Low temperature x-ray diffraction study on superconductivity

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Abstract. By using a low temperature x-ray diffractometer, we studied the superconductivity materials, optimal doped and under doped YBCOs and $PrOs_4Sb_{12}$ between 0.1 K and 300 K. At several temperatures whole profiles of x-ray reflection peak were measured and refined by the Rietveld method. By the Rietveld analysis we found that Pr atoms in $PrOs_4Sb_{12}$ is still oscillating with the amplitude of about 0.1Å at 0.18 K. For some reflection planes x-ray diffraction measurements with a small step size and a long stepping time were performed to accumulate more counts at certain temperatures The lattice constant *d* of optimal doped YBCO (OPT YBCO) shows the anomalous behaviours around the superconductivity transition temperature *Tc* and around spin gap temperature *T**. In OPT YBCO, the *I.I.* shows clear anomaly around *Tc*. The *I.I.* is related to the phonon frequency through a Debye-Waller factor.

1. Introduction

The role of phonon mechanism of high-*Tc* superconductivity is still a puzzle. The coefficient α of isotope effect is almost zero for optimally doped cuprates, but it becomes large in the under doped regime [1]. Meanwhile, there have been many searches for lattice anomalies at the superconducting transition temperature (*Tc*) [2]. Vibrational spectroscopy has shown softening of phonon modes involving the apical oxygen atoms in $YBa_2Cu_3O_7$ (YBCO) [3,4], and EXAFS experiments have revealed changes in the Debye-Waller factor of this atom at *Tc* [5]. A filled skutterudite $PrOs_4Sb_{12}$ with a heavy fermion superconductivity at *Tc*= 1.85 K is interested in. The quadrupolar fluctuation due to the CEF state and the charge fluctuation of the off-center motion of Pr atom in the huge cage seem to play a role for the Cooper pairing in superconducting phase. In the present paper x-ray diffraction experiments were carried out at low temperatures for YBCO and $PrOs_4Sb_{12}$. Temperature variations of lattice constants, full width at half maximum (*FWHM*) and integrated intensity(*I.I.*) of the x-ray diffraction spectrum were measured in detail. The *I.I.* can be described by the Debye-Waller factor, $I = I_0 exp(-k_B T sin^2\theta_B/M\omega^2)$, where I_0 is the scattered intensity from the rigid lattice, θ_B,; the scattering angle, *M*; the mass of the atom and ω; the frequency of the oscillator. Especially in the vicinity of the transition temperatures, measurements were performed while changing the temperature, by very small step. At some fixed temperatures, the Rietveld analysis was carried out, The Rietveld analysis gives the Debye-Waller factor which tells us the information of the lattice vibration. Except for under doped YBCO (UD YBCO), anomalous behaviors were observed in the *I.I.* in the vicinity of the transition temperatures.

2. Experiments

Two different types of cooling system were used in our low temperature x-ray diffraction experiments depending on the temperature range. Above about 10 K, a ^{4}He circulating cryocooler was used and below 10 K, a ^{3}He-^{4}He dilution refrigerator (D. R.). A D. R. itself 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. X-ray diffraction measurements for powder specimens were 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 with a step size of 0.01° and a step-counting time of 6 s. For some reflection planes x-ray diffraction measurements with a step size of 0.005° and a step-counting time of 60 s were performed to accumulate more counts at certain temperatures. From the observed profile the lattice constant *d*, the integrated intensity (*I. I.*) and also the *FWHM* were obtained. In these analyses the profile was fitted to a Pseude-Voight function.
Polycrystalline powder sample of $YBa_2Cu_3O_{7-x}$ was prepared by usual solid-state reaction method. The under doped powder was prepared by annealing the OPT YBCO powder at 500°C for a few hours in flowing nitrogen. The single crystal of $PrOs_4Sb_{12}$ was grown by the Sb-flux method. But for powder x-ray measurements, the single crystal was ground.

3. Results and Discussions

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 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, (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 the *d* value at *Tc* was observed, which excludes any possible structure phase transition or distortion at *Tc*. However, a clear kink can be observed in the d values in the vicinity of *Tc*. At the pseudo-gap opening temperature (*T**) of about 130 K, a tiny kink in the *d* values is also found, except for (113) reflection peak (not shown here). For the UD YBCO (*Tc* of 60 K), such kinks at *Tc* and also at *T** cannot be observed.

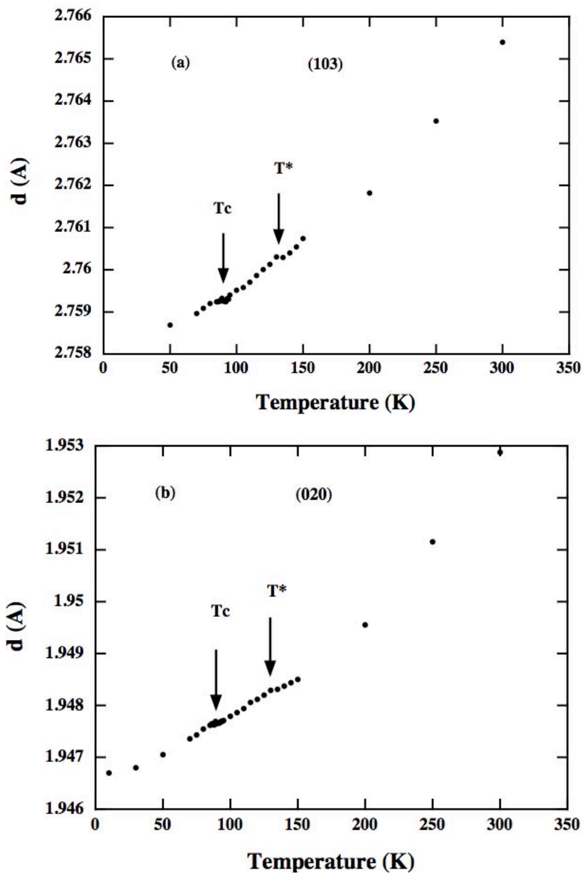

Figure 1. Temperature dependence of d-value of (a):(103) and (b):(020) reflections for OPT YBCOA. *Tc* and *T** are indicated by arrows**.**

The temperature dependence of the *I.I.* of the (103) + (013), (113), and (200) + (020) peaks for OPT YBCO is obtained. Because of the (103) and (013) peaks are too close to each other, it is hard to separate the *I.I.* of these peaks. However, when we express the intensity of the peak by a maximum of the peak height, both peaks show the similar temperature dependence. Then total intensity of 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.* of these peaks around *Tc* of 91 K. For the (113) (not seen here), and (013) + (103) peaks where the Debye-Waller factor is dominant by the c-axis motion of atoms, the *I.I.* increases suddenly when the sample becomes superconducting, implying that the phonon frequency related to the c-axis direction modes increases at *Tc*. For the (200) + (020) peaks, the *I.I.* shows an increase first at *Tc*, and then a decrease below *Tc*, which implies that there is a hardening of the phonon frequency related to the x-, and y-direction modes around or above *Tc*, followed by a softening below *Tc*. Xue et al. [6] reported a similar change at *Tc* in the *I.I.* of the (002) peak of MgB_2 which is a multi-band BCS superconductor. Above *Tc* the I.I. of (103) + (013) peaks decreases below 250 K with decreasing temperature, others increase. The anisotropic change in the *I.I.* regarding to the different crystallographic directions suggest that the coupling between the phonon and electron in different direction might be also anisotropic.

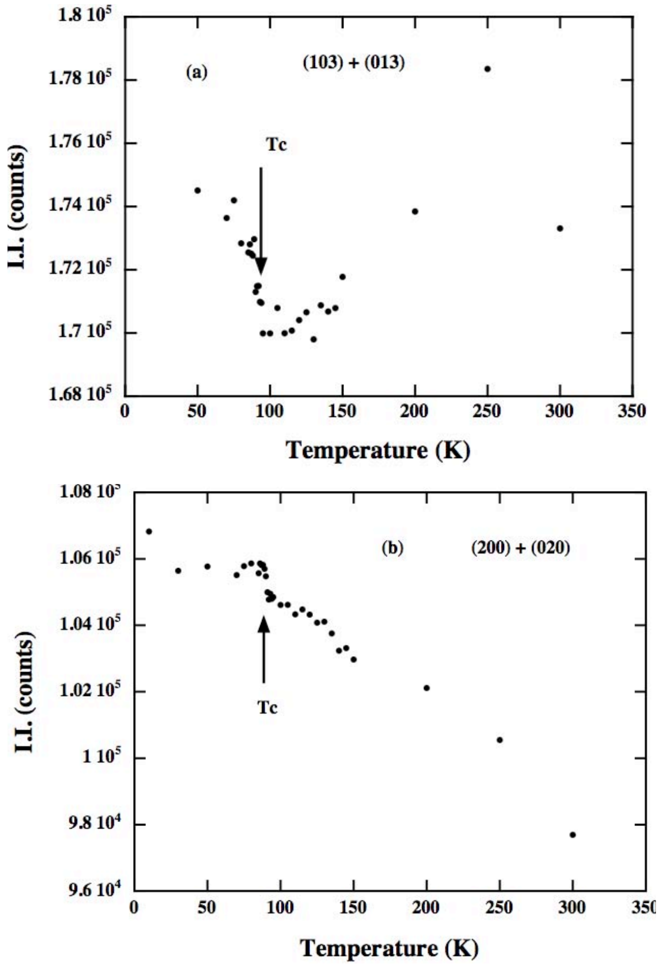

Figure 2. Temperature dependence of the integrated intensity for (a) (103) + (013) and (b) (200) + (020) reflection peaks for OPT YBCO.

3.2. $PrOs_4Sb_{12}$

At several temperatures between 0.1 and 300 K whole of reflection peaks were measured and refined by the Rietveld method. 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 (= $8\pi<u^2>$) is the isotropic displacement factor of the atom. At room temperature 300 K, *B* value was obtained for Pr atom to be 4.5 $Å^2$ which leads to the mean displacement amplitude $<u>$ ~ 0.25 Å. Compared with Pr atom, for Os and Sb atoms B parameters are very small. With decreasing temperature the value of *B* decreases till about 10 K, then it becomes nearly constant value of about 0.5 ~ 1 $Å^2$. Temperature variation of *B* parameter for Pr atom is shown in Fig. 3. Even though at such low temperatures as 0.1 K, Pr atoms are still moving to some extent, $<u>$ ~ 0.05 ~ 0.1 Å. To discuss the small temperature variation of Debye-Waller factor , the *I.I.* of some peaks was measured. In Fig. 4 the low temperature part of the *I.I.* of (420) reflection for $PrOs_4Sb_{12}$ is shown. It also shows a small peak at around *Tc* (= 1.8 K). In addition, the *I.I.* increases rapidly below about 0.5 K, suggesting the hardening of the lattice. Below 0.5 K the lattice was expanded as shown in Fig.5. A present the origin of this drastic change of the lattice is not known yet. T Karaki observed an anomalous behavior of the magnetic susceptibility in$PrOs_4Sb_{12}$ at around 0.5 K [7]. This suggests the change of the electronic state below 0.5 K due to the expansion of the lattice.

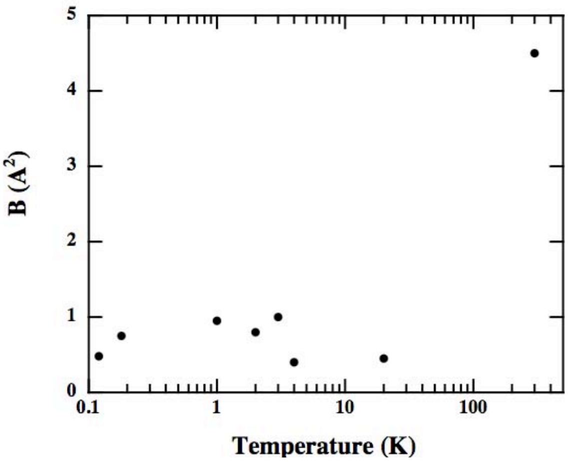

Figure.3. Temperature variation of *B* parameter of $PrOs_4Sb_{12}$.

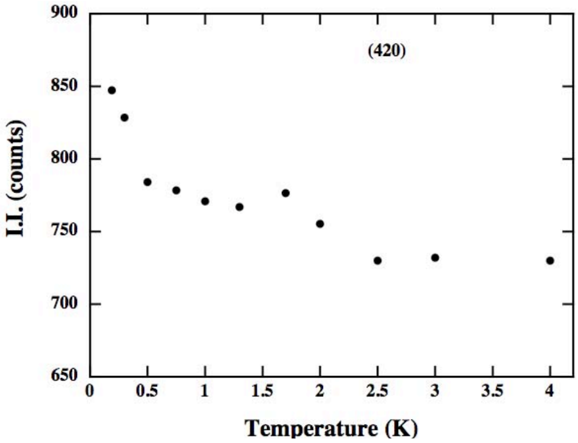

Figure 4. Temperature variation of the *I.I.* for (420) x-ray reflection of $PrOs_4Sb_{12}$.

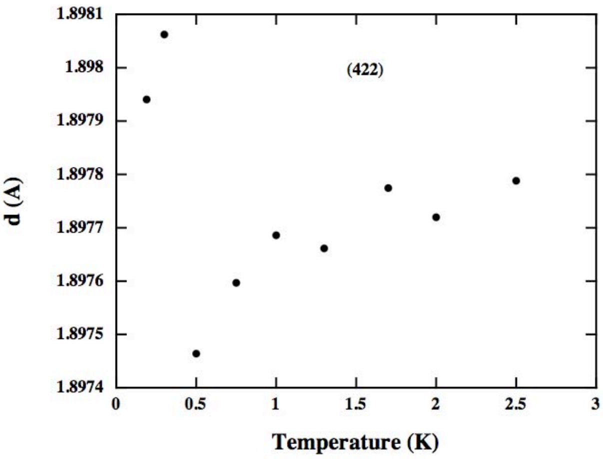

Figure 5, Temperature variation of lattice space *d* for (422) x-ray reflection of $PrOs_4Sb_{12}$.

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

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