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X-ray Diffraction Study of Spontaneous Strain in Superconducting $Ba_{0.6}K_{0.4}BiO_3$

H. Fujishita[a,b,1], T. Yamada[b], S. Nakada[b], H. Okamoto[c], S. Shitara[d], M. Kato[d], Y. Koike[d]

[a] *School of Mathematics and Physics, Kanazawa University, Kanazawa, 920-1192, Japan*
[b] *Division of Mathematical and Physical Sciences, Kanazawa University, Kanazawa, 920-1192, Japan*
[c] *School of Health Sciences, Kanazawa University, Kanazawa, 920-0942, Japan*
[d] *Department of Applied Physics, Tohoku University, Sendai 980-8579, Japan*

Abstract

The lattice parameter of $Ba_{0.6}K_{0.4}BiO_3$, which is a well-studied conventional superconductor, was measured by the X-ray Rietveld method between 10 K and room temperature. A very small change in the lattice parameter could be detected in the superconducting phase. The change could be attributed to a spontaneous strain generated in the superconducting phase by the coupling between a superconducting order parameter and the strain. Previously published data on $YBa_2Cu_3O_{6.5}$ and MgB_2 were analyzed, and the present results were compared with our previously obtained results on $La_{1.85}Sr_{0.15}CuO_4$. It was concluded that this coupling phenomenon is common to all superconductors.

Key words: Superconductors, crystal structure and symmetry, phase transitions
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1. Introduction

Structural changes in high-temperature superconductors have been studied extensively using a high-resolution diffractometers since the discovery of superconducting phase transition in $La_{2-x}Sr_xCuO_4$. Nevertheless, no significant anomalies have been detected in connection with the superconducting phase transition. Recently, lattice parameters of orthorhombic $YBa_2Cu_3O_{6.5}$ with a superconducting transition temperature T_c of 55 K were accurately measured by high-angle double-crystal X-ray diffractometry: A change in orthorhombicity $2(b-a)/(a+b) = tan^{-1}(b/a) - \pi/4$ at T_c was clearly detected [1]. The introduction of a new critical exponent has been considered necessary for explaining the difference between the observed orthorhombicity and that extrapolated from the normal state. An anomaly of the lattice parameter a of the hexagonal intermetallic superconductor MgB_2 was clearly observed by high-resolution pulsed neutron powder diffraction [2]: The a-axis thermal expansion became negative near its T_c of 39 K. The expected negative change in the thermal expansion coefficient at T_c was estimated to be approximately one-fifth of the observation based on the Ehrenfest relation for a second-order phase transition and the observed values of $dT_c/dP = -1.11$ K/GPa and the change in specific heat $\Delta C = 133$ mJ/mol·K. The thermal expansion of MgB_2 was also analyzed by introducing two Einstein temperatures, 222 K and 69 K, and two Grüneisen parameters, 1.33 and −0.304. The change in thermal expansion required by the Ehrenfest relation was concluded to be overwhelmed by the latter contribution.

A spontaneous strain, i.e., a secondary order parameter, is typically produced through the coupling between the strain e and the primary order parameter Q that is an atomic shift in structural phase transitions. In general, small spontaneous strains are produced in ferromagnets (i.e., spontaneous magnetostriction), where the order parameter Q is a spontaneous magnetization. However, the strain in invar alloys is known to be so large that the alloys show low thermal expansion in their ferromagnetic phases [3]. The free energy $G(Q,T)$ near the transition temperature can be written in its simplest form as follows using a Landau potential:

$$G(Q,T) = G_0(T) + \frac{1}{2}A(T-T_c)Q^2 + \frac{1}{4}BQ^4 + \frac{1}{2}Ce^2 - DeQ^2,$$

where A, B, C, and D are temperature independent positive constants. From the equilibrium condition for the strain, we can obtain the relation between the strain and

Email address: fujishit@kenroku.kanazawa-u.ac.jp (H. Fujishita)

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the order parameter as follows:

$$e = (D/C)Q^2.$$

The primary order parameter Q is zero above T_c, whereas it is nonzero below T_c. A spontaneous strain is defined in terms of a low-temperature phase lattice parameter a_{LT} and a high-temperature phase lattice parameter a_{HT} when extrapolated to the same low temperature (i.e., hypothetical lattice parameter of high-temperature phase at a low temperature) as follows [4]:

$$e = (a_{LT} - a_{HT})/a_{HT}.$$

We carried out precise lattice parameter measurements of the high-temperature superconductor $La_{1.85}Sr_{0.15}CuO_4$ [5]. We detected a change in the strain in the superconducting phase. We showed, for the first time, that the strain can be explained in terms of the coupling between the strain and the superconducting energy gap. We also showed that the strain of MgB_2 can be attributed to the coupling.

In the present study, we performed precise lattice parameter measurements of $Ba_{0.6}K_{0.4}BiO_3$, which is a well-studied conventional superconductor with a simple cubic perovskite structure, to clarify whether such a coupling is common to all superconductors. Further, we analyzed the published data on $YBa_2Cu_3O_{6.5}$ in terms of the coupling. We have published a part of this study previously [6, 7].

2. Experimental details

Polycrystalline samples of $Ba_{0.6}K_{0.4}BiO_3$ were synthesized in a very short heating time of several minutes at a temperature as low as 290°C using molten KOH. A mixture of KOH, BaO_2, and Bi_2O_3 (K:Ba:Bi = 55:0.6 :1 in molar ratio) was melted and reacted in a Teflon beaker at 290°C in air. The melt was quenched to room temperature. A black polycrystalline powder thus obtained was isolated by dissolving the KOH in distilled water, and then, it was dried at 150^oC in air. Details of sample preparation are given elsewhere [8]. The K-content x was estimated from the lattice parameter a using the relation $a = 4.3548 - 0.1743x$ [9]. The magnetization was measured in a magnetic field of 5 Oe after field cooling using a superconducting quantum interference device (SQUID) magnetometer, Quantum Design SP5000, to measure the superconducting transition temperature accurately.

X-ray diffraction patterns were measured using a Rigaku X-ray diffractometer, RINT2500, with a graphite counter monochromator and an X-ray generator with a rotating Cu anode. The generator was operated at 50 kV and 300 mA. A powder sample was obtained by grinding the polycrystalline powder. A platelike powder sample was mounted on a sample holder made of copper. The sample was fixed in a closed-cycle He gas refrigerator that was mounted on the diffractometer. The sample was cooled from room temperature to 10 K. Diffraction patterns were measured between 18° and 140° at a scanning speed of 2θ= 0.4°/min. Data were collected at every 2θ= 0.02°. Below 40 K, measurements were performed twice. The diffraction patterns were analyzed by the Rietveld method using the computer program RIETAN-2000 to obtain accurate lattice parameters [10]. The background levels were fitted by polynomial expressions through the analyses. Least-squares refinements were carried out to minimize the R-factor R_{wp}, which is defined as follows:

$$R_{wp} = \sqrt{\sum_i w_i(y_i - f_i)^2 \Big/ \sum_i w_i y_i^2},$$

where y_i and f_i are the observed and calculated intensities, respectively, at the i-th step. These intensities contain the background intensities. The weight w_i was taken to be equal to $1/y_i$. Calculations were carried out by a conjugate direction method on the basis of a cubic perovskite structure with the space group $Pm\bar{3}m$ (No.221) [11]. A few weak impurity peaks of unreacted Bi_2O_3 were detected; they were omitted from the calculations.

The phenomenological temperature dependence of the lattice parameter a above T_c was studied using the computer program KaleidaGraph.

3. Results

The result of profile fitting at 10 K is shown in Fig. 1, as an example. The R-factors of this fit were R_{wp} = 15.4%, R_p = 10.4%, and R_I = 8.7%. These values seem to be fairly large at first glance. However, the R-factors depend on not only the fitting but also the quality of the observed pattern, because the denominator in the equation of R_{wp} is the sum of the observed counts with background. The minimum observed count in Fig. 1 is less than 100 at $2\theta\sim$ 40°. Then, the ratio of the maximum count to the minimum one in Fig. 1 exceeds 900, which is several times that of the usual measurements. The large values of the present R-factors in appearance are mainly attributed to the high quality of our data. Thus, we cannot compare the R-factors of different measurements. We should judge the reliability

of the obtained parameters not by the R-factors but by the estimated standard deviations (esd's).

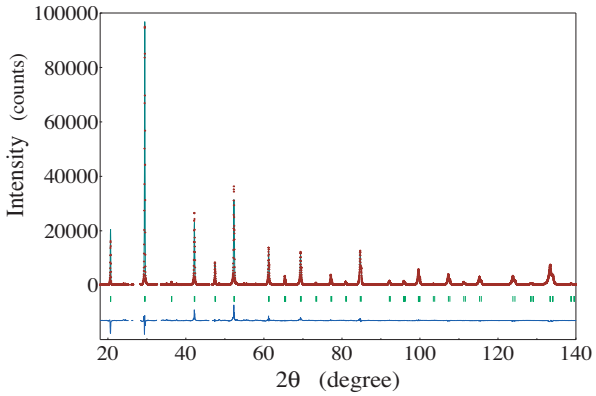

Figure 1: X-ray powder diffraction pattern and best-fit Rietveld refinement profile of $Ba_{0.6}K_{0.4}BiO_3$ observed at 10 K using CuKα radiation. A few weak impurity peaks of the unreacted Bi_2O_3 were detected; they were omitted from the calculations. The calculated pattern is shown by a green line passing though red data points in the upper portion. The short vertical green bars below the pattern indicate the positions of the allowed reflections. The blue line in the lower portion shows the differences between the observed and the calculated patterns.

In Fig. 2, the obtained lattice parameter a is delineated as a function of temperature along with the magnetization for comparison. Below 40 K, the lattice parameter was measured as an average of two measurements obtained at the same temperature, with an esd of $1/\sqrt{2}$. The magnetization showed a negative value below 26 K, indicating the superconducting transition temperature T_c to be 26 K.

To precisely estimate a_{HT} below T_c, we fitted a simple Einstein model to a above 26 K. The function is expressed as

$$ln(\frac{a}{a_o}) = A\Theta_E[exp(\frac{\Theta_E}{T}) - 1]^{-1},$$

where a_o is the lattice parameter a at $T = 0$, Θ_E is the Einstein temperature, and A is the scaling coefficient including the Grüneisen parameter. The results of the fitting and its extension below T_c are shown in Fig. 2 by a solid line, where Θ_E= 241 ± 3 K, and the error is the standard error. The coefficient of determination, R^2, of this fitting was 0.9998. The function accurately reproduced the data above T_c, while a_{HT} was almost temperature independent below T_c. A distinct deviation of a_{LT} from a_{HT} was observed in the superconducting phase.

Because a_{HT} was almost saturated in the superconducting phase of $Ba_{0.6}K_{0.4}BiO_3$, as shown by the red

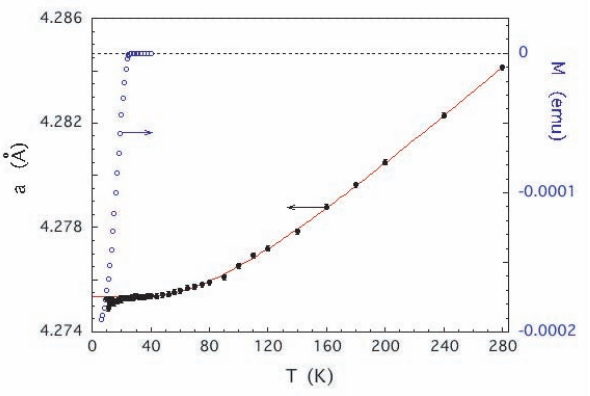

Figure 2: Plots of lattice parameter a (solid circles: lef-hand scale) and magnetization (open circles: right-hand scale) of $Ba_{0.6}K_{0.4}BiO_3$ versus temperature. The red solid line is the least-squares fit obtained using a simple Einstein model above T_c and its extension below T_c.

line in Fig. 2, the spontaneous strain was proportional to the difference between the low- and high-temperature lattice parameters, i.e., $a - a_{HT}$. A superconducting order parameter is an energy gap $\Delta(T)$, i.e., a Bardeen-Cooper-Schrieffer (BCS) gap, on a Fermi surface in the conventional superconductors. Figure 3 shows a comparison of the temperature dependence of the difference $|a - a_{HT}|$ with $\Delta^2(T)$. The difference was qualitatively proportional to $\Delta^2(T)$. Such a relationship is expected in the case of a linear-quadratic coupling between the strain and the order parameter.

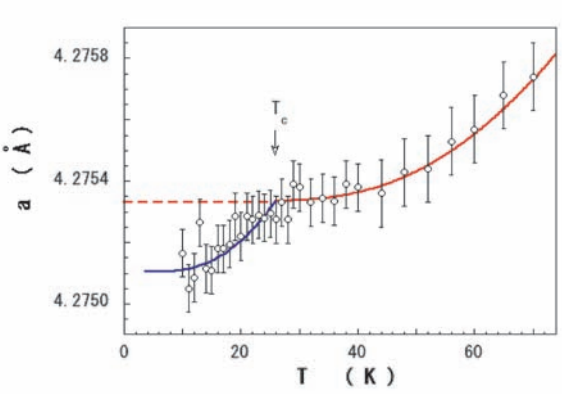

Figure 3: Comparison of the lattice parameter a (open circles) and the square of the BCS gap (blue solid line below T_c) of $Ba_{0.6}K_{0.4}BiO_3$. The red solid line and the broken line are the least-squares fits obtained using a simple Einstein model above T_c and its extension below T_c, respectively. (see text). The square of the BCS gap is reversed, whose origin is taken at $a(T_c)$ obtained by fitting.

4. Discussions

We could detect a very small change in the lattice parameter of $Ba_{0.6}K_{0.4}BiO_3$ below its superconducting transition temperature. This change can be explained as a spontaneous strain caused by coupling with the superconducting order parameter. We have previously obtained a similar result for $La_{1.85}Sr_{0.15}CuO_4$ [5]. The negative thermal expansion of a of the hexagonal intermetallic superconductor MgB_2 was clearly observed near its T_c of 39 K [2]. We suggested that the published data can be satisfactorily explained in terms of the coupling [5]. MgB_2 is now known to be a BCS superconductor showing two-band superconductivity [12]. Next, we analyzed the published data on the lattice parameter a of the orthorhombic high-temperature superconductor $YBa_2Cu_3O_{6.5}$ with T_c of 55 K [1]. The open circles in Fig. 4 show a obtained from Fig.4 in [1]. To precisely estimate a_{HT} below T_c, we fitted the simple Einstein model to a between 55 K and 100 K. The results of the fitting and its extension below T_c are shown in Fig. 4 by a broken line, where the Einstein temperature Θ_E= 112 ± 43 K. The coefficient of determination, R^2, of this fitting was 0.99996. The broken line shows a slight temperature dependence below T_c. The spontaneous strain e was obtained and compared with $\Delta^2(T)$. The solid line in Fig. 4 shows a calculated for $e \propto \Delta^2(T)$; i.e. $a_{LT} = a_{HT} + a_{HT}K\Delta^2(T)$, where K is a proportional constant. These values of a agree with the previously obtained data. Thus, the lattice parameter anomalies observed in $YBa_2Cu_3O_{6.5}$, $La_{1.85}Sr_{0.15}CuO_4$, MgB_2, and $Ba_{0.6}K_{0.4}BiO_3$ can be explained as a spontaneous strain caused by coupling with the superconducting order parameter.

We deduced the possible mechanisms of the coupling between the superconductivity and the strain. The mechanisms might be attributed to two kinds of electron-phonon interaction. First, let us consider a magnetovolume effect in invar alloys. The effect can be understood simply as follows, if we take into account an itinerant electron model based the Stoner theory: Ferromagnetism appears when a reduction in the exchange energy of electrons exceeds an increase in their kinetic energy caused by an exchange splitting of the electron band [13]. The increase in kinetic energy is suppressed by the expansion of the lattice parameters, which results in the magnetovolume effect. In the case of superconductors, the BCS energy gap opens up on a Fermi surface. The kinetic energy difference caused by the appearance of the gap is expressed as $\Delta^2/|V| - N(0)\Delta^2/2$, where V and $N(0)$ are the attractive interaction potential and density of states of electrons at the Fermi surface, respectively. Its leading term is canceled out by the attractive potential energy term [14]. Thus, an expansion of the lattice parameters might also suppress the increase in the kinetic energy in superconductors. This mechanism causes a positive strain ($e > 0$).

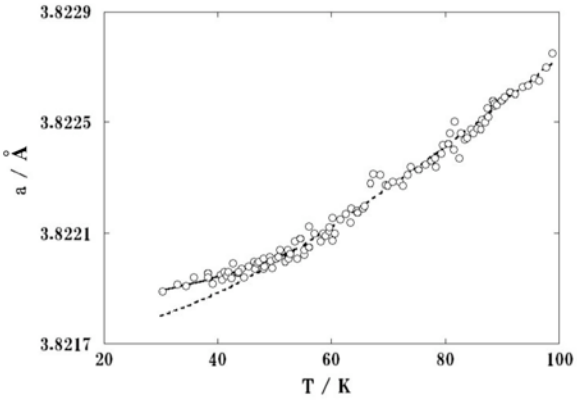

Figure 4: Comparison between the observed lattice parameter a (open circles) and the calculated one (solid line in superconducting phase) of orthorhombic $YBa_2Cu_3O_{6.5}$ (T_c= 55 K). The observed a values were obtained from Ref. 1. The broken line is the least-squares fit obtained using a simple Einstein model above T_c and its extension below T_c (see text).

Next, let us consider the relation between the superconductivity and the anharmonic interactions of phonons. The thermal expansion of lattice parameters is primarily caused by the anharmonic interactions. These interactions also destroy the dynamical independence of the phonons, which results in finite lifetimes of the phonons. The finite lifetime causes broadening of the lineshape of a phonon in inelastic neutron scattering experiments. An additional linewidth γ_q^{e-p} is caused by the electron-phonon interaction to the width of the phonon with wavenumber q and frequency ω_q. γ_q^{e-p} is expressed as $\gamma_q^{e-p} = \pi N(0)\hbar\omega_q^2\lambda_q$, where λ_q is the contribution of the phonon with q and ω_q to λ, the dimensionless electron phonon coupling parameter [15]. In the case of superconducting Nb with T_c of 9.2 K, changes in the linewidths of [110] phonons polarized [001] are observed clearly when the phonon energies are equal to $2\Delta(T)$ by inelastic neutron scattering measurements [16]: The linewidths decrease rapidly when $\hbar\omega_q < 2\Delta(T)$, whereas when $\hbar\omega_q > 2\Delta(T)$ on cooling, the linewidths increase slightly. The change in the sound attenuation constant that is proportional to γ_q^{e-p} was predicted on the basis of the BCS theory [17]. Then, it is plausible that these changes cause additional changes in the anharmonic interactions of phonons,

which results in additional expansion or contraction of the lattice parameters. This mechanism probably causes a negative strain ($e < 0$) rather than a positive strain, because the observed decreases in linewidths in Nb are more obvious than the enhancements.

Both of these mechanisms appear to be necessary for gaining a complete understanding the spontaneous strain in superconductors, because both positive e ($YBa_2Cu_3O_{6.5}$, $La_{1.85}Sr_{0.15}CuO_4$, and MgB_2) and negative e ($Ba_{0.6}K_{0.4}BiO_3$) are observed.

5. Conclusions

The spontaneous strain generated in the conventional superconductor $Ba_{0.6}K_{0.4}BiO_3$ in the superconducting phase can be explained in terms of the coupling between a superconducting order parameter and the strain. This coupling is common to all superconductors.

6. Acknowledgments

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