Out-of-plane thermal conductivity of the layered thermoelectric oxide $Bi_{2-x}Pb_xSr_2Co_2O_y$

I. Terasaki,[1,2,*] H. Tanaka,[1] A. Satake,[1] S. Okada,[1,2] and T. Fujii[1,2]
[1]*Department of Applied Physics, Waseda University, Tokyo 169-8555, Japan*
[2]*CREST, Japan Science and Technology Agency, Tokyo 108-0027, Japan*
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The out-of-plane thermal conductivity (κ_c) of $Bi_{2-x}Pb_xSr_2Co_2O_y$ is measured and analyzed. A low value of 4–8 mW/cm K is observed at 300 K, which is close to the minimum thermal conductivity. This implies the phonon mean-free path is of the order of the *c*-axis lattice parameter. The temperature dependence is also anomalous, and the positive temperature coefficient $d\kappa_c/dT>0$ is observed. These features can be understood semiquantitatively by a phenomenological expression of κ including the contribution of optical phonons.

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I. INTRODUCTION

Heat conduction is one of the most fundamental transport properties in solids.[1] The ratio of the thermal current density to the temperature gradient is known as the thermal conductivity κ, which has been studied for elementary and binary compounds with simple structures.[2] Nowadays, we study materials with more complicated structures consisting of three, four, or more elements. They have various force constants within the unit cell and tens of phonon branches, and often show a significant anisotropy in κ. However, the theoretical framework of the heat conduction has been basically unchanged since the 1960's,[3,4] and appears to be too simple to apply them for quantitative analyses. In addition, it has recently been established that the spin excitation is a good heat conductor in some magnetic insulators,[5–8] in which the spin-phonon interaction plays an essential role. Although the theoretical treatment of spin heat conduction has been extensively developed,[9,10] a generally agreed analysis procedure is not yet at hand. Thus, in order improve our understanding of heat conduction phenomena, we think it is important to supply reliable data of κ for complex materials.

We have studied the layered Co oxides as a possible thermoelectric material.[11–16] The thermoelectric material is a material that can generate electricity from heat through the Seebeck effect, and can pump heat through the Peltier effect. Its efficiency is characterized by the thermoelectric figure of merit $Z \equiv S^2/\rho\kappa$, where S and ρ are the Seebeck coefficient and the resistivity.[17] Thus κ is one of the most fundamental quantities for the thermoelectric materials, as important as ρ and S. Single crystals of the layered Co oxides were, however, very thin and small, and the heat loss seriously affected the κ measurement. In fact, there are only a few reports on the κ measurement of single crystals of the layered Co oxides.[18–20] Very recently, we have succeeded in measuring the in-plane κ (κ_{ab}) of various layered Co oxides by using the Harman method.[21] However, the out-of-plane κ (κ_c) has not yet been observed, because this is the most difficult direction to measure.

Among various layered Co oxides, $Bi_{2-x}Pb_xSr_2Co_2O_y$ is most suitable for the κ_c measurement, because large and (relatively) thick single crystals are available.[22] As shown in Fig. 1, $Bi_{2-x}Pb_xSr_2Co_2O_y$ is a layered oxide consisting of an alternate stack of the CoO_2 block and the $Bi_2Sr_2O_4$ block along the *c* axis.[23] The CdI_2-type CoO_2 block is responsible for electric conduction, which shows a large S and a low ρ. On the contrary, the NaCl-type $Bi_2Sr_2O_4$ block acts as a charge reservoir to stabilize the structure electrostatically. A notable feature is that the ions in this material are connected via various chemical bondings: the van der Waals coupling between the two Bi-O planes, the ionic bonding between Sr^{2+} and O^{2-}, and the covalent character between Co and O in the CoO_2 block. Thus the force constant is expected to be different within the unit cell, which would cause complicated phonon dispersion and thermal conduction. In this paper, we report on measurement and analysis of the *c*-axis thermal conductivity of $Bi_{2-x}Pb_xSr_2Co_2O_y$ ($x=0$, 0.4, and 0.6).

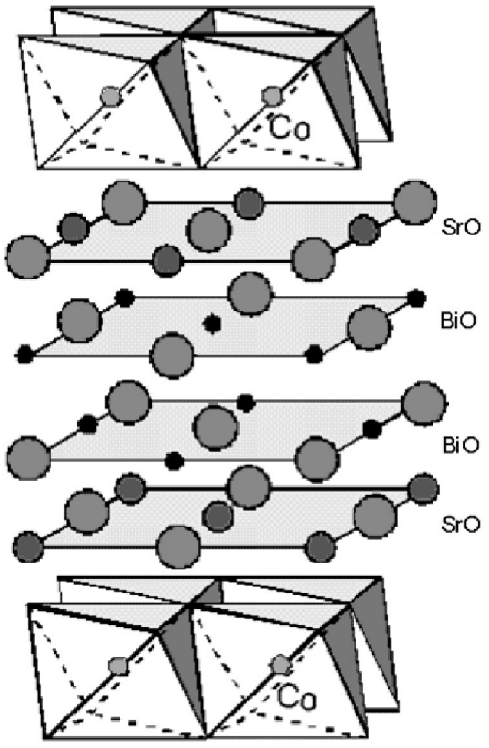

FIG. 1. Crystal structure of $Bi_{2-x}Pb_xSr_2Co_2O_y$.

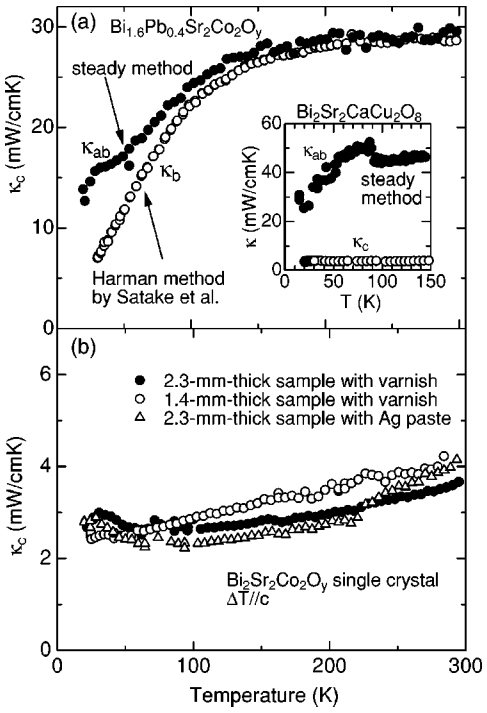

FIG. 2. (a) In-plane thermal conductivity of $Bi_{1.6}Pb_{0.4}Sr_2Co_2O_y$ measured by the Harman method and the steady method. The data for the Harman method are taken from Ref. 21. The inset shows the in- and out-of-plane thermal conductivities for a thick sample of $Bi_2Sr_2CaCu_2O_8$ single crystals stacked along the *c* axis with paste. (b) *c*-axis thermal conductivities of $Bi_2Sr_2Co_2O_y$ measured for different samples.

II. EXPERIMENTAL

Single crystals of $Bi_{2-x}Pb_xSr_2Co_2O_y$ were grown by the traveling-solvent-floating-zone technique. The detailed growth conditions and the characterization of the crystals were written previously.[23] The typical size of the crystals was 2 mm$\times$2 mm$\times$100 μm. We stacked pieces of crystals with varnish (GE 7031) along the *c* axis, and made a thick rectangular block of $2\times2\times3$ mm^3. We used the thermal conductivites of 0.44 and 0.22 *W*/mK at 300 and 77 K,[24] and estimated the thermal resistance of the varnish to be 2.0 and 4.0 K/W, respectively. These values are much smaller than the total thermal resistance (typically 750 K/W). Thus we can safely neglect the contribution of the varnish.

κ_c was measured using the block sample by the steady method with a temperature gradient of 0.5–1 K/mm. One edge of the sample was anchored to the cold head of a closed-cycle refrigerator, and the other edge was equipped with a resistance sheet heater and a 1.25-mm-diameter Si-diode thermometer (Lakeshore DT-421-HR).

III. RESULTS

First of all, we would like to examine the block sample consisting of thin crystals stacked with paste. Figure 2(a) shows the in-plane κ of $Bi_{1.6}Pb_{0.4}Sr_2Co_2O_y$ measured by the Harman method and the steady method. While we used one piece of thin single crystals for the Harman method,[21] we used the block sample for the steady method. As is clearly shown in Fig. 2, the two κ curves are in an excellent agreement except for the data below 50 K, where the Harman method is less accurate. As is well known, the thermal resistance of the varnish would be more serious at lower temperatures. Thus, if the thermal resistance of the glue were significant, the thermal conductivity would be measured to be lower than expected. But in reality, as shown in Fig. 2(a), the low-temperature data remain high at low temperatures, which implies that the thermal resistance of the glue is negligible. This is direct evidence that κ of the block sample reflects an intrinsic value.

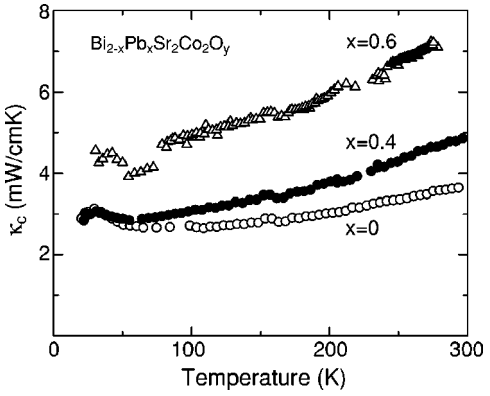

FIG. 3. Out-of-plane thermal conductivity of $Bi_{2-x}Pb_xSr_2Co_2O_y$.

We further examined the validity of a block sample for the high-temperature superconductor $Bi_2Sr_2CaCu_2O_8$. This compound exhibits similar mechanical properties attributed to the identical Bi_2O_2 layer, and can be a good reference for $Bi_{2-x}Pb_xSr_2Co_2O_y$. In the inset of Fig. 2(a) are shown the in- and out-of-plane κ's obtained through the steady method. A hump near 90 K is clearly seen in κ_{ab}, which is a hallmark of the onset of the high-temperature superconductivity. The temperature dependence and the magnitude of κ_{ab} are in good agreement with the data reported in the literature.[25] We measured κ_c using the same sample. The thermal-conductivity is anisotropic, but the thermal conductivity ratio of $\kappa_{ab}/\kappa_c=10$ is much less than the resistivity ratio $\rho_c/\rho_{ab}=10^4$. The electron thermal conductivity should be as anisotropic as the resistivity, implying that the phonon thermal conductivity is less anisotropic. The obtained κ_c is in reasonable agreement with Ref. 26, in which κ_c was measured for one piece of thin single crystal.

We will give additional pieces of evidence for the accuracy of the measurements. Figure 2(b) shows the *c*-axis thermal conductivity for three samples with different conditions. Although the volume fraction of the varnish is larger in the 1.4-mm-thick sample than in the 2.3-mm-thick sample, the obtained κ_c is in good agreement. This directly evidences that the thermal resistance of the varnish is negligibly small. We should also note that the sample with varnish and the sample with Ag paste (Dupont 4922N) give nearly the same κ_c, which again suggests that the glue does not affect the κ_c measurement seriously.

Figure 3 shows κ_c of $Bi_{2-x}Pb_xSr_2Co_2O_y$ ($x=0$, 0.4, and 0.6). The most important feature is that all the κ_c's are

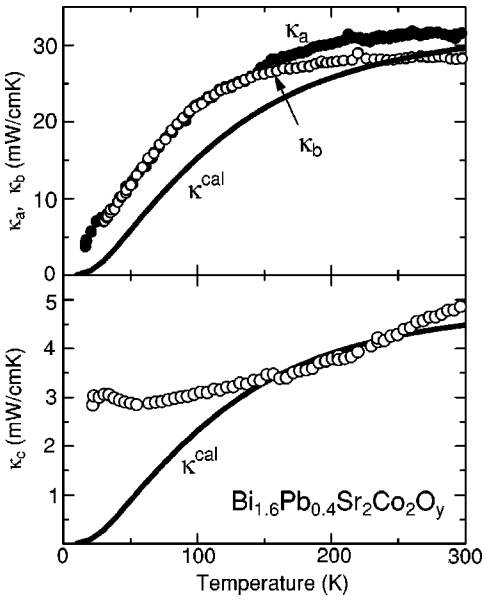

FIG. 4. Anisotropic thermal conductivity of $Bi_{1.6}Pb_{0.4}Sr_2Co_2O_y$.

4–8 mW/cm K at room temperature, which is as low as the minimum thermal conductivity suggested by Cahill *et al.*[27] They caluculated the minimum thermal conductivity to be 2.3 mW/cm K at 300 K for amorphous Se, whose sound velocity (1060 m/s) is close to the *c*-axis sound velocity (see below). This means that the phonon mean-free path is as short as the *c*-axis length. This could be assigned to the misfit layered structure, where the interface between the CoO_2 and the $Bi_2Sr_2O_4$ blocks could be a strong scatterer of phonons. The second feature to be pointed out is that the temperature dependence is positive ($d\kappa_c/dT>0$). κ is normally expected to be constant or decrease with T at high temperatures, because the temperature dependence of κ is determined by the phonon mean-free path.[14] The third feature is the Pb substitution effect, where κ_c increases with increasing Pb content. Note that the solid solution indeed enhances κ in this material, as is opposed to usual cases. The Pb substitution decreases the excess oxygen,[28] and removes the superstructure in the Bi-O plane.[23] Thus the Bi-O plane becomes flatter for larger x, which would make phonon mean-free path longer. We also note that the mass difference between Bi and Pb is so small that point-defect scattering due to Pb is negligible.

IV. DISCUSSION

Figure 4 shows the thermal conductivity of $Bi_{1.6}Pb_{0.4}Sr_2Co_2O_y$ along all the crystallographic axes. The *a*-axis thermal conductivity (κ_a) and the *b*-axis thermal conductivity (κ_b) are taken from Ref. 21. Since the in-plane anisotropy is small (although finite), we do not distinguish κ_a from κ_b, and call them κ_{ab} hereafter. The room-temperature resistivities are 5 mΩ cm for the in-plane direction (ρ_{ab}), and 10 Ω cm for the out-of-plane direction (ρ_c),[22] which are high enough for us to neglect the electron thermal conductivity. Thus the observed anisotropy κ_{ab}/κ_c is due to the anisotropy of the phonon contribution. The lattice vibration is a collective motion of all the atoms; it will be three dimensional even in the layered structure. Thus, it is not surprising that κ_{ab}/κ_c is much smaller than ρ_c/ρ_{ab}.

Let us analyze the observed κ with available theories. In a conventional insulator, we can employ the phonon-scattering theory,[3,4] in which we can express the phonon-scattering time $\tau(\omega,T)$ as a function of phonon frequency and temperature. We can further apply this theory to conventional semiconductors by the help of the Wiedemann-Franz law. In the present complex oxide $Bi_{2-x}Pb_xSr_2Co_2O_y$, however, we have to deal with tens of phonons of a different nature associated with the covalent, ionic, van der Waals bondings, which makes it unrealistic to assume a single value of $\tau(\omega,T)$. In addition, the charge and spin degrees of freedom exist in this material, which causes unusual magnetothermal conductivity at low temperatures.[29] Accordingly, we would like to go back to a more phenomenological expression instead of the conventional phonon-scattering theory.

The expression for κ that we adopt in this paper is

$$\kappa = Cv\ell/3 = Cv^2\tau/3, \tag{1}$$

where C, v, and ℓ are the specific heat, sound velocity, and mean-free path, respectively. This is a general phenomenological expression deduced from the classical Drude model,[1] which is independent of the microscopic details of the materials. We further assume that only C is dependent on temperature, and the anisotropy is predominantly determined by v. Although ℓ and τ depend on temperature, we leave them as constants. Their temperature dependence can be estimated from deviation of the measured κ from the calculation, as was done in the analysis of κ for the magnetic insulators.[7,8] In principle, C, v, and τ should be assigned to each phonon mode, but obviously it is impossible to obtain all of them from fitting. Instead, we use C, v, and τ as an average with respect to all the phonon modes.

Firstly, let us determine the sound velocity from the experimental data. In a conventional treatment of the transport phenomena, we have two kinds of approximation: the constant-ℓ and constant-τ approximation. κ_{ab}/κ_c is equal to v_{ab}/v_c in the former, while κ_{ab}/κ_c is equal to $(v_{ab}/v_c)^2$ in the latter. We will choose the better one by looking at the data for $Bi_2Sr_2CaCu_2O_8$. The sound velocities of $Bi_2Sr_2CaCu_2O_8$ were reported to be $v_{ab}=4400$ m/s and $v_c=3400$ m/s.[30] Then, the observed anisotropy $\kappa_{ab}^{ph}/\kappa_c=(\kappa_{ab}-L_0T/\rho_{ab})/\kappa_c$ is closer to $(v_{ab}/v_c)^2$ than to v_{ab}/v_c, which suggests that the constant-τ approximation is likely (note that L_0T/ρ_{ab} is the electron thermal conductivity for the in-plane direction, and L_0 is the Lorenz number). According to the Debye model, the average of the sound velocity $\overline{v}$ is given by

$$\overline{v^3} = v_{ab}^2 v_c = \frac{1}{6\pi^2 n}\left(\frac{k_B\theta_D}{\hbar}\right)^3, \tag{2}$$

where n is the atom density per unit volume. Putting $\theta_D=260$ K for $Bi_{2-x}Pb_xSr_2Co_2O_y$ (Ref. 31) into Eq. (2), we get $\overline{v}=2100$ m/s. From Fig. 4, κ_{ab}/κ_c is approximately equal

to 6, which gives $v_{ab}/v_c=2.5$. Eventually we get $v_{ab}=2800$ m/s and $v_c=1100$ m/s.

Next we will discuss the specific heat C. Usually the acoustic-phonon part C^{ac} is the predominant contribution for C, given by

$$C^{\mathrm{ac}} = 9nk_B\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x-1)^2} dx. \quad (3)$$

In this material, however, $d\kappa_c/dT>0$ is observed, which means that even at room temperature, the thermal excitation of phonons are not saturated. Since $\theta_D=260$ K, the phonon excited at room temperature should be assigned to optical phonons. Very recently, Hess and Buchner[32] have proposed the specific-heat contribution from optical phonons C^{opt} given by

$$C^{\mathrm{opt}} = 9nk_B\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x'^2 x^2 e^{x'}}{(e^{x'}-1)^2} dx, \quad (4)$$

$$x' = x + \frac{\Delta}{k_B T}, \quad (5)$$

where Δ is the minimum energy of the optical phonons. We further assume that all the phonon modes have the same sound velocity. Although this is an oversimplified assumption, we have no reliable theories for the thermal conduction due to optical phonons.

We estimate the third parameter τ from the room-temperature value. Then, the calculated thermal conductivity κ^{cal} is written by

$$\kappa_i^{\mathrm{cal}} = (C^{\mathrm{ac}} + C^{\mathrm{opt}}) v_i^2 \tau/3, \quad (i = ab, c). \quad (6)$$

Note that Eq. (6) includes only two fitting parameters, Δ and τ, which can be determined independently from the T dependence and the magnitude. The solid curves in Fig. 4 are those calculated for $\Delta/k_B=300$ K, and $\tau=1\times10^{-12}$ s. Then, the phonon mean-free paths are reasonably estimated to be 28 Å for the in-plane direction and 11 Å for the out-of-plane direction. In spite of our rough assumptions, the measured κ is in fair agreement with the calculation above 100 K, which implies that ℓ is as short as the lattice parameters, possibly owing to the lattice misfit. In particular, the estimated value of 11 Å is nearly equal to the c-axis length, which means that the lattice misfit is a strong scatterer to the out-of-plane phonons.

Finally, we would like to comment briefly on the temperature dependence of ℓ. Deviation from the calculation curves becomes remarkable below 100 K. This is because the mean-free path increases with decreasing T. The b-axis resistivity shows a broad minimum, and the Hall coefficient rapidly increases below 50 K. These are attributed to the opening of the spin-density-wave pseudogap.[23] We expect that the phonons will be less scattered by electrons below 50 K in the presence of the pseudogap. Thus the phonon mean-free path will be much longer, and the deviation is more remarkable below 50 K.[29] As is similar to the high-temperature superconducting cuprates,[33] the effects of the pseudogap are more serious in the out-of-plane directions, and the deviation is more significant than in the in-plane direction. Hess and Buchner found that the out-of-plane ℓ for $(\mathrm{La,Eu})_2\mathrm{CuO}_4$ increased up to 10^5 Å below 10 K,[32] as is similar to the present case.

V. SUMMARY

We have measured the out-of-plane thermal conductivity of $\mathrm{Bi}_{2-x}\mathrm{Pb}_x\mathrm{Sr}_2\mathrm{Co}_2\mathrm{O}_y$, which is as low as 4–8 mW/cm K at 300 K. This is very close to the minimum thermal conductivity proposed by Cahill *et al.*, suggesting the very short phonon mean-free path. We have compared it with the in-plane thermal conductivity, and have semiquantitatively explained the magnitude and the temperature dependence using a phenomenological expression of κ.

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*Electronic address: terra@waseda.jp

[1] N. W. Ashcroft and N. D. Mermin, in *Solid State Physics*, (Saunders, Philadelphia, 1976).
[2] G. A. Slack, Solid State Phys. **34**, 1 (1979).
[3] J. Callaway, Phys. Rev. **113**, 1046 (1959); J. Callaway and H. C. von Baeyer, *ibid.* **120**, 1149 (1960).
[4] E. F. Steigmeier and B. Abeles, Phys. Rev. **136**, A1149 (1964).
[5] K. Takenaka, Y. Fukuzumi, K. Mizuhashi, S. Uchida, H. Asaoka, and H. Takei, Phys. Rev. B **56**, 5654 (1997).
[6] Y. Ando, J. Takeya, D. L. Sisson, S. G. Doettinger, I. Tanaka, R. S. Feigelson, and A. Kapitulnik, Phys. Rev. B **58**, R2913 (1998).
[7] A. V. Sologubenko, K. Gianno, H. R. Ott, A. Vietkine, and A. Revcolevschi, Phys. Rev. Lett. **84**, 2714 (2000); Phys. Rev. B **64**, 054412 (2001).
[8] C. Hess, B. Buchner, U. Ammerahl, L. Colonescu, F. Heidrich-Meisner, W. Brenig, and A. Revcolevschi, Phys. Rev. B **64**, 184305 (2001); Phys. Rev. Lett. **90**, 197002 (2003).
[9] A. Klümper, and K. Sakai, J. Phys. A **35**, 2173 (2002).
[10] K. Saito and S. Miyashita, J. Phys. Soc. Jpn. **71**, 2485 (2002).
[11] I. Terasaki, Y Sasago, and K. Uchinokura, Phys. Rev. B **56**, R12 685 (1997).
[12] T. Kawata, Y. Iguchi, T. Itoh, K. Takahata, and I. Terasaki, Phys. Rev. B **60**, 10 584 (1998).
[13] Y. Ando, N. Miyamoto, K. Segawa, T. Kawata, and I. Terasaki, Phys. Rev. B **60**, 10 580 (1998).
[14] K. Takahata, Y. Iguchi, D. Tanaka, T. Itoh, and I. Terasaki, Phys. Rev. B **61**, 12 551 (2000).
[15] I. Terasaki, I. Tsukada, and Y. Iguchi, Phys. Rev. B **65**, 195106 (2002).

[16] T. Motohashi, R. Ueda, E. Naujalis, T. Tojo, I. Terasaki, T. Atake, M. Karppinen, and H. Yamauchi, Phys. Rev. B **67**, 064406 (2003).
[17] G. D. Mahan, Solid State Phys. **51**, 81 (1998).
[18] K. Fujita, T. Mochida, and K. Nakamura, Jpn. J. Appl. Phys., Part 1 **40**, 4644 (2001).
[19] R. Funahashi and M. Shikano, Appl. Phys. Lett. **81**, 1459 (2002).
[20] M. Shikano and R. Funahashi, Appl. Phys. Lett. **82**, 1851 (2003).
[21] A. Satake, H. Tanaka, T. Ohkawa, T. Fujii, and I. Terasaki, J. Appl. Phys. **96**, 931 (2004).
[22] I. Tsukada, T. Yamamoto, M. Takagi, T. Tsubone, S. Konno, and K. Uchinokura, J. Phys. Soc. Jpn. **70**, 834 (2001).
[23] T. Fujii, I. Terasaki, T. Watanabe, and A. Matsuda, Jpn. J. Appl. Phys., Part 2 **41**, L783 (2002).
[24] Lakeshore Specification Sheet: http://www.lakeshore.com/temp/acc/am_varnishts.html
[25] Y. Ando, J. Takeya, Y. Abe, K. Nakamura, and A. Kapitulnik, Phys. Rev. B **62**, 626 (2000).
[26] M. F. Crommie and A. Zettl, Phys. Rev. B **43**, 408 (1991).
[27] D. G. Cahill, S. K. Watson, and R. O. Pohl, Phys. Rev. B **46**, 6131 (1992).
[28] Y. Morita, J. Poulsen, T. Motohashi, T. Fujii, I. Terasaki, H. Yamauchi, and M. Karppinen, J. Solid State Chem. **177**, 3149 (2004).
[29] I. Terasaki, and T. Fujii, in *Proceedings of the 22nd International Conference on Thermoelectrics (ICT2003), Le Grand Motte, 17-21 August 2003* (IEEE, Piscataway, 2003), p. 207.
[30] M. Boekholt, J. V. Harzer, B. Hillebrands, and G. Guntherodt, Physica C **179**, 101 (1991).
[31] T. Yamamoto, K. Uchinokura, and I. Tsukada, Phys. Rev. B **65**, 184434 (2002).
[32] C. Hess and B. Buchner, Eur. Phys. J. B **38**, 37 (2004).
[33] L. B. Ioffe and A. J. Millis, Phys. Rev. B **58**, 11 631 (1998).