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H-T phase diagram of granular superconductors

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We propose an H-T phase diagram of granular superconductors based on the separate analyses of the intragranular critical fields and of an assembly of Josephson junctions. The model is examined experimentally and its predictions are applied to several problems of high-temperature superconductivity like the $H_{c2}(T)$ enhancement with a temperature reduction, the width of the $R(T)$ transition under an applied magnetic field, and a double-step $J_c(H)$ variation.

High-T_c superconducting ceramics are generally recognized as granular superconductors. The material is imagined as being built of grains of a good superconducting metal connected by a nonsuperconducting medium, through which the charge transfer can be either Josephson- or single-electron-tunneling-like. Despite the numerous works published, a clear understanding of the interplay and relative balance between the intra- and intergranular properties is still lacking. We devote this paper to this problem and propose an H-T phase diagram of the granular superconductors in which we introduce an effective critical field of the assembly of the intergranular Josephson junctions and compare it with the intragranular critical fields. The predictions of the model are verified by the experiments on the weakly coupled e-type high-T_c superconductors L-M-Cu-O (L =Pr, Nd, Sm; M =Ce, Th) and are applied to some well-known experimental results as the $H_{c2}(T)$ enhancement with a temperature reduction, width of the $R(T)$ transition under an applied magnetic field,[1] and a double-step $J_c(H)$ variation.[2]

Disordered superconductors are usually treated in two limits: homogeneous and inhomogeneous. The homogeneous limit is met when an effective superconducting coherence length $\xi(T)$ is larger than the inhomogeneity scale. For the granular case, this scale is the grain size d. As long as $\xi(T)$ is larger than d, the detailed structure of the disordered medium is unimportant and it behaves as an ordinary homogeneous dirty superconductor.[3] In the inhomogeneous limit $\xi(T) < d$, H_{c2} becomes structure sensitive. The order parameter is in general not destroyed uniformly everywhere in the sample at a well-defined critical field.

High-temperature superconductors should automatically be treated in the inhomogeneous limit[4] because their coherence length is much smaller than the typical grains dimensions and the intergranular junctions are the sites of a depressed order parameter.[5] We propose therefore to examine separately the response of the intra- and intergranular components to the applied magnetic field.

We imagine the sample to be built of large grains of a type-II superconductor surrounded by a matrix of Josephson junctions. For the bulk type-II superconductor the H-T phase diagram consists of two characteristic curves $H_{c1}(T)$ and $H_{c2}(T)$ emerging from zero at the same critical temperature T_{cg}. We wish to add to these two curves an additional one that characterizes an effective critical field of an assembly of Josephson junctions. At zero field a critical temperature of a single junction T_{cj} can be defined as the one at which the junction's characteristic coupling energy E_j exceeds the thermal energy of the order of kT. In the vicinity of the intragranular critical temperature T_{cg}, this can be written as

$$E_j = (\phi_0 I_{\text{eff}}/2\pi)[(T_{cg} - T_{cj})/T_{cg}] = k_B T_{cj} . \tag{1}$$

When magnetic field is applied, we assume that E_j remains proportional to the junction's critical current. The field-dependent critical temperature of a typical junction with a cross section S averaged for a wide distribution of the magnetic flux is then given by

$$\frac{\phi_0 I_{\text{eff}}}{2\pi} \frac{T_{cg} - T_{cj}(H)}{T_{cg}} \frac{1}{1+\pi\phi/\phi_0} = k_B T_{cj}(H) , \tag{2}$$

or in terms of the critical fields

$$\frac{\pi H_{cj}(T) S}{\phi_0} = \frac{T_{cg} T_{cj}}{T_{cg} - T_{cj}} \left(\frac{1}{T} - \frac{1}{T_{cj}} \right) . \tag{3}$$

The resulting H-T phase diagram of the granular superconductor is schematically shown in Fig. 1 by the solid lines. The $1/T$ dependence of the intergranular critical field is valid only in the limited range near T_{cg}; however, the most important basic difference between the temperature variation of the intragranular critical fields H_{c1} and H_{c2} and that of the junctions assembly in all the tempera-

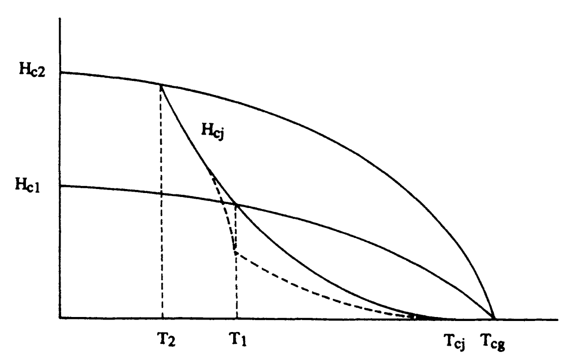

FIG. 1. Schematic H-T phase diagram of a granular superconductor (solid lines). The dashed lines correspond to the effective intergranular critical field as a function of an *applied* magnetic field.

ture range is that the first two vary with a negative second-temperature derivative ($d^2H_{c1,2}/dT^2<0$) with the finite values at zero temperature $H_{c1,2}(0)$, whereas the second varies with $d^2H_{cj}/dT^2>0$ and asymptotically increases when $T\to 0$. This assures an intersection of the $H_{cj}(T)$ curve with $H_{c1}(T)$ and $H_{c2}(T)$ at temperature T_1 and T_2,[6] respectively. The relative ratio between the inter- and intragranular critical fields varies with temperature reduction, that leads to a different response of the system to the applied field in three temperature ranges.

(1) $T_1 \le T \le T_{cj}(T_{cg})$: $H_{cj}(T)<H_{c1}(T)$. The intergranular Josephson-type tunneling is suppressed before the first vortice enters inside the grains.

(2) $T_2 \le T \le T_1$: $H_{c1}(T) \le H_{cj}(T) \le H_{c2}(T)$. The vortices start to enter inside the grains before the Josephson tunneling between the grains is suppressed. For an assembly of junctions with a distribution of E_j only a part of the Josephson junctions are destroyed when the field has reached H_{c1}.

(3) $T \le T_2$. The sample is perfectly coupled.

The phase diagram presented in Fig. 1 by the solid lines is based on the assumption of a homogeneous distribution of the magnetic flux in all the volume of the sample. This assumption is not met in granular superconductors with the grains size d significantly larger than the penetration depth λ in a low field limit. When the low field $H_{\rm appl}$ is applied all the magnetic flux can be considered to be concentrated in the intergranular regions and the effective local field H_e there is approximately equal to

$$H_e = H_{\rm appl} S_{\rm tot}/S_{\rm intergran}\,, \tag{4}$$

where $S_{\rm tot}$ is the total sample's cross section and $S_{\rm intergran}$ is the cross section of the intergranular regions. This intergranular flux accumulation breaks down when H_e exceeds H_{c1}. The additional vortices will accommodate themselves almost homogeneously all over the sample's volume, and the field density increase inside the junctions will fall down drastically. The physical state of the junctions will be influenced very little by the variation of the applied field at this point. As a result the effective critical temperature of the assembly of intergranular junctions becomes a two-step function of the *applied* magnetic field and is shown by a dashed line in Fig. 1.

Based on the diagram presented above we can make certain general qualitative predictions.

(1) The *measured upper critical field* is usually defined at the points where a certain fraction (10% or 50%) of the normal-state resistance is recovered. For a sample consisting of the mixture of strong and weak superconducting materials with comparable values of the normal-state resistances these definitions characterize mainly the suppression of the weakest component. In the temperature range $T_2 < T \le T_{cj}$, this relates mostly to the intergranular critical field $H_{cj}(T)$. A strong enhancement of the measured critical field with a temperature reduction is therefore expected down to the temperature T_2.

(2) The *width of the R(T) transition* under an applied magnetic field is equal to $\Delta T(H) = T_{cg}(H) - T_{cj}(H)$ is a nonmonotonic function of H. It has a minimum at $H=0$, broadens with an increase of the applied field until some maximum value and reduces to zero when the $H_{c2}(T)$ curve intersects the $H_{cj}(T)$ one. The same arguments can be applied to a magnetoresistance transition $R(H)$ at different temperatures.

(3) The critical current density $J_c(H)$ can be imagined as an analog of $T_{cj}(H)$ and therefore is expected to be a two-step function of an applied magnetic field.

The experimental examination of the model has been based on a direct measurement of the $T_{cj}(H)$ curve. We have shown in a previous work[7] that the separation and identification of the intra- and intergranular transitions can be reached by the resistance measurements of the e-type superconducting ceramics L-M-Cu-O (L = Pr, Nd, Sm; M = Ce, Th). We reproduce in Fig. 2 the resistance transition of the Sm-Ce-Cu-O sample measured as a function of temperature under different applied magnetic fields. Two general remarks should be made: (1) the sharp $R(T)$ transition at zero field widens strongly under low fields of the order of 0.1 kOe but becomes much sharper under fields of a few Tesla (see Fig. 2); (2) the critical field defined at 10% or 50% of the total resistance transition enhances strongly when temperature is reduced. Similar observations have been reported by other groups.[8]

The nonmonotonic transition is developed under moderate magnetic fields in which the resistance drops down to a nonzero minimum, increases with temperature reduction, and at last falls down. We understand the initial resistance drop unsensitive to the limited variation of the applied magnetic field as being caused by the intragranular transitions. The further resistance variation, very sensitive to the value of the low magnetic fields, is determined by the state of the intergranular junctions. Quasiparticle dominated tunneling ($dR/dT<0$) develops into the Josephson-type tunneling (resistance drop at low temperatures) when the temperature is reduced below an effective Josephson coupling temperature value $T_{cj}(H)$. This unique form of superconducting transition enables us to monitor explicitly the variation of the effective intergranular critical temperature as a function of applied magnetic field. We define $T_{cj}(H)$ as the temperature of the resistance peak maximum and present the results in Fig. 3. The intra- and intergranular transitions can be identified up to the field of 20 kOe and T_{cj} is found to fall

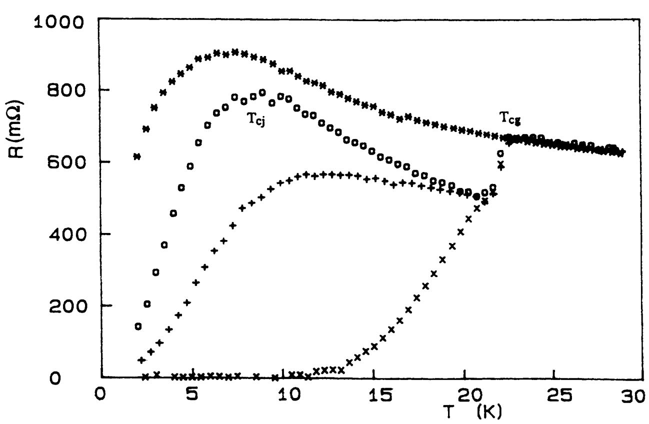

FIG. 2. $R(T)$ superconducting transition of the Sm-Ce-Cu-O sample measured under different applied magnetic fields: (×) −0.001 kOe; (+) −0.05 kOe; (□) −0.4 kOe; (*) −49.7 kOe.

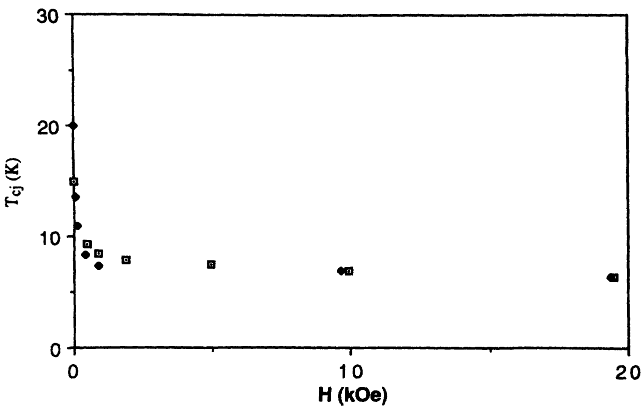

FIG. 3. The effective intergranular critical temperature T_{cj} of two samples [Sm-Ce-Cu-O (♦) and Nd-Th-Cu-O (⊡)] as a function of an applied magnetic field.

drastically under fields lower than a few hundred Oe and to almost saturate under higher fields.

The magnetoresistive transitions of the samples (Fig. 4) can be naturally divided in three stages with two characteristic break points, fields H_1 and H_2: (1) $0<H<H_1$. The resistance sharply increases with the field up to the value $R_1(H_1)$. (2) $H_1<H<H_2$. The resistance varies slowly or remains almost constant. (3) $H>H_2$. The resistance increases to the normal state value.

We relate the first steep increase of the resistance to the suppression of the intergranular Josephson junctions. There are two possible interpretations of the sharp change in the magnetoresistance curves at field H_1.

(1) All (or almost all) the Josephson junctions are suppressed. In this case the points $H_1(T)$ correspond to the junctions' critical-state curve $H_{cj}(T)$. R_1 should correspond to the intergranular contribution to the total sample's resistance, i.e., it has to meet the condition $R_1 \geq R_n - R_{\text{intragr}}$, where R_n is the normal-state resistance of the sample at temperature T, and R_{intragr} is a total intragranular resistance. (The resistance of a junction can be significantly higher than its normal-state value when the charge transfer is governed by the single electron tunneling between the superconducting grains.[7]) The total intragranular resistance of the sample can be defined to be equal to the initial resistance drop unsensitive to the limited variation of the applied magnetic field (Fig. 2). The normal-state resistance of the sample at temperatures below T_c can be extrapolated by the form: $R_n(T) = R_0 - A \ln T$, found in all the samples studied in the temperature range from T_c up to 100–200 K.[9]

(2) The effective field in the intergranular regions exceeds the value of the lower intragranular critical field H_{c1}. The additional flux will now accomodate itself not in the junctions but homogeneously in the volume of the sample. The rate of the flux increase in the junctions will fall down dramatically and the state of the junctions and therefore the sample's resistance will vary very slowly at this point. For an assembly of the junctions with a distribution of E_j this transition can occur when Josephson tunneling is suppressed in a small fraction of the junctions only. R_1 can then be lower than the total junctions resistance ($R_1 < R_n - R_{\text{intragr}}$). In this case H_1 relates to the intragranular critical field $H_{c1}(T)$.

We show in Fig. 5 the variation of H_1 and R_1 as a function of temperature. For the temperatures above 10 K $H_1(T)$ is found to be proportional to $1/T$. This dependence breaks down at lower temperatures where H_1 varies much slower with temperature decrease. Simultaneously, R_1 falls down well below the level of the normal-state intergranular resistance.

The variations of $H_1(T)$ and $R_1(T)$ correspond exactly to the predictions of the model discussed above with the H_{cj}-H_{c1} intersection at temperature about 10 K. The typical junctions' size can be calculated from Eq. (3) using an experimental value of the H_{cj} vs $1/T$ slope (see Fig. 5). By taking an average grain size to be 10 μm and a penetration length λ about 0.1 μm we obtain the effective intergranular field $H_e = 100\ H_{\text{appl}}$ [see Eq. (4)], which gives a reasonable junction's size of about $10^{-10}\ \text{cm}^2$.

The $H_2(T)$ points (Fig. 4) are also interpreted in the framework of the H-T phase diagram. At temperatures $T>10$ K the majority of the Josephson junctions is suppressed below the field H_1 and the total resistance of the sample varies weakly before the applied field reaches

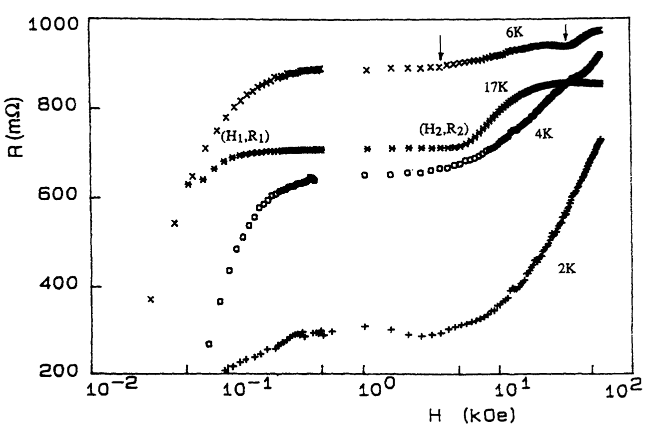

FIG. 4. Magnetoresistive superconducting transition of the Sm-Ce-Cu-O sample at different temperatures. Note the two-step resistance variation.

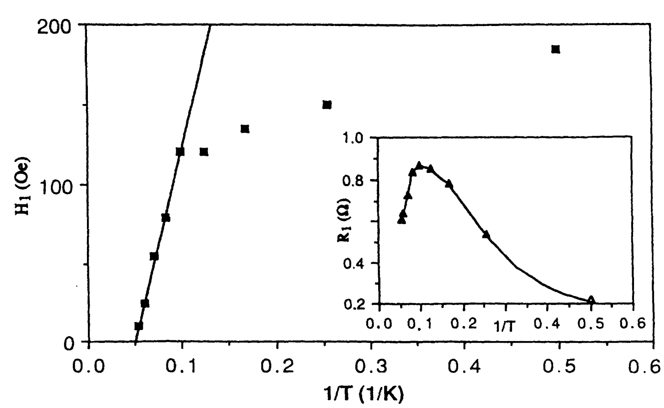

FIG. 5. Variation of the first break point coordinates R_1, H_1 (Fig. 4) as a function of $1/T$.

the level of the intragranular upper critical field. In this temperature interval H_2 corresponds to the lower limit of H_{c2}, i.e., of the weakest grains oriented with *a-b* planes perpendicular to the field.

At temperatures $T < 10$ K the break point at H_1 corresponds to the volume redistribution of the flux density, while a part of the junctions remains in the Josephson coupled state. A further increase of resistance now is caused either by the successful suppression of the remaining Josephson junctions or by the intragranular transitions at H_{c2}. The plateau therefore disappears and a smooth two-kink resistance increase is observed (see the 6 K curve in Fig. 4). For still lower temperatures the intergranular critical field $H_{cj}(T)$ exceeds significantly the intragranular critical field $H_{c1}(T)$ and a plateau between these two points is reestablished. The break point H_2 corresponds now to an intergranular critical field $H_{cj}(T)$.

To summarize briefly the experimental results: (1) we succeeded in separating and identifying the intra- and intergranular transitions; (2) in the vicinity of $T_{cj}(0)$, $H_{cj}(T)$ is found to vary proportionally to $1/T$; (3) we have found an intersection between the $H_{cj}(T)$ and $H_{c1}(T)$ curves; (4) we have found a plateau interval in the $T_{cj}(H)$ dependence; (5) the average upper critical field shows a typical upward tendency with temperature reduction; (6) the total resistance transition width was found to be a nonmonotonic function of the applied field in the *e*-type ceramics. (In other systems with higher H_{c2} values[10] only increasing transition width is usually observed in the limit of the applied fields.) All these results are in good agreement with the predictions of the proposed diagram.

The H-T phase diagram proposed here provides a simple qualitative understanding of several problems of the high-T_c superconducting ceramics, like an enhancement of the measured critical field, width of the transition under the field, or double-step field dependence of the critical currents. The first two of these phenomena have also been observed in single crystals. We should therefore reexamine the term "granular" superconductor. At the very early stages of high-T_c superconductivity Deutscher[4] has emphasized that "granularity" is an intrinsic property of the high-T_c superconducting materials caused by their very short superconducting coherence length, especially along *c* axis. Since then[11] several interpretations of the single crystalline properties have involved the interlayer Josephson-type coupling. It therefore will be very interesting to verify if the modified H-T phase diagram approach can be applied to the high-T_c single crystals as well.

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