

Crystal field, cluster formation and percolative superconductivity in $\text{ErBa}_2\text{Cu}_3\text{O}_x$

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ABSTRACT

Inelastic neutron scattering has been employed to study the crystal-field excitations of Er^{3+} in $\text{ErBa}_2\text{Cu}_3\text{O}_x$ ($6 < x < 7$). The lowest-lying crystal-field state exhibits a most unusual behavior versus the oxygen content x , which we interpret in terms of cluster formation in the superconducting CuO_2 planes. Three different cluster types are identified corresponding to local regions of semiconducting and metallic ($T_c \approx 60$ K, $T_c \approx 90$ K) character. The superconductivity is shown to result from the formation of a two-dimensional percolative network. A two-dimensional bond percolation model correctly predicts the critical oxygen contents associated with the two-plateau structure of T_c .

1. INTRODUCTION

It has been realised that the oxygen stoichiometry and oxygen defect structure are crucial quantities determining the occurrence or disappearance of superconductivity in the perovskite-type compounds $\text{RBa}_2\text{Cu}_3\text{O}_x$ (R denotes yttrium and most rare earths, $6 \leq x \leq 7$). The superconductivity of annealed samples exhibits a two-plateau structure of T_c versus x . $T_c = 90$ K superconductivity is found for $7.0 \geq x \geq 6.8$. T_c then decreases to 60 K, where it remains up to $x \approx 6.5$. For $x < 6.5$ the superconductivity deteriorates and is completely lost for $x < 6.4$. It is now generally believed that the superconducting properties are related to both the oxygen concentration and the oxygen ordering in the basal plane. Another important feature is the effect of phase separation which generates a coexistence of two different structural phases. While the disappearance of the superconductivity correlates almost exactly with the recently reported phase separation effects at $x \approx 6.4$ [1], the jump of T_c from 90 K to 60 K at $x \approx 6.8$ cannot be reconciled with the available structural data.

It is now well known that the variation of the oxygen concentration x results in charge redistributions in the superconducting CuO_2 planes. In our earlier work on $\text{HoBa}_2\text{Cu}_3\text{O}_x$ [2] and $\text{ErBa}_2\text{Cu}_3\text{O}_x$ [3,4] we have been able to observe these charge redistributions directly by means of neutron crystalline-electric-field (CEF) spectroscopy. The R^{3+} ions are sandwiched between the CuO_2 planes and thus constitute local probes that are susceptible to charge redistributions through the CEF potential experienced by the 4f electrons. We have put forward the idea that the energy spectra observed for $\text{RBa}_2\text{Cu}_3\text{O}_x$ are the result of a superposition of different local CEF spectra, and we have been able to account for the experimental data by a local symmetry model based

on combined statistical and geometrical considerations [2-4].

In the present work we provide new experimental data of the CEF interaction in $\text{ErBa}_2\text{Cu}_3\text{O}_x$ which clearly prove the formation of three different types of clusters in the superconducting CuO_2 planes. In particular, the observed energy spectra are interpreted as a superposition of two different metallic components and a semiconducting one, the relative weight of each component being extremely dependent upon the oxygen concentration x . The superconductivity can be shown to result from the formation of a two-dimensional percolative network, with the two-plateau structure of T_c being directly related to the variation of the proportions of the different cluster types versus the oxygen content x .

2. EXPERIMENTAL

The polycrystalline $\text{ErBa}_2\text{Cu}_3\text{O}_x$ samples were the same as those used in previous inelastic neutron scattering (INS) experiments [5-7]. The starting material was prepared by a standard sintering procedure. We treated the powdered material by a temperature controlled desorption-absorption procedure to yield the final oxygen contents of $x=6.09, 6.34, 6.45, 6.53, 6.78, 6.91$ and 6.98 . The samples were annealed from 920°C to room temperature at a rate of $1^\circ\text{C}/\text{min}$, but the cooling was interrupted for 5 hours every 200°C . Neutron diffraction proved the crystallographic single-phase character of the samples, and the two-plateau structure of T_c was established by DC magnetic susceptibility measurements.

The INS experiments were performed with use of the time-of-flight spectrometer IN4 at the high-flux reactor of the Institut Laue-Langevin at Grenoble with an incident neutron energy of 17.21 meV. Using a very good collimation we achieved an instrumental resolution (FWHM) of 0.3 meV for energy transfers $7 \leq \Delta E \leq 11$ meV. The samples were enclosed into cylindrical aluminum containers of 10 mm diameter and 50 mm height which were mounted in a helium cryostat to achieve temperatures $T > 10$ K. The raw data have been corrected for absorption, detector efficiency, background and phase space effects by standard procedures.

3. RESULTS

In our previous work [5-7] we have been able to observe all the seven excited CEF states of Er^{3+} in $\text{ErBa}_2\text{Cu}_3\text{O}_x$ resulting from the decomposition of the 16-fold degenerate ground-state J-multiplet $^4I_{15/2}$ due to the CEF interaction of either orthorhombic or tetragonal symmetry. The ground-state CEF excitations were found to be separated into a low-energy window ($\Delta E < 12$ meV) and into a high-energy window ($\Delta E > 65$ meV). All the CEF transitions were characterized by a monotonic behavior of their energies and intensities versus the oxygen content x , with the exception of the lowest-lying CEF state which was found to behave in a rather anomalous way. Therefore we investigated the low-energy CEF excitations of $\text{ErBa}_2\text{Cu}_3\text{O}_x$ in more detail under improved resolution conditions as discussed below.

Some of the observed energy spectra covering the ground-state transitions to the three lowest CEF states of $\text{ErBa}_2\text{Cu}_3\text{O}_x$ are shown in Fig. 1. The evolution of the scattering versus the oxygen content x behaves differently for the three CEF transitions A, B and C. While the energies of the CEF transitions B and C are almost independent of x and their intensities are slowly increasing when going from $x=7$ to $x=6$, the x -dependence of the CEF transition A exhibits a most unusual behavior: not only do we observe a major shift to lower energies and a significant decrease of the line intensity upon lowering the oxygen content x , but also is there evidence for real substructures associated with the CEF transition A. More specifically, the CEF transition A appears to be decomposed into three individual transitions A_1 , A_2 and A_3 , whose spectral weights distinctly depend on the oxygen content x .

4. DATA ANALYSIS

We have least-squares fitted the observed energy spectra to the conventional CEF model based on the previously derived CEF parameters [5,7]. The relative strengths of the lines A ($A = A_1 + A_2 + A_3$), B and C and their centers of gravity are determined by the transition

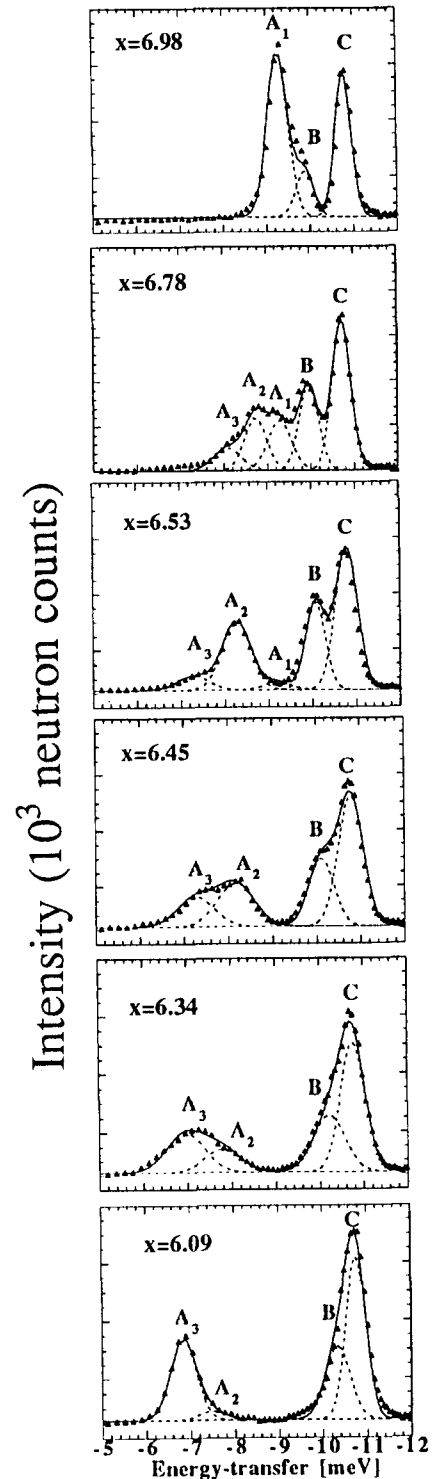


Fig. 1: Energy spectra of neutrons scattered from $\text{ErBa}_2\text{Cu}_3\text{O}_x$ at $T=10\text{K}$. The lines are the result of a least-squares fitting procedure as explained in the text.

matrix elements and energies resulting from the CEF parameters, respectively. The only fitting parameters are then a scaling factor for the intensity, two line width parameters (one for the transitions A_i and one for the transitions B and C) and three positional parameters for the CEF transitions A_i . All the transitions are approxi-

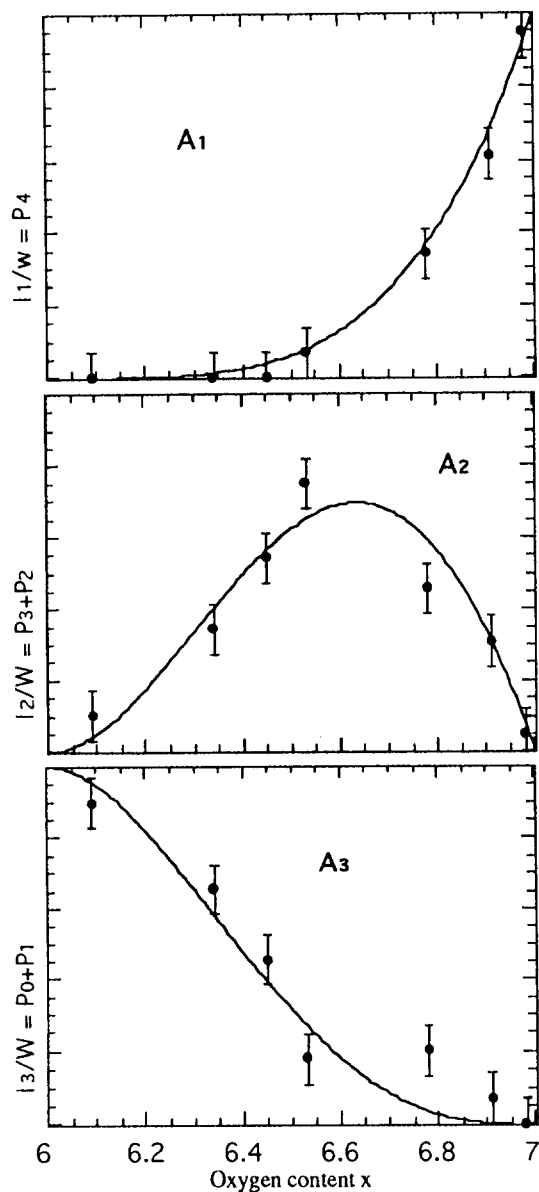


Fig. 2: Proportions of the lowest-lying CEF transitions A_i of $\text{ErBa}_2\text{Cu}_3\text{O}_x$ as a function of the oxygen content x . The lines refer to geometrical probability functions as explained in the text.

mated by Gaussian functions. We arrive at a decomposition of the observed energy spectra as indicated by the dashed lines in Fig. 1 which are found to be in excellent agreement with the experimental data. We immediately recognize that the transitions A_1 , A_2 and A_3 have maximum weight close to $x=7.0$, $x=6.5$ and $x=6.0$, respectively. With the CEF interaction being a local probe, there is no doubt that the above substructures originate from different local environments of the Er^{3+} ions which obviously coexist in the compound $\text{ErBa}_2\text{Cu}_3\text{O}_x$.

Our data and their interpretation provide clear experimental evidence for cluster formation. It is tempting to identify the three clusters associated with the transitions A_1 , A_2 and A_3 by two local regions of metallic ($T_c \approx 90$ K, $T_c \approx 60$ K) and a local region of semiconducting character, respectively. From our analysis it is straightforward to determine the x -dependent fractional proportions of the three cluster types as displayed in Fig. 2, however, care has to be taken of the variation of the transition probability of the lines A_i versus the energy transfer.

5. DISCUSSION

Our current understanding of the superconducting properties of $\text{ErBa}_2\text{Cu}_3\text{O}_x$ (and more generally all the $\text{RBa}_2\text{Cu}_3\text{O}_x$ compounds) involves a percolation mechanism of electric conductivity as recently discussed in both theoretical [8] and experimental [9] work. For $x=6$ the system is a perfect semiconductor. When adding oxygen ions into the chains, holes are continuously transferred into the CuO_2 planes[5,7]. By this mechanism the number of local regions with metallic character (associated with the CEF transition A_2) rises, which can partially combine to form larger regions. For some critical concentration a percolative network is built up, and the system undergoes a transition from the semiconducting to the conducting state (with $T_c \approx 60$ K). Upon further increasing the hole concentration a second (different) type of metallic cluster (associated with the CEF transition A_1) is formed which start to attach to each other and at the percolation limit induce a transition into another conducting state (with $T_c \approx 90$ K). For a two-dimensional square structure the critical concentration for bond percolation is $p_c = 50\%$ [10]. From the fractional proportions of A_2 and A_1 displayed in Fig. 2 we can then immediately determine the critical oxygen concentrations for the transitions from the semiconducting to the $T_c \approx 60$ K-superconducting state and to the $T_c \approx 90$ K-superconducting state to be $x_2=6.42$ and $x_1=6.86$, respectively, which is in excellent agreement with the observed two-plateau structure of T_c .

Combined statistical and geometrical considerations may be useful to understand the x -

dependent profiles of the fractional proportions of the three cluster types visualized in Fig. 2. In earlier publications [2-4] we have developed a local symmetry model and defined the probabilities $P_k(x)$ to have, for a given oxygen content x , k of the four oxygen chain sites $(0,1/2,0)$, $(1,1/2,0)$, $(0,1/2,1)$ and $(1,1/2,1)$ nearest to the Er^{3+} ion occupied. The fractional proportion of the cluster type A_1 exhibits the behavior predicted by the probability function $P_4(x)$ (i.e., all the oxygen chain sites being occupied). Similarly, the fractional proportions of the cluster types A_2 and A_3 follow the sum of the probability functions $P_3(x)+P_2(x)$ (i.e., one or two empty oxygen chain sites) and $P_1(x)+P_0(x)$ (i.e., one or none oxygen chain site being occupied), respectively. The above probability functions are shown in Fig. 2 by solid lines which excellently reproduce the experimental data.

6. CONCLUSION

We emphasize the role of neutron CEF spectroscopy among all experimental techniques as a unique and powerful tool to probe directly the local electronic configurations of the high- T_c perovskite-type compounds. Any attempts to unravel cluster formation effects in these compounds, for example by diffraction measurements, are likely to fail due to the rather small localization range anticipated for the different clusters. Indeed, a recently proposed ferromagnetic cluster model[8] predicts the local phases in the $\text{RBa}_2\text{Cu}_3\text{O}_x$ compounds to include only five plane copper ions, i.e., the localization range is restricted to a few unit cells only. While the semiconducting to metal transition may also be understood and related to the recently reported phase separation effects at $x \approx 6.4$ [1], the coexistence of two different types of metallic clusters can only be detected by local probes such as neutron CEF spectroscopy as outlined in the present work.

Financial support by the Swiss National Science Foundation is gratefully acknowledged.

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