Flux Trapping and Superconductive Glass State in La_2CuO_{4-y}:Ba

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Susceptibility and magnetic-moment measurements from 1.9 to 35 K in magnetic fields up to 1.5 T in powder samples of La_2CuO_{4-y}:Ba are reported. The diamagnetism observed in the zero-field-cooled state is considerably larger than under field cooling. The former is *metastable* like the magnetic moment induced after switching the field off. These observations indicate the existence of a superconductive glass state.

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In recent theories of granular superconductors, the existence of frustration[1] was pointed out. A larger cluster can support many supercurrent-carrying states of nearly equal energy. "The presence of a hierarchy of loops is crucial in defining its behavior in high magnetic fields."[2] Recently, Ebner and Stroud[3] presented a theory of diamagnetic response of coupled superconducting clusters up to high magnetic fields. In their model, superconducting grains, each small compared to the London penetration depth, are weakly coupled into closed loops. The picture they arrive at, in agreement with earlier works by them and others,[3] corresponds to a spin-glass. Hereafter, we call this state a superconductive-glass state. Some essential features are the difference in field-cooled and zero-field-cooled responses, the existence of a de Almeida-Thouless line separating metastable from stable regions, and nonexponential time dependences.

In this paper, we present magnetic data on the BaLaCuO system which exhibits superconducting-glass behavior with the properties predicted theoretically.[3] In a recent search for high-T_c superconductivity, Bednorz and Müller[4] reported resistivity measurements in this system. Upon cooling of the BaLaCuO samples, first a linear metallike decrease in resistivity occurs, followed by an approximately logarithmic increase interpreted as the beginning of localization. On further cooling of samples of certain compositions and heat treatment, a clear resistivity decrease in the 30- to 35-K range then occurs. A further reduction by up to 3 orders of magnitude follows, reminiscent of the onset of superconductivity. dc magnetic-susceptibility measurements have since been carried out by Bednorz, Takashige, and Müller[5] in ceramic samples. In small magnetic fields, the samples became diamagnetic at a slightly lower temperature than that of the last resistivity decrease. This was ascribed to the onset of percolative superconductivity. The amount of diamagnetic susceptibility was of the order of a percent of the complete Meissner effect of $-1/4\pi$, and could be suppressed with external magnetic fields of 1 to 5 T. It was then recognized that the diamagnetism in BaLaCuO is qualitatively similar to that observed in the superconducting $TaSe_3$ and $NbSe_3$ layer compounds. In these materials, χ is also of the order of a percent of $-1/4\pi$,[6] but occurs at quite different temperatures and fields.[7] The structural aspect is also analogous to the Ta/$NbSe_3$ compounds. A detailed powder x-ray analysis shows that the phase which becomes superconducting in the BaLaCuO system is the layerlike La_2CuO_4 phase (K_2NiF_4 structure) containing a few percent Ba.[8]

With the superconductive phase known, it has been possible to prepare nearly pure ceramic samples of this material.[8] Consequently, the diamagnetism is enhanced. Figure 1 shows the suppression of diamagnetism as a

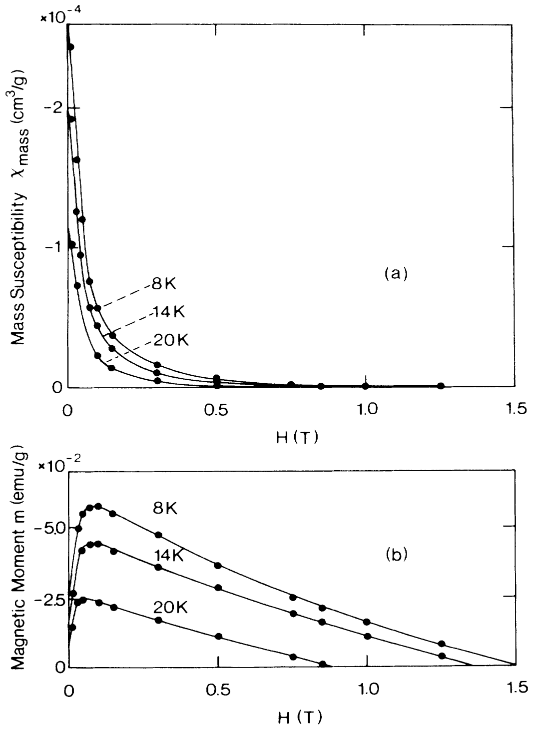

FIG. 1. Magnetic-field dependence (a) susceptibility and (b) magnetization of the Ba/La$\simeq$0.15/1.85 sample at three different temperatures after field cooling. Lines are guides to the eye.

function of external magnetic field at three different temperatures. The measurements were made with a BTI (Biomagnetic Technology, Inc.) variable-temperature susceptometer, model VTS 905. The sample consisted of 0.13 g of La_2CuO_{4-y} with about a ratio of Ba/La $\simeq 0.15/1.85$, and a total volume of 0.049 cm^3. Powder and ceramic samples gave the same results.[9] The susceptibility in Fig. 1(a) shows a nonsaturating increase for decreasing fields on the scale employed, as expected from simulations.[3] The magnetic moment m first rises, then goes through a maximum, and decreases almost linearly with increasing field. Both $\chi(H,T)$ and $m(H,T)$ are smaller for higher temperatures and almost scale with each other. It should be noted that these suppressing fields are not H_{c2} of the superconductor, but are related to phase slippings as discussed below.

From the above correspondence between theory and experiment, one is led to the expectation of a glass state. Figure 2 shows typical sequences supporting such an expectation. After zero-field cooling of the sample and then switching on of a 0.03-T field, χ is measured at point A. On then heating the sample, point B on curve 1 is reached. On cooling, a nearly temperature-independent susceptibility is measured. With further heating, point B is passed until point C is reached on curve 1. On cooling from C, a temperature-dependent slope smaller than that of curve 1 is followed. On further heating, curve 1 becomes reversible past point D. The same value D is reached by field cooling from 35 K. In field cooling past D, curve 2 is followed reversibly on a time scale of two hours.

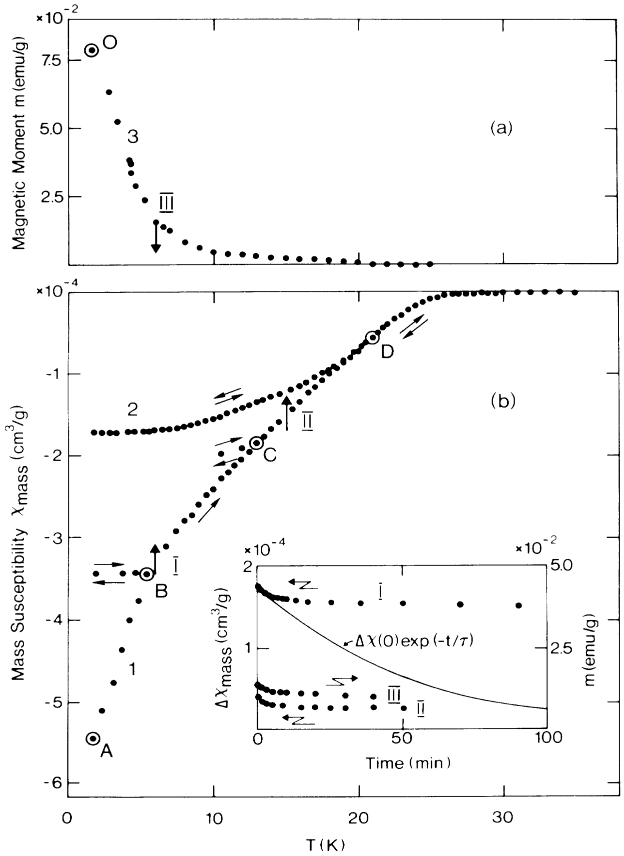

FIG. 2. Flux-trapping curve (3) and nonergodic values vs ergodic behavior of the susceptibility after zero-field and field cooling, respectively, as discussed in the text. Inset: Decay of metastable states, $\tau = 39$ min.

Figure 2(b) shows that on this time scale, a reversible and an irreversible trajectory of the system are present. Point D at $T^* = 21 \pm 1$ K and $H = 0.03$ T marks the ergodic limit. From measurement with different fields H, a quasi de Almeida-Thouless line $D(H,T^*)$ in the H-T plane is obtained.[10] Because of the tangential joining of the two trajectories 1 and 2, a sizable uncertainty in T^* is present. Nevertheless, the data points determined *first* were found *a posteriori* to fit a curve $H = 1.17 \times [1 - T^*(H)/\, T(0)]^{3/2}$, $T(0) = 23$ K, as shown. Theoretically, de Almeida and Thouless[10] derived the line separating ergodic and nonergodic regions, from the Sherrington-Kirkpatrick model with infinite-range spin interaction, to be $H = H_0[1 - T_g(H)/T_g(0)]^{\gamma}$, $\gamma = \frac{3}{2}$. T_g is defined for an infinitely slow sweep of T at fixed H, whereas T^* is obtained at finite sweep time. Therefore, necessarily, a difference between T^* and T_g exists. This and the exponent $\gamma \simeq 1.5$ were found in experiments on spin-glasses.[11,12] That $H(T^*)$ for the superconductive glass fits the exponent $\gamma = 1.5$ so well may be related to the longer range of forces present in a superconducting compound as compared to a magnetic system. Our fit is quite a bit better than that reported for the polar glass $KTaO_3$:Li system,[13] where possibly macroscopic inhomogeneities play a role.

When we field cool the sample and follow curve 2 to low temperature and then switch off the field, a positive remanent magnetization is observed, shown as point O in Fig. 2(a). This remanent magnetization results from flux trapping, and it is a proof of superconductivity in its own right. On heating of the sample at a rate of 0.3 K/min, curve 3 is followed. After a nearly linear decrease, $m(t)$ disappears around T^*, i.e., where the irreversibility of the susceptibility also disappears and curves 1 and 2 merge. This shows the consistency of all the data of Fig. 2, since above T^* reversibility exists, and no flux trapping can occur.

When the superconductor is in a nonequilibrium state, as for χ on curve 1 below T^* or for m on curve 3 (Fig. 2), it is metastable. Therefore, it tends to relax towards the stable state. The system can do that through a hierarchy of relaxational paths via phase slips.[3] The time evolution observed in such an experiment is necessarily longer than the time employed to reach the metastable state, for example, to switch off H to reach point O on curve 3. We have measured the decay of χ at points I and II of curve 1, and III of curve 3. The accuracy of the decays measured allows the statement that for short times they are exponential and later considerably slower. Very accurate measurements of the thermal remanent magnetization $\delta_{\rm TRM}$ in spin-glasses by Chamberlin, Mozurkewich, and Orbach[14] could be characterized by a "stretched" exponential form,

$$\delta_{\rm TRM}=\delta_0\exp[-C(\omega t)^{1-n}(1-n)] \ .$$

Such a Kohlrausch relaxation can be derived from models of hierarchically constrained dynamics[15] and the cooperative relaxation of a primary system of dipoles to a continuum of low-energy excitations.[16] We are presently improving the accuracy of our data to compare $m(T)$ curves to such an analytic form. This has been done for the polar glass state where the accuracy was not sufficient to distinguish between Kohlrausch and algebraic decays[13] as predicted by a mean-field model.[17] The long tail in these magnetic or polarization-versus-time curves has to be attributed to the fact that some clusters must wait to relax until a number of neighboring clusters simultaneously happen to be in the same favorable position.[11-16] In a transposition of the above picture to the superconductive-glass state, the phase coherence for a certain cluster has to become close enough to neighboring ones that if can relax. This becomes less probable when the system has evolved in time, and large volumes with different phase coherences are present.

An important aspect is whether this phase coherence has to occur *between* the $\mathrm{La_2CuO_{4-\mathit{y}}}$:Ba grains or within them. In our experiment, grain sizes have reached a volume $V=50\ \mu\mathrm{m}^3$. Our experiments are compatible with a penetration depth λ larger than the coherent regions, and our system is at best a dirty superconductor. According to Ref. 3, the low-field limit to reach a complete Meissner effect is $H_{c1}=\phi_0/2S$, where ϕ_0 is the flux quantum and S the homogeneous superconducting area. With our probing field H, we have not reached H_{c1}, and thus $S>\phi_0/2H=0.03\ \mu\mathrm{m}^2$. This means the single-phase area is smaller than that of a single grain with $S=V^{2/3}=14\ \mu\mathrm{m}^2$. Therefore, the superconductive glass state is present *in* the $\mathrm{La_2CuO_{4-\mathit{y}}}$:Ba grains, like what one thinks also exists in $\mathrm{Ta/NbSe_3}$ superconductors.[6] Furthermore, it should be noted that samples we prepared differently show no tendency to localization on cooling; a sharp onset of superconductivity and a much higher diamagnetism below T_c are seen. Therefore, S is still larger and the superconductive-glass features are considerably reduced in these samples.

In conclusion, the magnetic data in the $\mathrm{La_2CuO_{4-\mathit{y}}}$:Ba ceramic presented show all the features expected for a superconductive glass. These are the reduction in $\chi_{\rm diam}$ as a function of sizable magnetic field [Fig. 1(a)], the magnetic-moment dependence [Fig. 1(b)] as predicted,[3] and nonergodicity with respect to field versus zero-field cooling of $\chi_{\rm dc}$ (curves 1 and 2 in Fig. 2) yielding a quasi de Almeida–Thouless line (Fig. 3), $H(T^*)$. Switching off the field after field cooling induces a magnetic-moment proof of flux trapping. This metastable state as well as the one created by zero-field cooling and switching on a field show nonexponential decays as expected for a glass state with a hierarchy of relaxational paths (inset in Fig. 2).

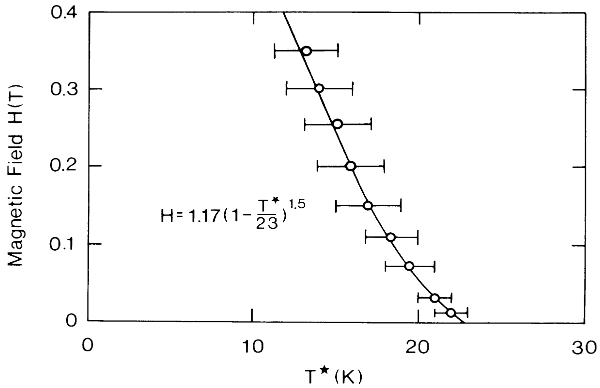

FIG. 3. Experimentally determined $H(T^*)$ line that separates ergodic from nonergodic areas together with an analytic expression for the quasi de Almeida–Thouless line.

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Note added.—Shih, Ebner, and Stroud[18] working with a model as in Ref. 7 also obtained a $T_g(H)$ line from Monte Carlo calculations.

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