Low temperature x-ray diffraction study on superconductivity

Y Xue¹, H Kaneko¹, Q Tao², Z Xu², N Takeda¹, Y Nemoto³, T Goto³ and H Suzuki¹

¹ Department of Physics, Kanazawa University, Kakuma-machi, Kanazawa, 920-1192, Japan
² Department of Physics, Zhejiang University, Hangzhou 310027, China
³ Graduate School of Science and Technology, Niigata University, Niigata 950-2181, Japan

hsuzuki@cphys.s.kanazawa-u.ac.jp

Abstract. Using a low temperature x-ray diffractometer, we studied superconductivity materials, optimally doped and underdoped YBCOs and PrOs₄Sb₁₂ between 0.1 K and 300 K. At several temperatures, whole profiles of the x-ray reflection peak were measured and refined by Rietveld analysis. By Rietveld analysis, we found that Pr atoms in PrOs₄Sb₁₂ are still oscillating at an amplitude of about 0.1 Å at 0.18 K. For some reflection planes, x-ray diffraction measurement with a small step size and a long stepping time was performed to accumulate more counts at certain temperatures. The lattice constant d of optimally doped YBCO (OPT YBCO) shows anomalous behaviours at around the superconductivity transition temperature Tc and around spin gap temperature T*. In OPT YBCO, the intensity of the reflection spectrum shows a clear anomaly at around Tc:

1. Introduction

The role of the phonon mechanism of high-Tc superconductivity remains unknown. The coefficient α of the isotope effect is almost zero for optimally doped cuprates, but becomes large for underdoped cuprates [1]. Meanwhile, there have been many searches for lattice anomalies at the superconducting transition temperature (Tc) [2]. Vibrational spectroscopy has shown the softening of phonon modes involving apical oxygen atoms in YBa₂Cu₃O₇ (YBCO) [3], and EXAFS experiments have revealed changes in the Debye-Waller factor of this atom at Tc [4]. A filled skutterudite PrOs₄Sb₁₂ has been reported to be the first Pr-based heavy-fermion superconductor with Tc= 1.85 K [5]. The quadrupolar fluctuation due to the CEF state and the charge fluctuation of the off-center motion of the Pr atom in the huge cage seem to play a role in Cooper pairing in superconducting phase. In the present paper, x-ray diffraction experiment was carried out at low temperatures for YBCO and PrOs₄Sb₁₂. The temperature variations in lattice constants, full width at half maximum (FWHM) and intensity of the x-ray spectrum were measured in detail. The intensity was defined as the integrated intensity [I. I.] of the diffraction spectrum. The intensity can be described by the Debye-Waller factor $I = I₀exp(-16π²k_B T sin² \theta / M \omega²)$, where $I₀$ is the scattered intensity from the rigid lattice, $\theta$ is the scattering angle, $M$ is the mass of the atom and $ω$ is the frequency of the oscillator. Particularly in the vicinity of
the transition temperatures, the measurements were performed while changing temperature in very small steps. At some fixed temperatures, Rietveld analysis was carried out. Rietveld analysis gives the Debye-Waller factor, which gives us information on the lattice vibration. Except for the underdoped YBCO (UD YBCO), anomalous behaviors were observed in the intensity of the x-ray diffraction spectrum in the vicinity of the transition temperatures.

2. Experiments
Two different types of cooling system were used in our low-temperature x-ray diffraction experiment depending on temperature. Above approximately 10 K, a $^4$He circulating cryocooler was used and below 10 K, a $^3$He-$^4$He dilution refrigerator (D. R.) was used. A D. R. reaches 20 mK, but with an x-ray beam, the lowest temperature in our experiment was about 120 mK, which achieved the thermal equilibrium of the specimen. The x-ray diffraction measurement for powder specimens was performed using the RINT 2500 system, Rigaku Co. An x-ray beam was generated by a rotating Cu anode. At several temperatures, entire profiles of reflection peaks were measured at a step size of 0.01° and a step-counting time of 6 s. For some reflection planes, the x-ray diffraction measurement at a step size of 0.005° and a step-counting time of 60 s was performed to accumulate more counts at certain temperatures. At each temperature, x-ray diffraction was measured 3 times. The standard deviation of the lattice constant $d$ was $3\times10^{-5}$. From the observed profile, the lattice constant $d$, intensity and FWHM were obtained. In these analyses, the profile was fitted to a pseudo-Voigt function. A polycrystalline powder sample of YBa$_2$Cu$_3$O$_{7-x}$ was prepared by a conventional solid-state reaction method. The underdoped (UD) powder was prepared by annealing the OPT YBCO powder at 500°C for a few hours in flowing nitrogen. The single crystal of PrOs$_4$Sb$_{12}$ was grown by the Sb-flux method. But for the powder x-ray diffraction analysis, the single crystal was ground.

3. Results and Discussion

3.1. OPT YBCO
A very sharp superconducting transition is observed at 91 K in the susceptibility for OPT YBCO. The oxygen content of the UD YBCO sample is estimated to be 6.65 according to the mass loss during the annealing in flowing nitrogen. However, the transition is a little broad for UD YBCO, which could result from the inhomogeneous distribution of oxygen content.

The temperature dependences of the lattice constant $d$-values were obtained for (103), (013), (113) and (020) reflections. Two of them, i.e., (103) and (020) are shown in Fig. 1. All $d$-values decrease with decreasing temperature, indicating a thermal contraction of the lattice. No sudden change in $d$ at $Tc$
was observed, which excludes any possible structural phase transition or distortion at \(T_c\). However, a clear kink can be observed in the \(d\) values in the vicinity of \(T_c\). A similar thermal expansion anomaly of YBCO near \(T_c\) has been reported by Lang et al. [6]. At the pseudo-gap opening temperature \(T^*\) of about 130 K, a tiny kink in the \(d\) values is also found, except for the (113) reflection peak (not shown here). For the UD YBCO \((T_c = 60\) K), no such kinks at \(T_c\) and \(T^*\) can be observed, which could result from an inhomogeneous distribution of oxygen content.

The temperature dependences of the integrated intensities \([I.I.s]\) of the (103) + (013), (113), and (200) + (020) peaks for OPT YBCO are obtained. Because the (103) and (013) peaks are too close to each other, it is difficult to separate the \(I.I.s\) of these peaks. However, when we express the intensity of the peak by the maximum of the peak height, both peaks show similar temperature dependences. Then the total intensity of the two peaks is shown in Fig. 2. For similar reason, the total \(I.I.\) of the (200) + (020) peaks is shown. The most striking feature in Fig. 2 is that there is a clear change in the \(I.I.s\) of these peaks at around \(T_c\) of 91 K. For the (113) (not seen here) and (013) + (103) peaks, where the Debye-Waller factor is predominant as a result of the c-axis motion of atoms, \(I.I.\) increases suddenly when the sample becomes superconducting. For the (200) + (020) peaks, \(I.I.\) shows an initial increase at \(T_c\), and then a decrease below \(T_c\). Xue et al. [7] reported a similar change at \(T_c\) in the \(I.I.\) of the (002) peak of \(\text{MgB}_2\), which is a multi-band BCS superconductor. Kim et al. measured the temperature-dependent (00l) x-ray Bragg peak intensities of YBCO and Hg1212 thin films [8]. They observed no anomaly at \(T_c\). On the other hand, the temperature-dependent \((1,2,12)\) neutron Bragg peak intensities of YBCO crystals have anomalies at \(T_c\) [9]. The observed temperature dependence of the intensity does not solely come from the dynamic displacement of atoms. Not only the phonon but also the changes in the static atomic positions within the cell affect the intensities. Therefore, together with the information on lattice parameters, we can extract useful information from the results. Above \(T_c\), the \(I.I.\) of (103) + (013) peaks decreases below 250 K with decreasing temperature; others increase. The anisotropic change in the \(I.I.\) depending on the crystallographic directions suggests that the coupling between the phonon and the electron in different directions might also be anisotropic.

### 3.2. \(\text{PrOs}_4\text{Sb}_{12}\)

At several temperatures between 0.18 and 300 K, whole reflection peaks were measured and refined by Rietveld analysis. From the Rietveld analysis, the Debye-Waller factor, which is defined here as \(T = \exp[-B(\sin(\theta)/\lambda)^2]\), was obtained for each atom. \(B = 8\pi^2<u^2>\) is the isotropic displacement factor of the atom. At room temperature of 300 K, \(B\)-value was obtained for the Pr atom to be 4.5 Å\(^2\), which leads to the mean square displacement amplitude \(<u^2> \approx 0.056 \text{ Å}^2\). Compared with those of the Pr atom, the \(B\)-values of the Os and Sb atoms are very small. With decreasing temperature, \(B\)-values decreases.
up to about 10 K, then becomes nearly constant at about 0.3 ~ 1 Å², which correspond to $\langle u^2 \rangle \sim 0.0076$ ~0.025 Å². Neutron powder diffraction analysis of PrOs₄Sb₁₂ was carried out by Kaneko et al. between 295 K and 7.7 K[10]. They also obtained the $B$-values for Pr to be 0.034 Å² at 295.1 K and 0.0062 Å² at 7.7 K. Their values are slightly smaller than ours. The temperature variation in our obtained $B$-value for the Pr atom is shown in Fig. 3. Even at such low temperatures as 0.18 K, Pr atoms still move to

![Figure 3](image3.png)  
**Figure 3.** Temperature variation in $B$-parameter of PrOs₄Sb₁₂.

some extent, $\Delta u \sim 0.11 \sim 0.15$ Å. To discuss the small temperature variation in Debye-Waller factor, the $I.Is$ of some peaks were measured. In Fig. 4, the low-temperature part of the $I.Is$ of the (420) reflection peak of PrOs₄Sb₁₂ is shown. It also shows a small peak at around $T_c (\sim 1.8$ K). In addition, $I.I.$ increases rapidly below about 0.5 K, suggesting the hardening of the lattice. Below 0.5 K, the lattice expanded as shown in Fig. 5. At present, the origin of this marked change of the lattice remains unknown. Karaki observed an anomalous behavior of the magnetic susceptibility of PrOs₄Sb₁₂ at around 0.5 K [11]. This suggests the change in the electronic state below 0.5 K due to the expansion of the lattice.

![Figure 4](image4.png)  
**Figure 4.** Temperature variation in $I.I.$ for (420) x-ray reflection of PrOs₄Sb₁₂.

![Figure 5](image5.png)  
**Figure 5.** Temperature variation in lattice space $d$ for (422) x-ray reflection of PrOs₄Sb₁₂.

**Acknowledgment**

This work was supported by a Grant-in Aid for Science Research from Japan Society for the Promotion of Science

**References**

[1] Pringle D J, Williams G V and Tallon J L 2000 Phys. Rev. B 62 12527
[2] Egami T and Billinge S J 1994 Prog. Mater. Sci 38 359
[3] Ranninger J 1991 Z Phys. B 84 167
[4] Conradson S D and Raitstick I D 1989 Science 243 117004
[5] Bauer E D et al. 2002 Phys. Rev. B 65 100506
[6] Lang M et al 1992 Phys. Rev. Lett. 69 482
[7] Xue Y et al. 2005 J. Low Temp. Phys. 138 1105
[8] Kim et al. 2003 Phys. Rev. B 67 092508
[9] Schweiss et al. 1994 Phys. Rev. B 49 1387
[10] Kaneko K, Metoki N, Matsuda T D and Kohgi M. 2006 J. Phys. Soc. Jpn. 75 034701
[11] Karaki T Private communication