# Thermal expansion of superconducting $Bi_2Sr_2CaCu_2O_8$

T. Asahi, H. Suzuki, M. Nakamura, H. Takano, and J. Kobayashi
*Kagami Memorial Laboratory for Materials Science and Technology, Waseda University, 2-8-26 Nishi-Waseda, Shinjuku-ku, Tokyo 169, Japan*

(Received 12 August 1996; revised manuscript received 21 November 1996)

Temperature dependences of thermal strains of superconducting $Bi_2Sr_2CaCu_2O_8$ were measured by using the two-dimensional reciprocal-lattice method of x-ray diffraction in the temperature range between 15 and 300 K. Accuracies of measuring the lattice strains attained $1.6\times10^{-6}$. Very small anomalies of the lattice constants and lattice volume took place at $T_c$ of the transition point. They were caused by definite discontinuities of the thermal-expansion coefficients. Using previously reported values of specific heat and isotropic compressibility a nearly temperature-independent equivalent Grüneisen parameter $\gamma_T$ was derived as $0.89\pm0.11$. From the extrapolation of the lattice volume of the high-temperature phase into the superconducting temperature region, additive lattice strains were found to appear spontaneously in the superconducting phase. From this fact it was concluded that a structural phase transition of the second order took place with the onset of superconductivity. [S0163-1829(97)03614-X]

## I. INTRODUCTION

In order to elucidate the origin of the superconductivity of the high-temperature superconductors (abbreviated HTSC's), it is indispensable to reveal temperature dependences of the lattice constants of any one of the typical HTSC's. Many workers have studied this problem. Their results have agreed only in a point that changes of the lattice constants accompanied by the onset of superconductivity were extremely small. However, it seems that decisive information on detailed behaviors of lattice constants has not been obtained yet.

Previous measurements of the thermal expansion of HTSC's have been focused mainly on $YBa_2Cu_3O_{7-\delta}$ (YBCO). According to x-ray studies,[1,2] accurate results could not be obtained when powder and twinned crystal specimens were used. Among reports of YBCO, those of You *et al.*[2] and Meingast *et al.*[3] seem to be specifically interesting. You *et al.*[2] used the ($\theta$-2$\theta$) coupled radial scanning method on (200), (020), and (006) reflections of YBCO. They found that the lattice constants, $a$, $b$, and $c$, showed unexpectedly large slope discontinuities near $T_c$ of the transition point, and strong fluctuations over the wider temperature range. However, to our surprise, $\alpha_a$ and $\alpha_b$, thermal-expansion coefficients of $a$ and $b$, became negative in the very low-temperature region. They suggest the possibility of the structural phase transition taking place at $T_c$. Meingast *et al.*[3] studied the capacitive dilatometry on YBCO, and found slight jumps of $\alpha_a$ and $\alpha_b$ at $T_c$. They ascribed them to the interaction with superconductivity, and ruled out the occurrence of an additional structural transition. Thus these investigations disclosed that anomalies of thermal expansions of the lattice really occurred at $T_c$, but fully convincing interpretations were not provided.

Exhaustive studies of thermal expansion have not been done on $Bi_2Sr_2CaCu_2O_8$ (BSCCO) by using untwinned specimens. X-ray powder diffractometry was adopted by Ye-Ning Wang *et al.*,[4] Mouallem-Bahout *et al.*,[5] and Gololobov *et al.*;[6] and single-crystal diffractometry was studied by Zhigadlo.[7] However, definite anomalies were not clearly found in the vicinity of $T_c$ in these investigations.

Thus looking at previous works, it seemed to us that decisive conclusions could not be drawn on the relation of lattice strains to the appearance of superconductivity. On the other hand, our recent optical study[8] by using the high accuracy universal polarimeter on BSCCO revealed that the superconducting phase ($S$ phase) appeared through the structural phase transition from the high-temperature phase ($H$ phase). Thus we felt it necessary to acquire accurate evidence of thermal expansion of the lattice of BSCCO in a wide temperature range including $T_c$. This paper reports our x-ray study of this problem.

## II. X-RAY MEASUREMENTS OF LATTICE STRAINS

In order to attain high accuracy for measuring thermal lattice strains, the two-dimensional reciprocal-lattice method[9] was adopted by using x ray. This method has been successfully applied to thermal-expansion measurements of various ferroelectrics.[10] For the present case, the method was considerably improved by reducing divergences of the incident x-ray beam to $7.8\times10^{-4}$ deg and $4.4\times10^{-4}$ deg along the horizontal and vertical directions, respectively, and by elongating the distance between the specimen and an x-ray counter to 2080 mm. As a result, the standard deviation of reading the reflection positions reached $3.1\times10^{-6}$, and accordingly the precision $\varepsilon$ of measurements of strains became $1.6\times10^{-6}$ by using reflections with the reflecting angle $\theta$ of 71.0 deg.

The specimens were prepared from the same crystal as was used for our optical study,[8] one with dimensions of $0.7\times0.5\times0.016$ mm$^3$ along $a$, $b$, and $c$ axes, respectively, and another with $0.8\times1.0\times0.024$ mm$^3$. The former was used for $a$-axis rotation, and the latter for $b$-axis rotation spectrometries. In order to examine the texture of the specimens, Weissenberg photographs of the two specimens were taken prior to the spectrometer study. It was strictly guaranteed that the specimens did not contain any twinning regions.

 

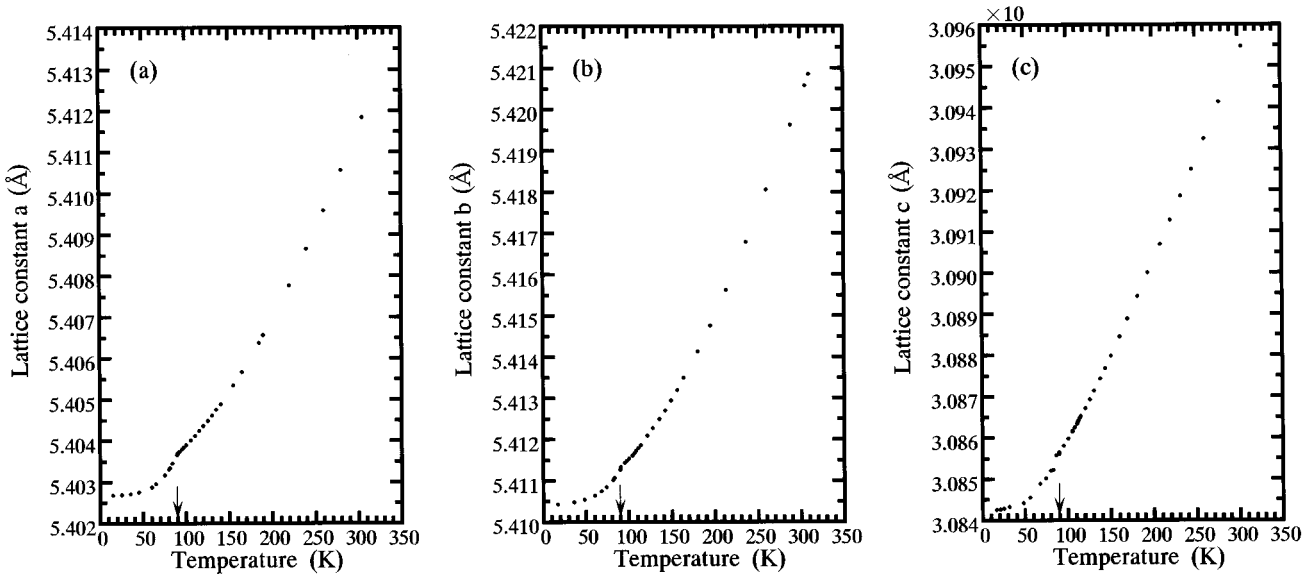


FIG. 1. Temperature dependences of the lattice constants, $a$ (a), $b$ (b), and $c$ (c), where the scale of the ordinate of (c) is taken as one order of magnitude larger than those of (a) and (b).

The lattice constants were also determined preliminarily from the two photographs. $c$ was determined by averaging $c$ values obtained from (0,0,34), (0,0,36), and (0,0,38) reflections of both films. $a$ was determined by averaging those values obtained from 15 ($h0l$) reflections distributed in the higher angle region ($2\theta \gg 100°$) of the $b$-axis photograph, and $b$ from 5 ($0kl$) reflections in the higher angle region of the $a$-axis film. The results were as follows: $a=5.41\pm0.01$ Å, $b=5.42\pm0.01$ Å, $c=30.96\pm0.02$ Å at 300 K. They coincided well with previous reports.[11]

The specimens for the spectrometer experiments were placed in the conduction-type cryostat. Temperatures of the specimens were kept constant within the accuracy of $\pm0.05$ K in the experimental temperature range between 15 and 300 K. The x-ray source was a rotating anode generator (RIGAKU RU200), and Cu $K\alpha$ radiation of 150 mA emission current was used. The reflections used for the spectrometry were (0,6,0) ($\theta=58.5$ deg) issued from the $a$-axis rotation specimen, and (0,0,38) ($\theta=71.0$ deg) and (6,0,20) ($\theta=81.5$ deg) from the $b$-axis rotation specimen.

First, we closely examined whether these reflections rotated around the center of the reciprocal lattice with the change of temperature. They did not rotate at all over the whole temperature range, confirming that axial angles $\alpha$ and $\beta$ were exactly $\pi/2$. It was not possible to prepare a specimen for the $c$-axis rotation, since the crystal was much too readily cleaved along the (001) plane. Therefore we could not check the change of the axial angle $\gamma$ by using the same method. However, as we found by previous optical work[8] that the optical indicatrix did not rotate at all around the $c$ axis when temperature varied, the invariance of $\gamma=\pi/2$ in the present temperature range was already known.

The temperature dependences of $a$, $b$, and $c$ are shown in Figs. 1(a), 1(b), and 1(c); where the scale of the ordinate of (c) is taken as one order of magnitude larger than those of (a) and (b). They similarly decreased with decrease of temperature, and manifested very small anomalies at $T_c$ of 90 K. The temperature dependence of the lattice volume $v=abc$ is depicted by a bold line in Fig. 2. Temperature dependences of the thermal-expansion coefficients along the three axes are indicated in Figs. 3(a), 3(b), and 3(c); e.g., $\alpha_a=(9.4\pm1.2)\times10^{-6}$ K$^{-1}$, $\alpha_b=(1.02\pm0.11)\times10^{-5}$ K$^{-1}$, and $\alpha_c=(1.64\pm0.16)\times10^{-5}$ K$^{-1}$ at 300 K. They manifested analogously distinct discontinuities at $T_c$. The temperature dependence of the volume thermal-expansion coefficient $\alpha_v$ is expressed by a bold line in Fig. 4, e.g., $(3.60\pm0.39)\times10^{-5}$ K$^{-1}$ at 300 K.

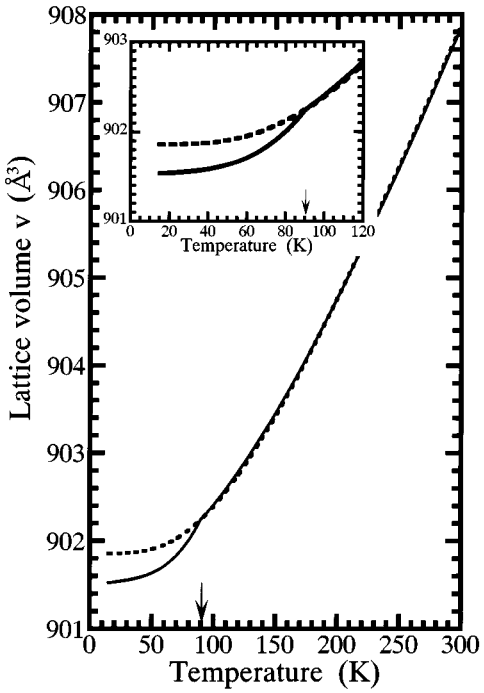


FIG. 2. Temperature dependences of observed (bold line) and calculated (dashed line) lattice volume $v$. Deflection of both lines from $T_c$ is shown in the inset on the enlarged scale.

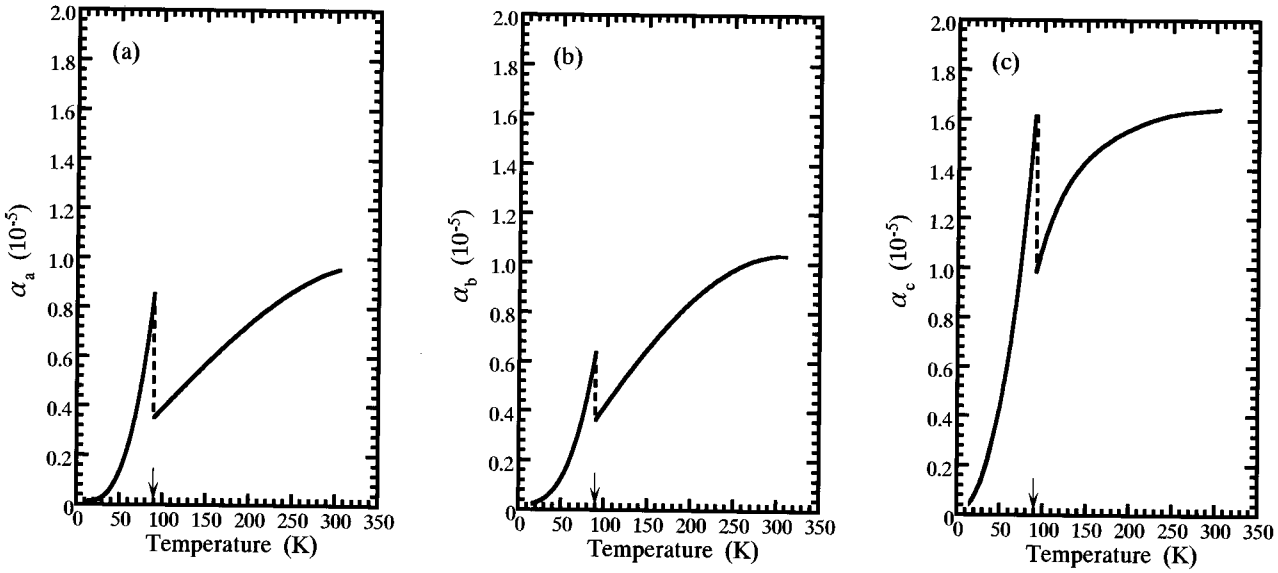


FIG. 3. Temperature dependences of thermal-expansion coefficients, $\alpha_a$ (a), $\alpha_b$ (b), and $\alpha_c$ (c).

### III. PHASE TRANSITION

It was found that the lattice constants and lattice volume exhibited very small anomalies at $T_c$ but each thermal-expansion coefficient manifested definite discontinuities at this point. However, it seemed that there were no investigations reporting the same result. Therefore we felt it necessary first to examine our results and previous results in terms of experimental accuracies, before we tried to draw conclusions.

Precisions of some relevant works for measuring lattice constants are shown in Table I. Horn *et al.*[12] studied powder specimens of YBCO. Their precisions were given in their paper. The precision of the work of You *et al.*[2] was calculated by us by using error bars shown in their paper. The precision of the dilatometry of Meingast *et al.*[3] was also calculated from error bars in their paper. Zhigadlo[7] used the two-dimensional representation method for studying BSCCO by x ray. However, the measurements were only confined to $c$, and the precision was evaluated from error bars. Mouallem-Bahout *et al.*[5] studied powder diffractometry on BSCCO, the precision being shown in their paper. Judging from Table I, the precision of the present work was approximately one order of magnitude better than those of other workers. Besides, our measurements were more accurate than other ones in having carefully ensured the absence of rotations of the reflections caused by lowering of the symmetry. Thus it would be well to consider that the present work could reveal thermal expansion of the lattice more accurately than other workers did.

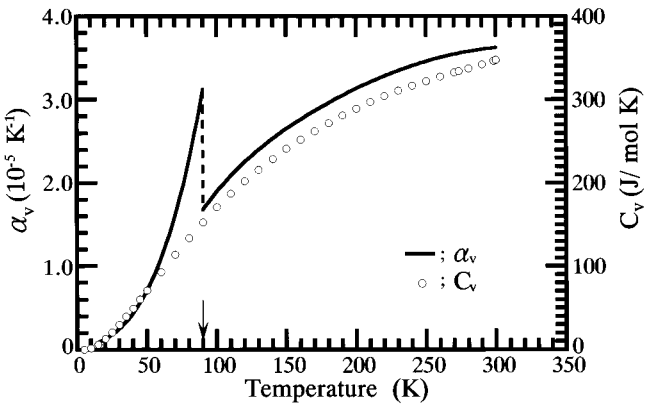


FIG. 4. Temperature dependences of volume thermal-expansion coefficient $\alpha_v$ (bold line) and specific heat $C_v$ (open circles).

Returning to BSCCO, Zhigadlo[7] found that large scatterings of $c$ values occurred both at 75–110 K and 220–245 K. They ascribed them to lattice instability, but excluded the occurrence of a phase transition around 75–110 K. Mouallem-Bahout *et al.*[5] found that no anomalies of $\alpha_a$ and $\alpha_c$ appeared at $T_c$ but $\alpha_a$ became negative below 50 K. They discussed both coefficients thermodynamically. As we obtained different results, it will be worthwhile to analyze our results on a thermodynamical viewpoint.

A volume thermal-expansion coefficient $\alpha_v$ is related to the equivalent Grüneisen parameter $\gamma_T$ within the quasiharmonic approximation.

$$\gamma_T = \frac{\alpha_v V}{\chi_T C_v}, \tag{1}$$

where $C_v$ is the specific heat at constant volume, $V$ is the molar volume, and $\chi_T$ is the isotropic compressibility. Gavarri *et al.*[13] measured $\chi_T = (16.7 \pm 3.1) \times 10^{-12}$ $Pa^{-1}$ at 300 K by using neutron diffraction. The temperature dependence of $C_v$ was measured by Gavrichev *et al.*[14] from 300 down to 10 K. Their results are represented by open circles and compared with $\alpha_v$ in Fig. 4. It is clear that temperature dependences of $\alpha_v$ and $C_v$ are almost parallel above $T_c$. It means that Eq. (1) holds in the $H$ phase of BSCCO with constant $\chi_T$ and $\gamma_T$. The temperature change of $\gamma_T$ was calculated as shown by open circles in Fig. 5 by using a constant value of $\chi_T$ given above. Thus it has been confirmed that $\gamma_T$ is independent of temperature above $T_c$. In other words, the $H$ phase of BSCCO is a perfect Grüneisen solid with

TABLE I. Precisions of various lattice strain measurements applied to HTSC's.

| Crystal | Experimental method | Precision | Authors |
|---|---|---|---|
| YBCO | X-ray diffraction | $\varepsilon_c = 6\times10^{-6}$ | Horn *et al.* (Ref. 12) |
| YBCO | X-ray diffraction | $\varepsilon_b = 7\times10^{-6}$ | You *et al.* (Ref. 2) |
| YBCO | Capacitive dilatometer | $\varepsilon_c = 3\times10^{-4}$ | Meingast *et al.* (Ref. 3) |
| BSCCO | X-ray diffraction | $\varepsilon_c = 1.0\times10^{-5}$ | Zhigadlo (Ref. 7) |
| BSCCO | X-ray diffraction | $\varepsilon_c = 3.6\times10^{-5}$ | Mouallem-Bahout *et al.* (Ref. 5) |
| BSCCO | X-ray diffraction | $\varepsilon_c = 1.6\times10^{-6}$ | Present work |

$\gamma_T = 0.89 \pm 0.11$. This value nearly equals $1.0 \pm 0.2$, derived by Gavarri *et al.*[13] at 300 K, and 1.08 by Mouallem-Bahout *et al.*[5] at 220 K.

As we knew $\alpha_v$, $\chi_T$, and $\gamma_T$ of the $H$ phase, it became possible to extrapolate $v$ of the $H$ phase below $T_c$ provided $C_v$ in the extended $H$ phase could be acquired. For this aim we determined Debye temperatures $\Theta_D$ as a function of temperatures from the $C_v$ vs $T$ relation given by Gavrichev *et al.*[14] They are shown by a bold line in Fig. 5, where data of the $S$ phase measured by Collocott *et al.*[15] are also depicted by open triangles. It was seen that $\Theta_D$ in the $H$ phase were approximately constant but began to decrease from about 90 K and converged to nearly constant values as given by Collocott *et al.*[15] Thus we could take $\Theta_D$ in the $H$ phase as 450 K. We calculated $v$ values of the $H$ phase by using these $\chi_T$, $\gamma_T$, and $\Theta_D$ in all the temperature range. They are shown in Fig. 2 by a dashed line. It coincides perfectly with the observed $v$ line above $T_c$. However, it is significant that it began to deflect from the observed $v$ line below $T_c$ as shown clearly in the inset. This fact shows that additional lattice strains take place spontaneously in the $S$ phase. This characteristic phenomenon can be more clearly demonstrated in Fig. 6(a) by representing the additive lattice volumes $\Delta v_S = |v_S - v_H|$ with respect to the temperature, where $v_S$ and $v_H$ are lattice volumes of the $S$ and $H$ phases below $T_c$. The temperature dependence of the thermal coefficient of $\Delta v_S$, is depicted in Fig. 6(b), where the same coefficient[8] of a gyration tensor component $g_{33}$ is also indicated for the sake of comparison. Both coefficients are quite similar. This fact indicates that the structural phase transition of the second order takes place with the onset of superconductivity at $T_c$.

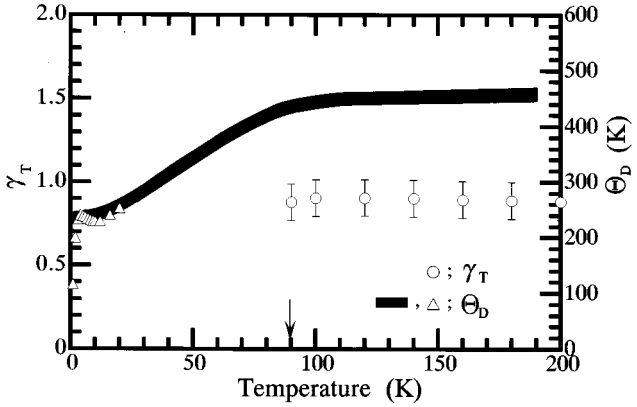


FIG. 5. Temperature dependences of Grüneisen parameter $\gamma_T$ (open circles) and Debye temperatures $\Theta_D$ (bold line).

## IV. CONCLUSION

We studied thermal expansion of the lattice constants and the lattice volume $v$ of BSCCO by using x ray in the temperature range between 15 and 300 K. Lattice constants and the lattice volume $v$ manifested analogously very small anomalies at $T_c$. It was found that these anomalies were caused by conspicuous discontinuities of each thermal-expansion coefficient.

Thermal expansion of BSCCO was discussed from a thermodynamical viewpoint. By using isotropic compressibility $\chi_T$ and specific heat $C_v$ in the high-temperature phase, BSCCO was found to be a perfect Grüneisen solid with an equivalent Grüneisen parameter $\gamma_T = 0.89 \pm 0.11$. $v$ of the $H$ phase was extrapolated into the superconducting region by

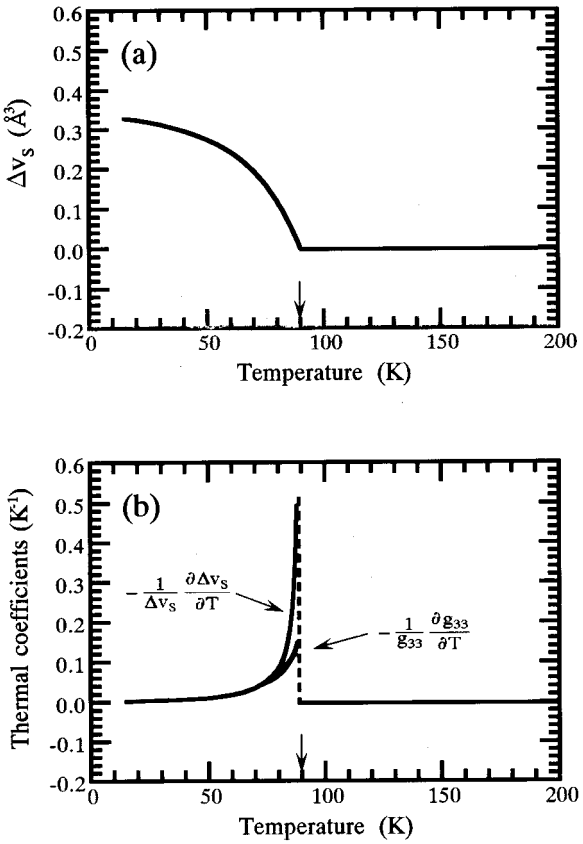


FIG. 6. Temperature dependences of spontaneous lattice volumes $\Delta v_S = |v_S - v_H|$ (a), and thermal coefficient $-1/\Delta v_S(\partial \Delta v_S/\partial T)$ (b). Thermal coefficient of a gyration tensor component $g_{33}$, $-1/g_{33}(\partial g_{33}/\partial T)$, is also shown in (b) for the sake of comparison.

using $\chi_T$, $\gamma_T$, and $\Theta_D$ of this phase. The extrapolated $v$ deflected significantly from observed $v$ below $T_c$, showing that additional lattice strains appeared spontaneously in the superconducting phase. Thus it was concluded that a structural phase transition of the second order took place together with the onset of the superconductivity at $T_c$.


## ACKNOWLEDGMENT

We express our gratitude to Dr. Y. Enomoto for supplying the specimens used in the present experiment.



[1] Hoydoo You, J. D. Axe, X. B. Kan, S. Hashimoto, S. C. Moss, J. Z. Liu, G. W. Crabtree, and D. J. Lam, Phys. Rev. B **38**, 9213 (1988).

[2] Hoydoo You, U. Welp, and Y. Fang, Phys. Rev. B **43**, 3660 (1991).

[3] C. Meingast, O. Kraut, T. Wolf, H. Wuhl, A. Erb, and G. Muller-Vogt, Phys. Rev. Lett. **67**, 1634 (1991).

[4] Ye-Ning Wang, Jin Wu, Hui-Min Shen, Jin-Song Zhu, Xiao-Hua Chen, Yi-Feng, and Zhong Zhao, Phys. Rev. B **41**, 8981 (1990).

[5] M. Mouallem-Bahout, J. Gaude, G. Calvarin, J. R. Gavarri, and C. Carel, Mater. Lett. **18**, 181 (1994).

[6] E. M. Gololobov, V. P. Popov, N. A. Prytkova, Zh. M. Tomilo, and N. M. Shimanskaya, Inzhenerno-Fiz. Zh. **60**, 88 (1991).

[7] N. D. Zhigadlo, Phase Transit. **43**, 167 (1993).

[8] J. Kobayashi, T. Asahi, M. Sakurai, M. Takahashi, K. Okubo, and Y. Enomoto, Phys. Rev. B **53**, 11 784 (1996).

[9] J. Kobayash, N. Yamada, and T. Nakamura, Phys. Rev. Lett. **11**, 410 (1963).

[10] For instance, J. Kobayashi, Y. Uesu, and Y. Sakemi, Phys. Rev. B **28**, 3866 (1983).

[11] S. A. Sunshine, T. Siegrist, L. F. Schneemeyer, D. W. Murphy, R. J. Cava, B. Batlogg, R. B. van Dover, R. M. Fleming, S. H. Glarum, S. Nakahara, R. Farrow, J. J. Krajewski, S. M. Zahurak, J. V. Waszczak, J. H. Marshall, P. Marsh, L. W. Rupp, Jr., and W. F. Peck, Phys. Rev. B **38**, 893 (1988).

[12] P. M. Horn, D. T. Keane, G. A. Held, J. L. Jordan-Sweet, D. L. Kaiser, F. Holtzberg, and T. M. Rice, Phys. Rev. Lett. **59**, 2772 (1987).

[13] J. R. Gavarri, O. Monnereau, G. Vaequier, C. Carel, and C. Vettier, Physica C **172**, 213 (1990).

[14] K. S. Gavrichev, V. E. Gorbunov, I. A. Konovalova, V. B. Lazarev, E. A. Tishchenko, and I. S. Shaplygin, Izvest. Akad. Nauk. Neorg. Mater. **26** (5), 1102 (1990).

[15] S. J. Collocott and J. G. Collins, Supercond. Sci. Technol. **4**, 202 (1991).