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MAGNETIC ANOMALIES IN THE RARE EARTH OXIDE
SUPERCONDUCTORS GDBA2CU3O(7-X) (U) NORTH CAROLINA UNIV
AT CHAPEL HILL DEPT OF CHEMISTRY W E HATFIELD ET AL
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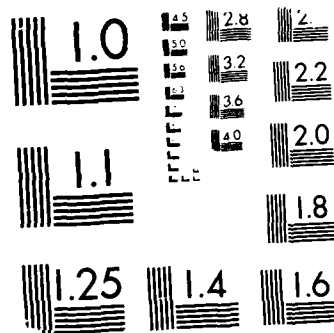
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19 ABSTRACT (Continue on reverse if necessary and identify by block number) The magnetic properties of $GdBa_2Cu_3O_{7-x}$ and $YbBa_2Cu_3O_{7-x}$ have been studied in low applied magnetic field by using pelleted sample. The magnetic behavior may be explained by the occurrence of a spin-glass state due to a granular superconductor. The model assumes superconducting grains which are small compared to the penetration depth, and these are coupled into closed loops. Cooling in zero-field, followed by the application of a field at a fixed temperature produces a metastable state resulting in frustration and spin-glass behavior.					
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Magnetic Anomalies in the Rare Earth Oxide
Superconductors $\text{GdBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{YbBa}_2\text{Cu}_3\text{O}_{7-x}$

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Magnetic Anomalies in the Rare Earth Oxide Superconductors
 $\text{GdBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{YbBa}_2\text{Cu}_3\text{O}_{7-x}$

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The discovery of high T_c superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ^{1,2} and this group's interest in the magnetic properties of rare earth compounds led to the study of paramagnetic analogs. Anomalous magnetic behavior in selected samples of two of these systems, $\text{GdBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{YbBa}_2\text{Cu}_3\text{O}_{7-x}$ is reported here. A spin - glass like transition is present at temperatures below T_c . The glassy behavior in an annealed pellet of $\text{GdBa}_2\text{Cu}_3\text{O}_{7-x}$ is shown in Figure 1. The flat regions in the diamagnetic shielding curve show flux trapping upon reversing the temperature and cooling in a field, proof that the sample is still a superconductor. The anomalous behavior observed in the diamagnetic shielding shows a time decay over a period of two weeks (Fig. 2) resulting in an increasingly broadened transition. After three weeks, the same sample displays typical superconductor behavior, however, a small residual component of the previous phase results in a slight decrease in the magnitude of the diamagnetic signal at 50 K. It is believed this transient glassy behavior is due to the sample being subjected to numerous thermal and magnetic cycles. The fact that subsequent samples lost this behavior after one series of such cycles confirms the metastability of this glassy state.

The Meissner signal for the sample showing the anomalous behavior and for the same sample after three weeks are essentially identical and show ~25% bulk diamagnetism. This is typical of a porous, granular superconducting composite.^{3,4} The magnetic susceptibility of a powdered sample of $\text{GdBa}_2\text{Cu}_3\text{O}_{7-x}$ (Fig. 3) is qualitatively

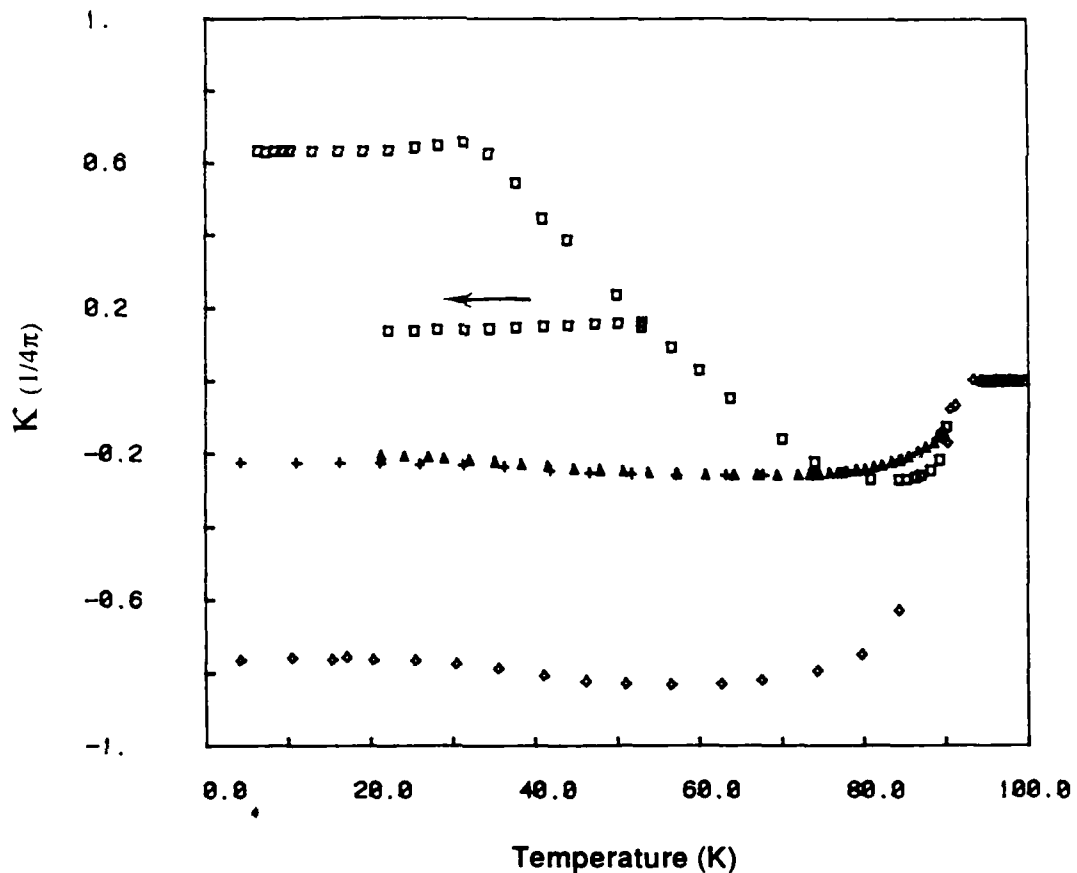


Figure 1. Volume susceptibility of $\text{GdBa}_2\text{Cu}_3\text{O}_{7-x}$ showing glassy behavior. Diamagnetic shielding (zero field cooled) signal of original sample $\square$, arrow demonstrates flux trapping upon cooling at 52°K. Meissner (field cooled) signal of original sample Δ . Diamagnetic shielding signal of same sample after three weeks $\diamond$ showing ~85% total flux exclusion. Meissner signal after three weeks +. All susceptibilities are corrected for porosity and demagnetization effects.

similar to Figure 1, except that no increase in the susceptibility below T_c is seen. The fact that the diamagnetic shielding is less than the previous amount of 75% for the pellet may be due to the smaller particle size of the powder.

The $\text{YbBa}_2\text{Cu}_3\text{O}_{7-x}$ sample (Fig. 4) is very similar to $\text{GdBa}_2\text{Cu}_3\text{O}_{7-x}$ since it also shows the glass-like behavior. The Meissner signal is ~10% of the value for total flux exclusion. The magnetization of the $\text{YbBa}_2\text{Cu}_3\text{O}_{7-x}$ specimen (Fig. 5) is typical of a "dirty" superconductor. As the field increases, the magnetization is linear beyond H_{c1} and

curves slowly due to the inability of flux to freely penetrate. Upon reversing the field, some of the flux is trapped at defect sites giving rise to the large hysteresis shown.

Several techniques have been used to determine sample purity. X-ray powder diffraction data give no evidence for a separate impurity phase. ICP-AES analysis yields an elemental stoichiometry of $\text{Gd}_1\text{Ba}_{1.922}\text{Cu}_{2.752}\text{O}_y$. Both of these techniques are accurate to within 5%. EPR spectroscopy (Fig. 6) at very high gain also yields none of the paramagnetic copper impurities witnessed by others.⁵ However, a broad Gd signal is observed at high gain indicating the possibility of a minor impurity phase (less than 0.5%). Perhaps the most convincing evidence lies in the susceptibility measurements. The Meissner signals show none or very small amounts of the large glass-like signal. Furthermore, paramagnetic impurities that give signals of this magnitude do not suddenly

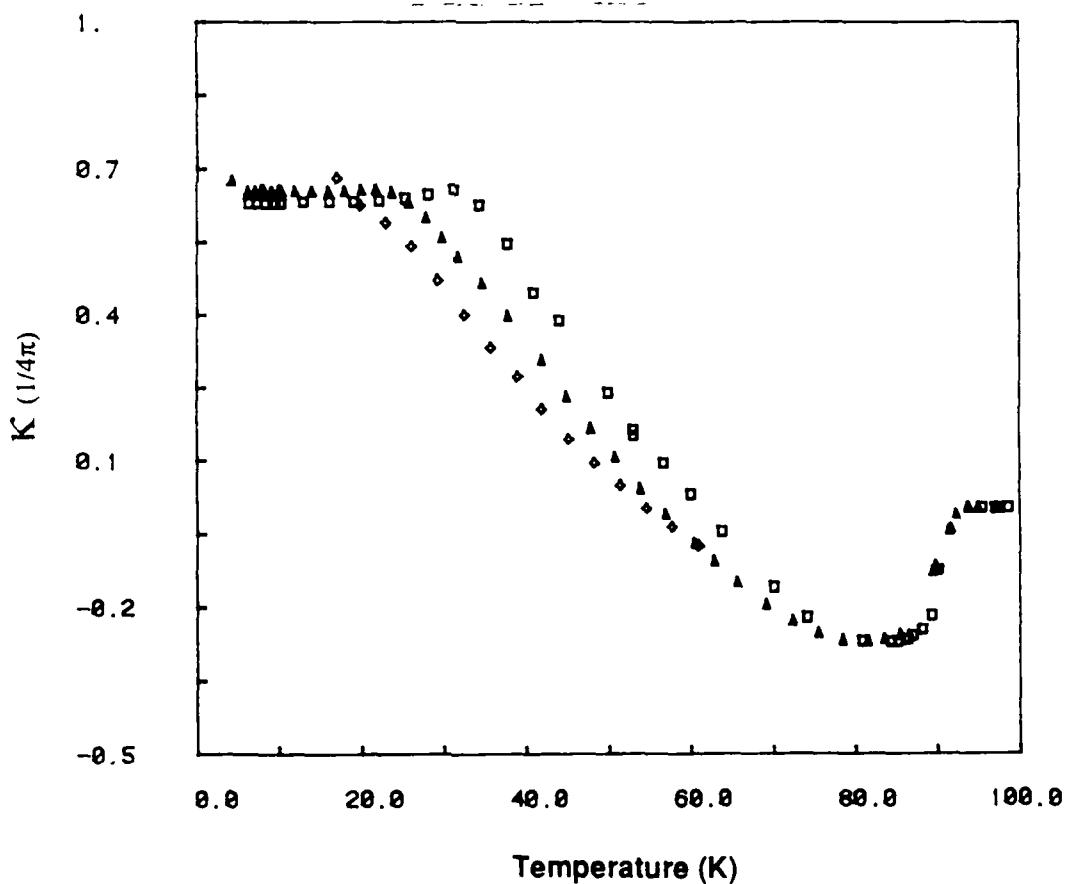


Figure 2. Diamagnetic shielding signal of $\text{GdBa}_2\text{Cu}_3\text{O}_{7-x}$ demonstrating signal decay over time: original sample $\square$, one day later Δ , after two weeks $\diamond$.

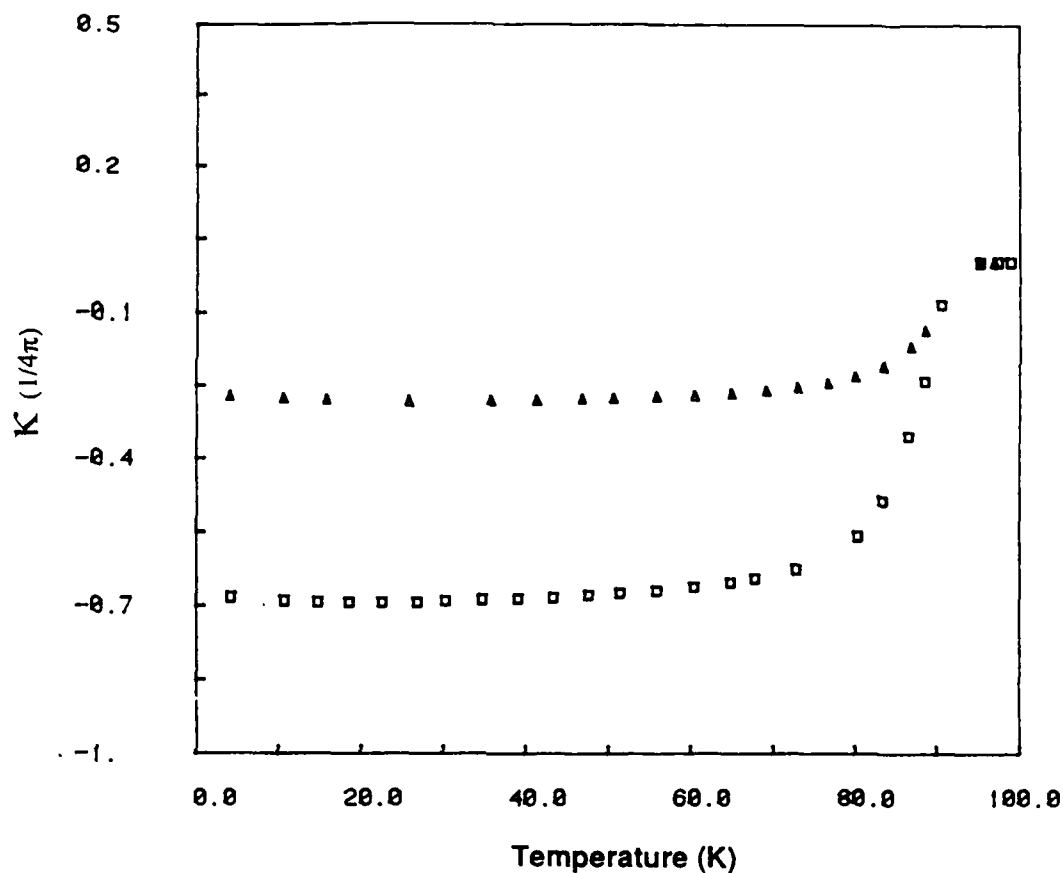


Figure 3. Volume susceptibility of a powdered sample of $\text{GdBa}_2\text{Cu}_3\text{O}_{7-x}$ showing typical superconductor behavior. The Meissner effect Δ is $\sim 25\%$ and the diamagnetic shielding $\square$ is $\sim 70\%$ of perfect diamagnetism.

dissipate. It can be conclusively stated that the signal is caused by some other phenomenon.

One explanation for this behavior is the occurrence of a spin-glass state due to a granular superconductor.^{6,7} The basic model involves superconducting grains, each small compared to the penetration depth, which are weakly coupled into closed loops. At finite fields, these clusters are frustrated, i.e., they cannot find a state which minimizes all bond energies simultaneously. Consequently, there are numerous competing ground states with nearly equal energy. Cooling in zero-field, followed by the application of a field at a fixed temperature, produces a metastable state resulting in frustration and spin-

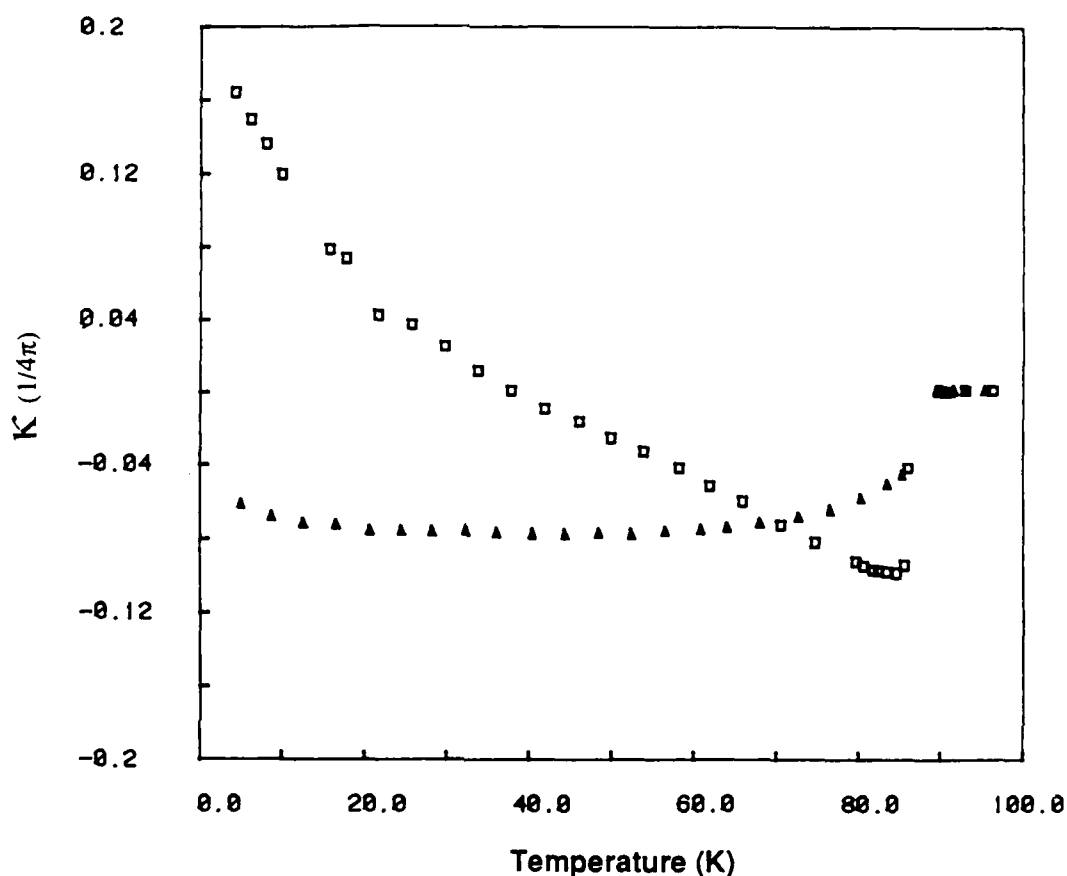


Figure 4. Volume susceptibility of $\text{YbBa}_2\text{Cu}_3\text{O}_{7-x}$. Diamagnetic shielding signal $\square$, Meissner signal Δ .

glass like behavior. If the sample is cooled slowly in a fixed field, the clusters are in equilibrium and a typical Meissner signal results.

This explanation, however, does not account for the large positive increase in the susceptibility. It accounts only for a decrease in the diamagnetism. Since X-ray powder diffraction and ICP-AES provide evidence that the impurities are less than 5%, small Gd impurities may form micromagnetic clusters resulting in spin-glass formation.^{8,9} The ZFC curve is a result of these clusters being frozen at some temperature $T < T_C$ in a frustrated manner. Upon warming, the rigid glass softens and the magnetic clusters relax. Thermal disorder then causes a time averaged magnetization which manifests itself in a decrease

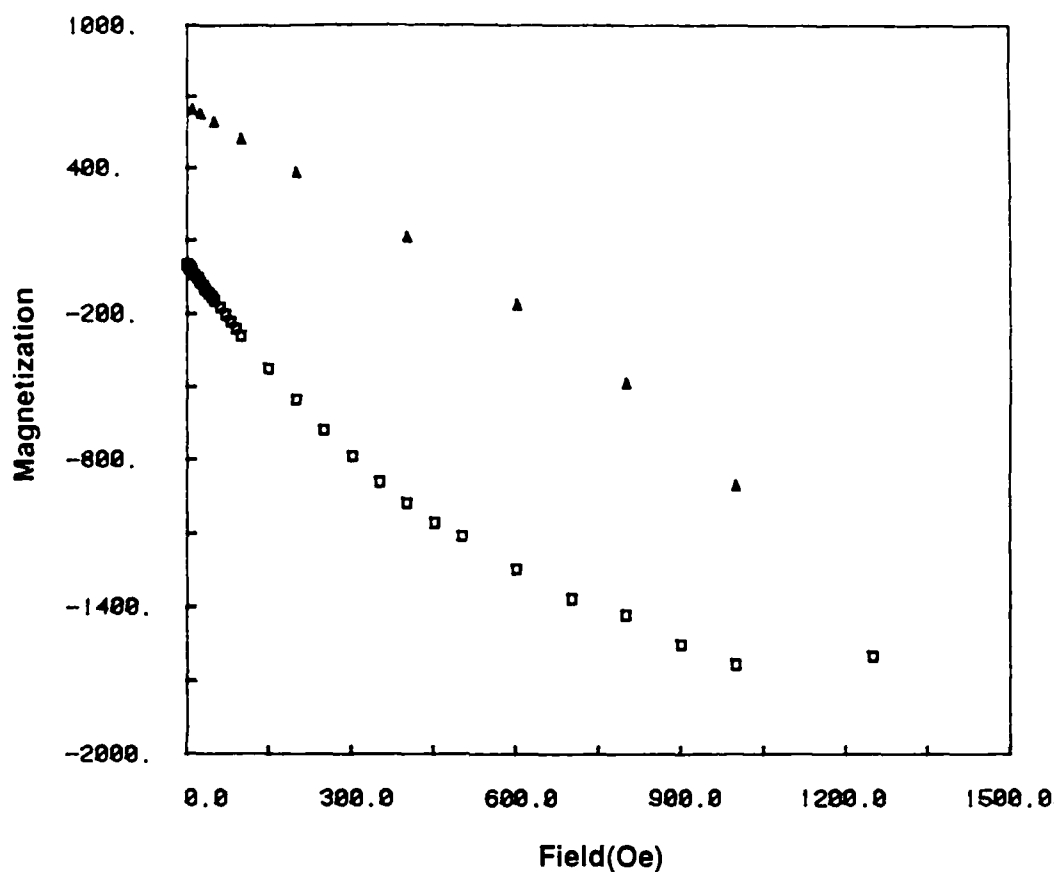
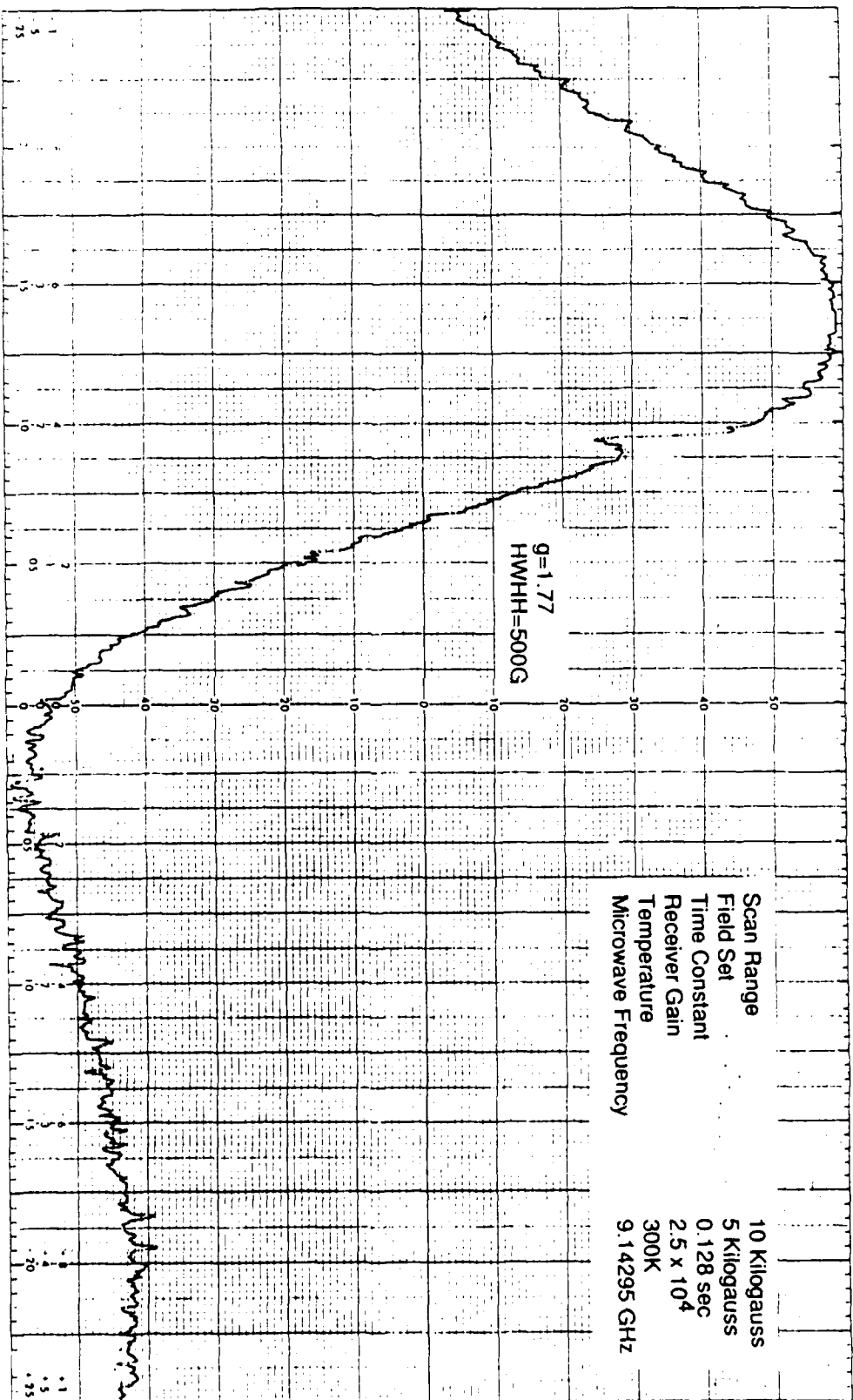


Figure 5. Magnetization of YbBa₂Cu₃O_{7-x} showing hysteresis due to flux trapping. Increasing field □ , decreasing field Δ .

Figure 6. (Next page) Room temperature X-band EPR signal of GdBa₂Cu₃O_{7-x} showing no copper impurities and a small Gd²⁺ signal. The small absorption at g = 2.00 is from a DPPH standard. The Gd²⁺ signal is not due to Gd₂O₃ which has g = 1.86 and HWHH = 330G.

in the susceptibility. In the FC curve, the temperature is gradually decreased and the cluster spins have time to minimize their energy, resulting in no net contribution to the magnetization by the impurity ions. Thermal and magnetic cycling may tend to break up these domain-like clusters. This may explain the transient nature of the observed glassy behavior.



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