TABLE I. Relative ion intensity as function of temperature (not corrected for fragmentation).

T (°C)	Al^+	Al_2^+	Al_3^+	Al_4^+	Al_5^+	Al_6^+
800	1	···	0.67	···	0.13	···
850	1	0.20	1.00	0.13	0.02	···
900	1	0.38	0.38	0.05	0.03	0.01
950	1	···	0.67	0.11	0.40	0.05
1000	1	0.10	0.14	0.10	0.02	0.008
1050	1	0.03	0.06	0.007	0.005	0.001
1100	1	0.02	0.03	0.002	0.005	0.003
1150	1	0.01	0.02	0.002	0.003	0.003
1200	1	0.005	0.01	0.002	0.002	0.0002

which then desorb. The surface lifetime of the adsorbed atom is an important variable in a heterogeneous process since surface diffusion and cluster formation occurs during that time. As the temperature is increased, the lifetime of the physisorbed atom decreases, even though the vapor density increases. These competing processes account for the results shown in Table I. Further, this mechanism is in agreement with W. Knauer's work.[4]

Increasing the surface area available for physisorption should enhance cluster growth. If, on the other hand, Al is strongly chemisorbed on a surface such as tungsten, it would not be able to migrate easily to form clusters. Hence, cluster size and distribution should be a strong function of surface migration rate, attachment rate, and desorption. Experiments to support our hypothesis are in progress.

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Magnetic susceptibility of sintered and powdered Y-Ba-Cu-O

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The real and imaginary parts of ac susceptibility of a sintered $Y_1Ba_2Cu_3O_{7-\delta}$ superconductor were measured before and after powdering. The temperature-dependent susceptibility may be separated into two contributions, one sensitive and the other relatively insensitive to the magnitude of the measuring field. The former is partially suppressed by coarsely crushing the sample. It is completely suppressed after finely powdering, whereupon the susceptibility curves become insensitive to the magnitude of the measuring field. Several models apparently consistent with the results are discussed.

The discovery of high-critical-temperature (high-T_c) superconductors has stimulated a remarkable range of scientific and technological research activity. These new copper-oxide-based ceramic materials, such as Y-Ba-Cu-O, have an orthorhombic, distorted perovskite structure, and exhibit superconductivity at temperatures above the boiling point of nitrogen. Substitution of rare-earth metals for yttrium does not appear to suppress the basic mechanism responsible for superconductivity. It is arguable whether these experimental facts are consistent with conventional theories for bulk, metallic superconductors.

Crucial to understanding the new materials is whether superconductivity is a bulk phenomenon and the role of dimensionality. From a materials perspective, the importance of particle size and sintering parameters must be determined. The influence of these parameters on the magnetic shielding and Meissner effects are thus of immediate interest. In this paper we study the decrease in diamagnetic susceptibility of sintered Y-Ba-Cu-O as it is crushed and finely powdered into presumably isolated grains.

There have been indications in high-T_c superconductors for the coexistence of two contributions to the magnetic susceptibility even in single-phase material.[1–6] Examination of the magnetic-field dependence of ac susceptibility is a particularly useful method for separating the two contributions.[3–6] It has been shown that moderate fields on the order of 80 A m^{-1} (1 Oe) are sufficient to suppress one of the contributions near T_c.[3,4] In fact, to achieve perfect diamagnetism just below T_c, fields on the order of 0.8 A m^{-1} (0.01 Oe) are required.[3] Some experiments, such as those presented here, involve comparing data for sintered and powdered samples.[6–9]

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We examined the real (χ') and imaginary (χ'') parts of ac susceptibility of a $Y_1Ba_2Cu_3O_{7-\delta}$ superconductor as functions of temperature both before and after grinding a sintered sample. As expected, there are two contributions to the total susceptibility.[3–6] Coarse grinding partially suppresses one of the contributions. Fine grinding totally suppresses it and also reduces the second contribution. Unlike the cases of the sintered and coarsely ground samples, the susceptibility curves for the finely ground sample are independent of the magnitude of the measuring field.[6]

To allow for an approximate comparison of sintered and powdered samples of different packing densities, mass susceptibility, rather than volume susceptibility, was calculated in all cases. The sintered sample was a prism, approximately $1.65 \times 2.45 \times 12.5$ mm^3, with the field applied along the long axis. No susceptibility corrections were made for the small demagnetization factor. The sample[10] was sintered at a pressure of 1.9 kPa and had a density of about 4.0 g cm^{-3}. It was annealed at about 950 °C in flowing oxygen for 6 h and slowly furnace-cooled to room temperature at a rate of 250 °C h^{-1}.

Susceptibility was measured upon warming after zero-field cooling. We used ac fields of 0.8 A m^{-1} (0.01 Oe) rms at 1 kHz, both with and without an 8 kA m^{-1} (100 Oe) dc bias field. Also used were ac fields of 800 A m^{-1} (10 Oe) rms at 1 kHz.

Figure 1 shows the susceptibility curves for the sintered sample. Measurements at 0.8 A m^{-1} (0.01 Oe) rms (curves *a*) show diamagnetic behavior below a critical temperature (T_c) of about 90 K. There is a sharp peak in χ'' at T_c. For such small measuring fields, the two contributions to the susceptibility are not separable.

With the addition of the dc bias field (curves *b*), a distinct bend appears in χ' at about 80 K with a corresponding peak in χ''. There is still a drop in χ' at T_c (which is slightly lower in temperature) but now only a plateau in χ'' at T_c. When the ac measuring field is increased to 800 A m^{-1} (10 Oe) rms (curves *c*), results show a slight peak in χ'' at T_c in addition to a major peak at about 75 K. These features indicate two contributions to the susceptibility of the material, one very sensitive to measuring field and the other relatively insensitive to field.[3,4] The field-dependent contribution does not appear above about 80 K, the temperature of the bend in χ'.

The sample was ground twice. It was first coarsely crushed with a hammer to particle sizes ranging from 10 to 900 μm. The powder was loosely packed into a cylindrical plastic holder of roughly the same dimensions as the original sintered sample. After susceptibility measurement, the coarse powder was finely powdered with a mortar and pestle to sizes ranging from 5 to 40 μm, with an average particle size of about 20 μm. The powder was again loosely packed into the holder and susceptibility was remeasured.

Susceptibility results after the first crushing are shown in Fig. 2. The magnitude of χ' at temperatures below the bend decreases and the lower-temperature peak in χ'' becomes smaller than in Fig. 1. Above the bend, however, χ' remains the same as before crushing. We hypothesize that the first crushing caused many of the grains to separate, but the grains themselves remained intact.

Measurements after the second grinding are plotted in Fig. 3. This time there is only one contribution to the susceptibility. There is no intermediate bend in χ' and the peaks in χ'' disappear. Curves for the three field conditions are almost identical. We hypothesize that the second grinding not only separated most of the grains but also reduced many in size.

To test the possibility of deoxygenation during the second grinding, the powder was annealed in flowing oxygen at 700 °C for 2 h, followed by a furnace cool to 200 °C at a rate of 100 °C h^{-1}. There was no significant change in the susceptibility curves. Finally, the powder was annealed above 750 °C in an argon atmosphere to remove oxygen. X-ray diffraction showed that the resulting particles were tetragonal. They were not superconducting.

Several models might explain the results. All are based on the existence of one intrinsic contribution to the suscepti-

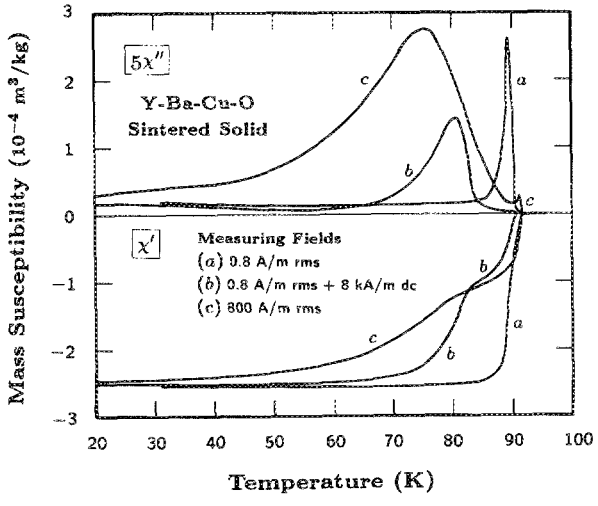

FIG. 1. ac susceptibility at 1 kHz for sintered solid Y-Ba-Cu-O for three different measuring fields. For clarity, χ'' is multiplied by 5. Except for the small-field data, there are two contributions to both χ' and χ''.

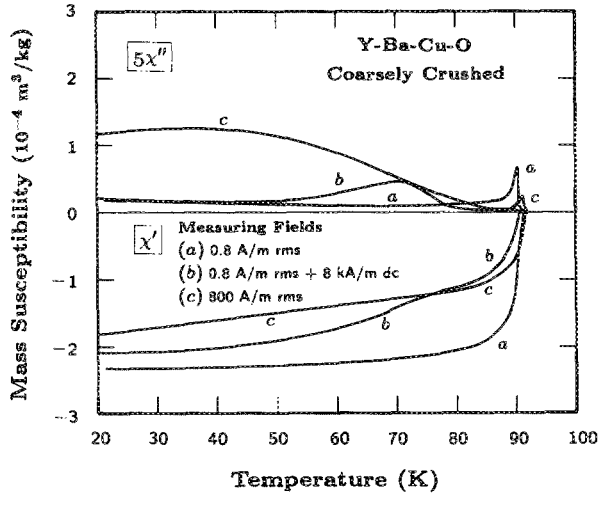

FIG. 2. ac susceptibility at 1 kHz for coarsely crushed Y-Ba-Cu-O for three different measuring fields. For clarity, χ'' is multiplied by 5. For all curves near T_c, χ' remains the same as before crushing.

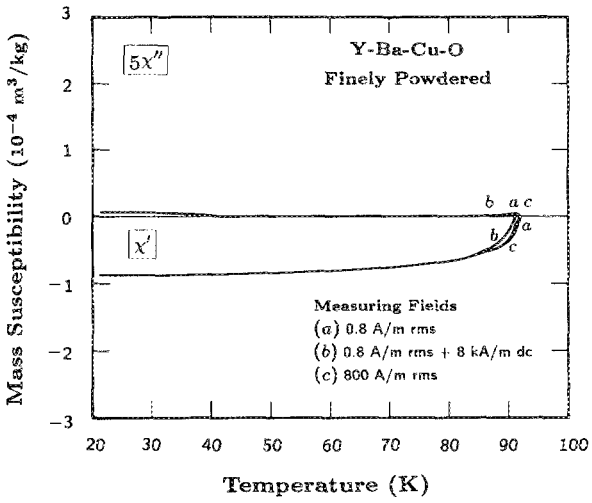

FIG. 3. ac susceptibility at 1 kHz for finely powdered Y-Ba-Cu-O for three different measuring fields. For all fields, χ'' is about zero. There is only one contribution to χ'.

bility that is relatively insensitive to field magnitudes and another contribution, arising from coupling, that is very sensitive.

The first model is that superconducting grains in the sintered sample are coupled by intergranular Josephson tunneling currents.[6–9,11–15] These currents are suppressed when fields are even moderately large or when the grains are well separated by grinding. In such states, the sample behaves as a collection of independent grains. Any grains of size less than one or even two orders of magnitude times the penetration depth would have their susceptibility measurably reduced.[11] The penetration depth has been estimated to be about 0.2 μm.[16]

A second model is that of percolation paths limited by anisotropy.[17] In moderate fields, conduction in the *a-b* crystallographic plane is much greater than along the *c* axis.[18–20] Owing to a distribution in grain orientations in the sintered sample, bulk shielding currents will include some *c*-axis conduction. In low fields, the shielding currents are not anisotropy limited, but in moderate fields, they are. In the latter case, however, the percolation path encloses a large area which gives rise to a significant susceptibility. When the sample is powdered, the percolation paths are destroyed. Only shielding currents within grains whose *a-b* planes are favorably aligned with the field (within a certain angle) contribute substantially to the susceptibility.

A third phenomenological model is that twinning planes[21,22] or antiphase boundaries,[23] seen by electron microscopy in orthorhombic Y-Ba-Cu-O, are a prerequisite for superconductivity in these materials. In the powdered state, residual diamagnetism, insensitive to field magnitude, is due to superconducting channels along the twinning planes in each particle.[22] When the particles are conglomerated into clusters of increasing size, the channels meet at grain boundaries and form a percolative network that constitutes superconducting paths for shielding currents.[21,22] The susceptibility is very sensitive to the applied field because of possible weak linking of the channels at the grain boundaries. Other theories also discuss superconducting grain boundaries[24–26] and twin-boundary effects.[27]

A resolution of the debate among researchers on the best model to describe these high-T_c materials awaits compelling experimental and theoretical results.

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Aging and field-effect studies of Cu island films at near liquid-nitrogen temperatures

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We report the results of the investigation carried out on the aging and field effect of discontinuous copper films deposited on glass substrates held at around 125 K. Using the scheme adopted in our earlier investigations, it was found that even at this temperature there is considerable increase in resistance. However, the agglomeration rate is much less than for films deposited at room temperature. The *I-V* characteristics of the films revealed an irreversible change in resistance following removal of the field. On stabilization, heating of the films revealed a decrease in resistance with temperature followed by an irreversible resistance increase beyond a transition temperature which was less than room temperature.

The instability in the physical properties of discontinuous films is a serious problem in exploiting the attractive properties of these films. This instability is seen as an increase in the post-deposition resistance with time. The resistance increase has been attributed to various causes.[1–6] Electron microscopy studies[5,6] indicated that mobility coalescence leading to an increase in the average interisland spacing was responsible for the post-deposition resistance increase. At high fields, the nonlinearity in *I-V* characteristics of island films has been reported by researchers and interpreted physically.[7–9] Earlier investigations have been carried out in our laboratory on the influence of different parameters on the aging behavior of copper and silver island films.[10,11] This study was carried out to test the validity of the thermally activated mobility coalescence model and its applicability to explain the aging behavior in island copper films.

Island films of copper (purity 99.999%) were deposited onto clean glass substrates at a pressure of 1×10^{-6} Torr. The purity of the copper was checked using x-ray photoemission spectroscopy (XPS). The substrates were maintained at a temperature of nearly 125 K by fixing them to a liquid-nitrogen-cooled cryostat. The film dimensions were 1×1 cm^2 with a substrate-to-source distance of 20 cm. The film resistance during and after growth was monitored using a Keithley electrometer. During deposition of the films, the rise in substrate temperature was not more than 5 K. Following stabilization of the film resistance with time, *I-V* characteristics were studied and the change in film resistance on application of a high field was noted. The temperature variation of resistance was studied from 125 K to room temperature by attaching a heater to the cryostat.

The films were studied under two different conditions:

(1) under ambient conditions with the application of glow discharge for 5–7 min, of initial resistance $R_0 = 0.18$, 1.3, 7.4, 14.5, 40, and 60 MΩ/□;

(2) dehydrated condition obtained using P_2O_5 and anhydrous $CaCO_3$ moisture traps inside the vacuum chamber for 48 h before depositing the film. During this period a

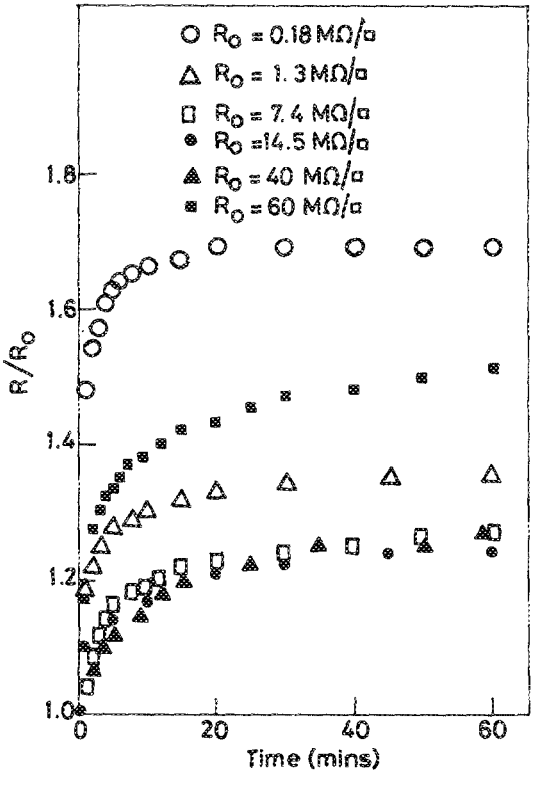

FIG. 1. Variation of normalized resistance with time for the films studied under condition (1).

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