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Magnetic and structural properties of superconducting $PrBa_2Cu_3O_y$ grown by the TSFZ method

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Abstract

We report the magnetic and structural properties of single crystal $PrBa_2Cu_3O_y$ grown by the travelling solvent floating-zone (TSFZ) method. Magnetic susceptibility measurements show that TSFZ $PrBa_2Cu_3O_y$ has a superconducting transition below 80 K. Zero-field-cooled magnetization shows diamagnetism with full volume fraction. The magnetic moment μ_{eff} approaches 2.0 μ_B, and is in good agreement with that of the Pr^{3+} ion in the presence of a crystal field. The as-grown TSFZ $PrBa_2Cu_3O_y$ is tetragonal and has a longer *c*-axis lattice constant than previously reported. Structural analysis revealed a larger *z* positional parameter of the Ba site in as-grown TSFZ $PrBa_2Cu_3O_y$. © 1998 Elsevier Science S.A.

Keywords: Magnetic moment; $PrBa_2Cu_3O_y$; Single crystal; Structural defects; Superconductor; TSFZ

1. Introduction

Most theories of non-superconductivity in $PrBa_2Cu_3O_y$ have argued that Pr is strongly hybridized with oxygen and has a mixed valence. This hybridization results in hole localization in the conduction band and the inhibition of superconductivity. Structural data obtained from Rietveld refinements of X-ray or neutron powder diffraction indicated that the $PrBa_2Cu_3O_y$ system is isostructural with superconducting $RBa_2Cu_3O_y$ analogs; no cation mixing between the Pr and Ba sites was observed in neutron powder diffraction refinements [1–7].

Recently, Blackstead et al. [8,9] reported thin film superconductivity in $PrBa_2Cu_3O_7$ with T_c~90 K. This sample exhibited a Meissner effect of at most 7% of the total volume. They consider that the key to observing superconductivity is sample preparation conditions that minimize the amount of Ba-site Pr. An improved preparation of superconducting $PrBa_2Cu_3O_7$ will provide important information on $PrBa_2Cu_3O_7$ [8].

We have reported on bulk superconductivity in single crystals of $PrBa_2Cu_3O_y$ [10]. These samples were grown by the travelling solvent floating-zone (TSFZ) method in an oxygen-reduced atmosphere. After oxygen annealing, the resistivity was zero below 80 K [10].

In the present study, the magnetic and structural properties of TSFZ $PrBa_2Cu_3O_7$ were obtained from tetragonal and twinned orthorhombic crystals.

2. Experimental

The starting feed and solvent materials were prepared from Pr_6O_{11}, $BaCO_3$ and CuO of 99.9% purity [10,11]. Single crystals of $PrBa_2Cu_3O_y$ were obtained from the product grown by the TSFZ method in an oxygen-reduced atmosphere. All the crystals were annealed in an oxygen atmosphere at 850°C for 24 h and then at 550°C for 77 h.

The single crystal X-ray diffraction method was used to confirm the crystallinity and to perform structural analysis on both the as-grown and annealed TSFZ $PrBa_2Cu_3O_y$ single crystals. An X-ray precession camera with imaging plate, and a four-circle diffractometer (Rigaku-AFC-7R) with monochromatized Mo Kα radiation were used in the experiment.

Magnetic susceptibility measurements were performed on annealed TSFZ $PrBa_2Cu_3O_y$ single crystals in the temperature range 5–300 K with a field of 5 and 5000 Oe using a Quantum Design Superconducting quantum inter-

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ference device (SQUID) magnetometer with field parallel (χ_c) or perpendicular (χ_{ab}) to the *c*-axis.

3. Results and discussion

3.1. Structural properties

X-ray diffraction data of the as-grown TSFZ $PrBa_2Cu_3O_y$ single crystal was collected on a four-circle diffractometer. The results of refinements of the average structure using 5961 reflections yielded the unweighted and weighted *R* factors, $R = 2.5\%$ and $wR = 3.0\%$, in space group *P4/mmm*. Fig. 1 shows a schematic structural diagram of tetragonal $PrBa_2Cu_3O_y$ and Table 1_lists the atomic coordinates and equivalent thermal parameters for the as-grown TSFZ $PrBa_2Cu_3O_y$ single crystal. The lattice parameters, $a = 3.9010$ and $c = 11.879$ Å, were refined by the least-squares method using 25 reflections with $2\theta > 36°$. It should be noted that the as-grown single crystal of TSFZ $PrBa_2Cu_3O_y$ has a longer *c*-axis lattice constant than previously reported. As shown in Table 1, the Ba site has a larger *z* parameter than reported for a flux $PrBa_2Cu_3O_y$ crystal [10]. This means that the atomic distance between the Ba atom and the Cu(1)–O(1) chain is relatively longer. The origin of the larger *z* parameter may be lattice defects, disordering of cations, and/or oxygen deficiency in the as-grown TSFZ $PrBa_2Cu_3O_y$ crystal [12]. This larger *z* parameter of the Ba site is considered to lead to a longer *c*-axis lattice constant in the as-grown TSFZ $PrBa_2Cu_3O_y$.

Table 1
Positional parameters and B_{eq} for as-grown $PrBa_2Cu_3O_y$ grown by the TSFZ method

Atom	*x*	*y*	*z*	B_{eq}
Pr	0.5000	0.5000	0.5000	0.480(2)
Ba	0.5000	0.5000	0.19052(2)	0.815(2)
Cu(1)	0.0000	0.0000	0.0000	1.097(6)
Cu(2)	0.0000	0.0000	0.35193(4)	0.539(3)
O(1)	0.0000	0.5000	0.0000	20000
O(2)	0.5000	0.0000	0.3706(2)	0.69(2)
O(4)	0.0000	0.0000	0.1526(3)	1.69(3)

Figs. 2 and 3 show precession photographs of as-grown and annealed TSFZ $PrBa_2Cu_3O_y$ single crystals, respectively. Ring-like diffusion can be observed in *h*0*l* reflections of the as-grown TSFZ $PrBa_2Cu_3O_y$ crystal, as shown in Fig. 2. This phenomenon is considered to be caused by growth defects inside the plane which contains the *c*-axis.

Fig. 3 shows a precession photograph of the *h*0*l* reflections of the annealed single crystal. The ring-like diffusion observed for the as-grown TSFZ $PrBa_2Cu_3O_y$ single crystals is not evident. This means that annealing improves the crystallinity. Annealed TSFZ $PrBa_2Cu_3O_y$ is orthorhombic with space group *Pmmm*, $a = 3.8620$, $b =$

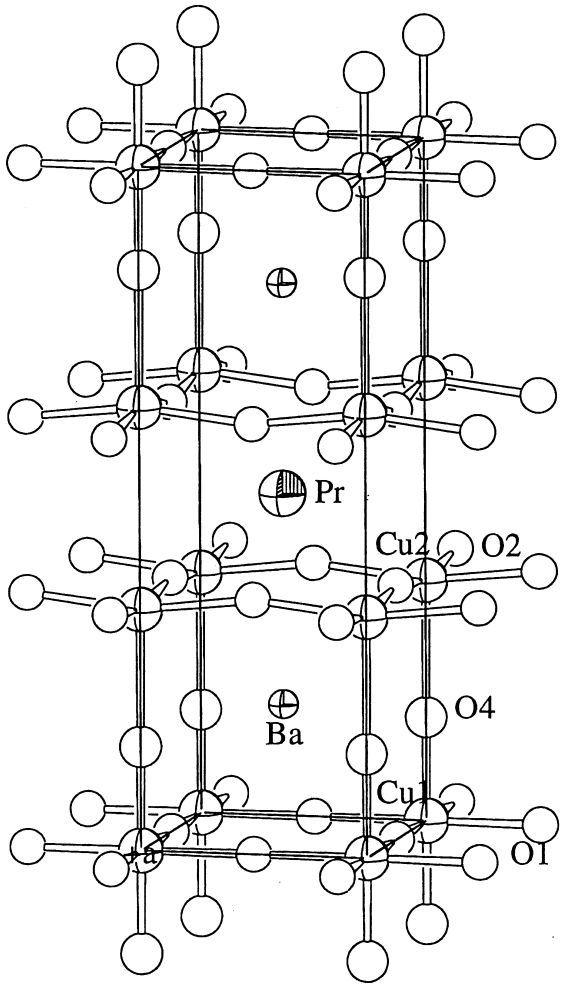

Fig. 1. Schematic diagram of the structure of the tetragonal phase of TSFZ $PrBa_2Cu_3O_y$.

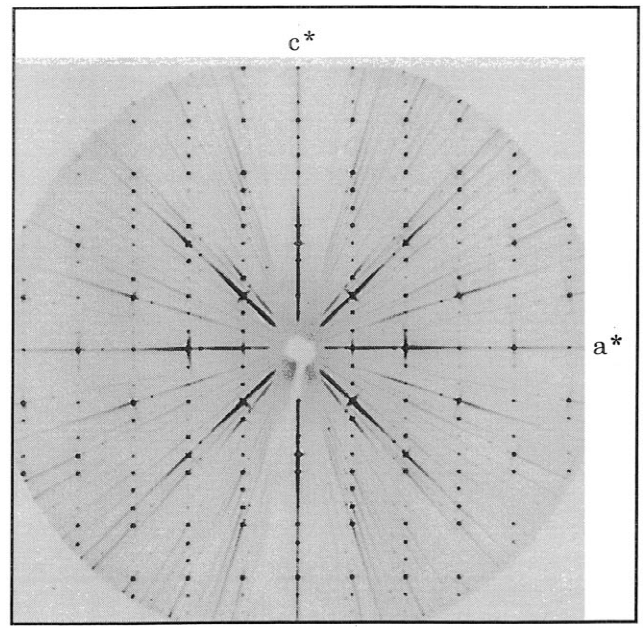

Fig. 2. Precession photograph of the *h*0*l* diffraction for as-grown TSFZ $PrBa_2Cu_3O_y$.

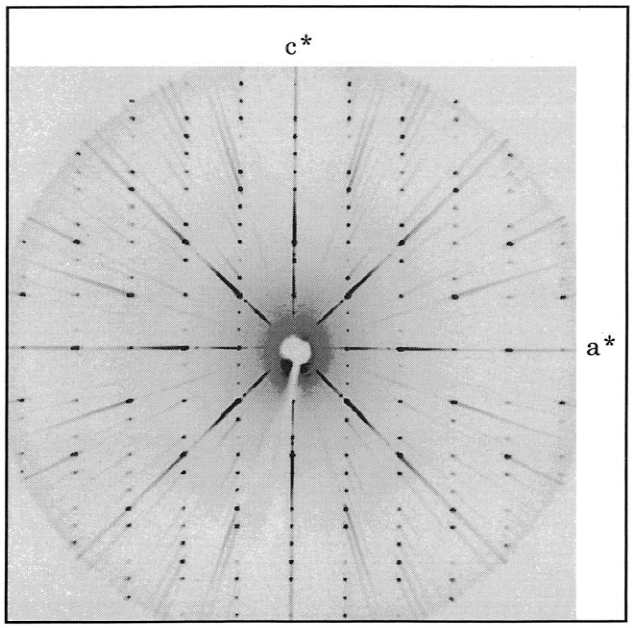

Fig. 3. Precession photograph of the *h*0*l* diffraction for annealed TSFZ $PrBa_2Cu_3O_y$.

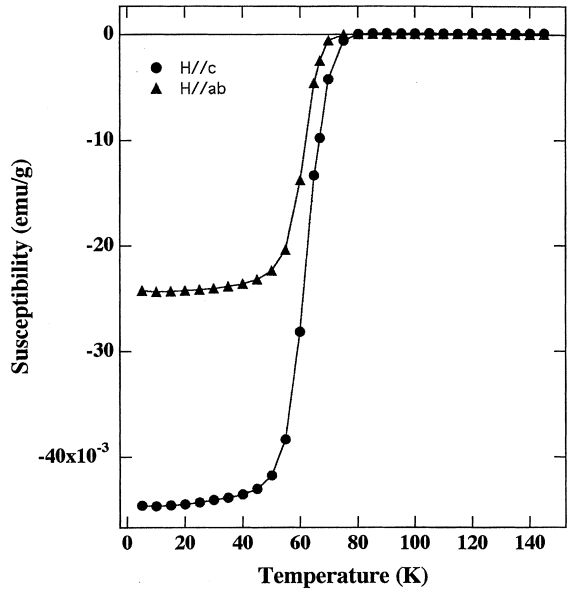

Fig. 4. Temperature dependence of the magnetic susceptibility of $PrBa_2Cu_3O_y$ crystals at an applied magnetic field of 5 Oe for two field orientations *H* parallel to the *c*-axis and the *ab* plane.

3.9128 and $c = 11.694$ Å, as calculated from the precession photograph. The structural parameters and oxygen content of detwinned TSFZ $PrBa_2Cu_3O_y$ could not be obtained since the as-grown TSFZ $PrBa_2Cu_3O_y$ single crystal was converted into a twinning crystal after annealing and the sample was very small. However, the *c*-axis parameter obtained approached the value for that of an oxygen-annealed sample grown by the flux method. Our X-ray structural analysis of TSFZ $PrBa_2Cu_3O_y$ suggests that, in the as-grown TSFZ $PrBa_2Cu_3O_y$ single crystal, there are lattice defects, oxygen deficiency, disordering of cations, or a combination of these factors. Relaxation of the defects leads to a decrease in the *c*-lattice parameter of annealed TSFZ $PrBa_2Cu_3O_y$.

An orthorhombic–tetragonal phase transition was observed between the as-grown and annealed TSFZ $PrBa_2Cu_3O_y$ single crystals. The *hk*0 reflections split in the annealed TSFZ $PrBa_2Cu_3O_y$ crystal. A twinned TSFZ $PrBa_2Cu_3O_y$ crystal was observed. This local crystallographic variation before and after the orthorhombic–tetragonal transition, and near the transition, provides important information for understanding both the superconducting and non-superconducting crystals.

Details of the investigation of the structure of the as-grown and detwinned TSFZ $PrBa_2Cu_3O_y$ will be published elsewhere.

3.2. Magnetic properties

The as-grown TSFZ $PrBa_2Cu_3O_y$ single crystals did not exhibit superconductivity. Fig. 4 shows the magnetic susceptibility of the annealed TSFZ $PrBa_2Cu_3O_y$ single crystals. The superconducting transition temperature T_c was observed below 80 K at an applied magnetic field of 5 Oe and the transition width was about 10K. The sample was annealed in an oxygen atmosphere at 850°C. The magnetic field was applied perpendicular to the *ab* plane. The directional susceptibility of TSFZ $PrBa_2Cu_3O_y$ single crystals shows $\chi_c > \chi_{ab}$ below T_c for all compounds studied. This result is in agreement with that of Jayaram et al. [13].

The magnetization at 5 K decreases linearly with applied magnetic field. The demagnetization factor is estimated to be ~0.85 [14]. Taking into account this demagnetization effect, the value of perfect diamagnetism corresponds to a volume fraction of about 100% of the specimen. The field-cooled magnetization shows a Meissner effect of about 15% of the total volume. The result indicates that this superconductivity is bulky.

The inverse magnetic susceptibility (χ^{-1}) is shown in Fig. 5. The measurements were performed from 5 to 300 K in an applied field of 0.5 T. Diamagnetic susceptibility was observed below 70 K in TSFZ $PrBa_2Cu_3O_y$ when the magnetic field was 0.5 T. From a fit with the Curie–Weiss law ($\chi = \chi_0 + C/(T + \Theta)$) to calculate the susceptibility above 100 K, $\chi_0 = 8.5 \times 10^{-4}$ emu mol^{-1} and an effective magnetic moment of $\mu_{eff} \sim 2.0\ \mu_B$ were obtained. The magnetic properties of TSFZ $PrBa_2Cu_3O_y$ have several features in common with other praseodymium oxides [15,16]. However, Li et al. [17], using neutron techniques, found that the effective moment of $PrBa_2Cu_3O_y$ was 0.74 μ_B for $T \ll T_N$, and the Neel temperature was 17 K. However, in our sample, traces of antiferromagnetism of Pr atoms was not observed from 5 to 300 K. These differences of T_N for $PrBa_2Cu_3O_y$ might possibly arise

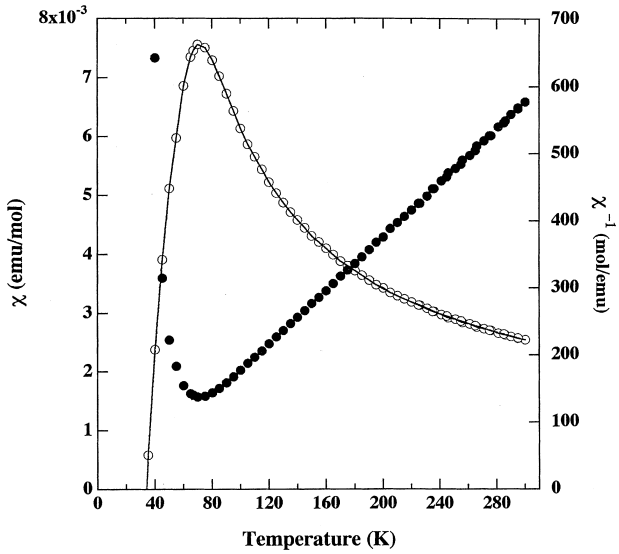

Fig. 5. Temperature dependence of the inverse susceptibility of $PrBa_2Cu_3O_y$ single crystals. The solid lines represent fits of the data to a Curie–Weiss law of the form $\chi = \chi_0 + C/(T + \Theta)$, from which the effective Pr charge state is subsequently estimated.

from the disordering of cations in the TSFZ $PrBa_2Cu_3O_y$ crystal.

In contrast to a previous paper reporting that there are no carriers in the CuO_2 plane of $PrBa_2Cu_3O_7$ [6], the bulk superconductivity of our samples indicates that there are probably carriers in the CuO_2 plane. Holes generated by oxidization would be distributed in the CuO_2 plane, the CuO chain and Pr, probably hybridized with oxygen. The distribution of holes would be sensitive to the electronic structure of Pr hybridized with the neighboring oxygen and CuO_2 plane, which would be affected by the local crystal structure and/or the inter-site substitution of cations. In the model proposed by Fahrenbacher et al. [7], hybridization of Pr and surrounding oxygen would be sensitive to crystallographic differences. Characterization of the local structure and the electronic state of Pr would be good tests for the model of Fahrenbacher et al. [7] and provide the answer to the mechanism for the distribution of the holes.

Our experimental results show that the properties of TSFZ $PrBa_2Cu_3O_y$ are sensitive to the conditions of synthesis. The idea that such crystallographic differences, or electronic state, valence state, may give a means for understanding TSFZ $PrBa_2Cu_3O_y$ has been put forward by several groups [18]. It is important to check the change in the antiferromagnetic order of the TSFZ $PrBa_2Cu_3O_y$ crystal by specific heat measurements or other methods. We therefore suggest that information on changes in the lattice and valence state is an important framework for discussing the physical properties of not only superconducting crystals of TSFZ $PrBa_2Cu_3O_y$ but non-superconducting $PrBa_2Cu_3O_y$.

4. Summary

We have shown that superconducting TSFZ $PrBa_2Cu_3O_y$ exhibits a number of interesting phenomena. The Ba site has a larger z parameter and the atomic distance between the Ba atom and the Cu(1)–O(1) chain is relatively longer in as-grown TSFZ $PrBa_2Cu_3O_y$ crystals. This may be caused by lattice defects, disordering of cations, and/or oxygen deficiency. This larger z parameter of the Ba site is considered to lead to a longer c-axis lattice constant in as-grown TSFZ $PrBa_2Cu_3O_y$. The c-axis lattice parameter decreases with relaxation of the defects after annealing. For superconducting TSFZ $PrBa_2Cu_3O_y$, we show that the magnetic susceptibility manifests features characteristic of Pr^{3+}, but not mixed valence. We find that the properties of $PrBa_2Cu_3O_y$ are sensitive to the conditions of synthesis and it is possible to obtain both superconducting and non-superconducting crystals.

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