Reentrant superconductivity in a composite formed by YBa$_2$Cu$_3$O$_{7-\delta}$ and Ammonium Terbium Oxalate.

Rodolfo E. López-Romero and Dulce Y. Medina

División de Ciencias Básicas e Ingeniería, Universidad Autónoma Metropolitana-Azcapotzalco, Av. San Pablo No 180, Col. Reynosa-Tamaulipas, C.P. 02200 México D.F., México.

R. Escudero
Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México. A. Postal 70-360. México, D.F.

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We present a study of reentrant behaviour in a composite formed by a Hight-T$_c$ superconductor, YBa$_2$Cu$_3$O$_{7-\delta}$ and Ammonium Terbium Oxalate, Tb(H$_2$O)(C$_2$O$_4$)$_2$·NH$_4$. The composite has a transition temperature about 92 K, and it presents a reentrant behaviour resulting of the coexistence between superconductivity and magnetism. According to this study the values and shape of the critical magnetic fields were dramatically reduced in a similar form as in other known reentrant superconductors.

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I. INTRODUCTION

Among the many interesting characteristics of some superconductors, reentrant behaviour in superconductivity is a quite important topic of study. Some superconductors displaying this behaviour are those that have a magnetic ion in its crystal structure. A classical example very well known is ErRh$_4$B$_4$, it is a reentrant compound found by Ferting many years ago [1]. Many others were discovered with this characteristic [2–4]. The physics related to the reentrant process occurs because the competition between superconductivity and magnetism. This phenomenon is actual and important topic of study, it was first addressed by Ginzburg [5], he studied the possibility of coexistence of superconductivity and ferromagnetic materials. Quite important to mention is that in BCS theory these two phenomena are antagonist and mutually excludents. In BCS the phenomenon arises by the creation of Cooper pairs mediated by virtual phonons connecting the two electrons and resulting in ordered antiparallel spins; the BCS manner of Cooper pairs formation. If paramagnetic impurities are in the superconducting bulk those magnetic ions could break Cooper pairs, destroying superconductivity, depending on the strength of the magnetic interactions, then a new spins ordering will be arises. This new arrange causes breaking of pairs because a type of ferromagnetic order; parallel spins, and the resulting parallel configuration will bring the destruction of the superconducting state; thus, reentrant superconducting behaviour will arise.

In a possible reentrant superconductor, if the intensity of the magnetic interactions are strong enough will affect and influence the behavior of the superconducting state. Accordingly, the magnetic interactions could give additional information to have a better understanding of a superconductor and in that manner to obtain more insight into the microscopic mechanisms and electronic properties. Then some of the basic phenomena related to the coupling and formation of the Cooper pairs will be related to this elementary excitations.

The reentrant behavior in superconductors is well know since early times. As mentioned it may occur when a superconductor is doped with paramagnetic impurities, the interplay results in pair breaking and total destruction of superconductivity. This phenomenon has been explained by Abrikosov and Gor‘kov [6], they study the interplay introducing the form that magnetic ions play an important role in the exchange interaction of both conducting electrons an magnetic ions [4, 7, 8].

As was mentioned, in BCS theory the two phenomena are mutually excludents. In many compound, however recently it has been observed that more types of superconductors involved different forms of pair formation, meaning that the nature of pair coupling will be different to the mediated by phonons. Thus, the superconducting state will be different as in the BCS model. Among those new materials, the Fe-Based compounds are a type of the new materials [9]. New studies by different researchers in the superconducting field have discovered many new example of these materials not following BCS theory, with different manners to form the Cooper pairs mediated with different processes of coupling.

The effect of the influences of a magnetic field in a superconductor is most notable at temperatures below the superconducting transition. In this situation the influence of the magnetism is quite clear because the transition temperature decreases due to the diminution of the number of Cooper pairs. The most clear consequence of these interactions between superconductivity and magnetic field results in the reentrant superconducting behavior. These interactions create a competition between both, magnetism and superconductivity, growing and reinforcing with decreasing temperature, although those changes will be at different rates. Depending of the strengths and magnitude of those processes, one or the other could be predominant. In some cases the superconducting state could be destroyed or simply reduced.
In other situations the two interacting energies, one to create Cooper pairs, the other to energize magnetic interchanges could be in equilibrium [7]. Those processes are very dependent on temperature. Normally, the energy for Cooper pairs formation increases when the temperature decreases, but this is not always the case for the ferromagnetic interactions, it can be decreases, or increases depending on many factors; i.e. type of crystal structure, type of different transitions, and or other modification related with temperature. Accordingly in some materials the superconducting pair will be only reduced. The reentrant characteristic in superconducting materials was for the first time observed by Ferting [1] in the compound \( \text{ErRh}_4\text{B}_4\). Posteriorly it was seen in other compounds as \( \text{HoMo}_6\text{Se}_{8} \) [2], also in \( \text{HoNi}_2\text{B}_2\text{C} \) [3, 4], and in others.

In this research we present a study of the reentrant behaviour in a composite formed by a ceramic superconductor and a luminescent material. The experiments were carried out using \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) particles and two luminescent materials; \( \text{Tb(H}_2\text{O})(\text{C}_2\text{O}_4)_2\cdot\text{NH}_4 \), or \( \text{Y}_2\text{O}_3:\text{Eu}^{3+} \). Two composites to different proportions in weight between its components were prepared. Both were characterized by magnetic susceptibility as function of temperature and magnetic field applied. Only the composite \( \text{YBCO} - \text{Tb(H}_2\text{O})(\text{C}_2\text{O}_4)_2\cdot\text{NH}_4 \) presents reentrant superconductivity. The critical fields were evaluated in the composite 10% superconductor - 90% Tb oxalate and we found a drastic reduction of them due to the coexistence between superconductivity and magnetism. Initially idea of the research was to study the influence of the luminescent materials into the superconductor under UV illumination at low temperatures.

### A. EXPERIMENTAL PROCEDURE

The materials used for this investigation were a ceramic superconductor and two different luminescence materials. The ceramic superconductor, YBCO, presents a high transition temperature, \( T_C = 92 \text{ K} \), and the amount of superconducting material was determined by two modes of measurements, Zero Field Cooling (ZFC) and Field Cooling (FC) under small magnetic field, 100 Oe. The two luminescence compounds were Ammonium Terbium Oxalate, \( \text{Tb(H}_2\text{O})(\text{C}_2\text{O}_4)_2\cdot\text{NH}_4 \), and Yttrium-Europium Oxide, \( \text{Y}_2\text{O}_3:\text{Eu}^{3+} \) [10, 11]. The use of these two compounds is because they are excellent photoluminescence materials.

The composites were prepared using the ceramic superconductor and one luminescent material; \( \text{YBCO} - \text{Tb(H}_2\text{O})(\text{C}_2\text{O}_4)_2\cdot\text{NH}_4 \), and \( \text{YBCO} - \text{Y}_2\text{O}_3:\text{Eu}^{3+} \). Only the composite with ammonium terbium oxalate gave a reentrant characteristic.

The preparation of the ceramic superconductor was using a known procedure as already published in the literature, starting from \( \text{BaCO}_3 \), \( \text{Y}_2\text{O}_3 \), and \( \text{CuO} \) [12]. Subsequently, the ceramic was grounded and suspended in high pure acetone to evaluate the particle size according to precipitation time. Only we used particles in range about 500 and 350 nm.

The composites were prepared by homogeneous precipitation method, starting from a aqueous solution of rare-earth nitrates, ammonium oxalate and a certain amount of superconducting particles. This solution was ultrasonically dispersed for 30 minutes in a sealed flask. After, the solution was heated at 75° C for two hours with magnetic stirring. The resulting mixture was washed three times with 30 ml of pure acetone to remove the ammonium oxalate excess. Finally, the resulting compounds were dried at 60° C. Only in the case of \( \text{YBCO@Y}_2\text{O}_3:\text{Eu}^{3+} \) composite it was heated at 400° C for five minutes. With this procedure both, yttrium and europium nitrates, trans-
forms to oxides.

II. RESULTS AND DISCUSSION

As above mentioned the main idea of this research was to study the influence of luminescent compounds in the superconducting properties.

The characteristics of the ceramic superconductor are shown in Fig. 1, top figure. There we also display the characteristics of the composite formed with the Tb oxalate at different compositions Superconductor - Tb oxalate: 10:90 and 15:85 (in weight). In these three figures the data was obtained in two modes of measurements, ZFC and FC. At low temperature is seen the reentrant behaviour, both middle and bottom figure show in the

FIG. 2: (Color on-line) $\chi(T)$ measurements for the composite YBCO - Tb(H$_2$O)(C$_2$O$_4$)$_2$ · NH$_4$ at 100 Oe. The amounts of superconducting material are 10, 15, 100%.

FIG. 3: (Color on-line) Isothermal magnetic measurement, $M - H$, in mode ZFC from 2 to 110 K for composite Super:Tb oxalate 10:90%. This figure shows the decreasing of the critical fields $H_{C1}$ and $H_{C2}$ with temperature.

FIG. 4: (Color on-line) The critical fields of one composite with 10% superconductor and 90% Tb oxalate. The graphs were plot using data of Fig 3. The critical fields were determined in a conventional manner. Note the dramatic reduction and shape of them. This is clearly due to the coexistence between superconductivity and magnetism in the composite. In this case the calculation of $\kappa$ was quite reduced at a value around 1.6 in comparison to $\kappa \geq 70$ in YBa$_2$Cu$_3$O$_7$ single-crystal [13]. The dotted lines are a guide for the eye.

FIG. 5: (Color on-line) Magnetization - Temperature (MT) in ZFC mode at H=100 Oe in YBCO - Y$_2$O$_3$:Eu$^{3+}$ composite. This composite is not reentrant as mentioned in the main text. Note also that in this figure in black dots, the pure ceramic superconductor has an upturn at low temperatures which is due to ferromagnetism because surface oxygen vacancies, as was mentioned by other authors [14, 15].
two modes of measurements the reentrance characteristic. In Fig. 2, the main figure and the inset shows only the ZFC measurement. The three curves show three different compositions in the composite. The inset shows that 10, and 15 % of superconductor are reentrant.

Figure 3 shows the isothermal $M - H$ characteristics from 2 to 110 K for the composite YBCO - Tb(H$_2$O)(C$_2$O$_4$)$_2$·NH$_4$ with composition 10:90%. From this figure we obtained the variation with temperature and magnitudes of the critical fields $H_{C2}$ and $H_{C1}$. Fig. 4 presents the behaviour of the critical fields, note the curvature at low temperatures. These curvatures marks the temperature when the external magnetic field energy initiate the breaking the superconducting behavior. This shape is the remarkable characteristic in reentrant superconductors and is when both phenomenons coexist; superconductivity and magnetism [17–19].

It is interesting to mention that these results extracted from Fig. 3 and plotted in Fig. 4 indicate that the magnitude of the critical fields shows a dramatically reduction, with magnitudes as small as $\approx 300$ Oe and 2 kOe for $H_{C1}$ and $H_{C2}$, respectively. Accordingly, the critical second magnetic field is enormously reduced. This is perhaps the most important discovery in this new reentrant superconducting composite. Evaluating the Ginzburg-Landau parameter from Fig. 4, it was quite reduced at around 1.6 in comparison to $\kappa \geq 70$ in YBa$_2$Cu$_3$O$_{7-\delta}$ single-crystal [13].

On the other hand, in Fig. 5 is shown the $\chi(T)$ characteristic in the YBCO - Y$_2$O$_3$:Eu$^{3+}$ composite. In it was not seen reentrant behaviour. In this composite we show different proportions of superconducting material from 10 to 100% and it never becomes reentrant, perhaps because the magnetic response of the Y oxide is smaller than in the Tb oxalate. An additional observation related to the behavior in the pure ceramic superconductor, black dots of Fig. 5, is that at low temperatures it seen an upturn in $\chi(T)$ which we attributed to defects and oxygen vacancies on the surface of the superconductor, this has been also observed by other researchers [14–16]. Lastly in Fig. 6 is displayed an electron microscopy picture of the composite YBCO - Tb oxalate. In there, white areas are particles of YBCO, while the grey areas are the Tb oxalate.

In order to have a better information of the Tb oxalate, in Fig. 7 we show the magnetic characteristics. Top figure is the magnetic susceptibility, $\chi - T$ determined at 5 Tesla in ZFC and FC modes. The bottom figure displays isothermal measurements determined at temperatures from 1.7 to 300 K. Tb oxalate is superparamagnetic with a blocking temperature $\approx 18$ K.

III. CONCLUSIONS

We found a new reentrant superconductor formed by a Hight-$T_c$ superconductor and a luminescent material.
Two composites were prepared with different luminescent compounds, the composite with ammonium terbium oxide presented reentrant behavior. According to this study values and shape of the critical magnetic fields, $H_{C1}$ and $H_{C2}$, were dramatically reduced, implying that the Ginzburg-Landau parameter ($\kappa$) has a small value of 1.6 in the composite 10:90%. We concluded that the reentrant behavior is because the coexistence between superconductivity and magnetism in the composite. As mentioned before the main idea of this study was to see the influence of a superconductor in the luminescent properties, as already published by other authors in MgB$_2$ [20], but however the investigation was deviated to study this new characteristics.

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