Equilibrium Phase with Broken Time-Reversal Symmetry in Ceramic High-T_c Superconductors

Hikaru Kawamura[1] and Mai Suan Li[1,2]
[1]*Faculty of Engineering and Design, Kyoto Institute of Technology, Sakyo-ku, Kyoto 606, Japan*
[2]*Institute of Physics, Polish Academy of Sciences, 02-668 Warsaw, Poland*
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Possible occurrence of an equilibrium thermodynamic phase with spontaneously broken time-reversal symmetry is studied in a model ceramic superconductor with anisotropic pairing symmetry. It is shown by Monte Carlo simulations that such a "chiral-glass" phase is stable even under the influence of screening. Critical exponents associated with the chiral-glass transition are close to those of the Ising spin glass. [S0031-9007(97)02438-1]

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Recent experiments have revealed that cuprate high-T_c superconductors have an anisotropic pairing symmetry, probably of the $d_{x^2-y^2}$-wave type [1]. Naturally, one may expect that such an anisotropic nature of the superconducting order parameter could give rise to novel thermodynamic properties not encountered in the conventional *s*-wave superconductors. In bulk single crystals, however, this appears not to be the case since the $d_{x^2-y^2}$-wave order parameter is characterized by a single phase variable of the condensate as in the conventional superconductors. By contrast, in ceramic or granular samples, the situation may well differ because ceramic samples can be regarded as a random Josephson network and the anisotropic superconducting order parameter largely modifies the properties of the Josephson junction. One remarkable effect is the appearance of the "π junction" characterized by the *negative* Josephson coupling across which the order parameter changes the phase by π. Indeed, such π junctions were invoked by Sigrist and Rice [2] to explain the paramagnetic Meissner effect observed experimentally in certain high-T_c ceramics [3,4].

Among a variety of macroscopic thermodynamic properties of superconductors, the type and the nature of possible thermodynamic phases is of central importance. For example, considerable attention has recently been paid to the possible phase of *random* high-T_c superconductors in applied magnetic fields. While the existence of a vortex-glass phase with zero linear resistance was predicted [5], recent simulations suggest that the screening effects eventually destabilize it [6].

Meanwhile, one of the present authors (H. K.) recently proposed that a novel thermodynamic phase might occur *in zero external field* in certain ceramic high-T_c superconductors [7]. This phase is characterized by a spontaneously broken time-reversal symmetry with keeping a U(1) gauge symmetry, and is called a "chiral-glass phase." The order parameter is then a "chirality," quenched-in half a vortex, which represents the direction of the local loop-supercurrent circulating over grains. The frustration effect, which arises due to the random distribution of π junctions, is essential to realize the chiral-glass phase. The existence of this phase has some experimental support from the recent ac susceptibility measurements [8].

However, the theoretical analysis of Ref. [7] was based on an analogy to the *XY* spin glass [9], and completely neglected the effects of screening (coupling of the condensate to fluctuating magnetic fields). Thus, the fate of the proposed chiral-glass phase in the presence of screening is not yet clear. It should be noted that the screening effect could be substantial in intergranular ordering of ceramic high-T_c materials, since the length unit to be compared with the penetration depth is the grain size ($\sim 1\ \mu$m) rather than the short coherence length of the Cooper pair. As the screening effect makes the otherwise long-ranged interaction between chiralities short ranged, one may wonder if it would eventually wash out a sharp phase transition and destabilize the chiral-glass phase, just as it destabilizes the vortex-glass phase of type-II superconductors in a field.

In the present Letter, we study by extensive Monte Carlo simulations the question whether the hypothetical chiral-glass phase is really stable in the presence of screening. Our calculation is based on a simple three-dimensional lattice model introduced by Domínguez *et al.* [10]. The linear [10] and nonlinear [11] susceptibilities of this model were studied, but neither of the previous simulations was fully equilibrated, and the question about the existence of a true equilibrium phase remains open. By performing an equilibrium simulation based on an extended ensemble method recently proposed by Hukushima and Nemoto [12], we have found that there indeed exists a stable chiral-glass phase with a spontaneously broken time-reversal symmetry even in the presence of screening. Critical exponents characterizing the chiral-glass transition are determined.

We consider the Hamiltonian given by [10,11]

$$\mathcal{H} = -\sum_{\langle ij\rangle} J_{ij}\cos(\theta_i - \theta_j - A_{ij}) + \frac{1}{2\mathcal{L}}\left(\frac{\phi_0}{2\pi}\right)^2 \sum_p (\vec{\nabla}\times\vec{A})^2, \tag{1}$$

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where θ_i is the phase of the condensate at a grain on the ith site of a simple cubic lattice, $\vec{A}$ the fluctuating gauge potential, ϕ_0 the flux quantum, $\mathcal{L}$ the self-inductance of a loop (an elementary plaquette), J_{ij} the Josephson coupling, and the lattice curl is the directed sum of A_{ij}'s round a plaquette. The first sum in Eq. (1) is taken over all nearest-neighbor bonds on the lattice, whereas the second sum is over all elementary plaquettes on the lattice. Quenched randomness occurs only in the distribution of J_{ij}, which is assumed to be an independent random variable taking the values J or $-J$ with equal probability ($\pm J$ distribution), each representing 0 and π junctions. While our simulation is performed for this particular distribution of J_{ij}, one could expect from experience in spin-glass studies that the results would be rather insensitive to the details of the distribution, e.g., a slight asymmetry between $\pm J$ or the detailed form of the distribution.

Note that, contrary to the well-studied vortex-glass (gauge-glass) models, the present Hamiltonian defined in zero field keeps the time-reversal symmetry, and the frustration arises from the random distribution of the negative coupling, *not* from external magnetic fields. The bare Josephson penetration depth in units of lattice spacing is given by $\lambda_0 = 1/\sqrt{\tilde{\mathcal{L}}}$, where $\tilde{\mathcal{L}}$ is the dimensionless inductance defined by

$$\tilde{\mathcal{L}} = (2\pi/\phi_0)^2 J \mathcal{L} \,. \tag{2}$$

Magnetization per plaquette is given by

$$m = (4\pi S N_p)^{-1} \sum_{p \in \langle xy \rangle} \vec{\nabla} \times \vec{A} \,, \tag{3}$$

where S is the area of a plaquette and the sum is taken over all N_p plaquettes on the $\langle xy \rangle$ plane. The local chirality may be defined at each plaquette by the gauge-invariant quantity [7,11],

$$\kappa_p = 2^{-3/2} \sum_{\langle ij \rangle}^{p} (J_{ij}/J) \sin(\theta_i - \theta_j - A_{ij}) \,, \tag{4}$$

where the sum runs over a directed contour along the sides of the plaquette p. Note that the chirality is a pseudoscalar in the sense that it is invariant under global U(1) gauge transformation, $\theta_i \to \theta_i + \Delta\theta$, $A_{ij} \to A_{ij}$, but changes its sign under global Z_2 time-reversal transformation, $\theta_i \to -\theta_i$, $A_{ij} \to -A_{ij}$.

We choose the gauge where the A_{ij}'s along the z direction are fixed to be zero, and impose free boundary conditions on all sides of the lattice [13]. Simulation is performed according to the version of an extended ensemble method of Ref. [12], where the whole configurations at two neighboring temperatures of the same sample are occasionally exchanged. Most extensive calculations are made for the inductance $\tilde{\mathcal{L}} = 1$, which corresponds to the bare penetration depth λ_0 equal to one lattice spacing. We expect that the effect of screening should manifest itself for this inductance even for rather small lattices studied here, which contain $L \times L \times L$ sites with $L = 4, 6, 8, 10$. The sample average is taken over 1540 ($L = 3$), 1000 ($L = 4$), 500 ($L = 6$), 300 ($L = 8$), and 100 ($L = 10$) independent bond realizations. We run in parallel two independent replicas with the same bond realization and computed the overlap between the chiral variables in the two independent replicas,

$$q = N_p^{-1} \sum_p \kappa_p^{(1)} \kappa_p^{(2)} . \tag{5}$$

In terms of q, the Binder ratio of the chirality is calculated by

$$g_{\mathrm{CG}} = (3 - [\langle q^4 \rangle]/[\langle q^2 \rangle]^2)/2 \,, \tag{6}$$

where $\langle \cdots \rangle$ represents the thermal average and $[\cdots]$ represents the average over bond disorder. Since the present spin-glass-like model possesses the link variables in addition to the site variables, an equilibrium simulation is rather hard even with the new efficient algorithm. Typically, for a given sample, we prepare 20 temperature points and perform 1.5×10^5 exchanges per temperature of the whole system, combined with the same number of standard "single-spin-flip" Metropolis sweeps [12]. Equalibration is checked by monitoring the stability of the results against at least three-times longer runs for a subset of samples.

Figure 1(a) displays the size and temperature dependence of g_{CG} for $\tilde{\mathcal{L}} = 1$. The data of g_{CG} for $L = 3, 4, 6, 8$ all cross at almost the same temperature $T \sim 0.28$–0.29, suggesting the occurrence of a finite-temperature chiral-glass transition at $T_c = 0.286 \pm 0.01$ (T is measured in units of J). Via a standard finite-size scaling, the chiral correlation-length exponent is estimated to be $\nu_{\mathrm{CG}} = 1.3 \pm 0.2$ [see Fig. 1(b)]. A similar finite-size scaling analysis has also been made for the chiral-glass susceptibility $\chi_{\mathrm{CG}} = N_p[\langle q^2 \rangle]$ (not shown here), yielding the chiral critical-point-decay exponent $\eta_{\mathrm{CG}} = -0.2 \pm 0.2$. The obtained chiral-glass exponents are reasonably close to the values determined previously for the model without screening, $\nu_{\mathrm{CG}} = 1.5 \pm 0.3$ and $\eta_{\mathrm{CG}} = -0.4 \pm 0.2$ [7,9], and are also close to the spin-glass exponents of the three-dimensional Ising spin glass [14]. Thus, our present result seems consistent with the view that the screening effect is irrelevant at the 3D chiral-glass transition and that it lies in the universality class of the Ising spin glass. Anyway, the occurrence of an equilibrium ordered phase appears to be clear, and is in sharp contrast to the vortex-glass problem where the screening is found to destabilize the equilibrium ordered phase [6]. Presumably, such a difference comes from the fact that the broken symmetry is a discrete Z_2 symmetry here while it is a continuous U(1) symmetry in [6].

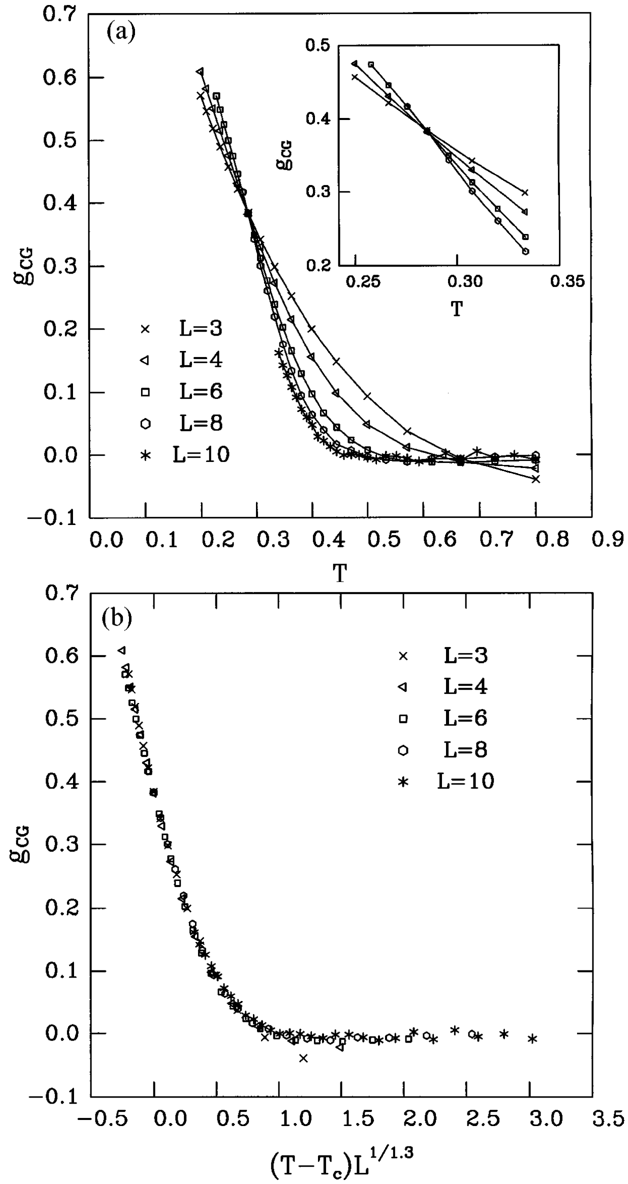

FIG. 1. (a) The temperature and size dependence of the Binder ratio of the chirality g_{CG} for $\tilde{\mathcal{L}} = 1$. Inset is a magnified view around the transition temperature $T_c \sim 0.286$. (b) Finite-size scaling plot of g_{CG} with $T_c = 0.286$ and $\nu_{CG} = 1.3$.

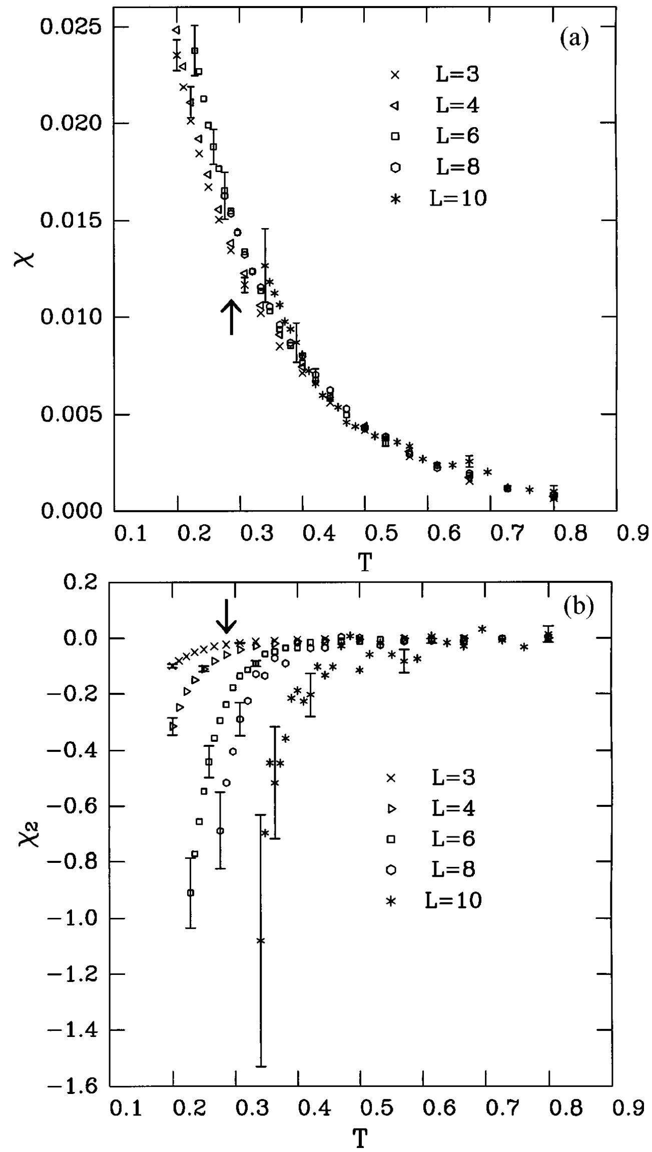

FIG. 2. The temperature and size dependence of the zero-field linear susceptibility χ (a), and of the zero-field nonlinear susceptibility χ_2 (b), for $\tilde{\mathcal{L}} = 1$. χ_2 is given in units of $(4\pi S/\phi_0)^2$. An arrow represents the location of the transition point.

We have also computed the zero-field linear and nonlinear susceptibilities, χ and χ_2 defined by $\chi \equiv dm/dH$ and $\chi_2 \equiv (1/6)d^3m/dH^3$ (H is the external field), via fluctuations of the magnetization (3). As can be seen from Fig. 2(a), the equilibrium χ is paramagnetic over an entire temperature range studied, including in the disordered phase $T > T_c$, without a clear anomaly at T_c. In shorter simulations on the same model where the full equilibration is not achieved, χ tends to get smaller and sometimes becomes negative [11]. It should be noted that the sign of χ is in fact a nonuniversal property: Effects not taken into the present model, such as intragranular supercurrents, could give additional diamagnetic contribution in real systems, and could easily change the sign of the observed χ. By contrast, on general theoretical grounds, the nonlinear susceptibility χ_2 is expected to show a negative divergence at the transition point where the time-reversal symmetry is spontaneously broken in a spatially random manner [7,11]. Indeed, as shown in Fig. 2(b), we have observed a behavior fully consistent with this expectation. The exponent associated with this negative divergence is estimated as $\gamma_2 \sim 4.4$.

We also made similar calculations for other inductances including $\tilde{\mathcal{L}} = 3, 4, 5$ in order to study the inductance dependence of the ordering. As expected, the chiral-glass transition temperature monotonically decreases as

$\tilde{\mathcal{L}}$ increases. The obtained phase diagram in the T-$\tilde{\mathcal{L}}$ plane is sketched in Fig. 3. There appears to be a finite critical value of the inductance, $5 \lesssim \tilde{\mathcal{L}}_c \lesssim 7$, above which there is no equilibrium chiral-glass transition.

The dimensionless inductance $\tilde{\mathcal{L}}$ given by Eq. (2) is a highly sample-dependent quantity. Our present result suggests that an equilibrium chiral-glass state could be realized in the type of samples with smaller $\tilde{\mathcal{L}}$, but largely suppressed for the samples with larger $\tilde{\mathcal{L}}$. One may roughly estimate the typical value of $\tilde{\mathcal{L}}$ in real granular samples: If one models a loop as a cylinder of radius r and height h, its inductance is given by $\mathcal{L} = 4\pi^2 r^2/h$. Putting $r \sim 1$ μm, $h/r \sim 0.01$, and $J \sim 20$ K (these values are chosen to mimic the sample used in Ref. [8]), one gets $\tilde{\mathcal{L}} \sim 10^{-2}$. Since this value is considerably smaller than the possible $\tilde{\mathcal{L}}_c$, an equilibrium chiral-glass phase may well occur in such samples. By contrast, if the sample has too large a grain size or too strong Josephson coupling, an equilibrium chiral-glass phase may not be realized. Another requirement is that the grains must be connected via weak links into an infinite cluster, not decomposed into finite clusters. Obviously, finite-cluster samples cannot exhibit a chiral-glass transition, although the paramagnetic Meissner effect is still possible [2]. The chiral-glass transition could be detected by standard magnetic measurements looking for a negative divergence of χ_2 or an aging phenomenon [15]. Recently, a sharp negatively divergent anomaly of χ_2 was reported in a $YB_2C_4O_8$ ceramic sample by the ac method [8], which might be a signal of the chiral-glass transition. It may also be possible to detect a spontaneously induced flux in the chiral-glass state by muon spin relaxation or by electron holography in zero external field.

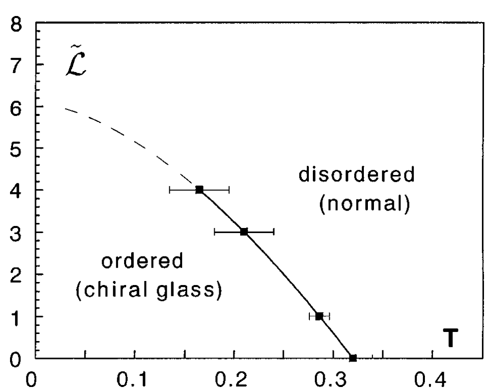

FIG. 3. A phase diagram in the T-$\tilde{\mathcal{L}}$ plane. Renormalized inductance $\tilde{\mathcal{L}}$ is defined by Eq. (2). The data point at $\tilde{\mathcal{L}} = 0$ is taken from Ref. [9].

In summary, we have shown by extensive Monte Carlo simulations that an equilibrium zero-field phase with spontaneous broken time-reversal symmetry, a chiral-glass phase, is possible in certain ceramic superconductors with anisotropic pairing symmetry. This phase is truly stable even in the presence of screening. It is interesting to experimentally search for this novel phase, since it could be realized only in anisotropic superconductors such as d-wave superconductors.

The numerical calculation has been performed on the FACOM VPP500 at the supercomputer center, Institute of Solid State Physics, University of Tokyo. One of the authors (M. S. L.) thanks the Japan Society for Promotion of Science for the award of a fellowship.

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