

## Unusually large $T_c$ enhancement in superconducting $\text{PrBa}_2\text{Cu}_3\text{O}_x$ under pressure

Jinhua Ye

*National Research Institute for Metals, 1-2-1 Sengen, Tsukuba 305, Japan*

Zhigang Zou

*Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba 305, Japan*

Akiyuki Matsushita

*National Research Institute for Metals, 1-2-1 Sengen, Tsukuba 305, Japan*

Kunihiko Oka

*Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba 305, Japan*

Yoshikazu Nishihara

*Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba 305, Japan  
and Faculty of Science, Ibaraki University, Bunkyo 2-2-1, Mito 310, Japan*

Takehiko Matsumoto

*National Research Institute for Metals, 1-2-1 Sengen, Tsukuba 305, Japan*

(Received 5 February 1998)

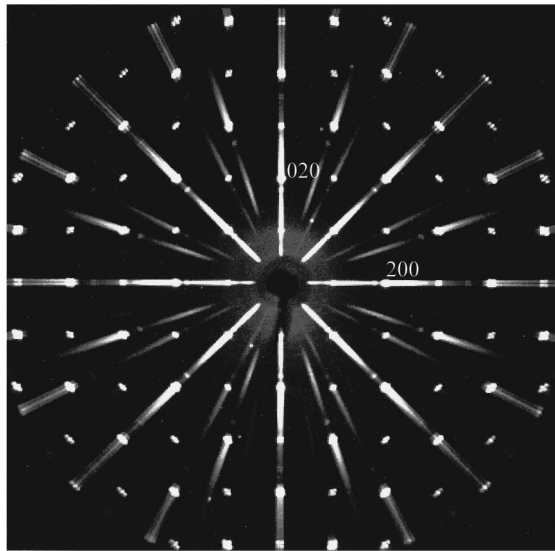
Pressure effects on  $T_c$  of superconducting  $\text{PrBa}_2\text{Cu}_3\text{O}_x$  were investigated by electrical-resistance measurements under hydrostatic pressure up to 10 GPa, using single crystals with different oxygen contents. Large positive-pressure coefficients of  $T_c$ ,  $dT_c/dP$ , with a maximum of +7.4 K/GPa, have been observed. The zero-resistance  $T_c$  was enhanced to 105 K at a pressure of 9.3 GPa, and still keeps positive value of  $dT_c/dP$ . The maximum  $T_c$  increase was as large as 50 K. The unusually large  $T_c$  enhancement far exceeds that observed for the isostructural  $\text{YBa}_2\text{Cu}_3\text{O}_x$  compounds, while x-ray diffraction under high pressure indicates that the compressibility of  $\text{PrBa}_2\text{Cu}_3\text{O}_x$  is about  $6.9 \times 10^{-3} \text{ GPa}^{-1}$ , a value comparable to that of  $\text{YBa}_2\text{Cu}_3\text{O}_x$ . [S0163-1829(98)50326-8]

Since the discovery of the high- $T_c$  oxide superconductors in 1986,  $\text{PrBa}_2\text{Cu}_3\text{O}_x$  (Pr123) has been believed as the exceptional material being nonsuperconducting among the isostructural  $R\text{Ba}_2\text{Cu}_3\text{O}_x$  ( $R$ =rare earth) compounds. A huge number of papers have been published to report and explain the nonsuperconductivity of the Pr123 compound, as well as the suppressing effects of Pr substitution to the superconducting  $R$ -Ba-Cu-O systems for these several years (for example, Refs. 1–8). Some nice models, such as magnetic pair breaking, hole filling, carrier localization, and so on, have been proposed to explain the phenomena. Among them, the model that the hybridization of Pr  $4f$  and O  $2p$  orbitals leads to the localization of holes sounds most plausible and is widely accepted at present. The  $T_c$  decrease with increasing pressure observed in  $(\text{Y}_{1-x}, \text{Pr}_x)\text{Ba}_2\text{Cu}_3\text{O}_x$  for  $x > 0.4$  (Ref. 9) seems to be a good supporting fact to this idea.

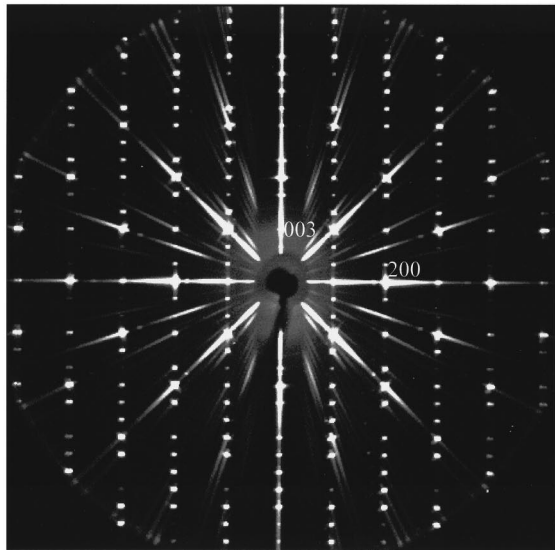
However, superconductivity in  $\text{PrBa}_2\text{Cu}_3\text{O}_x$  thin films has been recently reported by Blackstead *et al.*,<sup>10</sup> and very recently by Usagawa *et al.*<sup>11</sup> On the other hand, Zou *et al.*<sup>12</sup> have grown superconductive Pr123 single crystals by the traveling-solvent floating-zone (TSFZ) method. Further investigations<sup>13,14</sup> to the crystals revealed the following items: (1) the atomic ratio of metallic elements is close to 1:2:3 stoichiometry, (2) the valence state of Pr is +3, and (3) the structure is isostructural to  $\text{YBa}_2\text{Cu}_3\text{O}_x$  (Y123) compounds. Although some differences have been revealed be-

tween the structure of the present superconducting and the conventional semiconducting Pr123, such as a longer  $c$ -axis lattice parameter coming from a slight modification of the structure, the clarifying of the mechanism appears to still be needed. As a means to help understanding about the origin of the superconductivity, pressure dependence of  $T_c$  in a  $\text{PrBa}_2\text{Cu}_3\text{O}_x$  crystal with optimum oxygen content was measured, and a remarkable  $T_c$  enhancement has been observed and briefly reported.<sup>13</sup> In this paper, we report the details of the studies of the pressure effects on the superconducting and structural properties of the  $\text{PrBa}_2\text{Cu}_3\text{O}_x$  single crystals with different oxygen contents, by means of electrical resistance measurement and x-ray diffraction.

Two Pr123 single crystals grown by TSFZ method with different  $T_c$ 's (sample A,  $T_{c(\text{zero})} = 56.5$  K, size:  $0.75 \times 0.25 \times 0.20 \text{ mm}^3$ , sample B,  $T_{c(\text{zero})} = 81$  K, size:  $0.90 \times 0.40 \times 0.30 \text{ mm}^3$ ) were used for the investigation of pressure effect. The bulk superconductivity of the samples was recognized from the magnetic susceptibility measurement using a superconducting quantum interference device variable temperature susceptometer.<sup>12</sup> The single crystallinity of the crystals was confirmed using an x-ray precession camera. Figures 1(a) and (b) show the precession photograph of the  $hk0$  and  $h0l$  reflections of the sample A (taken after unloading). The crystal is orthorhombic, which can be recognized from the splitting of  $hk0$  reflections. The lattice parameters



(a)



(b)

FIG. 1. Zero layer x-ray precession photographs of the  $\text{PrBa}_2\text{Cu}_3\text{O}_{6.6}$  single crystal in (a) [001] and (b) [100] zone axes.

were  $a = 3.883(1) \text{ \AA}$ ,  $b = 3.948(1) \text{ \AA}$ , and  $c = 11.823(3) \text{ \AA}$ . A very weak ringlike diffusing can be observed in strong reflections of  $h0l$ , indicating existence of stacking faults along the  $c$  axis introduced during single-crystal growth. This is consistent with the observation from a scanning electron microscope photograph that a growth pattern along  $c$  axis is visible in the surface of the as-grown TSFZ crystal.<sup>12</sup> The defects might have relevance to the relatively larger superconducting transition width observed in the samples.

Since the sample size is very small, it is difficult to determine the oxygen content of the sample directly using an appropriate chemical analysis method. Here, we presumed that the relation between  $T_c$  and oxygen content as reported for isostructural  $\text{YBa}_2\text{Cu}_3\text{O}_x$  (Ref. 15) is also available in  $\text{PrBa}_2\text{Cu}_3\text{O}_x$ , and estimated oxygen content from the value of  $T_c$ . The oxygen contents in samples A and B as estimated were about 6.6 and 6.8, respectively.

The temperature dependence of the electrical resistivity

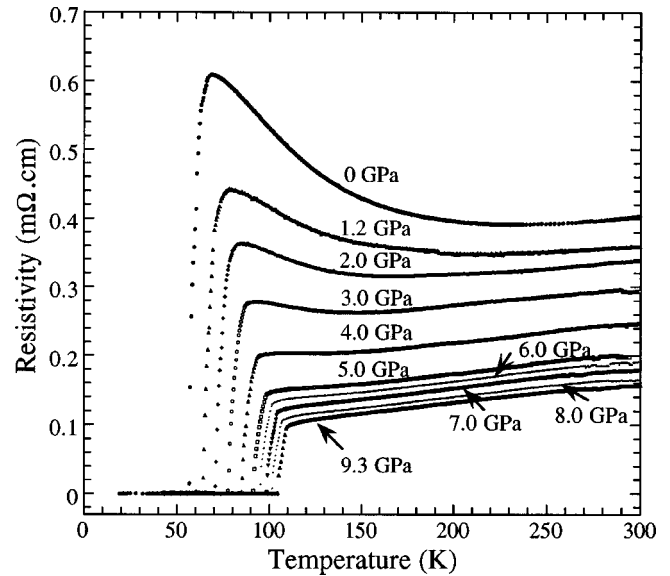


FIG. 2. Temperature dependence of electrical resistivity of  $\text{PrBa}_2\text{Cu}_3\text{O}_{6.6}$  measured at various pressures.

under high pressure up to 10 GPa was measured using a cubic anvil apparatus, which consists of six anvil tops made of tungsten carbide. Fluorinert liquid was used as the pressure transmitting medium to generate hydrostatic pressure. The gasket with a Teflon inner cell is made of a mixture of amorphous boron and epoxy resin. The pressure was changed at room temperature. As soon as the pressing procedure was accomplished, the sample started to cool. The electrical resistivity was measured with the usual four-probe dc method (on  $ab$  plane). Au wires were used as lead wire for the samples. The contact between Au wires and sample was made with Ag paste. The electrical current applied during measurement was 1 mA, 5 mA, and 10 mA. The measurement was in the Ohmic condition. In fact, the measured data fell on the same temperature-resistivity curve.

The structural changes of the compounds under high pressure were investigated using a Mao-Bell-type diamond anvil cell (DAC) at room temperature. The sample, powdered from single crystals of Pr123, was loaded in a brilliant-cut diamond anvil. A 4:1 mixture of methanol:ethanol was used as the pressure transmitting medium. The pressure was determined by using the ruby fluorescence method. X-ray diffraction was carried out using Si(111)-monochromatized  $\text{Mo } K\alpha$  radiation. A collimator with a diameter of  $300 \mu\text{m}$  was used to confine the x-ray beam on the sample. The intensity data were recorded on a bended imaging plate placed behind the DAC, and read out in a scanning step of  $50 \mu\text{m}$ . The two-dimensional diffraction patterns were then integrated into one-dimensional  $2\theta$ - $I$  data from which lattice parameters under pressure were calculated by the Rietveld refinement.<sup>16</sup>

Figure 2 shows the temperature dependence of electrical resistivity  $\rho$  of  $\text{PrBa}_2\text{Cu}_3\text{O}_{6.6}$  measured at various pressures. It can be seen that the temperature dependence of electrical resistivity in the normal state displays a semiconducting behavior at ambient pressure. With increasing pressure, the magnitude of  $\rho$  decreases rapidly, and the semiconducting behavior at normal state tends to be depressed and transfers

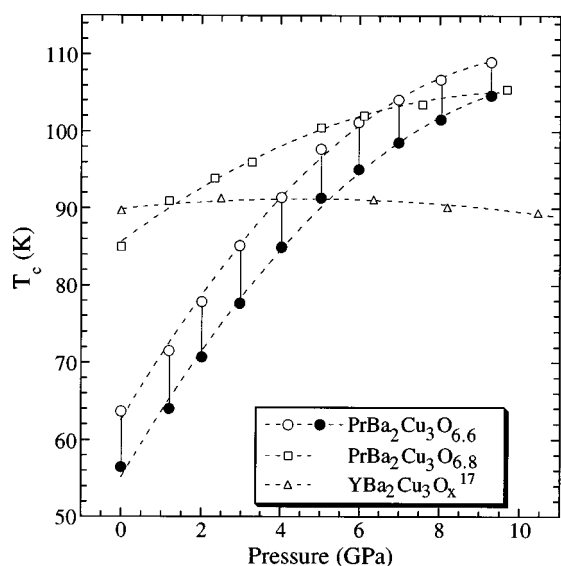


FIG. 3. Pressure dependence of superconducting transition temperature in  $\text{PrBa}_2\text{Cu}_3\text{O}_x$  single crystals. Open and solid circles represent onset  $T_c$  and zero-resistance temperature of  $\text{PrBa}_2\text{Cu}_3\text{O}_{6.6}$ , while open squares are onset  $T_c$  of  $\text{PrBa}_2\text{Cu}_3\text{O}_{6.8}$ . Triangles refer to onset  $T_c$  of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  ( $x = 6.85 \sim 7.0$ ) single crystals.<sup>17</sup> The dotted lines are guides to the eye.

into metallic behavior above 5 GPa. For higher pressure range,  $\rho$  decreases further but much more slowly. The decrease of  $\rho$  and the suppression of semiconducting behavior with increasing pressure indicate a significant increase in the carrier density with the pressure in the oxygen deficient Pr123 compound. For sample B, where the oxygen content approaches the optimum value, the temperature dependence of electrical resistivity in the normal state is metallic for whole pressure range.

Along with the decrease in electrical resistivity with increasing pressure, the superconducting transition temperature in both samples shows a significant increase. Figure 3 plots the pressure dependence of  $T_c$  observed in the two  $\text{PrBa}_2\text{Cu}_3\text{O}_x$  single crystals, along with those reported for  $\text{YBa}_2\text{Cu}_3\text{O}_x$  ( $x = 6.85 \sim 7.0$ ) (Ref. 17) as a comparison. In the figure, the open and solid circles represent the value of on-set and zero-resistance temperature of  $T_c$  for  $\text{PrBa}_2\text{Cu}_3\text{O}_{6.6}$ . The squares represent the on-set  $T_c$  value of  $\text{PrBa}_2\text{Cu}_3\text{O}_{6.8}$ , in which the transition width of the sample was about 4 K. The triangles refer to on-set  $T_c$  of Y123, which was determined from the one-set of the ac susceptibility by Klotz *et al.*<sup>17</sup> It can be seen from the figure that  $T_c$  in Pr123 samples was enhanced rapidly with increasing pressure. The enhancement rate  $dT_c/dP$  ( $P$ : pressure) at initial stage was about 7.4 K/GPa for  $\text{PrBa}_2\text{Cu}_3\text{O}_{6.6}$  and 3.8 K/GPa for  $\text{PrBa}_2\text{Cu}_3\text{O}_{6.8}$ . The maximum value of onset and zero-resistance  $T_c$  enhanced under pressure in  $\text{PrBa}_2\text{Cu}_3\text{O}_{6.6}$  is 109 K and 105 K at 9.3 GPa, and in  $\text{PrBa}_2\text{Cu}_3\text{O}_{6.8}$ , 106 K and 102 K at 9.7 GPa, respectively. Zero-resistance  $T_c$  in both samples exceeds 100 K, and still shows potential to increase. It is notable that in  $\text{PrBa}_2\text{Cu}_3\text{O}_{6.6}$ , the net  $T_c$  increase from ambient pressure to 9.3 GPa is about 50 K, which is probably the champion data among various high- $T_c$  superconductors reported up to now. In Y123 with the optimum oxygen concentration, by contrast, the  $T_c$  changes little with pressure

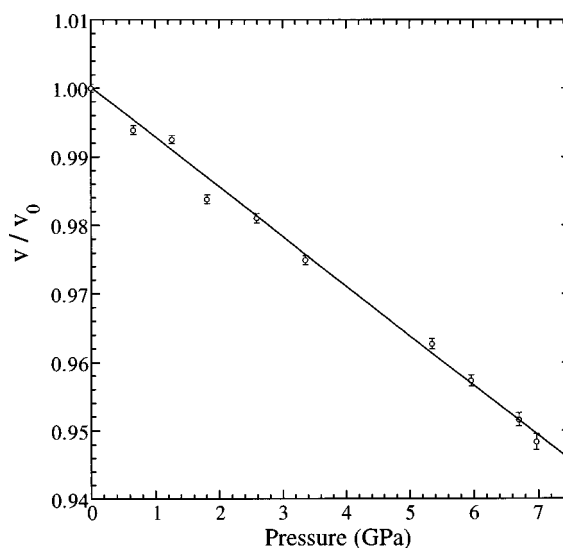


FIG. 4. Relative volume change of  $\text{PrBa}_2\text{Cu}_3\text{O}_x$  ( $x \sim 6.6$ ) under hydrostatic pressure.  $V_0$  is the unit cell volume at ambient pressure. The solid line is a guide to the eye.

around 92 K up to  $\sim 3$  GPa and decreases with pressure above 4 GPa. For other  $R\text{Ba}_2\text{Cu}_3\text{O}_x$  ( $R123$ ) superconductors, the pressure effects on  $T_c$  were reported to increase slightly with increasing rare-earth size.<sup>18,19</sup> However, zero-resistance temperature above 100 K has not been observed in a series of  $R123$ . Although there is a paper<sup>20</sup> reporting that the onset  $T_c$  of a Y123 polycrystalline sintered sample exceeded 100 K at 14.9 GPa, the maximum enhanced zero-resistance  $T_c$  in their sample was lower than 80 K. Therefore our results demonstrate unambiguously that the pressure coefficient for Pr123 is a large positive value, and the pressure enhanced  $T_c$  value far exceeds those observed in other isostructural  $R123$  superconductors.

It is proposed that hole localization due to strong hybridization between Pr  $4f$  and O  $2p$  orbitals is a main origin resulting in the nonsuperconductivity of the conventional Pr123 compound.<sup>6-8</sup> If we assume that the application of pressure decreases the distance between Pr and O(2) atoms, the hybridization between Pr  $4f$  and O  $2p$  orbitals might be expected to increase under high pressure. This increasing hybridization may lead to the stronger localization of carrier, and result in the negative pressure effects in  $\text{PrBa}_2\text{Cu}_3\text{O}_x$ , as observed in the Pr doped  $\text{YBa}_2\text{Cu}_3\text{O}_x$  compounds.<sup>9</sup> However, the present research shows opposite results with this expectation, raising a question as to the explanation of the nonsuperconducting Pr123.

One of the key parameters controlling the  $T_c$  value of the superconducting cuprates is considered to be the carrier concentration in the  $\text{CuO}_2$  planes.  $T_c$  as a function of hole concentration is found to follow a parabolic curve for many hole doped high- $T_c$  superconductors. Under high pressure, the hole concentration in  $\text{CuO}_2$  plane increases due to the carrier transfer from Cu-O chain, which is caused by the structure modification, leading to the increase in  $T_c$ . The initial hole concentration in  $\text{CuO}_2$  plane at ambient pressure thus has a sensitive influence on the pressure effect, as indicated by some theoretical and experimental studies.<sup>21,22</sup> From this point of view, the difference observed in the pressure coefficient of the two  $\text{PrBa}_2\text{Cu}_3\text{O}_x$  samples with different oxygen

content are understandable. However, the maximum  $T_c$  enhanced in Pr123 far exceeds the limit observed in Y123. And, it is of great interest to notice that the maximum enhanced  $T_c$  in Pr123 even exceeds those reported for  $\text{YBa}_2\text{Cu}_3\text{O}_x$ ,<sup>23</sup> where there exists double Cu-O chains being considered responsible for the large pressure effects compared to the Y123 compound, which contains a single Cu-O chain.

Since the Pr123 has the same layered orthorhombic perovskite crystal structure as other R123 compounds, the maximum  $T_c$  enhanced under pressure should be comparable to the R123 superconductors, as the  $T_c$  at ambient pressure behaves. This is indeed in  $\text{RBa}_2\text{Cu}_3\text{O}_x$  superconductors, where the maximum  $T_c$  enhanced under high pressure was reported about the same for different rare earth.<sup>24</sup> Therefore, the unusually high  $T_c$  observed in our experiment indicates that the pressure effects in Pr123 could not be explained by a simple carrier transfer model. Initial differences in carrier distribution of Pr123 coming from its different rare-earth element, as well as some other factors unknown at present may also contribute to the  $T_c$  increase.

Figure 4 shows the relative volume change of  $\text{PrBa}_2\text{Cu}_3\text{O}_x$  ( $x \sim 6.6$ ) under high pressure measured using a diamond anvil cell up to 7 GPa. In accordance with an increase in the applied pressure, unit cell volume showed a monotonical decrease. No trace of structural transition could

be recognized. The compressibility,  $-d \ln V/dP$  varied slightly with the oxygen content of the sample. The average  $-d \ln V/dP$  value was about  $6.9 \times 10^{-3} \text{ GPa}^{-1}$ , which is only slightly larger than that reported for Y123 ( $6.4 \times 10^{-3} \text{ GPa}^{-1}$ ),<sup>25</sup> but smaller than that in Y124 ( $8.2 \times 10^{-3} \text{ GPa}^{-1}$ ).<sup>26</sup> The compressibility of such a magnitude seems difficult to give out a good explanation to the unusually large  $T_c$  enhancement in Pr123. Further study of the structural parameters of Pr123 under high pressure is in progress, which is believed to supply more concrete information of carrier distribution in the compound.

In summary, our  $T_c(P)$  measurement of superconducting Pr123 revealed a large positive pressure effect, which is opposite those reported for the Pr-substituted Y-Ba-Cu-O compounds with high Pr concentration. The pressure coefficient of  $T_c$ ,  $dT_c/dP$ , was found to decrease with increasing oxygen content of the compound, in a similar manner as the isostructural Y123 compound behaves.<sup>27</sup> However, the maximum enhanced  $T_c$  value ( $T_{c(\text{zero})} = 105 \text{ K}$ ) far exceeds the limit observed for Y123 compounds. The unusually large  $T_c$  enhancement suggests that superconducting state, including carrier distribution in the present compound, should be reconsidered.

The authors thank Dr. J. Tang and T. Kosaka for technical assistance.

- <sup>1</sup>L. Sonderholm, K. Zhang, D. G. Hinks, M. A. Beno, J. D. Jorgensen, C. U. Segre, and I. K. Schuller, *Nature (London) (London)* **328**, 604 (1987).
- <sup>2</sup>J. K. Liang, X. T. Xu, S. S. Xie, G. H. Rao, X. Y. Shao, and Z. G. Duan, *Z. Phys. B* **69**, 137 (1987).
- <sup>3</sup>Y. Dalichaouch, M. S. Torikachvili, E. A. Early, B. W. Lee, C. L. Seaman, K. N. Yang, H. Zhou, and M. B. Maple, *Solid State Commun.* **65**, 1001 (1988).
- <sup>4</sup>L. J. Peng, P. Klavins, R. N. Shelton, H. B. Radousky, P. A. Hahn, and L. Bernardz, *Phys. Rev. B* **40**, 4517 (1989).
- <sup>5</sup>J. Fink, N. Nucker, H. Romberg, M. Alexander, M. B. Maple, J. J. Neumier, and J. W. Allen, *Phys. Rev. B* **42**, 4823 (1990).
- <sup>6</sup>K. Takenaka, Y. Imanaka, K. Tamasaku, T. Ito, and S. Uchida, *Phys. Rev. B* **46**, 5833 (1992).
- <sup>7</sup>R. Fahrenbacher and T. M. Rice, *Phys. Rev. Lett.* **70**, 3471 (1993).
- <sup>8</sup>A. I. Liechtenstein and I. I. Mazin, *Phys. Rev. Lett.* **74**, 1000 (1995).
- <sup>9</sup>J. J. Neumeier, M. B. Maple, and M. S. Torikachvili, *Physica C* **156**, 574 (1988).
- <sup>10</sup>H. A. Blackstead, J. D. Dow, D. B. Chrisey, J. S. Horwitz, M. A. Black, P. J. McGinn, A. E. Klunzinger, and D. B. Pulling, *Phys. Rev. B* **54**, 6122 (1996).
- <sup>11</sup>T. Usagawa, Y. Ishimaru, J. Wan, T. Utagawa, S. Koyama, and Y. Enomoto, *Jpn. J. Appl. Phys., Part 2* **36**, L1583 (1997).
- <sup>12</sup>Z. Zou, K. Oka, T. Ito, and Y. Nishihara, *Jpn. J. Appl. Phys., Part 2* **36**, L18 (1997).
- <sup>13</sup>Z. Zou, J. Ye, K. Oka, and Y. Nishihara, *Phys. Rev. Lett.* **80**, 1074 (1998).
- <sup>14</sup>J. Ye, Z. Zou, K. Oka, Y. Nishihara, and T. Matsumoto (unpublished).
- <sup>15</sup>J. D. Jorgenson, B. W. Veal, A. P. Paulikas, L. J. Nowicki, G. W. Crabtree, H. Claus, and W. K. Kwok, *Phys. Rev. B* **41**, 1863 (1990).
- <sup>16</sup>F. Izumi, *J. Crystallogr. Soc. Jpn.* **27**, 23 (1985), in Japanese.
- <sup>17</sup>S. Klotz, W. Reith, and J. S. Schilling, *Physica C* **172**, 423 (1991).
- <sup>18</sup>C. C. Kim, E. F. Skelton, M. S. Osofsky, and D. H. Liebenberg, *Phys. Rev. B* **48**, 6431 (1993).
- <sup>19</sup>J. G. Lin, C. Y. Huang, Y. Y. Xue, C. W. Chu, X. W. Cao, and J. C. Ho, *Phys. Rev. B* **51**, 12900 (1995).
- <sup>20</sup>M. W. McElfresh, M. B. Maple, K. N. Yang, and Z. Fisk, *Appl. Phys. A: Solids Surf.* **A45**, 365 (1988).
- <sup>21</sup>J. J. Neumeier and H. A. Zimmermann, *Phys. Rev. B* **47**, 8385 (1993).
- <sup>22</sup>C. C. Almasan, S. H. Han, B. W. Lee, L. M. Paulius, M. B. Maple, B. W. Veal, J. W. Downey, A. P. Pauliks, Z. Fisk, and J. E. Schirber, *Phys. Rev. Lett.* **69**, 680 (1992).
- <sup>23</sup>E. N. Van Eenige, R. Griessen, R. J. Wijngaarden, J. Karpinski, E. Kaldis, S. Rusiecki, and E. Jilek, *Physica C* **168**, 482 (1990).
- <sup>24</sup>J. Tang, Y. Okada, Y. Yamada, S. Horii, A. Matsushita, T. Kosaka, and T. Matsumoto *Physica C* **282–287**, 1443 (1997).
- <sup>25</sup>W. H. Fietz, M. R. Dietrich, and J. Ecke, *Z. Phys. B* **69**, 17 (1987).
- <sup>26</sup>H. A. Ludwig, W. H. Fietz, M. R. Dietrich, H. Wuhl, J. Karpinski, E. Kaldis, and S. Rusiecki, *Physica C* **167**, 335 (1990).
- <sup>27</sup>W. H. Fietz, R. Quenzel, H. A. Ludwig, K. Grube, S. I. Schlachter, F. W. Hornung, T. Wolf, A. Erb, M. Klaser, and G. Muller-Vogt, *Physica C* **270**, 258 (1996).