Title
SYSTEMATICS OF COMPLEX FRAGMENT EMISSION IN NIOBIUM INDUCED REACTIONS

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Almost from the time the 90K superconducting transition was first observed[1] in $YBa_2Cu_3O_{7-x}$ (YBCO), various phenomena suggestive of superconductivity at much higher temperatures, frequently in the range 200-240K, have been reported. More recently there has been a growing recognition of the importance of both the oxygen content and the ordering of the oxygen vacancies in determining superconducting properties. On page xxx of this issue, Laegreid et al. report[2] calorimetric evidence for an ordering process that occurs near 220K and is correlated with the occurrence of superconductivity. The magnitude of the specific heat anomaly at 220K is approximately proportional to the "discontinuity" in specific heat at 90K, the latter being taken as a measure of the completeness of the transition to the superconducting state. Although different interpretations of the 220K anomaly are possible at this time, it seems clear that the anomaly will provide a clue to the nature of the superconductivity in this interesting and important system.

Specific heat measurements have generally been regarded as the ultimate test for distinguishing bulk superconductivity from superconducting filaments, which might occupy only a small fraction of the sample volume. Measurements of resistivity or, to a lesser degree, of magnetic susceptibility can be misleading in this respect, but a measurement of the specific heat gives the average of that property over the whole volume of the sample. The electronic specific heat, C_e, of a BCS superconductor that exhibits a sharp transition to the superconducting state is represented in Figure 1. In the normal state, realized in fields that exceed the critical field, the specific heat is $C_{en} = \gamma T$, where γ is a constant proportional to the density of electronic states at the Fermi level. In the superconducting state, there is a discontinuity, $\Delta C(T_c)$, at the critical temperature, T_c, and at lower temperatures the specific heat, C_{es}, has an approximately exponential dependence on temperature. The linear term characteristic of the normal state is absent and $C_{es}/T \rightarrow 0$ as $T \rightarrow 0$. The exponential temperature dependence of C_{es} reflects the condensation of the electrons into Cooper pairs and the consequent development of a gap in the density of states.

In principle, the completeness of the superconducting transition could be determined either by measuring $\Delta C(T_c)$ (which is proportional to the fraction of the sample that goes superconducting) or by looking for a residual linear term $\gamma' T$, in zero applied field (which is proportional to the fraction that remains normal). Both methods depend on a knowledge of γ. The former is rendered uncertain, even for BCS superconductors, by the variation of $\Delta C(T_c)$ from the weak-coupling limit, $1.43\gamma T_c$, to as much as $2.5\gamma T_c$ in cases in which the coupling is strong. For the new high-T_c materials in particular there are several problems associated with the application of these criteria: (1) In addition to C_e the quantity measured always includes the lattice specific heat, C_1. Because T_c is so high, C_1 is by far the larger contribution at T_c and $\Delta C(T_c)$ is only of the order of 1% of the total specific heat. This difficulty in determining $\Delta C(T_c)$ can be alleviated by measuring C both in zero magnetic field and in a field large enough to suppress the superconducting transition by several degrees. (2) The transitions observed to date are relatively broad, and $\Delta C(T_c)$ must be determined by a construction similar to that in Fig. 2 of the paper[2] by Laegreid et al. (3) At low temperatures the critical field is very high, of the order of 100T, and γ has not been measured directly.

Furthermore, for the new superconducting oxides there are special reasons to think that a linear term in the specific heat in zero field is not necessarily an indication of an incomplete transition to the superconducting state. The electron-phonon coupling which is generally believed to be the basis for the attractive interaction between electrons that leads to superconductivity in all other materials (heavy-fermion compounds possibly excepted) may not be able to account for the superconductivity of the new materials. Other mechanisms are being considered. For one of these, the resonant-valence-bond, RVB, model[3], the superconductivity is "gapless", the temperature dependence of C_{es} differs from that of the BCS theory, and a linear term in C_{es} is an intrinsic property of the superconducting state. Another possible origin of a linear term is the existence of "two-level-systems", TLS, as suggested by sound-velocity data[4]. These TLS are associated with double minima in the potential energy of an atom (presumably oxygen atoms in YBCO) between which tunneling can occur, and are responsible for the well known linear term in the specific heat of amorphous materials. To date, all specific heat measurements on YBCO and on the superconducting lanthanum-alkaline earth-copper oxides show a linear term in the specific heat in zero field. These linear terms <u>can</u> be accounted for on the basis of incomplete transitions to the superoconducting state, but other origins such as TLS or the gapless superconductivity of the RVB model are certainly not ruled out. In the case of the lanthanum oxides the wide variation in the values of γ' suggests that they arise at least in part from residual normal material, but for YBCO there are a number of reports of γ' values in the range 6-8 mJ/mole K^2. The small variation in γ', apparently independent of oxygen content, might be taken as support for the RVB model. However, it is clear that the answer to the question of the origin of the zero-field linear term must await further measurements on well characterized samples.

Laegreid et al. do not report[2] low-temperature data and γ' is therefore unknown for their samples. The data for sample UK1 near 90K show a transition width similar to those observed in careful measurements in other laboratories, but a relatively low value of $\Delta C(T_c)$. Their sample B39/2, for which $\Delta C(T_c)$ is substantially greater (but for which the data are not shown) would appear to be more like the "best" samples that have been studied elsewhere. It is therefore reasonable, for the purpose of comparison with the 220K anomaly, to take their values of $\Delta C(T_c)$ (ΔC_p in their notation) as a measure of the extent or "quality" of the superconducting transition.

Laegreid et al. discuss a number of possible origins[2] of the 220K specific heat anomaly, and conclude that the most likely explanation lies in the ordering of the oxygen system. As they note, there now exists considerable evidence that it is ordering of the oxygen in the CuO chains that is important for superconductivity. Furthermore, it is clear that high oxygen content favors good superconducting properties. The authors do not propose a model that relates the ordering to their specific heat results, but since they observe a larger 220K anomaly for the better samples, one must infer that the entropy change associated with ordering is greater in the samples with the higher oxygen content. However, since the samples with lower oxygen content have a larger number of oxygen vacancies, one might have naively expected a greater entropy change for those samples.

The antiferromagnetic ordering in other copper oxides affords another interesting comparison with the 220K anomaly. It is known[5] that CuO orders magnetically at ~230K. (Because the molal entropy change associated with the ordering in CuO is about the same as that associated with the 220K anomaly in YBCO, it is not possible to attribute this anomaly to CuO impurities). Furthermore, there is evidence for antiferromagnetic ordering in La_2CuO_4 at similar temperatures[6], although the Neel temperature is a strong function of oxygen content. For both La_2CuO_4 and CuO the magnetic moment per copper atom is ~0.4 to ~0.5μ_B, quite different from larger moments associated with conventional antiferromagnetic ordering in ionic copper salts. In spite of the differences in chemical composition and crystal structure among these compounds, and in spite of the lack of clear-cut magnetic evidence in the case of YBCO, one should consider the possibility of antiferromagnetic ordering as the origin of the 220K anomaly in that material.

It may well be the case that oxygen ordering rather than antiferromagnetism or some other ordering phenomenon explains the anomaly observed by Laegreid et al[2]. More investigation will be necessary before we can be certain. There is little question, however, that the discovery of the 220K specific heat anomaly in YBCO provides another piece of evidence which will be useful in unraveling the riddle of high temperature superconductivity.

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Figure Caption

The electronic specific heat of a BCS superconductor in the normal and superconducting states.

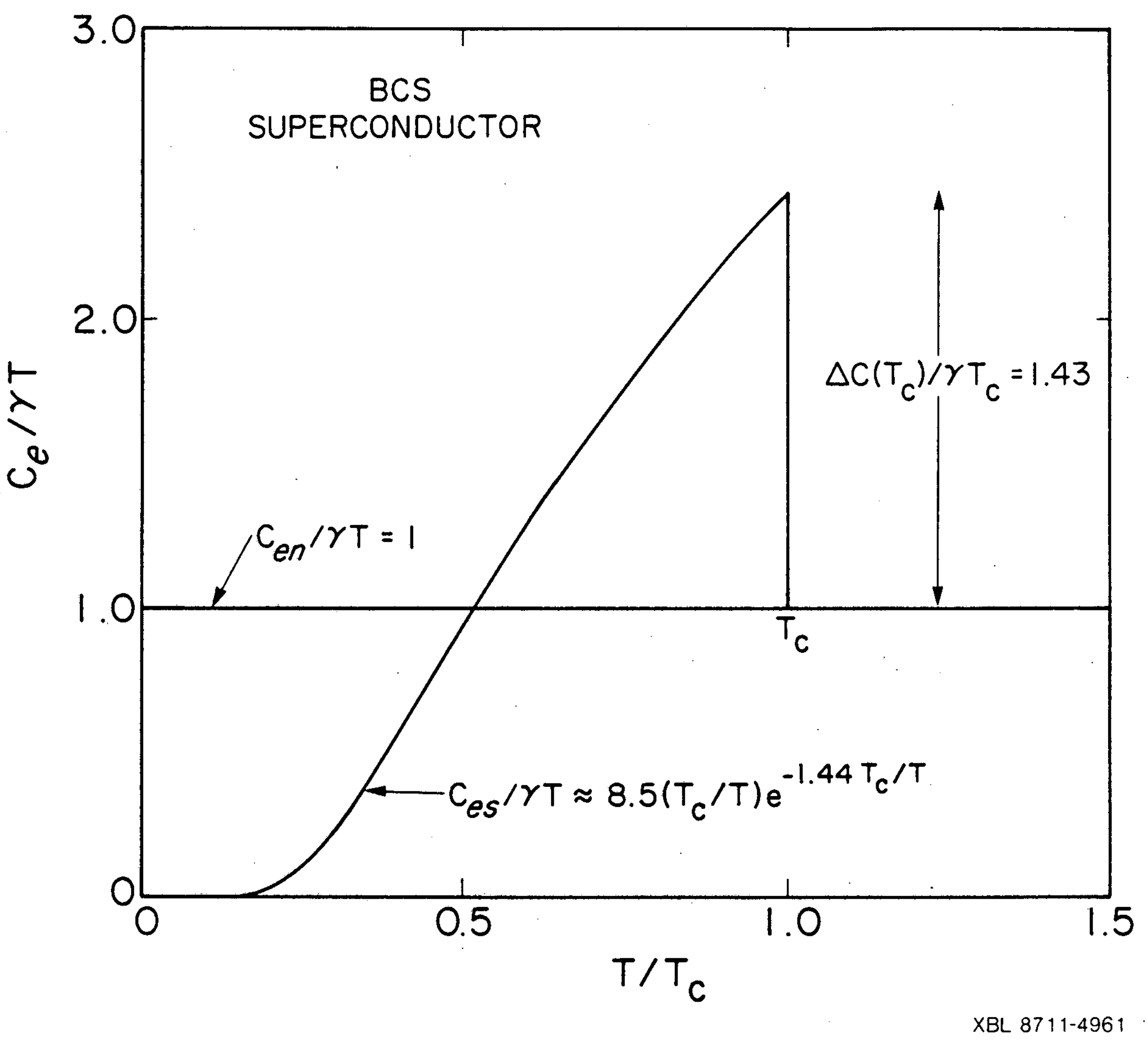
BCS
SUPERCONDUCTOR
3.0
2.0
1.0
0
0
0.5
1.0
1.5
$C_e/\gamma T$
T/T_c
$C_{en}/\gamma T = 1$
T_c
$\Delta C(T_c)/\gamma T_c = 1.43$
$C_{es}/\gamma T \approx 8.5(T_c/T)e^{-1.44\,T_c/T}$
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Fig. 1

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