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Magnetic relaxation in sintered $Tl_2Ca_2Ba_2Cu_3O_x$ and $YBa_2Cu_3O_{7-x}$ superconductors

M. E. McHenry and M. P. Maley
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

E. L. Venturini and D. L. Ginley
Sandia National Laboratory, Albuquerque, New Mexico 87185
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We have characterized the time dependence of the zero-field-cooled magnetization for sintered pellets of the Tl 2:2:2:3 and Y 1:2:3 superconductors. The magnetic relaxation in both cases is large and exhibits a logarithmic time dependence. The temperature dependence of the relaxation rate $A=dM/d\ln(t)$ has been characterized for both materials for applied fields of 1, 2, 3, and 10 kG. The relaxation rate for the Y 1:2:3 sintered material is comparable to that observed in similar sintered materials and in single crystals. The Tl 2:2:2:3 material exhibits similar relaxation spectra with a weaker temperature dependence at a given field consistent with stronger pinning in this material. The temperature dependence of the relaxation is analyzed using a phenomenological relaxation model to yield an average pinning energy (0.33 eV at $H=1$ kG) and its field dependence.

Logarithmic decay of magnetization with time has been observed in conventional superconductors[1] and successfully explained in terms of thermally activated motion of vortices.[2] This form of relaxation is also of current interest in that it is one of the signatures of the superconducting glass state.[3] Logarithmic time dependence of the magnetization has been observed to be a prominent feature in the recently discovered high-T_c oxide superconductors, $La(Ba)_2CuO_4$,[3,4] $YBa_2Cu_3O_{7-x}$,[5-8] $Bi_4Sr_3Ca_3Cu_4O_y$,[9] and $Tl_2Ca_2Ba_2Cu_3O_x$.[10] The purpose of this paper is to describe relaxation in the Tl 2:2:2:3 materials as a function of temperature and field and to compare features of the relaxation with those observed in the Y 1:2:3 material.

The study of the magnetic relaxation in these oxide materials offers considerable insight in that large thermal energies are accessible because of their high T_c's.[8] Characterization of the temperature dependence of the relaxation allows for a description of the distribution of pinning energies in the material $f(E)$ as well as the average pinning energy $E(H)$. In the analysis of our data we have considered several phenomenological models for the time dependence of the magnetization. One of these is the Richter model[11] which has found extensive use in the analysis of magnetic relaxation in ferromagnets and which we have found to parallel the essential physics contained in the Anderson flux creep model.[2] In this model the logarithmic time dependence arises from a distribution of activation energies. The time-dependent deviation of the magnetization from the equilibrium magnetization M_{eq} is determined by an Arrhenius rate expression $\lambda_i=\lambda_0 \times\exp(-E_i/k_BT)$ and an assumed varying distribution of activation energies bounded above and below by the energies $E_1(\approx 0)$ and E_2. Of considerable interest in this model is the derivative of the magnetization with respect to $\ln(t)$ denoted as A. For typical experimental data, short-time data reveal[12] that A may be expressed

$$A=\frac{d[M(t)-M_{eq}]}{d\ln(t)}=\left[\frac{kT}{E_2}\right](M_0-M_{eq}). \quad (1)$$

In the Bean[13] model M_0-M_{eq} can be related to J_{c0}, the critical current density in the absence of thermal activation. Thus, the form[1] is essentially similar to that proposed by Yeshurun and Malezemoff[8] in their adaptation of the Anderson flux creep model, if E_2 is associated with U_0 the average pinning potential energy. It is important to keep in mind in this model that (1) is pertinent only to intermediate times $l/\lambda_1 \ll t \ll 1/\lambda_2$.

Another form for the relaxation[14] of current interest is the so-called Kohlrausch law[15] which arises from a consideration of hierarchically constrained dynamics. In this model individual relaxation events do not occur in parallel, as is supposed in the Richter model. Rather, some of the relaxation events are not able to occur until other events pave the way. This yields series-coupled relaxation events in which the time-dependent magnetization follows a stretched exponential form

$$M(t)-M_{eq}=(M_0-M_{eq})\exp[-(t/\tau)^{\beta}]. \quad (2)$$

The Kohlrausch law is not explicitly used in the analysis of the data here, since we are considering only simple linear fits. However, considering the short time, small relaxation behavior $[(t/\tau)^{\beta}\ll 1)]$ of the Kohlrausch law it is possible to show that $\ln(1-x)=\beta\ln(t/\tau)$ (where x represents the reduced magnetization $[M(t)-M_{eq})/(M_0-M_{eq})]$. For small x, $\ln(1-x)$ reduces to $-x$ so that the Kohlrausch law lends itself to logarithmic time fits in the small relaxation regime. Typically, for $x<0.2$, the maximum error in assuming small $(t/\tau)^{\beta}$ will not exceed 20% which in turn can be reduced significantly by truncating the range of times fit. From (2) it is easy to show that $\ln(\tau)=M_0-M_{eq}/A=E/kT$, as in the previously discussed flux creep and Richter models.

Another form for the relaxation of the magnetization that has been considered is the power-law expression,[16] which is used extensively in the analysis of relaxation of magnetization in spin-glass materials. The form for the

magnetic relaxation in this case is

$$M(t)-M_{eq}=(M_0-M_{eq})\left[\frac{t}{\tau_0}\right]^{\beta}, \quad (3)$$

in which the relaxation exponent β takes the place of A in the previous expression, i.e., $\beta=d\Delta M(t)/d\ln(t)$. In this model β represents a suitably normalized relaxation rate and, thus, is a direct measure of the thermal energy, activation barrier ratio.

In each of these models, Arrhenius plots of $(M_0-M_{eq})/A$ or $1/\beta$, respectively, vs $1/T$ will yield an average activation energy. Each model should be capable of accurately extracting the activation energy, though the pertinent time scale for the various models will differ. The Richter model, because of the restriction to times where the distribution function of activation energies is only slowly varying, should prove to have the most limited time scale, while the Kohlrausch expression should be useful over longer times. In the experimental durations considered here (1 h) the flux creep and Richter models have proved adequate descriptions of the relaxation.

Samples of $YBa_2Cu_3O_{7-x}$ were prepared from commercial[17] powder with a 10-μm average grain size. The powder was cold-pressed to 50 000 psi and then fired in oxygen. The annealing cycle consists of a ramp to 965 °C at 200 °C/h, holding at 965 °C for 10 h, cooling to 400 °C at 25 °C/h, holding at 400 °C for 20 h, and then cooling to room temperature at 25 °C/h.

The room-temperature resistivity of this material is about 2600 $\mu\Omega$ cm with a midpoint of 92 K, a 10% to 90% width of 2.5 K, and zero resistance near 89 K. dc susceptibility measurements in a 100-Oe field showed a 93-K onset, a 74-K midpoint, and 95% of $4\pi\chi$ flux exclusion at 7 K. The Meissner effect in 100 Oe was 24% of $4\pi\chi$ flux exclusion at 7 K. Magnetometer magnetization loops, M vs magnetic field H, were made at 7, 65, and 75 K. Hysteresis in these data is indicative of intragranular critical currents. Values of J_c determined using the Bean model,[5] $J_c=15\Delta M/R$ where ΔM is the hysteresis in gauss, R is a typical particle size in cm, and J_c is in A cm^{-2}, are 1.8×10^6 at 7 K, 6.8×10^3 at 65 K, and 3.4×10^3 at 75 K, all at $H=0$ in the remanent state. These values are similar to those measured in single crystals, although with a more rapid fall off with increasing temperature.

Samples of the $Tl_2Ca_2Ba_2Cu_3O_x$ were similarly processed by sintering constituent powders. The materials were produced from high-purity oxides (>99.99%) stored under Ar until used. The oxides were mixed, ground, and pressed in a 1″ die at 24 000 lbs. for 7 min. The pressed pellet was then sintered for 15 min in the air at 850 °C on a Pt sheet. The pellet was crushed, ground, and repressed. It was subsequently resintered at 850 °C for 15 min and then annealed in 1 atm flowing O_2 at 900 °C for 12 h with a 5-h slow cool. Magnetometer magnetization H loops were made at 5, 30, 60, and 77 K, again revealing a strong temperature dependence of J_c. An average grain size of 20 μm was employed to yield critical current densities of 14, 3, 1.2, and 0.5×10^5 A/cm^2 for the respective temperatures.

Magnetization versus time measurements were made using an SHE superconducting quantum interference device magnetometer. The procedure for acquiring the magnetic relaxation data consisted of cooling in zero field (ZFC) and, after attaining a stable temperature, application of the field. The first magnetization point was taken after the 3 min required to latch the field. Subsequent magnetization points were taken every 2 min for the duration of the experiment (typically 1 h). Between runs the field was removed and the sample heated to above its T_c in order to expel all remaining flux. The equilibrium magnetization values (M_{eq}) were approximated as the magnetization of a slowly field-cooled sample at the temperature in question. It was ascertained that negligible relaxation occurred from this field-cooled state.

Figure 1 illustrates typical time dependences of the magnetization at various temperatures for a Tl 2:2:2:3 sample cooled initially in zero field upon application of a field of a 1 kG. The magnetization M in each case is normalized by the initial magnetization value M_1 as given by the first measured data point ($t_1=200$–250 s). The magnetization is seen to change by approximately 15% at 60 K within a 1 h measurement period. This is to be contrasted with the case of $YBa_2Cu_3O_{7-x}$ samples in which the relative change was 15% at 40 K. This value is comparable to that reported for single crystals of $YBa_2Cu_3O_{7-x}$.[18] The stronger temperature dependence of the Y 1:2:3 sample is a clear manifestation of the weaker pinning evident for Y 1:2:3 as compared to Tl 2:2:2:3.

Figure 2 shows results of fits of the $M(t)$ behavior for an applied field of 1 kG and temperature of 50 K for the Tl 2:2:2:3 sample. These results are typical of fits to the relaxation data. For all but the highest fields and temperatures the M vs $\ln(t)$ fit, as predicted by the Richter and flux creep models, offers an excellent fit to the data over the entire duration of the experiment. Even at high temperatures and fields one or more decades of linear M vs $\ln(t)$ behavior can be observed. Figure 2(b) shows the result of a $\ln(M-M_{eq})$ vs $\ln(t)$ fit ($H-1$ kG, $T=50$ K). These fits are generally of comparable quality to M vs $\ln(t)$ at low temperatures and fields. At high temperature and fields, indicative of larger kT/E values, the power-

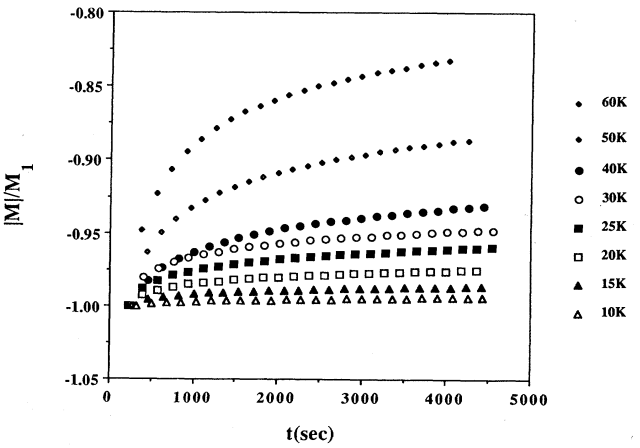

FIG. 1. $M(t)$ vs t as a function of temperature for the Tl 2:2:2:3 material.

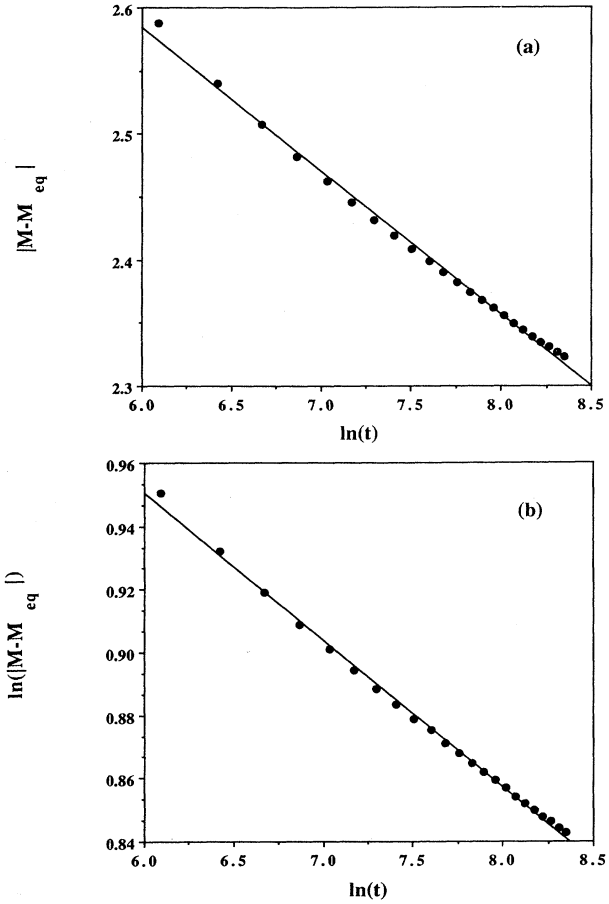

FIG. 2. Fits of the $M(t)$ data to (a) the flux creep model [M vs $\ln(t)$] and (b) a power-law model [$\ln M$ vs $\ln(t)$].

law fits are actually of somewhat higher quality. However, for the $M(t)$ data reported here the difference in the two fits rarely yields a difference of more than 0.01 in the linear regression coefficient. The improvement in using the power-law fits, typically weighs more heavily in the short and long time intervals, and, thus, the improvement might be more dramatic for extended experimental times. Finally, a procedural note on the determination of the equilibrium magnetization M_{eq} is in order. The equilibrium magnetization is taken to be the field-cooled value of the magnetization at a particular temperature and field. Even though this value is also subject to pinning corrections, at low temperatures $M_{fc}/M_{zfc}(0) \approx (5\% - 10\%)$, while at higher temperatures equilibration is fast. Further, no appreciable relaxation is observed from the field-cooled state indicating it to be a quasiequilibrium state.

Given the high quality of the M vs $\ln(t)$ fits it is convenient to use this analysis to further investigate the Tl 2:2:2:3 material because of ease of comparison with a variety of published data analyzed in this manner. Figure 3(a) shows the relaxation spectra $A = dM/d\ln(t)$ vs T for applied fields of 1, 2, 3, and 10 kG, respectively. Notable in these spectra are peaks that are progressively shifted to lower temperatures with higher applied fields. The origin of these peaks has been recently explained by Yeshurun and Malezemoff[8] as originating from the competing effects of an explicit linear T term and an implicit decreasing of J_c with T. Figure 3(b) shows relaxation spectra, again at $H = 1$, 2, 3, and 10 kG for the Y 1:2:3 material. Striking in the comparison of the Y 1:2:3 and Tl 2:2:2:3 spectra is the fact that for all fields the relaxation spectra is shifted to higher temperatures for the Tl 2:2:2:3 material. This is a clear indication of the stronger pinning in the Tl 2:2:2:3 material. Even on a reduced (T/T_c) temperature scale the Tl peaks are shifted higher showing that the increased T_c of the Tl material can be only partly responsible for the higher pinning energies.

Figure 4 shows an Arrhenius plot of $E/kT = M_0 - M_{eq}/A$ vs $1/T$ for a 1 kG field for the Tl 2:2:2:3 material. In the case of fits to the 1 and 2-KG data low-temperature data was excluded (20 K and < 10 K, respectively) because of severe deviation from linearity. This deviation at low temperatures can be understood by considering that the applied field is significantly less than $H^*(T)$, the field at which the entire volume of an average grain has been penetrated by the field. For these low fields and temperatures the flux-penetration volume is less than the sample volume. The predictions of (1) are borne out in this figure. The slope of Arrhenius curves yields the activation energy or, alternatively, the average pinning en-

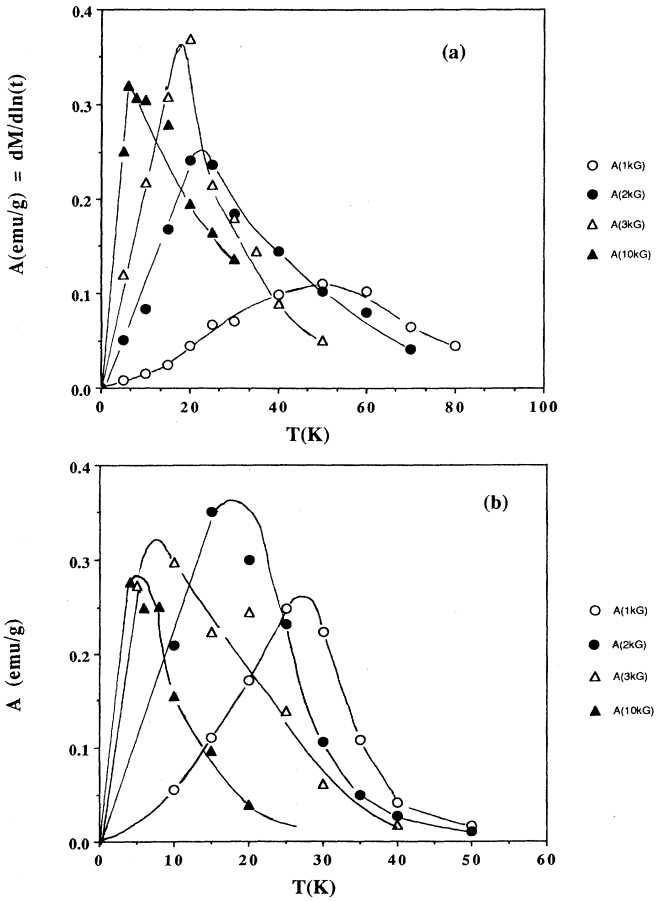

FIG. 3. Logarithmic relaxation parameter $A = dM/d\ln(t)$ as a function of temperature for (a) Tl 2:2:2:3 and (b) Y 1:2:3.

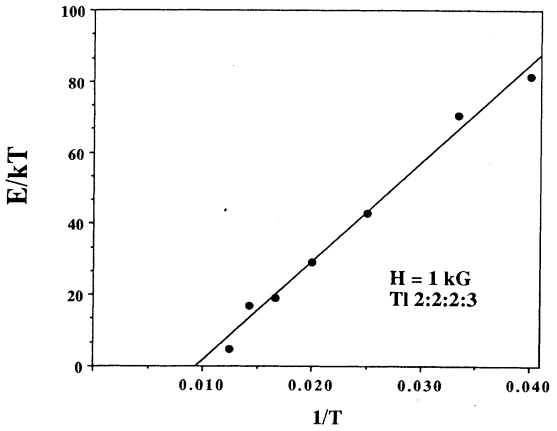

FIG. 4. Arrhenius plot of $E/kT=(M_0-M_{eq})/A$ vs $1/T$ for the Tl 2:2:2:3 material in $H=1$ kG.

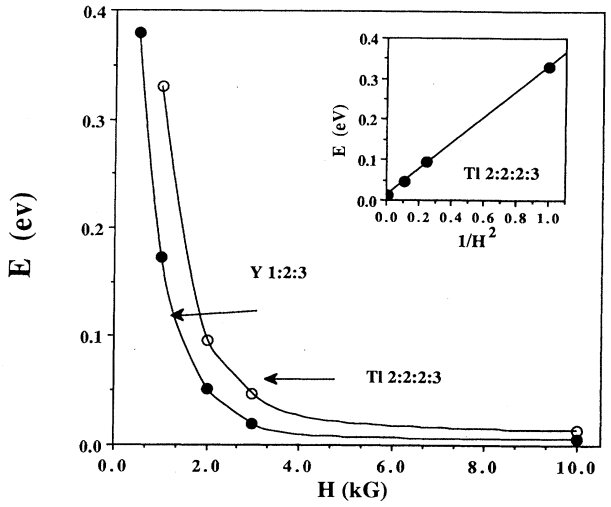

FIG. 5. Field dependence of the apparent activation energy E for the Tl 2:2:2:3 and Y 1:2:3 materials. Inset shows the fit to $E=A/H^2$ for the Tl 2:2:2:3 material.

ergy. This energy was seen to be strongly field dependent with a large decrease in the slope with increasing field.

Figure 5 illustrates the field dependence of the pinning energy as deduced from the Arrhenius plots for all fields examined. Figure 5 compares the $E(H)$ behavior for the Tl 2:2:2:3 material with similarly derived $E(H)$ values for the Y 1:2:3 material. This comparison shows convincingly that the pinning barriers are stronger for the Tl 2:2:2:3 material. This result is quite interesting in light of the fact that the Tl 2:2:2:3 material is an untwinned material. This suggests that if twins are important pinning centers in the Y 1:2:3 material then even stronger pinning centers exist in the Tl 2:2:2:3 material. It is worth pointing out that recent experiments on Bi material reveal much weaker pinning than in either the Y 1:2:3 or Tl 2:2:2:3 materials here reported. In the $Bi_4Sr_3Ca_3Cu_4O_y$ material a relative relaxation ($|M|/M_0$) of $\sim 40\%$ was observed at 15 K in this material.[9] Flux creep measurements on conventional superconductors[19,20] have previously observed a field dependence of U_0, the average pinning potential, that is monotonically decreasing toward zero at B_{c2}. This presumably reflects the field dependence of the relevant activation volume. As shown in Fig. 5, the magnetic field dependence for the Tl material is considerably steeper ($\approx 1/B^2$ dependence as shown in the inset).

Logarithmic time-dependent magnetic relaxation has been observed for a polycrystalline Tl 2:2:2:3 oxide superconductor and compared to a similar Y 1:2:3 material. Large magnetic relaxation is observed in both cases consistent with the fact that thermal energies represent a substantial fraction of the average pinning energy. Fitting of the magnetization versus time data with Richter (M vs $\ln t$) and power law [$\ln(M-M_{eq})$ vs $\ln t$] shows accurate fits for both expressions for experimental times of 1 h or less. The Tl 2:2:2:3 material exhibits relaxation spectra which are shifted to higher temperatures as is consistent with significantly larger pinning energy barriers in the Tl material. Arrhenius plots reveal an activation energy of 0.33 eV for the Tl material at 1 kG and 0.18 eV for the Y 1:2:3 material in the same field. The activation energy is strongly field dependent.

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