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SPECIFIC HEAT MEASUREMENTS OF HIGH-T_c SUPERCONDUCTOR $YBa_2Cu_3O_7$ BETWEEN 78 K AND 260 K

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High-precision specific heat measurements of the single-phase high-T_c superconductor $YBa_2Cu_3O_7$ have been performed in the temperature range between 78 K and 260 K. A distinct jump in the C/T vs. T plot, which is associated with the superconducting phase transition in this compound is observed at $T_c = 91.8$ K. The value of $\Delta C/T_c$ is estimated to be 48 ± 2 mJ/mol K^2. The γ-value, the coefficient of the linear term in the specific heat calculated from the static susceptibility above T_c, is 36 ± 2 mJ/mol K^2, which is comparable to the values for A-15 compounds. The ratio $\Delta C/\gamma T_c$ results in the value 1.33, which is close to 1.43, the weak-coupling BCS value. An anomalous large temperature variation of the Debye-temperature Θ_D suggests the existence of anomalous phonon modes in this crystal structure.

1. Introduction

The recent discovery of high-T_c superconductors in $La_{2-x}(Ba,Sr,Ca)_xCuO_{4-y}$ systems, and subsequently in $(RE)Ba_2Cu_3O_7$ systems, where (RE) represents most of the rare-earth elements have raised the fundamental question whether the mechanism of high-T_c superconductivity is due to a conventional electron–phonon mediated interaction or not. It seems that the obtained superconducting transition temperature T_c is too high to be explained by a conventional electron–phonon mechanism even by making use of the currently available strong-coupling theory by Allen and Dynes [1] that may explain T_c's as high as about 40 K, but not 90 K or more. Although calculations of the superconducting transition temperature T_c are not very accurate, the present theories are simply not about to account for superconductivity at 90 K. Various superconducting properties investigated so far, like upper critical fields H_{c2} [2], critical current J_c [3–5], superconducting gap Δ [6, 7], etc. obtained from samples of different quality, show anisotropic behavior, which suggests a significant anisotropic electronic structure in this compound. This anisotropy which is expected in this system with its special crystal structure with ordered oxygen vacancies [8] has recently been demonstrated by band calculations by Massidda et al. [9] and Yu et al. [10]. In addition, the lack of an oxygen-isotope effect [11–12] is remarkable and is not commonly found in ordinary superconductors.

The main concern in this paper is to investgate the thermodynamical properties of the high-T_c superconducting state as well as the normal state properties of $YBa_2Cu_3O_7$. Although it may be very hard to identify the superconducting Cooper-pairing mechanism by thermodynamics, the comparison of the results with known thermodynamical relations may help to solve the main problem in this compound.

2. Sample preparations

A large amount of the single-phase $YBa_2Cu_3O_7$ was prepared by the standard powder-ceramics technique, as described previously [13–14]. The purities of the starting materials Y_2O_3, $BaCO_3$ and CuO are 99.9%, 99.3% and 99.9%, respectively. In the present case, an additional heat treatment at 700°C for 12 hours in an oxygen flow atmosphere was applied. For the specific heat measurement, the final product was ground to powder.

The sample was checked by Debye–Scherrer X-ray investigations and no appreciable impurity phase was found.

AC- and dc-susceptibilities and ac-resistivity measurements were additionally done to determine T_c as well as to confirm the quality of the sample. Superconductivity was observed at 92.8 K with a resistive transition width of 0.8 K, as shown in fig. 1a. The resistivity was zero at 91.3 K. Susceptibility also showed a sharp transition at 92.5 K as seen in fig. 1b.

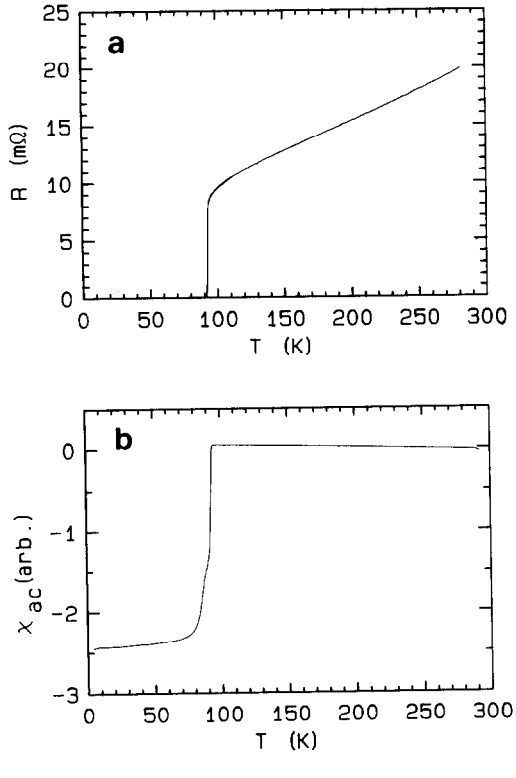

Fig. 1. Temperature dependence of the ac-electrical resistivity (a) and the ac-susceptibility (b) at 90 Hz of $YBa_2Cu_3O_7$.

Moreover, the structure and the content of oxygen of this sample were further characterized by thermal neutron scattering analysis at room temperature. A weak trace of $BaCuO_2$ (<1%) as a main impurity phase, as well as very weak reflections, which could be assigned to be unreacted BaO and Y_2O_3, were detected.

The structure established by the neutron diffraction performed at ECN (Energy Research Center, Petten, The Netherlands) is orthorhombic with Pmmm symmetry. The lattice parameters were determined to be $a = 3.8235(1)$ Å, $b = 3.8858(1)$ Å and $c = 11.6762(6)$ Å, in good agreement with previous results [8, 13, 15]. A high degree of ordering of oxygen vacancies in the *ab* plane was concluded in order to fit the neutron powder data consistently by a Rietveld analysis. The content of oxygen atoms in the unit cell was deduced to be between 6.95 to 7.00, indicating a high quality of the sample.

3. Experiments

Specific heat measurements have been performed in a high-precision adiabatic calorimeter [16, 17] between 78 K and 260 K. The calorimeter was checked by measuring standard samples of synthetic sapphire and of n-heptane. The absolute difference from the accepted data was within 0.2%. In our measurements, a powdered $YBa_2Cu_3O_7$ sample with mass of 26.334 g or 0.03953 mol (one mol means the number of atoms or molecules of the compound which corresponds to Avogadro's number, 6.02217×10^{23}) was used. The measurements (5 runs) were repeated carefully under different experimental conditions to ensure the accuracy and to avoid systematic error during long measuring time. In all the measurements, a heatpulse of 28 mW was applied to the sample. To promote the heat conduction in the powdered sample, about 1000 Pa helium gas at 300 K was introduced in the adiabatic can.

4. Results

The molar specific heat, between 78 K and 260 K is depicted in fig. 2. In this figure, all of the five runs are included. A small but distinct anomaly in the smoothly increasing specific heat is clearly visible at the superconducting critical temperature of 91.8 K. The specific heat around the superconducting transition temperature is shown in an extended scale in fig. 3.

Fig. 4 also shows the data of the specific heat but now in a C/T *vs.* T plot. The peak around T_c is somewhat broadened with a width of about 2 K. The solid line was drawn to determine T_c as well as the height of the jump, assuming an ideal superconducting transition. The superconducting transition temperature determined in this way is 91.8 K which corresponds to the temperature where the resistivity is completely zero and the ac-susceptibility drops sharply. Furthermore, the anomaly in the specific heat starts at 93 K where the resistivity begins to drop markedly.

The value of $\Delta C/T_c$ obtained in this way is 48 ± 1.0 mJ/mol K^2. In order to obtain this value, a smooth extrapolation of the lattice part of the specific heat about T_c was carried out, assuming a smooth variation of the Debye temperature between 100 K and T_c, as described later.

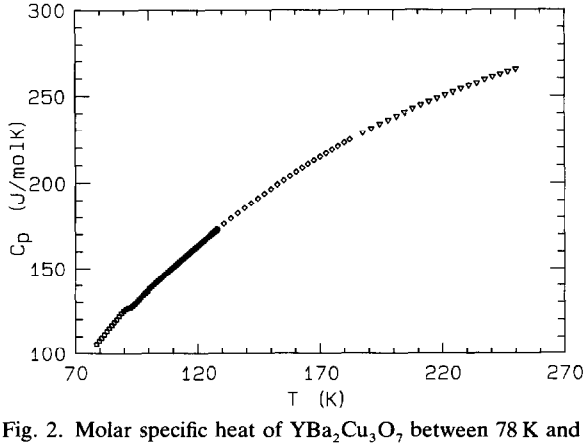

Fig. 2. Molar specific heat of $YBa_2Cu_3O_7$ between 78 K and 260 K. All five runs are included with different symbols. A tiny but clear anomaly is seen as 91.8 K, where the resistivity and the susceptibility show the superconducting phase transition.

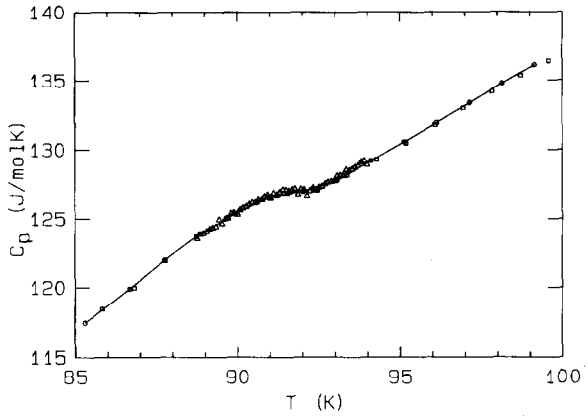

Fig. 3. Molar specific heat of $YBa_2Cu_3O_7$ around the superconducting transition temperature in an enlarged scale between 85 K and 100 K. A distinct step is visible in the rapidly changing specific heat.

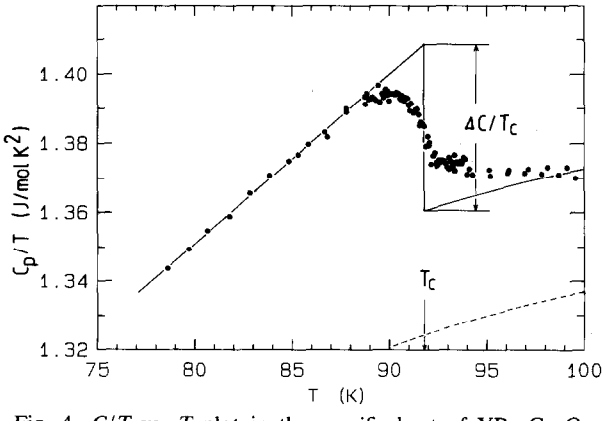

Fig. 4. C/T vs. T plot in the specific heat of $YBa_2Cu_3O_7$ between 75 K and 100 K. The dotted curve is an estimated phonon contribution to the specific heat (see text).

5. Discussions

The specific heat measurements performed on $YBa_2Cu_3O_7$ provide important information concerning the thermodynamical properties in this system. The rather sharp anomaly observed at the superconducting transition temperature of 91.8 K exactly coincides with the observed transitions in resistivity and ac-susceptibility. The jump in the C/T vs. T plot amounts to about 3.5% of the total specific heat, which is mainly due to the phonon contribution. These observa-

tions, at least, prove that the high-T_c superconductivity in this system is not a filamental, surface or granular property but a real bulk property.

The extrapolated specific heat jump at $T_c = 91.8\,K$ is estimated to be $\Delta C/T_c = 48 \pm 2\,mJ/mol\,K^2$, by assuming that the temperature dependence of the phonon contribution is smooth around T_c. The calculated phonon contribution to the specific heat is also shown in fig. 4 by the dotted curve. For this calculation, the temperature dependence of the Debye-temperature is extrapolated to T_c from the values obtained between 100 K to 126 K. The Debye temperature at T_c is calculated to be $444 \pm 1\,K$, which is significantly higher than that at low temperatures [18] and much lower than that at 250 K, where these values are 359 K and 512 K, respectively. As the temperature variation of the Debye temperature in usual cases is related to the special shape of the phonon density of states and the unharmonicity of the lattice vibrations, it is reasonable to attribute the large variation of the Debye temperature in this case to a special feature of the vibration modes due to the peculiar crystal structure in this system, which can be understood by the ordered oxygen vacancies. Indeed, large vibration amplitudes of the oxygen atoms O_1 and O_4 in this crystal have been claimed from neutron diffraction measurements.

From the results of static susceptibility measurements, shown in fig. 5 as an example, which were independently performed on several $YBa_2Cu_3O_7$ samples, it was found that the temperature independent part of the susceptibility does not vary from sample to sample, although the Curie constants and paramagnetic Curie–Weiss temperatures are strongly sample dependent. The results were fit to the expression

$$\chi(T) = \chi_0 + C/(T - \Theta)\,.$$

In this way, the value of χ_0 was deduced to be $4 \times 10^{-9}\,m^3/mol$ and C and Θ were found to vary in between $1.5 \times 10^{-7}\,Km^3/mol$ and $1.8 \times 10^{-6}\,Km^3/mol$ and between 10 K and 34.5 K, respectively. The core contribution to the diamagnetism is estimated to be roughly

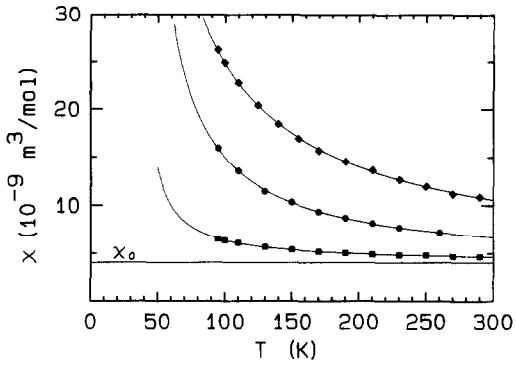

Fig. 5. Temperature dependences of the static susceptibility of $YBa_2Cu_3O_7$ above T_c.

$-2.26 \times 10^{-9}\,m^3/mol$ ($Y^{3+} = -1.5$, $Ba^{2+} = -3.02$, $Cu^{2+} = -1.5$ and $O^{2-} = -1.5$ in unit of $10^{-10}\,m^3/mol$). As a result, the calculated coefficient of the linear term in the specific heat is about $36 \pm 3\,mJ/mol\,K^2$, using the relation $\chi_0/\gamma(0) = 3\mu_B^2/\pi^2 k_B^2$. This value is of comparable order of magnitude as the values of A-15 compounds, for instance, $30.3 \pm 1.0\,mJ/mol\,K^2$ for Nb_3Ge [19].

Taking this value into account, the value of $\Delta C/\gamma T_c$ is calculated to be 1.33, by using the experimental value of $\Delta C/T_c = 48\,mJ/mol\,K^2$. This value is slightly lower than 1.43, which is expected by BCS weak-coupling theory. Since the estimation of the γ-value from the susceptibility χ_0 has an uncertainty from 10% to 20%, we believe that this value $\Delta C/\gamma T_c = 1.33$ is in good agreement with BCS weak-coupling theory, and that, at least from this experiments, there is no evidence from strong-coupling.

Furthermore, according to Rutger's formula, the jump of the specific heat can be related to the slope of the critical field at T_c by

$$\Delta C(T_c)/T_c = (V/4\pi)\left(\frac{\partial B_c}{\partial T}\right)^2_{T=T_c},$$

where B_c is the thermodynamical critical field and V, the molar volume. We calculate the value $(\partial B/\partial T)_{T=T_c} = 2.24 \times 10^{-2}\,T/K$.

In conclusion, it is clear that the experimental results suggest a weak-coupling mechanism in high-T_c superconductivity in the $YBa_2Cu_3O_7$ sys-

tem. In this case, the superconducting transition temperature can generally be expressed by

$$T_c = T^* \exp(-1/g) ,$$

where g is an effective coupling constant and T^*, a characteristic temperature. Since $T_c \sim 100\,\mathrm{K}$, T^* must be considerably higher than 100 K, which corresponds to an energy scale between 10 meV to 100 meV. Such a relatively high energy scale strongly suggests that it is very well possible that the coupling mechanism is not of an ordinary electron–phonon type. As pointed out earlier, and previously [13–14], it appears that the mechanism of the high-T_c superconductivity at 90 K strongly involves a very peculiar structural aspect in this compound, as there are the very loosely bound oxygen atoms O_1 and O_2, and the specially arranged oxygen vacancies. It is very intriguing to look for a new type of mechanism, for instance, excitonic modes [16], negative U centers [21] or resonating valence bond [22].

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