCPF for phase phonons) takes the reference Hamiltonian to be strictly harmonic, but with effective spring constants selected so as to minimize $F_r$. Thus, using (1) for $F_r$,

$$F \leq E_h - TS_h + \left( \sum_{\langle ij \rangle} [E_{ij} \left[ 1 - \cos(\phi_i - \phi_j) \right] - \frac{1}{2} K (\phi_i - \phi_j)^2] \right) + \omega_q^2 \sum_q \sin^2(\frac{1}{2} \vec{q} \cdot \vec{R}_j),$$

(7)

where $E_h = \langle H_h \rangle$ and $H_h$ with

$$H_h = \frac{U}{2} \left[ \sum_{\langle ij \rangle} \frac{K}{U} \sum_i \phi_i^2 + \frac{1}{2} K \sum_{\langle ij \rangle} (\phi_i - \phi_j)^2 \right]$$

(8)

and $\langle \rangle$ denotes a thermodynamic average with respect to the harmonic reference system. Because of the Gaussian nature of the harmonic Hamiltonian we note that

$$\langle \cos(\phi_i - \phi_j) \rangle = \exp[-\frac{1}{2} (\langle (\phi_i - \phi_j)^2 \rangle)]$$

(9)

so that

$$F_r = E_h - \sum_{\langle ij \rangle} \left[ E_{ij} - \frac{K}{2} \sum_i \phi_i^2 \right] = 0$$

(10)

where $D_{ij} = \langle (\phi_i - \phi_j)^2 \rangle$.

The minimization condition on $F_r$ is now

$$\frac{\delta F_r}{\delta K} = \frac{\delta F_r}{\delta D_{ij}} + \frac{\delta F_r}{\delta D_{ij}} \frac{\delta D_{ij}}{\delta K} = 0.$$  

(11)

From the general relation $F_r = -k_B T \ln Z_h$ (where $Z_h$ is the partition function of the harmonic Hamiltonian), the first term on the right-hand side of (11) can be shown to vanish identically:

$$\frac{\delta F_r}{\delta K} = \frac{\delta F_r}{\delta K} - \frac{1}{2} K \sum_{ij} D_{ij} = 0.$$  

(12)

The condition on the trial-free energy is thus

$$K = E_h \exp(-D_{ij}/2),$$

(13)

since $F_r$ does not depend on $D_{ij}$. To evaluate $D_{ij}$ we Fourier transform in order to use the equipartition theorem. For $N$ grains in the lattice we write, in the notation of Choquetard,\textsuperscript{18}

$$\phi = \frac{1}{\sqrt{N}} \sum_i \exp(-i \vec{q} \cdot \vec{R}_i) \phi_i$$

(14)

from which

$$D_{ij} = \frac{4}{N} \sum \langle |\phi| \rangle \sin^2(\frac{1}{2} \vec{q} \cdot \vec{R}_j)$$

(15)

with $\vec{R}_j = \vec{R}_i - \vec{R}_j$. (Here $\vec{R}_i$ is a lattice vector and the sum runs over the first Brillouin zone.) We observe that the harmonic Hamiltonian may be written in the canonical form

$$H_h = \frac{1}{2} \sum_{\vec{q}} (P_{\vec{q}} P_{-\vec{q}} + \omega_q^2 Q_{\vec{q}} Q_{-\vec{q}})$$

(16)

with

$$P_{\vec{q}} = \frac{p_{\vec{q}}}{\sqrt{M}},$$

$$\omega_q^2 = \frac{4K}{MN} \sum_{\vec{q}} \sin^2(\frac{1}{2} \vec{q} \cdot \vec{R}_j),$$

$$Q_{\vec{q}} = \sqrt{M} \phi_{\vec{q}},$$

and the quantity playing the role of the mass $M$ in the Hamiltonian (1) is $M = \frac{\hbar^2}{4U}$. The equipartition theorem requires that for the harmonic Hamiltonian at a temperature $k_B T = 1/\beta$ (Ref. 18)

$$\omega_q^2 \langle Q_{\vec{q}} Q_{-\vec{q}} \rangle = \frac{k_B}{2} \coth \frac{\beta}{2} \omega_q.$$  

(17)

We then have immediately for this scalar problem that

$$\langle |\phi_q|^2 \rangle = \frac{\hbar^2}{2Mk_B} \coth \frac{\beta}{2} \omega_q.$$  

(18)

Equations (10), (13), (15), and (18) constitute a complete prescription for the thermodynamics of the Hamiltonian (2) within the SCPF approximation, given the dispersion relation $\omega_q$. In what follows we shall adopt the Debye approximation as a reasonable description of the low-energy excitations of the full anharmonic Hamiltonian (1). In this model

$$\hbar \omega_q = \hbar \omega_0 q a = \hbar \omega_0 \Theta \left( q / q_D \right),$$

(19)

where $\omega_0 = \sqrt{K/M}$ is the natural frequency of one harmonic oscillator, $\Theta$ is the Debye temperature, and the phase-phonon spectrum is cut off at the Debye wavevectors $q_D$, given by $q_D^2 = 6\pi^2 N/\Omega$, where $N$ is the number of grains in the sample volume $\Omega$. Henceforth we will assume there to be one grain per simple cubic cell of side $a$. We then find, substituting for $M$,

$$\langle |\phi_q|^2 \rangle = \frac{1}{qa} \left( \frac{U}{K} \right)^{1/2} \coth \beta \omega_q \sqrt{UK}$$

(20)

so that, with the substitution

$$\sum_{\vec{q}} = \frac{\Omega}{(2\pi)^3} \int d\vec{q}$$

in (15), we have

$$D_{ij} = D_{NN},$$

$$\frac{1}{\pi^2} \left( \frac{U}{K} \right)^{1/2} \int_0^{q_D} \frac{d\sigma}{x} x \left( \frac{1}{x} - \sin x \right) \coth \beta \sqrt{UK} x,$$

(21)
where we have used the fact that $D_0$ is evaluated for the nearest-neighbor distance $R_{NN}(=\alpha$ for the simple cubic lattice). In terms of the convenient dimensionless quantity $\alpha = z E_J/U$ (where $z = 6$ is, as above, the number of nearest neighbors in the lattice), the self-consistency condition becomes

\[
K/E_J = \exp \left[ -\frac{1}{2\pi^2} \left( \frac{z}{\alpha} \right)^{1/2} \int_0^\alpha \frac{d\theta}{\sqrt{T^*}} \int_0^{\pi} d\chi \left( \frac{1 - \sin \chi}{\chi} \right) \coth \frac{x}{T^*} \right]^{1/2},
\]

with $T^* = k_B T / (z E_J) = T / 2 T_c^{MF}$.

The solution of Eq. (22) for each value of $T^*$ and $\alpha$ yields the value of $K/E_J$ [or, alternatively, $\Theta_p(T)$] which minimizes the test free energy. Once this quantity is known, the expectation value of the phase order parameter takes the form

\[
\langle \cos \phi_i \rangle = \langle \exp (i \phi_i) \rangle = \exp \left( -\frac{1}{2} \langle |\phi_i|^2 \rangle \right),
\]

where

\[
\langle |\phi_i|^2 \rangle = \frac{1}{N} \sum_q \langle |\phi_q|^2 \rangle = \frac{1}{2\pi^2} \left( \frac{z}{\alpha} \right)^{1/2} \int_0^\alpha d\theta \int_{-\pi}^{\pi} d\chi \frac{1}{\sqrt{T^*}} \coth \frac{x}{T^*} \left( \frac{K}{E_J} \right)^{1/2},
\]

with $K/E_J$ determined from (22) above. The order parameter as calculated from Eqs. (22) and (23) is shown in Fig. 1 as a function of temperature for several values of $\alpha$. The phase-ordering temperature $T_c$ is clearly suppressed by increasing the charging energy. For $U = 0$ the integration in (24) may be done analytically and the value of $T_c^*$ is found to be

\[
\lim_{U \to 0} T_c^* = k_B T_c / (z E_J) = \frac{2\pi^2}{qe} \left[ q_d a - Si(q_d a) \right]
\]

($= 0.5706$ for $z = 6$, simple cubic),

with $e$ the base of natural logarithms and $Si$ the sine integral. The SCPP approximation gives a first-order phase transition (with infinite slope of the order parameter) at $T_c$. This feature is an artifact of the approximation, and hence it is of limited value in estimating critical properties. Nonetheless, the reasonable agreement for the $U = 0$ simple cubic phase-ordering temperature with the mean-field estimate suggests that the approximation is semiquantitatively reliable except insofar as the order of the transition is concerned (and away from the extreme anharmonic region, $\alpha \to -1$).

The remarkable inhibition of phase ordering by particle charging is demonstrated in Fig. 2, where the transition temperature is shown as a function of $\alpha$. For values of $\alpha$ less than

\[
\alpha_c = \frac{\sqrt{2e}}{4\pi^2} \left( \frac{q_d a}{q_d a} \right)^2 \left( -1 - \cos q_d a \right) \right)^{1/2}
\]

($= 0.9798$ for $z = 6$, simple cubic),

there is no phase ordering at finite temperatures, in this model. (Simanek's mean-field calculation for $T = 0$ gives $\alpha_c = 1.8$.) As $\alpha \to \alpha_c$, $T_c \propto (\alpha - \alpha_c)^{-1/4}$.

Note that no trace of reentrant superconductivity is exhibited in this approximation. For any given temperature the order parameter is monotonically reduced to zero as the charging energy is increased.
Apart from the vicinity of $\alpha_*$, where the SCPP approximation is probably inadequate, it is tempting to regard reentrance as an artifact of finite temperature mean-field theory, where the thermal fluctuations due to long-wavelength phonons are clearly neglected. The discrete eigenvalues of the Mathieu equation correspond to a set of distinct Einstein oscillator frequencies which in mean-field theory have replaced the arbitrarily low-energy phonons present for long wavelengths and low temperatures. Previous authors have found reentrance within mean-field theory in the region $0.5 < \alpha < 1$, where we find no phase transition at all. We will investigate this question further in Sec. VI.

IV. SPECIFIC HEAT

The heat capacity is given by

$$C_v = -T \frac{\partial}{\partial T} \left[ \frac{\partial F_i}{\partial T} + \frac{\partial K}{\partial T} \right]_v = T \left( \frac{\partial S_h}{\partial T} \right)_v,$$

(27)

where we have identified $S_h = -\theta F_h/\theta T$ and noted that the minimization of the test free energy $F_i$ with respect to $K$ requires the second term in square brackets to vanish for any temperature. Now for a collection of oscillators

$$S_h = -k_B \sum_q \left[ \ln(1 - \exp(-x)) - x/\exp(x) + 1 \right],$$

(28)

where $x = \beta \theta \omega_q$. Thus in the Debye model

$$\frac{dx}{dt} = -\frac{\theta D}{\theta_D} \frac{d\theta D}{dt} + \frac{q}{q_D T^2} \frac{d\theta D}{dt},$$

(29)

so that

$$C_v = k_B \left[ 1 - \frac{T}{\theta_D} \frac{d\theta D}{dt} \right] \sum_q \frac{x^2 e^x}{(e^x - 1)^2},$$

(30)

or, replacing the sum with the corresponding Debye model integral,

$$C_v(T) = 3Nk_B \left( \frac{T}{\theta_D} \right)^{1/2} \left[ 1 - \frac{T}{\theta_D} \frac{d\theta D}{dt} \right] \int_0^{\theta_D/(T/2)} \frac{x^2 e^x}{(e^x - 1)^2},$$

(31)

with $\theta_D(T)$ deduced from Eq. (22).

Equation (31) leads to characteristic behavior in two limiting regimes. First, as $T \to 0$, $\theta_D(T)$ approaches a constant, the integral assumes the value $4\pi^2/15$, and we find a characteristic $T^2$ specific heat of electronic origin. $\theta_D(T=0)$ may be extracted from numerical solution of (22). In this limit

$$\Theta^2_D = \frac{2q_D a}{\sqrt{2\pi}} \exp \left[ -\frac{1}{2} \frac{q_D a}{\Theta^2_D} \frac{1}{\alpha} \left( \frac{q_D a}{\Theta^2_D} \right)^2 \right],$$

(32)

where $\Theta^2_D = k_B \Theta_D(T=0)/zE_f$; this is equivalent to Eq. (3.15) of Ref. 8 for $z = 6$. The quantity $C_v/(Nk_B T^2)$ for low temperatures is shown as a function of $\alpha$ in Fig. 3.

For high temperatures ($T \gg \Theta_D$), if there were no phase ordering $C_v$ would tend to the "classical"

Dulong-Petit value $Nk_B$, where $N$ is the number of grains in the lattice. As $U \to 0$, $\Theta_D$ is reduced and the "classical" high-temperature region is expected to expand; we find

$$\lim_{U \to 0} \frac{C_v(T)}{Nk_B} = \frac{1}{2} \left[ 1 + \frac{1}{\ln u} \right],$$

(33)

where $u$ is the solution to the self-consistent equation

$$u = \exp(1 - t/u),$$

(34)

with $t = T^*/T_c^*$, $u = eK/E_f$, and $T_c^*$ is given in (25). Within this approximation, as $T \to T_c$,

$$C_v \to \frac{1}{2} \left[ 1 + 1/[2(1 - t)^{1/2}] \right] Nk_B,$$

but the behavior near $T_c$ cannot be relied upon because of the spurious first-order transition predicted by the SCPP model. The character of the predicted divergence of $C_v$ near $T_c$ is presumably the same for all values of the charging energy, though $T_c$ itself depends weakly on $\alpha$ for large $\alpha$. In reality for the Hamiltonian (1) near $U = 0$, $C_v$ is expected to behave as $(T_c - T)^{-\alpha}$ with $\alpha = 0.02$, appropriate to the $d = 3$ $XY$ model, (23) (rather than with $\alpha = \frac{1}{2}$).

![Figure 3](image)

**FIG. 3.** Coefficient of $T^3$ low-temperature phase-ordering specific heat as a function of $\alpha$. 

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as predicted by self-consistent phonons).

The general behavior of the specific heat for several values of $\alpha$ is shown in Fig. 4. For small $\alpha (\leq 2)$ the $T^3$ behavior persists up to the singularity in $d\Theta_T/dT$; for intermediate values a linear $T$ dependence develops. The temperature range of this region and the slope of $C_p$ in the linear region both depend on $\alpha$. A remarkable feature of this figure is that even for $U/(kT_0) = 1/500$ a well-defined $T^3$ and linear region are discernible before the curve asymptotically approaches the $U = 0$ value. Thus the inclusion of even a tiny charging energy in the Hamiltonian (1) qualitatively changes the low-temperature behavior of the system. Since (1) obviously admits of phononlike excitations at low temperature, this is not unexpected. We will return to this matter later; in Sec. V we will examine the expected effects of a simple form of disorder on the picture implicit here.

V. EFFECTS OF DISORDER

The model investigated above is clearly a gross oversimplification of a genuine superconducting composite, in which the grains are randomly distributed. In particular, one expects a broad (and temperature-dependent) distribution of Josephson coupling energies as well as of charging energies (because of fluctuations in particle sizes and proximities). Moreover, we make the tacit assumption that there exist nearest-neighbor Josephson couplings, which in the aggregate span the entire sample, in order for there to be a true thermodynamic phase transition. In the language of percolation theory there is then an infinite cluster of Josephson-coupled superconducting grains. The simple lattice of grains we have described above clearly corresponds to a configuration with every grain present with probability $p = 1$.

In this section we consider, as a crude model for a nonideal granular superconductor, a simple cubic lattice for which the grain sites are randomly occupied with an average site occupation probability $p_c < p < 1$, where $p_c (= 0.316)$ is the percolation threshold probability for a simple cubic lattice in three dimensions. Below this value of $p$, by definition of $p_c$, the probability that an infinite connected path of Josephson couplings exists is zero. Clearly this approach remains a rather stylized description of a structurally disordered granular sample, but we expect this model to mimic qualitatively the physical effects of dilution of the grain-number density. (The corresponding bond percolation problem, which will not be considered here, seems more naturally related to a reduction in the average strength of the intergrain Josephson coupling, which will also, in general, be very important.) Qualitatively, we expect in this model that the phase-ordering temperature $T_c(p, U) < T_c(1, U)$ for $p < 1$, for any value of the charging energy $U$. Likewise, the critical value $\alpha_c(p) = (zE/JU)_c$ below which there is no finite-temperature phase transition will increase with decreasing $p$, corresponding to the usual inhibition of ordering by structural disorder.

To pursue the subject further, even qualitatively, we need (i) an estimate of how phonon frequencies (i.e., effective spring constants) scale with the site-occupation probability $p$, and (ii) a criterion for the occurrence of the phase-ordering transition. Because of the difficulty of treating both disorder and anharmonicity simultaneously, we will abandon the SCPP approximation for a diluted system and will adopt below a purely harmonic description of the site-diluted lattice of superconducting grains, i.e., we will make the small-angle approximation to (1). Since such a system is known not to "melt," i.e., the long-range phase order does not disappear for any finite temperature, we will supplement this harmonic description with a "Lindemann's Law": we estimate the transition to occur when $\langle |\phi|^2 \rangle$, the mean-square fluctuation in the phase, exceeds a specific value, determined below.

In the harmonic model [see Eq. (24) with $K/E_j = 1$]

$$\langle \cos \phi \rangle = \exp \left[ -\frac{1}{2} \langle |\phi|^2 \rangle \right] = \exp \left[ -\frac{1}{4\pi^2} \left( \frac{1}{\alpha} \right)^{1/2} \int_0^\alpha dx x \coth \frac{x}{\sqrt{x}} \frac{1}{T^2} \right].$$

(35)

In the mean-field theory discussed briefly in Sec. II, the phase-ordering transition in the absence of charging effects
(α → ∞) occurred at $T_c^{* \text{MF}} = k_B T_c^{\text{MF}}/z E_j = \frac{1}{T}$. In this limit (35) becomes

$$\lim_{\alpha \to \infty} \langle \cos \phi_n \rangle = \exp \left( -\frac{z}{4\pi^2} T^* q_0 a \right), \quad (36)$$

which provides a natural Lindemann criterion for the mean-square phase fluctuation,

$$\langle \phi^2 \rangle = \frac{z}{4\pi^2} (q_0 a)$$

$$= 0.5924 \quad \text{for} \quad z = 6, \quad \text{simple cubic}. \quad (37)$$

It should be noted that this is relatively small. [For $T = 0$, (35) reproduces Eq. (4.1) of Ref. 8.] In this Lindemann’s Law harmonic theory $\alpha_c = 2.532$, as compared to 0.98 for the self-consistent phonon theory above, so that we expect the harmonic theory to be less reliable for small $\alpha$ where the effects of phonon anharmonicity are more pronounced.

As a simple, nonrigorous estimate of the effects of site dilution on the elastic stiffness constant we will use the results of Harris and Kirkpatrick for the scaling of the spin-wave stiffness constant $D$ for a three-dimensional site-diluted simple cubic classical spin model. $D$ is defined by the long-wavelength isotropic ferromagnet spin-wave dispersion relation, $\omega_q = D q^2$. Since the equation of motion for spin waves is first order in time and that for phonons (elastic waves) is second order [giving rise to the relation $\omega^2 = c^2 q^2 = (\omega_0 q_0)^2 q^2$ in the Debye model] we will argue that the effects of site dilution on phonon frequencies are reasonably described by the substitution

$$\frac{\Theta_D(p)}{q_0(p)} = \frac{\Theta_D(p = 1)}{q_0(p = 1)} \left( \frac{D(p)}{D(1)} \right)^{1/2}, \quad (38)$$

where $q_0(p)$, the Debye wave vector, satisfies $q_0^2 = 6\pi^2 N p / \Omega$. [The quantity $D(p) / D(p = 1)$ is displayed in Fig. 8 of Ref. 25.] The harmonic Lindemann approximation above then leads to a simple result in the classical limit:

$$\lim_{U \to 0} \frac{T_c^*(p)}{T_c(p = 1)} = \frac{D(p)}{D(1)} \frac{1}{p^{4/3}} \quad (39)$$

and

$$\alpha_c(p) = \left[ \frac{q_0 a (p = 1)}{\sqrt{z}} \right]^{2/3} \frac{p^{4/3}}{D(p)/D(1)}. \quad (40)$$

For general $\alpha$, $T_c$ must be determined numerically.

The general behavior of $T_c^*(\alpha, p)$ is shown for this model in Fig. 5. For a fixed value of charging energy $\alpha$, $T_c$ is rapidly reduced upon diluting the lattice until no phase ordering is possible ($T_c = 0$). The critical value of $p$ below which $T_c = 0$ is shown as a function of $\alpha$ in Fig. 6.

Although the details of the simplified treatment of lattice site dilution given in this section are not likely to be quantitatively reliable, they do suggest how the phase-ordering transition and its critical temperature are modified by this rather restricted form of disorder. While fluctuations in the Josephson couplings $E_j$ and the charging energies $U$ are obviously beyond the scope of this treatment, we can conclude that the phase-ordering transition depends sensitively on the topological connectedness of the disordered granular metal, at least for dilute systems ($p \gtrsim p_c$).
VI. DISCUSSION

Perhaps the most intriguing feature of the treatment above is the prediction that for temperatures well below \( T_c \) there will be a phononlike \( T^0 \) specific heat which is electronic in origin. Moreover, this phenomenon may have measurable effects since we may estimate the ratio of "phase-phonon" to lattice-phonon heat capacities at sufficiently low temperatures to be of order (here we take \( k_B \Theta_D \equiv E_J \equiv k_B T_c \))

\[
\frac{C_p^{\text{phase}}}{C_p^{\text{ionic}}} \geq \frac{1}{3} \left( \frac{\Theta^0}{T_c} \right)^3 \frac{N_{\text{grain}}}{N_{\text{ion}}} .
\]

(41)

For 50-A radius Al grains (containing \( \sim 3 \times 10^4 \) ions/grain) with \( T_c \sim \frac{1}{2} \) K and \( \Theta^0 \sim 400 \) K, this ratio is of order 5000!

This prediction is founded on a number of assumptions:

(i) The physical system consists of a collection of superconducting particles electrically isolated from one another by, e.g., oxide coats of finite resistivity, or the host medium itself;

(ii) the phase-ordering temperature is well below the single-grain ordering temperature \( T^0 \) so that the Hamiltonian (1) with temperature-independent coefficients could be used;

(iii) the average site-occupation fraction \( p \) in this lattice model exceeds the percolation threshold appropriate to the charging energy of an average grain (for real samples this will imply a fairly substantial volume-filling fraction of superconductor in the composite sample); and

(iv) the "phase phonons" are well-defined excitations, i.e., are long lived on an appropriate time scale.

We consider these points in more detail below. We shall occasionally use the simple mean-field estimate \( k_B T_c^{\text{MF}} = \frac{\alpha}{2} E_J \) below, since away from the vicinity of \( \alpha_c \), the phase-ordering transition temperature depends only weakly on charging energy.

To make criterion (i) more precise we may use a simple mean-field argument following Patton et al.\(^{26}\) for the pure (\( p = 1 \)) periodic system in the limit \( \alpha \rightarrow \infty \). This leads to the implicit equation

\[
k_B T_c = \frac{zE_J(T_c)}{2} = \frac{z}{2} \frac{\Delta}{2e} J^{\text{max}} ,
\]

(42)

using \( E_J = (\hbar/2e)J^{\text{max}} \), with \( J^{\text{max}} \) the maximum Josephson current which can be carried by a nearest-neighbor junction. Ambegaokar and Baratoff\(^{27}\) have established that for a junction between two identical superconductors

\[
J^{\text{max}} = \frac{\pi \Delta}{2e} \frac{1}{R} \tanh \frac{\Delta}{2k_B T_c} ,
\]

(43)

where \( \Delta \) is the gap in the superconductor and \( R \) is the normal-state junction resistance. We will inter-

pret \( R \) here as the nearest-neighbor intergrain resistance in the nondiluted lattice. Hence the mean-field result may be written

\[
k_B T_c = \frac{\pi}{8} \left( \frac{R_{0}^{2}}{R} \right) \Delta(T_c) \tanh \frac{\Delta(T_c)}{2k_B T_c} ,
\]

(44)

where \( R_0 = \hbar/2e^2 = 4114 \) \( \Omega \). Within the weak-coupling BCS theory \( \Delta(T_c)/\Delta(0) \) is a universal function of \( T_c/T^0_c \); with \( \tilde{R} = R/zR_0 \) the expression

\[
\frac{T_c}{T^0_c} = a \tilde{R} + 1/(1 + b \tilde{R})
\]

(45)

gives an excellent fit to the full (mean-field) results of Patton et al. for \( T_c(R)/T^0_c \) and becomes exact in the limits \( R \rightarrow 0 \) and \( R \rightarrow \infty \). The coefficients are \( a = 8e^2/\pi^2 = 1.444 \) and \( b = a - 14\xi(3)/\pi^2 = 0.9099 \), with \( \xi = \text{Euler's constant and } \xi \text{ the Riemann zeta function. It is found that } T_c/T^0_c \text{ decreases monotonically as the normal-state intergrain resistance } R \text{ increases. The phase-ordering temperature has fallen to half the single-grain value for } \tilde{R} = 1.025, \text{ corresponding to an intergrain resistance (for our simple cubic lattice) of } \sim 25 \text{ k}\Omega. \text{ If one takes a typical intergrain junction resistance for a real composite to be } \sim 10 \text{ k}\Omega \text{ with } x_{\text{eff}} \sim 10, \text{ one finds } T_c/T^0_c \gg 0.9, \text{ so that the independent existence of a phase-ordering transition would, in principle, be difficult to ascertain. However, while } T^0_c \text{ is expected to be only weakly concentration dependent, the site-dilute percolation model predicts that } T_c \text{ will (as demonstrated in Sec. V) drop rapidly with decreasing } p. \text{ Hence, for a real sample } T_c \text{ and } T^0_c \text{ may be well separated because of percolation effects.}

Patton et al.\(^{26}\) go on to estimate the width of the critical region using a Ginzburg-Landau free-energy functional for the phase-ordering transition in conjunction with the Ginzburg criterion. They find

\[ |(T_c - T)|_{\text{crit}}/T_c \sim 1/2 .\]

For such a relatively broad transition one might expect precursor effects well above \( T_c \), in analogy with the fluctuation effects for a zero-dimensional superconductor above \( T^0_c \). Thus even a system for which \( T_c - T^0_c \) may exhibit some features arising from phase phonons.

We turn next to point (iv) above. A useful criterion for intergrain properties may be established as follows. The grain charging energy \( U \) is in general related to the intergrain capacitance \( C \) and \( E_J \) is related to the nearest-neighbor normal junction resistance. The phase phonons will be well-defined excitations if their characteristic frequency exceeds the \( RC \) damping rate associated with the leaking out of charge over the finite conductance of a nearest-neighbor junction, or,

\[
\omega_0 = \frac{2}{\hbar} \sqrt{UE_J} \gg \frac{1}{RC} .
\]

(46)

The energy required to transfer a Cooper pair from
one grain to a nearest neighbor [or \( U/2 \) in Eq. (1) above] is

\[ U \equiv (2e)^2/C. \quad (47) \]

Thus

\[ \omega_0 = \left( \frac{8eI_{\text{max}}}{\hbar C} \right)^{1/2}, \quad (48) \]

which may be recognized as the "Josephson plasma frequency" appropriate to the situation. Using (43), the criterion (46) becomes

\[ RC \gg \frac{\hbar}{4\pi \Delta}, \quad (49) \]

where we have assumed that for temperatures of interest \( \text{tanh}(\Delta/2k_BT) \sim 1 \). Taking (for low temperatures) the simple BCS result \( \Delta(0) \approx 2k_BT_c^0 \), we find a simple criterion for the intergrain \( RC \) time constant

\[ RC \gg \frac{1}{8\pi} \frac{k_BT_c^0}{k_BT_c^m}. \quad (50) \]

For \( T_c^0 \approx 1.2 \, \text{K} \) (appropriate to Al) this requires \( RC \gg 0.25 \, \text{ps} \) or, for a nominal intergrain normal resistance of 10 k\( \Omega \), \( C \gg 0.025 \, \text{fF} \). We may use the mean-field result \( k_BT_c^m = zE_J/2 \) to identify

\[ \omega_0 = \frac{4}{\hbar} \frac{k_BT_c^0}{k_BT_c^m}, \quad (51) \]

so that, equating (48) and (51) and using (50), the inequality (46) becomes an inequality for \( \alpha \):

\[ \alpha \gg \frac{1}{4\pi^2 z} \left( \frac{T_c^0}{T_c^m} \right)^2. \quad (52) \]

Since in general \( T_c \leq T_c^0 \), the entire regime \( \alpha \geq \alpha_c ( \approx 1) \) remains a region of well-defined phase phonons (which are very anharmonic near \( \alpha_c \)).

If assumptions (i)–(iv) above are not fully satisfied for real systems, e.g., due to distributions of the parameters of (1), the estimate (41) of the phase-phonon contribution to the \( T^3 \) specific heat will naturally be much too large. In any case, one expects on general grounds that the specific heat associated with phase ordering itself is small in comparison to the single-grain ordering. The corresponding phase-ordering entropy change through the transition is expected to be smaller by a factor of order 1/N than the figure for the single-grain transition since there are of order one phase and \( N \) electronic degrees of freedom per grain.

Coefficients of the \( T^3 \) term in the specific heat for \( T > T_c^0 \) have in fact been measured for granular superconductors in the form of thick films \( \text{28–30} \) and are observed to be considerably enhanced (approximately a factor of 3) relative to the bulk.\( \text{31} \) For \( T < T_c^0 \) the assumption has been that the \( T^3 \) contribution is unmodified by single-grain (and phase) ordering. That this is roughly true is indicated by the reasonable agreement between the superconducting electronic contributions to \( C_V \) (obtained by subtracting from \( C^\text{cal} \) an estimate of the phonon contribution, fit to the \( T^3 \) data above \( T_c^0 \)) and existing theoretical expressions which neglect charging effects.

Even though granular superconducting composites depart considerably from the extremely idealized picture discussed above, experimental detection of possible charging energy-induced "phase phonons" is, in principle, simple. The signature of the "phase phonon" specific heat would presumably be a fairly strong dependence of its \( T^3 \) specific-heat coefficient on applied magnetic field for \( T < T_c \), roughly given by the smeared-out envelope of the Josephson supercurrent–magnetic field diffraction pattern for one junction, \( \sin(aH)/(aH) \). (The current results of Rogovin and Nagel\( \text{12} \) regarding the field dependence of the critical current for ultrasmall Josephson junctions may be relevant for this problem.)

VII. SUMMARY AND CONCLUSIONS

We have presented above a simple finite-temperature self-consistent phonon (SCPP) calculation for the phase-ordering transition in a lattice model of a granular superconductor well below its single-grain ordering temperature. We have examined the temperature dependence of the order parameter (and find no reentrance within the range of validity of the SCPP procedure). We also find the expected suppression of the ordering temperature by particle charging. The phase-ordering specific heat is phononlike (\( \sim T^3 \)) at low temperatures, diverging at the phase-ordering transition. The qualitative modifications of the transition due to site dilution of the lattice are examined within a harmonic approximation, using an estimate of phonon softening obtained from spin-wave stiffness results of Harris and Kirkpatrick. The effects of this form of disorder on the transition temperature are determined, as is the critical charging energy below which phase ordering is impossible. Criteria for possible observation of phase-phonon effects are presented; a simple experiment is suggested.

It is clear that the phenomena associated with particle charging and the phase-ordering transition are sufficiently complex that more theoretical work is necessary to understand, for example, whether or not reentrant behavior is conceivable for large enough charging energies. Heat-capacity measurements for low temperatures in the presence of applied magnetic fields should also be of interest in determining whether a discernible electronic phase-phonon \( T^3 \) component is present.
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11See, for example, Refs. 1 and 2.

12If one allows for a rapid increase in the intergrain resistance as the temperature is reduced, it can be argued (B. Patton, private communication) that, in accordance with Eq. (45) below, $T_c$ is suppressed to zero, thus giving rise to a reentrant normal phase at very low temperatures. This possibility depends on the explicit temperature dependence of the parameter $E_\phi$, which we have neglected above.

13Efetov (Ref. 3) has argued that for reasonably close-packed granular systems the diagonal approximation (i.e., taking the charging energy to be of the form $(U/2) \sum_n n^2 \tilde{n}_n^2$ rather than $(U/2) \sum_n n \tilde{n}_n$) is likely to be valid. In Sec. V, it is argued that for a phase-ordering to occur, sites must be present with a probability $p > n_c \sim \frac{1}{3}$. This will require for a random composite, roughly speaking, a metal volume filling fraction $f > \frac{1}{3}$; since $f = R^3/r_\sigma^3$ (where $R$ is an average spherical grain radius and $r_\sigma$ is the mean intergrain spacing) the percolation condition is $r_\sigma/R < 1.9$. This is a relatively dense structure, suggesting the validity of a diagonal charging energy approximation. (On the simple cubic lattice the nearest-neighbor distance divided by the grain radius is constrained to be $> 2$.) Reference 10 also discusses this point.


15The usual Goldstone theorem applies only to short-range forces; the situation for long-range (e.g., Coulomb) forces is more subtle, but we expect, following Efetov's argument (Ref. 3) that $U$ in the Hamiltonian (1) plays the role of a Hubbard on-site occupation energy, and that the effective charging potential is of short range because of screening by quasiparticles at finite temperature. Alternatively, one may regard $U$ as the Coulomb self-energy of a charged metal grain. See also Refs. 10 and 11.

16The situation is similar to that for Weiss molecular-field theory, where low-temperature spin waves are omitted by the approximation.

17See, for example, R. P. Feynman, Statistical Mechanics (Benjamin, New York, 1972), p. 67.


21Lozovik and Akopov (J. Phys. C 14, L31 (1981)) have used a self-consistent procedure which omits (in our notation) the term $\tau_{SA}$ in Eq. (7); they nonetheless find a phase diagram in qualitative agreement with ours.

22Simanek (Ref. 10) has very recently examined the corrections to the usual mean-field picture due to the constraint $-\pi \leq \phi \leq \pi$ and finds no reentrance. Off-diagonal contributions to the charging energy term cause a weak reentrance for $0.99 < \alpha < 1$. Y. Imry and M. Strongin (unpublished) have also used only 2$\pi$-periodic wave functions in the mean-field equations and find a phase diagram similar to our Fig. 2.


31Interestingly enough, finite-size effects themselves will give rise to an enhanced $T_\delta^c$ specific heat at low temperatures simply because a larger fraction of the lattice in a small crystalline particle is near a (quasifree) surface, resulting in a general softening of phonon frequencies and hence a reduced effective grain Debye temperature. Enhanced phonon specific heats may also be due to the amorphous nature of the host medium in which the superconducting grains are embedded.