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Scaling of the irreversibility line in a low temperature superconducting oxide

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We have studied the critical field and irreversibility line on the magnetization of the ceramic oxide $LiTi_2O_4$. The irreversibility line scales with the critical field while the coherence length of the material changes by a factor of two. This universal behavior indicates that the origin of the irreversibility line does not depend on extrinsic factors and relies solely on the intrinsic superconducting parameters of the material.

One of the most interesting features of the high temperature superconductivity in ceramics is the existence [1] of an irreversibility line in the magnetic field H versus temperature T phase diagram. For temperatures and fields above this line system is in the stable, thermodynamic state regardless of the path along which the point T,H is reached. For temperatures and fields below this line the system shows pronounced hysteresis, the state is defined by the previous history of the experiment and the critical current is finite. The origin and cause of this new phase boundary to our knowledge has not been ascertained, to date. It is therefore of the utmost importance to characterize the dependence of the irreversibility line on the properties of the sample, in order to find the constraints theories should take into account. In this paper we present experimental evidence which shows that the irreversibility line scales with the upper critical field. This indicates that the irreversibility line is a thermodynamic property which depends only on the intrinsic superconducting properties of the material and not on extrinsic factors.

The irreversibility line was first identified [1] as the locus of points at which the zero-field-cooling (ZFC) and field-cooling (FC) magnetization meet. Several models have been proposed to explain this unique phase line which is apparently not present in conventional superconductors. The various models include a quasi Thouless-de Almeida line [1,2] in a spin-glass analogy, vortex depinning due to thermal fluctuations, [3] melting of the flux line lattice due to the competition between thermal fluctuations and elastic energy [5–8] and freezing of the flux line lattice in a glassy state [9]. In general the various models can be classified into two categories; one that depends on extrinsic properties of the superconductor (grain size, twin boundaries, oxygen deficiency, etc.) and theories that only depend on the intrinsic thermodynamic properties (coherence length, critical temperature, etc.). Experimentally, Malozemoff et al. [4] reported that the irreversibility line is weakly frequency dependent. Recently, Civale et al. [10] presented evidence that the irreversibility line does not depend on the density of pinning centers. Using low field decoration techniques Gammel et al. [11] observed a vortex lattice at 4.2 K and no magnetic pattern at 77 K in $YBa_2Cu_3O_{7-\delta}$ single crystals

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suggesting a possible melting of the vortex lattice. However, Safar et al. [12] showed that the irreversibility line obtained from magnetization measurements and the melting transition detected in vibrating reed experiments do not coincide at low fields in Bi–Sr–Ca–Cu–O ceramics, indicating a different origin. Therefore, to date there is no conclusive experimental evidence capable of discerning between these various models.

$LiTi_2O_4$ is a ceramic superconductor with a critical temperature between 11 and 14 K [13,14]. The reason for this variation is not fully understood at present. Recently [15] it was shown that the superconductivity in $LiTi_2O_4$ presents the same granular characteristics as the high temperature ceramic superconductors. Although it shares the ceramic and granular superconducting character with the high-T_c oxides it has a cubic spinel structure [13] and therefore is expected to be isotropic.

$LiTi_2O_4$ ceramic samples were prepared according to two different methods. Samples prepared following the recipe of Johnston et al. [13] exhibit X-ray diffraction (XRD) patterns characteristic of $LiTi_2O_4$ with impurities of Ti_2O_3. In an attempt to improve sample quality, the method of Harrison et al. [16] was also followed. The XRD pattern of this second set of samples showed an improved yield of $LiTi_2O_4$, although some Ti_2O_3 was still present. The resistivity of these samples is similar to the results of Johnston [13] with values typically of the order of 0.1 Ωcm and almost temperature independent down to the superconducting transition. This transition is observed around 12–14 K, although in some samples a non-zero resistance tail was observed down to 7 K.

Magnetization measurements in the field range 100 Oe to 50 kOe and in the temperature range 7 to 15 K were performed in a SHE SQUID magnetometer at the University of California-San Diego (UCSD) and a Quantum Design SQUID magnetometer at the Katholieke Universiteit Leuven (KUL). Measurements were performed on different samples and on the same sample after several room temperature dry atmosphere "aging" cycles. Experimental problems have been reported [17] related to the sample travel length in SQUID magnetometers. In order to check our results measurements were taken in the SHE magnetometer with travel length 50% longer than the standard one. No significant differences were found. The ZFC and FC magnetization were measured as a function of temperature for different applied fields.

It was found, as has been previously reported [15], that the sample characteristics changed as a function of aging time. This degradation process is not understood at present. While the as prepared samples present an irreversible behavior in the magnetization for the whole temperature range, a reversible zone develops for aged samples. The conclusions presented here are universal for all samples which present an irreversibility line, although the mechanism by which it is suppressed in the as prepared samples has not been ascertained.

Fig. 1 shows typical results of ZFC and FC curves for different applied fields as a function of temperature. Based on these data we identify two lines in the H versus T phase diagram. The upper critical field, H_{c2}, is defined as the onset of the diamagnetic behavior. Although this definition can be affected by thermodynamic fluctuations we do not expect the

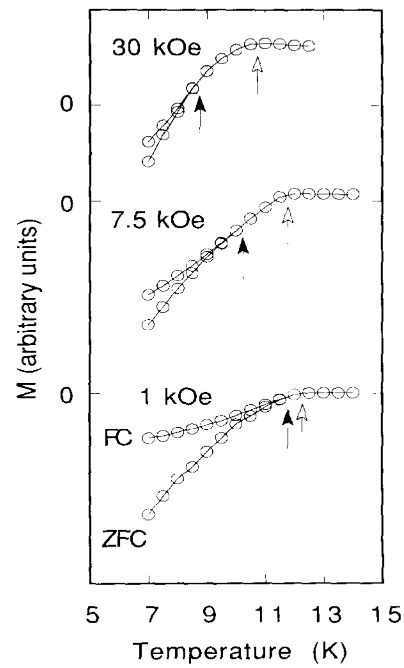

Fig. 1. ZFC and FC magnetization for sample 2 as a function of temperature. Data for $H = 1$ kOe, 7.5 kOe and 30 kOe are included. Open arrows indicate the onset of the diamagnetic signal, i.e. the upper critical field. Full arrows indicate the temperature at which irreversibility begins, i.e. the irreversibility point.

difference to be significant due to the low value of T_c and the 3-dimensional character of the material. This hypothesis is confirmed by the fact that other criteria for the definition of H_{c2}, like extrapolation of the linear part, coincide with the onset within our experimental error bar. The appearance of irreversibility at a lower temperature indicates the irreversibility point, (T^*, H^*). The irreversibility line is experimentally defined as those fields and temperatures at which the ZFC and FC curves begin to differ in more than the experimental noise, typically 0.1% of the maximum signal.

Fig. 2 shows the upper critical field H_{c2} as a function of reduced temperature, $t=T/T_c$ which for all samples studied is linear within the experimental accuracy. However, it is evident that there is a wide spread in the value of the slope. Through the Landau–Ginzburg relation

$$H_{c2}(t)=\frac{\phi_0}{2\pi\xi^2(0)}(1-t)\,, \tag{1}$$

where ϕ_0 is the flux quantum and $\xi(0)$ is the zero temperature coherence length we find that the latter is changing by more than a factor of two in this set of samples. Table 1 shows the critical temperature, critical field slope and calculated coherence length for the samples shown in fig. 2.

Fig. 3 shows a universal (T,H) phase diagram which includes results for the irreversibility line, (T^*, H^*). The field data have been normalized by the

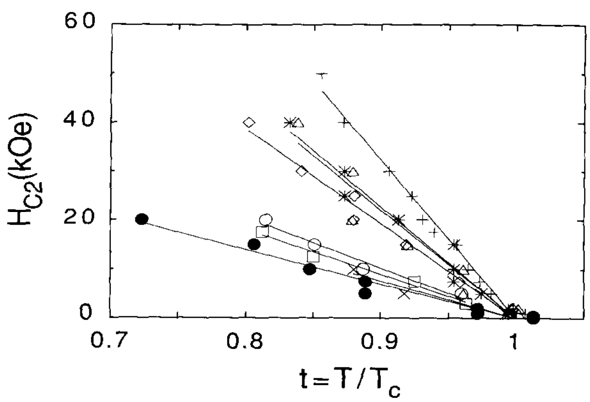

Fig. 2. Critical field, H_{c2}, as a function of reduced temperature, t. Solid lines indicate linear fits to the data. (○) sample 1a, (□) sample 1b, (×) sample 1c, (★) sample 2, (+) sample 3, (△) sample 4, (×) sample 5a and (◇) sample 5b.

Table 1
Critical temperature, T_c, slope of the critical field as a function of reduced temperature, dH_{c2}/dt, and calculated coherence length at zero temperature, $\xi(0)$, for the set of samples. Different number indicate different samples. Same number and different letter indicate different aging at room temperature in dry atmosphere for the same sample.

Sample	T_c (K)	$-dH_{c2}/dt$ (kOe)	$\xi(0)$ (Å)
1a	13.81	103	57
1b	13.23	90	60
1c	12.09	70	69
2	12.31	227	38
3	11.92	322	32
4	12.27	220	39
5a	13.35	76	66
5b	12.78	193	41

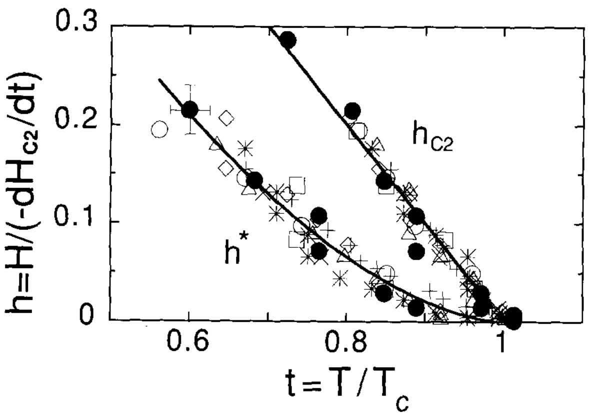

Fig. 3. Normalized critical field, h_{c2}, and irreversibility line, h^*, vs. reduced temperature, t, phase diagram. Fields have been normalized by the slope of the critical field as a function of reduced temperature, dH_{c2}/dt. Symbols for different samples are the same as in fig. 2. The same symbol is used in h_{c2} and h^* for a given sample. Solid lines indicate $h_{c2}=(1-t)$ and $h^*=a(1-t)^b$ where $a=1$ and $b=1.7$ are the least-square-best-fit coefficients. One of the data points shows a typical error bar.

slope of the critical field as a function of reduced temperature. The figure shows that within the experimental uncertainty the irreversibility line follows a universal behavior in this phase diagram. A power law fit to the normalized data, $h^*=a(1-t)^b$ renders $a=1$, $b=1.7$ and has been included in the graph as a solid line.

This universal behavior in a set of different samples with H_{c2} changing by factors of four or coherence lengths changing by more than a factor of two, clearly indicates that the mechanism by which the irreversibility line is originated does not depend on extrinsic factors and relies solely on the intrinsic superconducting parameters of the material.

In this sense, the data presented here favors models based only on the thermodynamic properties (like the melting theories) rather than ones based on extrinsic factors (like depinning theories). If the pinning energy, i.e. the extrinsic factors, scale with H_{c2} it may imply that extrinsic factors are responsible for the irreversibility line. This would be the case if superconductivity is completely destroyed at the site of a defect. Although from our data this possibility cannot be ruled out this seems to be unlikely due to the relative large value of $\xi(0)\approx 50$ Å and the fact that all pinning centers, which are random in nature, would have to behave in the same way. An additional point not clarified by the present experiments is the reason for the irreversibility line not to appear in the as-prepared samples. If the irreversibility line is an intrinsic property there must be a competition between this thermodynamic process and pinning. If the defects are strong enough to provide individual pinning they will override the irreversibility transition and the reversible zone will not be observed. In this framework we could speculate that one of the effects of the aging process is to decrease the pinning strength. Table 1 show that the effect of the aging on sample 1 and sample 5 is opposite. In effect dH_{c2}/dt decreases in sample 1 while it increases in sample 5. This indicates that the aging process is not simply an increase in the dirtiness of the sample, i.e. a decrease in the electronic mean free path, which would lead to an increase of dH_{c2}/dt.

It may be argued that in $LiTi_2O_4$ the temperatures are too low to allow melting of the flux line lattice. However ref. [6] shows that the distance over which a vortex wanders is

$$\Lambda_L=\left(\frac{8\pi^2 L k_B T}{\phi_0 H_{c1}}\right)^{1/2} \tag{2}$$

which for $L=1$ cm for the sample length, $T=10$ K and $H_{c1}(0)=120$ Oe [15] is reduced only by a factor of 3 with respect to the high temperature superconductors [6]. This is due to $H_{c1}(0)$ being lower than in the high-T_c oxides and the weak square root dependence on T. The fact that the irreversibility line is not exclusive to high temperature oxides has also been proved by its observation in other low critical temperature superconductors like $PbMo_6S_8$ [18] and recently for $Ba_{0.625}K_{0.375}BiO_3$ [19].

In conclusion we have measured the ZFC and FC magnetization of a set of $LiTi_2O_4$ samples in which the coherence length changes by more than a factor of two. Although due to this fact the absolute value of the critical field changes by more than a factor of four the irreversibility line is a universal function of reduced field, $h=H/(dH_{c2}/dt)$, and reduced temperature, $t=T/T_c$. This scaling behavior with the upper critical field indicates that the origin of the irreversibility line is thermodynamic in origin and does not depend on extrinsic factors.

The origin of the degradation process and the process by which the reversible zone in the magnetization originates remains unanswered.

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