Comparison of various methods to determine experimentally the irreversibility line in superconductors

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An attempt has been made to determine the irreversibility temperatures $[T_r(H)]$ via the merger of zero-field-cooled and field-cooled magnetizations, via the vanishing of the isothermal hysteresis, and via the appearance of the differential paramagnetic effect in specimens of lead and niobium. The first method appears to define a lower limit on $T_r(H)$ and does not necessarily indicate a true thermodynamic region near $T_c(H)$. The differential paramagnetic effect, however, is a qualitative feature whose presence is sufficient to imply reversibility.

The magnetic phase diagram of high-temperature superconductors (HTSC's) is considered to be divided into a thermodynamic region near the superconducting-normal phase boundary [$T_c(H)$ line] and a nonequilibrium region below an irreversibility (H_r, T_r) line.[1] The commonly used magnetic methods to experimentally determine this irreversibility line are as follows:

(i) Müller, Takashige, and Bednorz[2] had introduced temperature-dependent measurements of field-cooled (M_{FC}) and zero-field-cooled (M_{ZFC}) magnetizations in a constant field H and identified the temperature below which these are different with $T_r(H)$. As noted by Malozemoff,[3] $M_{ZFC}(T)$ and $M_{FC}(T)$ approach each other asymptotically, and so the precise value of $T_r(H)$ should be determined by the resolution of the experimental data. Another manifestation of this is the observation by Xu *et al.*[4] and Xu and Suenaga[5] that the measured $T_r(H)$ values strongly correlate with the extent of hysteresis.

(ii) The isothermal $M(H)$ measurements can also be used to map the irreversibility line. Finnemore *et al.*[6] emphasized that the width of hysteresis $\Delta M(H)$ becomes negligible near $H_{c2}(T)$ in a HTSC compound and the magnetization curve in that region yields equilibrium response. Kritscha *et al.*[7] have recently adapted this method in an attempt to determine $H_r(T)$ values; however, this procedure is more laborious.

(iii) An out-of-phase ac susceptibility $\chi''_H(T)$ measured in a constant dc field H is often used to quote the $T_r(H)$ value. While the temperature at which $\chi''_H(T)$ peaks is referred to as $T_r(H)$, the analyses used[8] assume that the sample is irreversible as soon as $\chi''_H(T)$ is nonzero. The difference between actual and the quoted $T_r(H)$ values is therefore large when the peak in $\chi''_H(T)$ is broad. Even at the low frequencies employed in such ac methods, there are contributions to $\chi''_H(T)$ from the electrodynamics of the normal state,[9–11] possibly from the thermodynamic superconducting state[12] as well, which are usually ignored, but which can further complicate the analyses of the $\chi''_H(T)$ data to yield a true $T_r(H)$.

(iv) The existence of a reversible magnetization response close to $T_c(H)$ should give rise to a paramagnetic signal when in-phase ac susceptibility $\chi'_H(T)$ is measured in a constant H. This, identified in type-I superconductors and referred to as the differential paramagnetic effect (DPE) by Hein and Falge,[13] has only recently[14–16] been used to test the existence of the reversible region in HTSC compounds.

The results obtained by the various methods described above often show some disagreement for the same system (see, for instance, Ref. 7). Further, while a DPE in $\chi'_H(T)$ has been observed in Tl- (Refs. 14 and 15) and Bi- (Ref. 15) based HTSC compounds, this effect has not been observed in $YBa_2Cu_3O_7$.[16] Hein *et al.*[16] assert that this absence of the DPE "forces one to conclude that the reversible region in M_{ZFC} and M_{FC} scenarios is not a thermodynamically reversible one." M_{ZFC} and M_{FC} measurements have also been used in recent years to identify $T_r(H)$ in conventional superconductors,[17–21] and careful measurements on specimens of a type-I superconductor Pb resulted in an inference[21] that the observed irreversibilities in some situations may not be a material (bulk) characteristic. Besides the qualitative disagreements referred to above, there have also been differences in detail. For instance, most studies indicate that $T_r(H)$ satisfies a power-law relation $1 - T_r(H)/T_c(0) = aH^q$, with the exponent q in the range $\frac{1}{2}$–$\frac{3}{4}$ in HTSC's.[1] Detailed measurements show a somewhat larger value of q in some thin-film specimens of HTSC's;[4] Rössel *et al.*,[20] Sägdahl *et al.*,[22] and de Rango *et al.*[23] find different values for q in different H regions in $PbMo_6S_8$, $YBa_2Cu_3O_7$, and Bibased (2:2:2:3) compounds, respectively.

Motivated by these various approaches, we have used methods (i), (ii), and (iv) to study the (H_r, T_r) line in two specimens of conventional superconductors Pb and Nb. We have chosen a type-I and -II material since the physical basis of irreversibility in the two cases are different. We can thus dwell on the relative efficacy of various methods in general, to detect the magnetically reversible region. Since the problems in analyzing $\chi''_H(T)$ are aggravated[9,16] for these metallic superconductors, we shall not use method (iii) for reporting $T_r(H)$ data in the present report. Our detailed measurements in the given Nb specimen bring out the fact the merger of $M_{\text{ZFC}}(T)$ and $M_{\text{FC}}(T)$ is indeed asymptotic, and it seems to correspond to critical-current density $J_c(T)$, decaying to zero as $T \rightarrow T_c(H)$,[24] and not necessarily to thermodynamic reversibility below $T_c(H)$. The results in the Pb specimen reinforce the belief that the observation of DPE, however, is a qualitative feature, the presence of which is sufficient to imply the existence of a reversible region of magnetization near the $T_c(H)$ line.

The Pb disk (diameter $=4.15$ mm and thickness $=2.15$ mm) and Nb powder specimens used have been subjected to some experimental work reported earlier.[19,21,25] Figures 1(a) and 1(b) show the isothermal magnetic hysteresis data recorded using a Quantum Design superconducting quantum interference device (SQUID) magnetometer in the two specimens. The data are recorded at discrete field values at close intervals. The continuous lines in Fig. 1(b) are smooth curves drawn through data points. The Pb disk specimen in Fig. 1(a) is oriented with its cylindrical axis perpendicular to the magnetic field, so as to avoid the setting up of persistent surface currents which can give rise to large hysteresis.[21] A noteworthy difference between the two curves of Fig. 1 is the persistence of hysteresis in the Nb specimen up to its H_{c2} value [see inset, Fig. 1(b)]. In contrast, the Pb specimen appears to have large reversible region [Fig. 1(a)] near its $H_c(T)$. However, the FC and ZFC magnetization values at 4.7 K in the Pb specimen are different up to at least 300 Oe (see Ref. 21 for details). The $M_{\text{ZFC}}(T)$ and $M_{\text{FC}}(T)$ curves for different H values merge as the temperature is raised above 4.7 K. The $T_r(H)$ values so determined[21] obey an apparent power-law behavior with $q \simeq 1$. We have recorded $M_{\text{ZFC}}(T)$ and $M_{\text{FC}}(T)$ data in Nb powder as well to much higher accuracy than done earlier[19] at $H=20$, 50, 100, 200, 300, 400, 600, 1000, and 3000 Oe. Figure 2 displays temperature dependence of ZFC and FC susceptibility values at a few selected fields, viz. $H=20$, 100, and 3000 Oe. The arrows mark the merger temperatures designated as $T_r^{(21)}(H)$, at nominal resolution. Figure 3 contains plots of the difference susceptibility $\Delta\chi[\equiv\chi_{\text{ZFC}}(T)-\chi_{\text{FC}}(T)]$ versus temperature at $H=20$, 100, and 3000 Oe. From such data one can

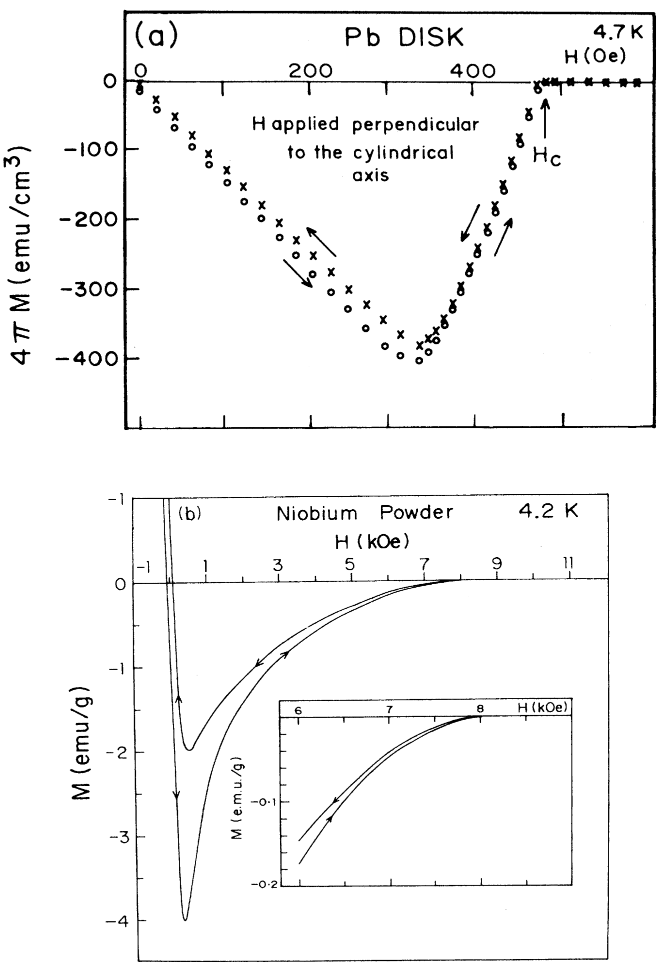

FIG. 1. (a) Isothermal magnetization hysteresis data in disk-shaped lead specimen at 4.7 K. (b) Isothermal magnetization hysteresis curve in niobium powder specimen at 4.2 K. The inset shows the forward and reverse hysteresis curves near the H_{c2} value on an expanded scale; the two curves are seen to asymptotically merge at H_{c2}.

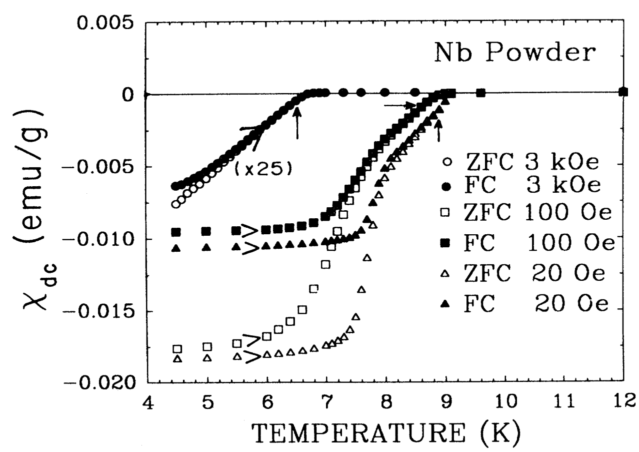

FIG. 2. Temperature dependence of zero-field-cooled and field-cooled susceptibilities in $H=20$, 100, and 3000 Oe in a niobium powder specimen. The arrows mark the merger temperatures $[T_r^{(21)}(H)]$ at which the pairs of curves appear to merge at nominal resolution.

pick out the temperatures [to be designated as $T_r^{(22)}(H)$] at which $\Delta\chi$ approaches zero to a resolution level which is 5–10 times smaller than the nominal level of merger values $T_r^{21}(H)$. It is apparent that $T_r^{(21)}(H) < T_r^{(22)}(H) < T_c(H)$. $T_c(H)$ may be viewed as the asymptotic limit of the values of T_r if the (H_r, T_r) line coincides with the $T_c(H)$ line. Figure 4 shows the plots of $\ln[1-T_r(H)/T_c(0)]$ vs $\ln H$ in Nb powder for three sets of $T_r(H)$ data, viz., $T_r^{(0)}(H)$ [$\equiv T_c(H)$], $T_r^{(21)}(H)$, and $T_r^{(22)}(H)$. If we attempt to reconcile the data in Fig. 5 to a power-law relationship $1-T_r(H)/T_c(0)=aH^q$, the exponent q will vary with H, as also noted earlier by others.[20,22,23] It may, however, be stated here that in the midfield region (10^2–10^3 Oe), $T_c(H)$, $T_r^{(22)}(H)$, and $T_r^{(21)}(H)$ data fit to a power-law with $q=0.67$, 0.55, and 0.34, respectively.

The in-phase ac susceptibility χ'_H in the Pb and Nb specimens has been investigated in the frequency interval 21–210 Hz with the energizing fields in the range 0.3–2.0 Oe rms and with applied dc field (H) up to 300 Oe. Figure 5 shows the χ'_H data in the Pb specimen recorded at 21 Hz in a rms field of 1 Oe at $H=0$ (Earth's field), 100, and 300 Oe (data recorded at $H=5$, 10, 20, 30, and 200 Oe are not shown for brevity). In nominal zero field, only the diamagnetic response is observed across the normal-to-superconducting transition (curve a, Fig. 5), while in finite field (even as small as 5 Oe) a strong paramagnetic response (DPE) emerges and it precedes the onset of the diamagnetic response. The paramagnetic peak (DPE) broadens as the dc field increases (cf. curves b and c, Fig. 5). We may identify the temperature of onset of a paramagnetic response as $T_c(H)$ and the onset of a diamagnetic response as $T_r^{(1)}(H)$ in Fig. 5. The $T_r^{(1)}(H)$ values compare favorably with the irreversibility temperature values obtained from the merger of $M_{ZFC}(T)$ and

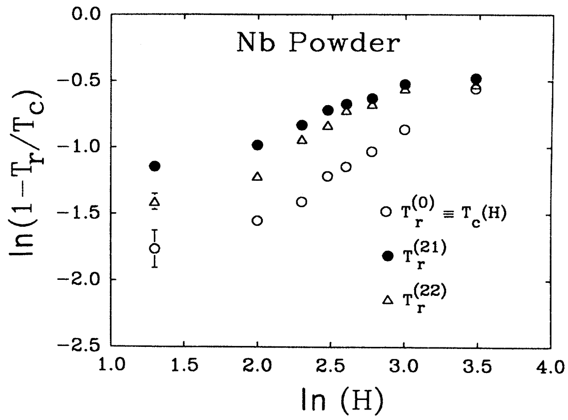

FIG. 4. Log-log plot of $1-T_r(H)/T_c(0)$ vs H for three sets of $T_r(H)$ values in a niobium powder specimen.

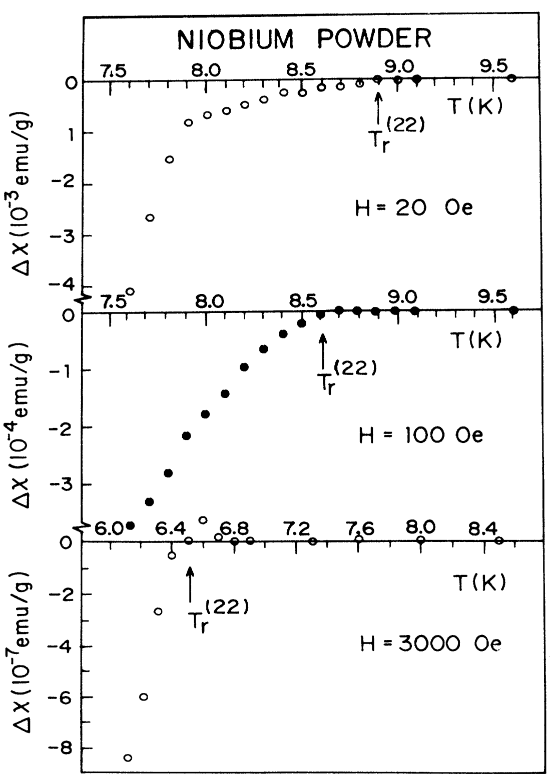

FIG. 3. Temperature dependence of difference susceptibility $\Delta\chi$ [$\equiv\chi_{ZFC}(T)-\chi_{FC}(T)$] in $H=20$, 100, and 3000 Oe in a niobium powder specimen. The arrows mark the temperature [$T_r^{(22)}(H)$] at which $\Delta\chi$ appears to vanish at high resolution.

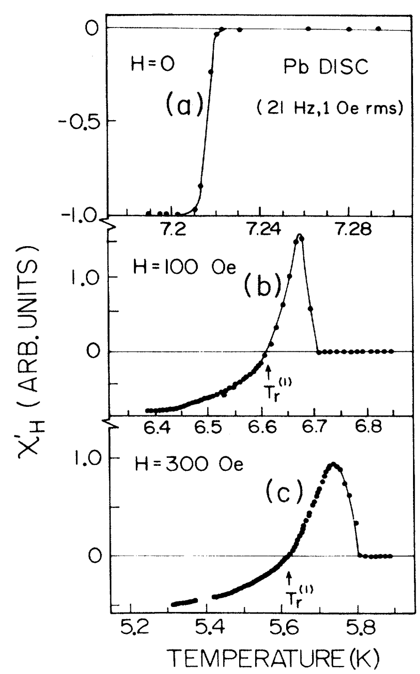

FIG. 5. Temperature dependence of in-phase susceptibility $\chi'_H(T)$ in a Pb disk specimen measured at 21 Hz with energizing field of 1 Oe rms in $H=0$ (Earth's field), 100, and 300 Oe.

$M_{FC}(T)$ data in the same Pb specimen in Ref. 21. The $T_c(H)$ and $T_r^{(1)}(H)$ values in Pb also appear to fit a power-law relationship with $q \simeq 1$. Since the DPE is an effect that emerges in an ac measurement, there is a question whether the frequency used is low enough to investigate the time-independent irreversibilities. The frequency we have used (21 Hz) is at the lower end of the frequencies normally used in ac susceptibility measurements. In Fig. 6 we compare our χ''_H data as the frequency is changed from 21 to 210 Hz. The change is perceptible, but small, and gives us the confidence that 21 Hz is a low enough frequency for the Pb specimen under study.

We could not observe any paramagnetic response (DPE) in the niobium power specimen. We believe that this failure to observe the DPE is a consequence of the absence of a true thermodynamic region near the $T_c(H)$ line. In this specimen the situation is that, even though $M_{ZFC} \rightarrow M_{FC}$ as $T \rightarrow T_r^{(22)}(H)$, the width of the hysteresis $\Delta M(H)$ at $T = T_r^{(22)}(H)$ remains finite. The latter approaches zero as $T \rightarrow T_c(H)$ (or $H \rightarrow H_{c2}$). This would be consistent with earlier observations[19,26,27] of superconductors that an isothermal hysteresis loop defines the envelope within which $M_{FC}(H)$ values lie. It clearly implies that $\Delta m(H)$ values near $H_{c2}(T)$ are larger than the differences $[M_{FC}(H) - M_{ZFC}(H)]$. This feature has been noted by Nakao *et al.*[28] in magnetic hysteresis data recorded in very high fields in single-crystal specimens of $YBa_2Cu_3O_7$. They observed finite $\Delta M(H)$ values in the region where M_{ZFC} values were expected to merge with M_{FC} values from the data of Welp *et al.*[29] These facts appear to tie up well with the reported absence of the DPE in specimens of $YBa_2Cu_3O_7$.[16]

To summarize, we have obtained data on the irreversibility temperature by different methods in two specimens of conventional superconductors. The T_r values determined from the asymptotic merger of M_{ZFC} and M_{FC} curves are shown to be dictated by the resolution of the data. The vanishing of $\Delta M(H)$ in isothermal measurements appears to be a better criterion for determining $T_r(H)$—a feature also noted recently by Suenaga *et al.*[30] in Nb_3Sn. The differential paramagnetic effect[16] appears to give a qualitatively clear signature of the reversibility phenomenon. The T_r values obtainable from the DPE are in general expected to be higher than those determined from dc magnetization data. This is easily verified by a comparison of the recent data of Khoder, Couach, and Jorda[14] with the other representative values available in the literature.[4] It may be cautioned here that the failure to observe the DPE in a routine measurement need not be used to emphatically rule out the existence of reversible region in superconductors having very high κ values, as for HTSC's. A very careful search[14] is necessary to observe the DPE in such superconductors.

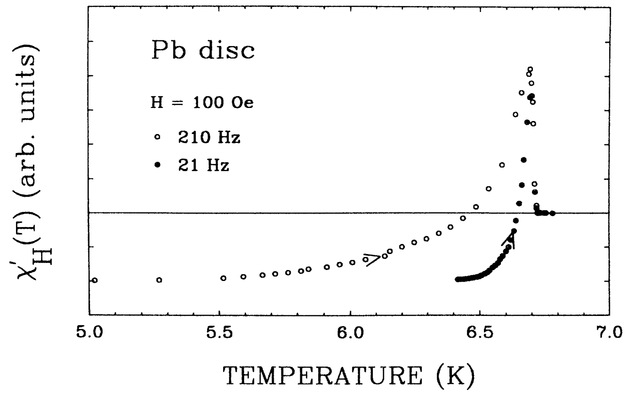

FIG. 6. $\chi'_H(T)$ vs temperature at $H = 100$ Oe in a Pb disk specimen at two different frequencies (21 and 210 Hz).

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