PHYSICAL PROPERTIES OF SINGLE-PHASE HIGH-T_c SUPERCONDUCTOR YBa$_2$Cu$_3$O$_7$

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Transport and thermodynamical properties as well as structural investigations in the well-characterized 90 K-class high-T_c superconductor YBa$_2$Cu$_3$O$_7$ are presented, especially in relation to the fundamental mechanism of the high-T_c superconductivity. High-precision specific heat measurements around $T_c = 91.8$ K reveal that the value of $\Delta C/T_c$ is 48 ± 2 mJ/mol K^2. This value results in the fact that the value of $\Delta C/\gamma T_c$ is 1.33, which is close to 1.43, the weak-coupling BCS value, provided that the coefficient, γ, of the linear term in the specific heat is 36 ± 2 mJ/mol K^2.

1. Introduction

Recently, there has been an explosive number of papers on high-T_c superconductivity around 40 K in La$_{2-x}$(Ba, Sr, Ca)$_x$CuO$_{4-y}$ systems, subsequently above 90 K in (RE)Ba$_2$Cu$_3$O$_7$ systems, where (RE) means most of the rare-earth elements. These activities were undertaken not only because of the importance for practical applications but also because of the fundamental question whether the electron–phonon interaction is responsible for the high-T_c superconductivity or not. Although the theoretical calculations of T_c values are not so accurate, the observed T_c value seems to be too high to be accounted for by ordinary electron–phonon coupling mechanisms. In addition, some unusual phenomena in these systems are known to exist. First of all, the superconducting properties are closely related to magnetism, indicating that magnetic interaction may be involved in the superconductivity. Be-

sides that, physical parameters which characterize the superconducting state are highly anisotropic, suggesting a highly anisotropic electronic structure in this system. Next, yttrium can be replaced by most of the rare-earth elements without any effect on T_c, even though they are strongly magnetic. In the case of GdBa$_2$Cu$_3$O$_7$, antiferromagnetic ordering below 2.23 K has been observed [1], which coexists with the high-T_c superconducting phase. Moreover, by neutron diffraction experiments, thermal vibrations of certain oxygen atoms are very pronounced, which is also predicted by the strong temperature dependence of the Debye temperature deduced from specific heat experiments [2]. Finally, a linear temperature dependence of the resistivity up to around 750 K without an appreciable residual resistivity [3], occurrence of precursor effect of the superconductivity well above T_c and an anomalous upturn in the specific heat at low temperatures are noteworthy in YBa$_2$Cu$_3$O$_7$.

So far, many approaches have been proposed to account for high-T_c superconductivity by taking into account the specific features of this compound. From an experimental point of view, it is most important to establish the fundamental parameters with sufficient accuracy in well qualified samples in order to compare them with available theories.

It is the purpose of this paper to report our recent studies on electrical, magnetic, transport and thermodynamical as well as structural properties in well-characterized samples.

2. Sample preparation and characterization

All samples for the present experiments were prepared by a standard ceramics technique as described previously [4].

The samples were checked by X-ray powder analysis and confirmed to be of a single-phase orthorhombic structure. Some of the samples were also investigated by thermal neutron scattering experiments at ECN (Energy Research Center, Petten, The Netherlands). A small amount of BaCuO$_2$ (<1%) as a main impurity phase as well as very weak lines, which could be assigned to unreacted BaO and Y$_2$O$_3$, were detected. The lattice parameters determined by neutron measurements are $a = 3.8235(1)$Å, $b = 3.8858(1)$Å and $c = 11.6762(6)$Å, in good agreement with previous work [5–6]. Highly ordered oxygen vacancies in a peculiar structure were confirmed. The importance of the oxygen atoms in a certain ordered manner in the unit cell has been stressed [7]. The number of oxygen atoms in a unit cell was determined to be in the range from 6.95 to 7.00.

3. Electrical resistivity

The resistivity was measured by a conventional ac as well as a dc four-points method. The contacts were made with a silver epoxy-type of glue.

One example is shown in fig. 1. In the inset, the detailed behavior around T_c is shown. In

general, the absolute value of the resistivity strongly depends on the preparation methods. As long as the sample is treated under the same conditions described above, the main factor seems to be the density of the sample, indicating that porosity and grain boundary effects are dominant. If the material is partially melt, the sample becomes harder and denser but the resistivity does not improve and the second phase becomes appreciable in the X-ray pattern. A typical value of the resistivity is roughly between 350 μΩcm and 1000 μΩcm at room temperature, but the intrinsic resistivity is expected to be significantly lower. In fig. 1, a remarkable case is shown with a resistivity of only 350 μΩcm at room temperature and 127 μΩcm at 100 K due to an improved heat-treatment and additional densification. These numbers are comparable to the transition metal alloys and intermetallics. The superconductivity occurs at $T_c = 91$ K with the width $\Delta T_c = 0.9$ K. The calculated density of this sample was as high as 86% of the theoretical density.

The temperature dependence of the resistivity is approximately expressed by $\rho(T) = BT$ in a wide temperature range between 120 K to 750 K with a temperature coefficient, $B = 1.0 \sim 1.2$ μΩcm/K. Above 750 K the resistivity increases more rapidly [8].
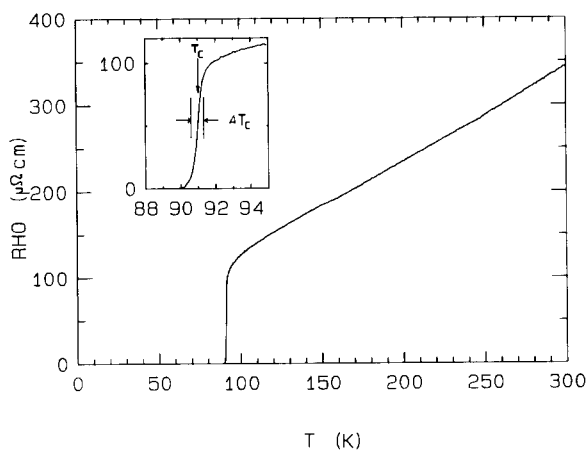

Fig. 1. Temperature dependence of the ac-electrical resistivity of YBa$_2$Cu$_3$O$_7$. The inset shows the resistivity around its superconducting transition temperature $T_c = 91.0$ K. The width defined by 10% and 90% of the resistivity is 0.9 K.

4. Susceptibility

Temperature dependence of ac- and dc-susceptibility were measured in the normal state as well as in the superconducting state in several samples with different heat-treatments. The Curie–Weiss plots of three samples are shown in fig. 2. The susceptibility in the normal state is fit to the formula $\chi(T) = \chi_0 + C/(T - \Theta)$, where χ_0 stands for the temperature-independent part of the susceptibility, C, for the Curie constant and Θ, for the Curie–Weiss temperature. Both C and Θ vary over the different samples in the range of $(1.5 \sim 18) \times 10^{-7}$ K m^3/mol and $10 \sim 35$ K, respectively. However, χ_0 does not change, being 4×10^{-9} m^3/mol. Consequently, the estimated effective moment varies from 0.18 to 0.62 μ_B/Cu, If the same moment is assumed at every Cu site. It is interesting to note that the Θ value is positive, indicating ferromagnetic interaction between the moments. However, further studies are necessary to clarify these points. The possibility for contribution from magnetic impurity phases such as BaCuO$_2$ can not be excluded. The inset in fig. 2 shows the superconducting transition in the ac-susceptibility.

5. Specific heat

High-precision specific heat measurements have recently been performed by Miltenburg et al. [2] below and above the superconducting transition temperature. The most interesting part is depicted in fig. 3, where the C/T vs. T plot is chosen. In this plot, a clear jump is observed in $\Delta C/T_c$ centered at 91.8 K, which directly proves the bulk superconducting phase transition. Its value amounts to 48 ± 2 mJ/mol K^2, 3.5% of the total C/T at T_c, assuming that the specific heat due to the lattice contribution smoothly changes across T_c.

From the value of $\chi_0 = 6.26 \times 10^{-9}$ m^3/mol after correction of diamagnetic contributions the coefficient, γ, of the linear term of the specific heat can be calculated. By using the relation $\chi_0/\gamma = 3\mu_B^2/\pi^2 k_B^2$, we find $\gamma = 36 \pm 2$ mJ/mol K^2. Therefore, $\Delta C/\gamma T_c$ is equal to 1.33, which is

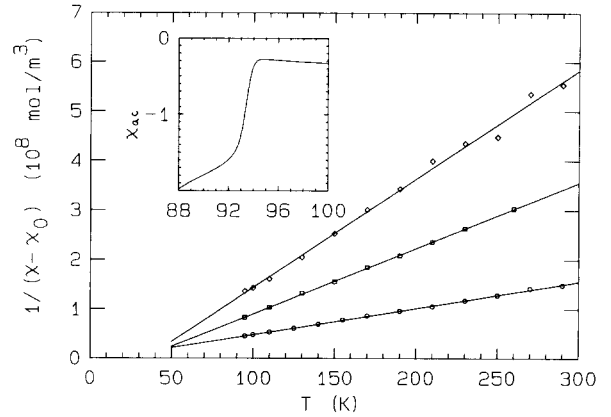Fig. 2. A set of Curie–Weiss plots of the susceptibility of YBa$_2$Cu$_3$O$_7$ above T_c. Heat-treatment was changed in the three samples. The inset shows an example of the ac-susceptibility around T_c.

close to the value of 1.43, the weak-coupling BCS value.

In fig. 4, the specific heat at low temperatures is presented in a C/T vs. T^2 plot. Assuming the simple relation, $C(T) = \gamma T + \beta T^3$, in this temperature range, γ and β can be reasonably deduced to be 5.53 ± 0.50 mJ/mol K^2 and 0.421 ± 0.02 mJ/mol K^4, which give rise to $\Theta_D = 389 \pm 1$ K.
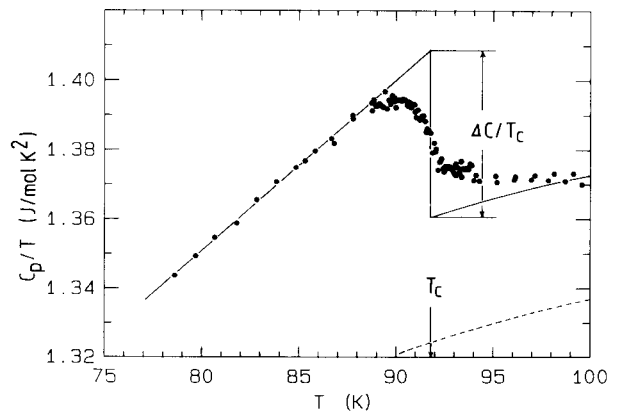

Fig. 3. C/T vs. T plot of the specific heat of YBa$_2$Cu$_3$O$_7$ around the superconducting transition temperature in an enlarged scale between 75 K and 100 K. T_c and $\Delta C/T_c$ are obtained to be 91.8 K and 48 ± 2.0 mJ/mol K^2, respectively. A distinct step is visible in the rapidly changing specific heat. The dotted line shows the lattice contribution.

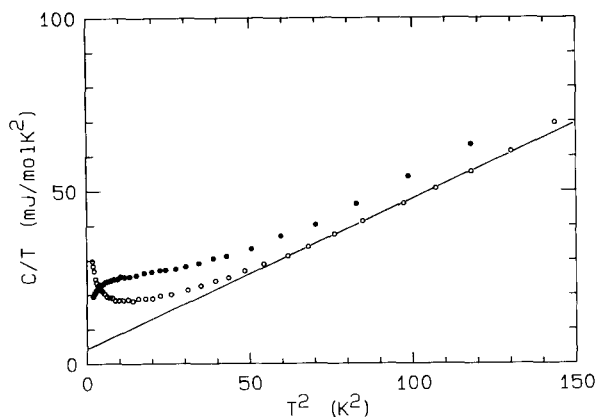Fig. 4. An example of the C/T vs. T^2 plots of the specific heat of $YBa_2Cu_3O_7$ below 12 K under magnetic fields $H = 0\,T(\bigcirc)$ and and $5\,T(\bullet)$.

As clearly seen in fig. 4, C/T has a marked upturn below 3 K, indicating the existence of additional degrees of freedom at low temperatures. Since this upturn has a significant magnetic field dependence, it is natural to attribute it to magnetic origins. The estimated extra entropy down to 1.4 K is about 43.2 mJ/mol, which is only 0.25% of the $3R\ln2$, the value that is expected for Cu^{2+} free spins. Although this upturn behavior looks interesting, the possibility of contributions from small amounts of impurity phases (~0.5%) cannot be ruled out, as already pointed out above. However, the origin of the non-zero γ value at low temperatures is not yet understood clearly.

6. Summary

The specific heat analysis around the superconducting phase transition suggests that there is not necessarily evidence for strong coupling and that the weak-coupling theory can reasonably be applied to this system. Regardless of the detailed electronic structure, the superconducting transition temperature in this case can be simply reduced to $T_c = T^* \exp(-1/g)$, where T^* stands for a characteristic temperature associated with the energy scale for the formation of Cooper-pairs, and g for an effective coupling constant.

Since T_c is approximately 100 K, T^* naturally results in several hundreds of Kelvin, corresponding to an energy scale between 10 and 100 meV. We believe that this high energy scale can hardly be attained by the ordinary electron–phonon interacting mechanism.

Acknowledgements

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