Normal-state spin gap of Bi-based superconductors

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The thermoelectric power (TEP) $S(T)$ and resistivity $\rho(T)$ were measured for underdoped and overdoped $Bi_{1.8}Pb_{0.2}Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta}$ ($n=1,2$) samples with different oxygen contents. A specific heat measurement was also conducted for the $n=2$ system. We found that $S(T)$ exhibited a significant enhancement below a characteristic temperature T_g for these samples, as observed in underdoped samples of $YBa_2Cu_3O_{7-\delta}$ and $YBa_2Cu_4O_8$. Such an anomaly in $S(T)$ below T_g suggests that an energy gap exists in the normal states of underdoped and overdoped Bi-based superconductors ($n=1$ or 2). The normal-state gap temperature (T_g) increases with decreasing oxygen content in both $n=1$ and 2 systems. A downturn behavior in $\rho(T)$ with the opening of a normal-state gap was also observed for some overdoped samples. On the other hand, the experimental data also showed that $S(T)$ had a positive slope at high temperatures for the heavily overdoped samples of the $n=1$ system, while all the overdoped samples of the $n=2$ system had a negative slope in $S(T)$ within the whole measured temperature range. This suggests that the Bi_2O_2 layers are metallic and make a contribution to the TEP in the heavily overdoped region of the $n=1$ system, but are insulating in the whole overdoped region of the $n=2$ system. In addition, specific heat measurements for the $n=2$ system reveal that a decrease in oxygen content results in the occurrence of phase segregation. [S0163-1829(97)04521-9]

I. INTRODUCTION

It is known that understanding of the nature of unusual normal-state transport properties of high-temperature superconductors (HTSC's) is necessary to clarify the pairing mechanism. Hence investigations on normal-state properties have been one of the most attractive topics in HTSC research. A wealth of experimental and theoretical work has been published in this area. It has commonly been realized that normal-state resistivity shows a linear behavior in temperature from T_c up to hundred degrees kelvin for the optimally doped samples and a Fermi-liquid-like behavior for overdoped samples, i.e., $\rho \propto T^{\alpha}$, with α changing from 1 to 2. For underdoped samples, normal-state resistivity exhibits a downturn at low temperature due to the opening of a normal-state (NS) gap.[1] Such an anomalous transport behavior associated with the NS gap in underdoped samples provides important evidence for the magnetic scattering mechanism of charge carriers. The NS gap phenomenon has attracted a lot of attention in recent years due to its intimate relation with superconductivity.

The NS gap phenomenon was first observed in NMR and inelastic neutron scattering measurements of $YBa_2Cu_3O_{7-\delta}$ (Y123).[2,3] Loram *et al.* also observed the NS gap in Y123 by means of high-precision differential heat capacity measurements. The NS gap temperature T_g and energy E_g determined from C_p are nearly consistent with that from NMR.[4] Recently, Tallon *et al.*[5] found that thermoelectric power (TEP) can also probe the same gap as does the heat capacity and NMR. The TEP becomes significantly enhanced as the NS gap opens. Besides Y123, the NS gap behavior was also detected in other HTSC's, such as $YBa_2Cu_4O_8$ (Y124),[1,6] $La_{2-x}Sr_xCuO_4$ (La214),[7] and $Tl_2Ba_2CuO_{6+\delta}$.[7] From experimental results so far, it is widely believed that the NS gap is specific to the underdoped region and the NS gap temperature decreases with an increase in doping level, whereas the NS gap seems to merge into the superconducting gap in the overdoped region. But whether this type of relation of the NS gap and carrier concentration is suitable for other superconducting compounds still remains an open question.

For Bi-based superconductors, there are few reports on the NS gap in the literature. Only Walstedt *et al.*[8] observed the NS gap phenomenon in $Bi_2Sr_2CaCu_2O_8$ by NMR. Whether the NS gap phenomenon appears in $Bi_2Sr_2CuO_y$ or not is not clear up to now. In order to clarify the NS gap features in Bi-based superconductors, recently we have prepared $Bi_{1.8}Pb_{0.2}Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta}$ ($n=1,2$) samples with different oxygen contents and systematically investigated the NS gap behavior of these samples by means of TEP and resistivity. Our experimental data show that a NS gap exists well above T_c in both underdoped and overdoped samples of $Bi_{1.8}Pb_{0.2}Sr_2CuO_{6+\delta}$ (Bi2201) and $Bi_{1.8}Pb_{0.2}Sr_2CaCu_2O_{8+\delta}$ (Bi2212) and that the NS gap temperature increases with decreasing oxygen content.

II. EXPERIMENTAL METHODS

Polycrystalline samples of $Bi_{1.8}Pb_{0.2}Sr_2CuO_{6+\delta}$ and $Bi_{1.8}Pb_{0.2}Sr_2CaCu_2O_{8+\delta}$ were synthesized using conventional solid-state reaction of stoichiometric oxides and carbonate in air. Sets of samples with different δ values were obtained by annealing the sintered samples at various temperatures and

TABLE I. Different treatment conditions of $Bi_{1.8}Pb_{0.2}Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta}$ ($n=1,2$).

$n=1$	Treatment conditions	$n=2$	Treatment conditions
$A1$	cooled in furnace	$A2$	cooled in furnace
$B1$	N_2 700 °C×2.5 h	$B2$	quenched in air
$C1$	O_2 10^{-5} atm 550 °C×2.5 h	$C2$	O_2 10^{-5} atm 550 °C×0.5 h
$D1$	O_2 10^{-5} atm 630 °C×2.5 h	$D2$	O_2 10^{-5} atm 550 °C×2.5 h+ O_2 10^{-8} atm 550 °C×2.5 h
$E1$	O_2 10^{-5} atm 630 °C×2.5 h+ O_2 10^{-5} atm 650 °C×1.5 h+ O_2 10^{-8} atm 650 °C×2 h	$E2$	O_2 10^{-5} atm 550 °C×5 h+ O_2 10^{-8} atm 550 °C×10 h

oxygen partial pressures. The detailed treatment conditions are listed in Table I. X-ray-diffraction analysis showed that the sintered samples were free of impurity phase and that all the samples still remained single phase after treatment under different conditions. Furthermore, x-ray-diffraction and electron-diffraction analyses, which will be published in a separate paper, also revealed that a progressive structure change occurred with decreasing oxygen content in both Bi2201 and Bi2212 systems.

Resistivity was measured using a standard four-probe method in a closed-cycle helium cryostat. The available lowest temperature for the helium cryostat is 11 K. The TEP of the sample was measured by a differential method.[9] The temperature at the two ends of the measured sample was controlled automatically within a precision of 0.01 K. The emf of the sample was indicated by a Keithley 181 nanovoltmeter with an error less than 0.2 μV. Calibrated by pure Pb, the error of the TEP measurement system was smaller than 0.1 μV/K. For the Bi2212 series the specific heat was also measured using a continually increasing temperature method.[10]

III. EXPERIMENTAL RESULTS

Figure 1 shows the temperature dependence of resistivity (ρ) for the Bi2201 samples annealed under different conditions. The gradual increase in resistivity from the sample $A1$ to $E1$ reflects a progressive decrease in the oxygen content of the Bi2201 phase. The temperature dependence of ρ is approximately linear within the measured temperature region (11–290 K) for samples $A1$ and $B1$, and superconductivity is not observed above 11 K in the two samples. For samples $C1$ and $D1$, superconductivity appears at about 20 K (T_c^{onset}) and the normal state $\rho(T)$ exhibits a marked downward curvature below 180 and 187 K, respectively. For sample $E1$, T_c^{onset} decreases to 14 K and the transport in the normal state shows a semiconductinglike behavior.

$S(T)$ for the Bi2201 samples annealed under different conditions is plotted against temperature in Fig. 2. The $S(T)$ value increases progressively with decreasing in the oxygen content from sample $A1$ to $E1$. Samples $A1$, $B1$, and $C1$ have negative values for $S(T)$ within the measured temperature region (90–290 K), while for samples $D1$ and $E1$, $S(T)$ changes sign from negative to positive around 160 and 210 K, respectively. These five samples exhibit a common feature in the S-T curves. Namely, $S(T)$ becomes significantly enhanced below a certain characteristic temperature, as observed in underdoped samples of $YBa_2Cu_3O_{7-\delta}$ and $YBa_2Cu_4O_8$.[5] The characteristic temperatures are, respectively, 120, 130, 180, 190, and 210 K for samples $A1$, $B1$, $C1$, $D1$, and $E1$. Additionally, another noteworthy phenomenon is that for samples $B1$ and $C1$ the slope of $S(T)$ changes from positive to negative around 250 and 220 K, respectively.

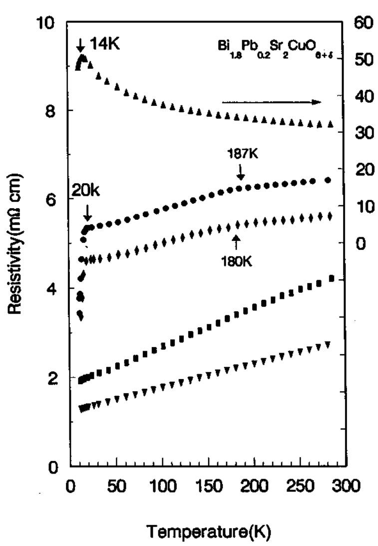

FIG. 1. Temperature dependence of resistivity for samples $A1$ (▼), $B1$ (■), $C1$ (♦), $D1$ (●), and $E1$ (▲).

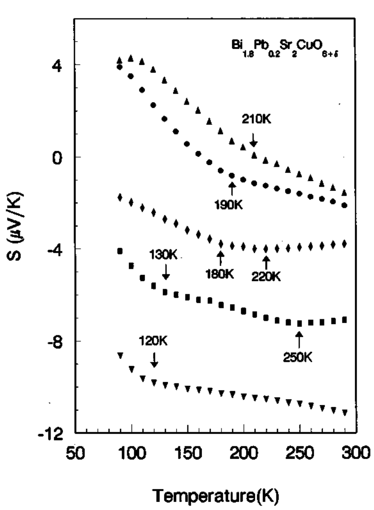

FIG. 2. Temperature dependence of TEP for samples $A1$ (▼), $B1$ (■), $C1$ (♦), $D1$ (●), and $E1$ (▲).

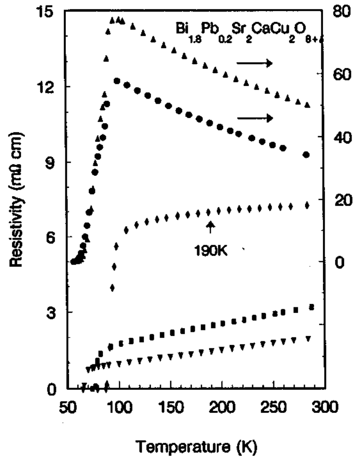

FIG. 3. Temperature dependence of resistivity for samples $A2$ (▼), $B2$ (■), $C2$ (♦), $D2$ (●), and $E2$ (▲).

The temperature dependence of ρ for the Bi2212 samples treated under different conditions is shown in Fig. 3. The increase in normal-state resistivity similarly reflects that the oxygen content of the Bi2212 phase decreases gradually from sample $A2$ to $E2$. The reduction in the oxygen content of the Bi2212 phase induces a remarkable change in the superconductivity and temperature dependence of normal-state resistivity. Here T_c (midpoint in transition) is about 67, 78, 92, 80, and 81 K for samples $A2$, $B2$, $C2$, $D2$, and $E2$, respectively. The temperature dependence of ρ exhibits a linear behavior for samples $A2$ and $B2$, but semiconductivity for samples $D2$ and $E2$. For sample $C2$ the $\rho(T)$ deviates downward from linearity around 190 K.

Figure 4 gives the temperature dependence of S for the Bi2212 samples treated under different conditions. The TEP of the Bi2212 phase also changes from negative to positive with decreasing oxygen content, as observed in the Bi2201 system. Moreover, the steep enhancement behavior below a certain temperature is observed as well in samples $B2$, $C2$, $D2$, and $E2$. The characteristic temperatures at which $S(T)$ starts to be enhanced steeply are 150, 190, 200, and 210 K, respectively, for samples $B2$, $C2$, $D2$, and $E2$. Compared with the Bi2201 system, a different feature for the Bi2212 system is that the slope of $S(T)$ does not change from positive to negative at high temperature.

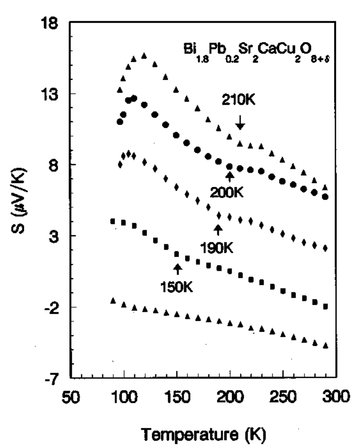

FIG. 4. Temperature dependence of TEP for samples $A2$ (▼), $B2$ (■), $C2$ (♦), $D2$ (●), and $E2$ (▲).

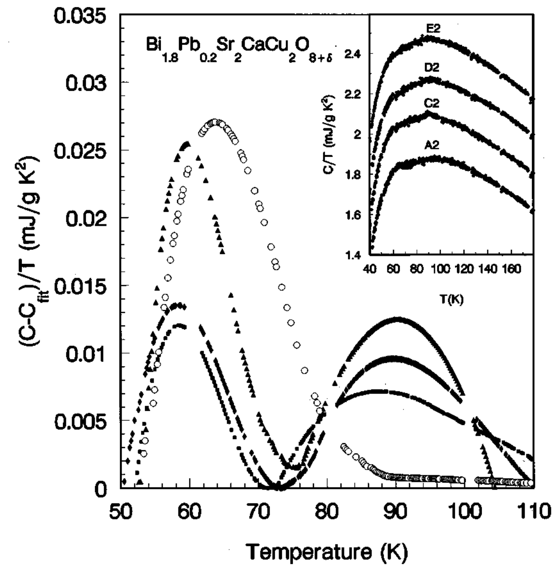

FIG. 5. Fitted curves of $(C-C_{\rm fit})/T$ vs T for samples $A2$ (○), $C2$ (▲), $D2$ (♦), and $E2$ (■). The inset shows the measured values of C/T for samples $A2$, $C2$, $D2$, and $E2$. In the interest of clarity, the curves of $C/T-T$ for samples $C2$, $D2$, and $E2$ are shifted upward by 0.2, 0.4, and 0.6, respectively.

The specific heat measurement results $(C/T-T)$ for sets of Bi2212 samples are shown in the inset of Fig. 5. Here $\Delta C/T$ is obtained by subtracting $C_{\rm fit}/T$ from C/T. Figure 5 gives the fitted curves of $(C-C_{\rm fit})/T$. From Fig. 5, it can be seen clearly that the phase segregation phenomenon occurs with the removal of oxygen in the Bi2212 system. Sample $A2$ contains only a superconducting phase with T_c of $\sim$64 K [called the lower-T_c phase (LTP) hereafter], while a superconducting phase with T_c of $\sim$90 K [higher-T_c phase (HTP)] appears besides the LTP for sample $C2$ and T_c of the LTP decreases to $\sim$60 K. For samples $D2$ and $E2$ with much less oxygen content, T_c of the LTP decreases to $\sim$58 K and its volume fraction decreases markedly, while T_c of the HTP still remains $\sim$90 K for sample $D2$, but decreases to $\sim$87 K for sample $E2$. Combining with the resistivity and TEP data shown in Figs. 3 and 4, we can deduce that a fraction of the Bi2212 phase exhibiting semiconductivity exists in the two samples besides the LTP and HTP.

IV. DISCUSSION

Presland *et al.*[11] have also studied the influence of oxygen content on T_c of the Bi2212 phase by annealing $Bi_{1.9}Pb_{0.2}Sr_2Ca_{0.9}Cu_2O_{8+\delta}$ at different temperatures. Their experimental data showed that these annealed samples all resided in the overdoped region in the phase diagram and T_c ranged from 64 to 92 K [T_c(max)]. Our annealed samples of $Bi_{1.8}Pb_{0.2}Sr_2CaCu_2O_{8+\delta}$ also show a similar change in T_c. It is apparent that both the LTP and HTP reside in the overdoped region in samples $A2$, $B2$ and $C2$, $D2$, while the HTP with T_c of 87 K in sample $E2$ appears to lie in the underdoped region. For the Bi2201 phase, it is known that an optimized T_c can rise to a maximum of 25 K by the La substitution for Sr.[12] Hence it can be thought that samples $A1$, $B1$, $C1$, and $D1$ are located in the high-hole-concentration side of $T_c(\max)$, while sample $E1$ with a T_c^{onset} of 14 K lies in the underdoped region. The semiconducting behavior in resistivity for sample $E1$ is also likely to arise from a phase segregation.

As mentioned above, the TEP in the normal state shows anomalies for overdoped and underdoped samples of the Bi2201 and Bi2212 systems; i.e., $S(T)$ is enhanced significantly below a certain characteristic temperature. In accordance with the work of Tallon *et al.*,[5] we can think that such a strong enhancement in $S(T)$ is related to the smooth opening of a NS gap. Moreover, the downturn behavior in $\rho(T)$ with the opening of a NS gap is simultaneously observed in the samples of $C1$, $D1$, and $C2$, and the NS gap temperature T_g determined from the ρ-T curve is nearly consistent with that from the TEP. These facts suggest that a NS gap exists in both the overdoped and underdoped regions of the Bi2201 and Bi2212 systems. However, it should be noted that the ρ-T curve does not show the features associated with the NS gap opening for samples $A1$, $B1$, $E1$, $B2$, $D2$, and $E2$ though the steep enhancement in $S(T)$ below T_g reflects the existence of a NS gap in these samples. This implies that the TEP can reflect the modification in the NS excitation spectrum more sensitively than the resistivity. The TEP data shown in Figs. 2 and 4 also reveal that the T_g increases with decreasing oxygen content for both Bi2201 and Bi2212 systems.

Walstedt *et al.*[8] have observed the existence of a NS gap by NMR for the 77 and 90 K superconducting phases of Bi2212, and the NS gap temperatures for the two phases are 90 and 190 K, respectively. It is clear that T_g determined from the TEP agrees well with that from NMR for the 90 K superconducting phase. We have already pointed out that phase segregation exists in the Bi2212 system. Obviously the HTP's in samples $B2$, $C2$, $D2$, and $E2$ are responsible for the observed NS gap behavior, while T_g of the LTP should be smaller than 90 K.

The TEP shows a negative slope for most HTSC's, which is characteristic of the CuO_2 planes. The positive slope in $S(T)$ data was observed only in Y124 and Y123 with $\delta<0.19$.[5,13] The presence of a positive slope in $S(T)$ of the two systems arises from the contribution of the oxygenated Cu-O chains.[5,14] As described above, the positive slope behavior in $S(T)$ is also observed in samples $B1$ and $C1$, but does not appear in the Bi2212 system. It is obvious that such a positive slope behavior in $S(T)$ in the Bi2201 phase should similarly be related to the transport in non-CuO_2 planes. For Bi-based superconductors, band structure calculations show that the Bi_2O_2 layers are metallic and play a similar role as the Cu-O chains. However, many experiments have demonstrated that the Bi_2O_2 layers are insulating for the Bi2212 phase. But the above $S(T)$ data of the Bi2201 system seem to support the results of band structure calculations. Namely, the Bi_2O_2 layers for the heavily overdoped Bi2201 phase are metallic and have a contribution to the TEP, thus producing the positive slope in $S(T)$ at high temperature. Yet it is surprising that sample $A1$ with the highest doping level does not exhibit a positive slope in $S(T)$ within the measured temperature range. We think the temperature at which the slope in $S(T)$ changes from positive to negative may be larger than 290 K.

For undoped $Bi_2Sr_2CaCu_2O_{8+\delta}$ (undoped Bi2212), a series of overdoped samples with T_c ranging from 60 to 90 K can be obtained as well by varying the oxygen content. Obertelli *et al.*[14] have studied the TEP of these overdoped samples. From their experimental data, it can be seen that the varying behavior of $S(T)$ with oxygen content in the undoped Bi2212 system is nearly consistent with our results shown in Fig. 4. This suggests that overdoped samples of the $Bi_2Sr_2CaCu_2O_{8+\delta}$ system reside in almost the same hole concentration region as the $Bi_{1.8}Pb_{0.2}Sr_2CaCu_2O_{8+\delta}$ system. Nevertheless, it is worthwhile to note that the undoped Bi2212 system does not display anomalies in the normal state $S(T)$ and the temperature dependence of S is linear above T_c. This implies that a NS gap does not exist in the overdoped samples of the undoped Bi2212 system. This is an indication that the hole concentration is not the only factor determining the NS excitation spectrum. It is known that $Bi_2Sr_2CaCu_2O_{8+\delta}$ possesses a strong incommensurate modulation. Onoda and Sato[15] have pointed out that a modulation wave causes a swelling of each layer, i.e., the displacements of Bi, Sr, and Cu in the chains which run along the c axis. Yet the Pb substitution for Bi suppresses such an incommensurate modulation, thus decreasing the relative displacements of Bi, Sr, and Cu atoms.[16] This type of strong local structure distortion accompanied by incommensurate modulation in the undoped Bi2212 phase might be responsible for the disappearance of the NS gap. On the other hand, it is known that samples in the overdoped and underdoped regions for the Bi2201 phase can also be obtained by the La substitution for Sr.[12,17,18] But the $S(T)$ and resistivity data of La-doped samples did not exhibit anomalies associated with a NS gap (see Ref. 18). This phenomenon should similarly be related to the microstructure characteristics. As a result, it can be believed that the microstructure characteristic is an important factor determining the NS excitation spectrum.

V. CONCLUSION

In summary, we have studied the normal-state transport properties of underdoped and overdoped samples of $Bi_{1.8}Pb_{0.2}Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta}$ ($n=1,2$) by means of resistivity and TEP measurements. Meanwhile, the specific heat measurements were conducted for the $n=2$ system. From these experimental investigations and analyses, the following conclusions may be drawn.

(1) An energy gap exists in the normal states of both underdoped and overdoped samples of $Bi_{1.8}Pb_{0.2}Sr_2CuO_{6+\delta}$ and $Bi_{1.8}Pb_{0.2}Sr_2CaCu_2O_{8+\delta}$. The NS gap temperature increases with decreasing oxygen content in both systems.

(2) A phase segregation phenomenon appears for the Bi2212 samples annealed at higher temperature and lower oxygen partial pressure; i.e., the LTP with T_c of ~ 60 K, the HTP with T_c of ~ 90 K, and a fraction of Bi2212 exhibiting semiconductivity generally coexist in these samples.

(3) The Bi_2O_2 layers are metallic and make a contribution to the TEP at high temperatures for the heavily overdoped Bi2201 samples, but are insulating for the Bi2212 samples with any doping level.

Furthermore, by comparing our $S(T)$ data with that reported for the undoped Bi2212 and La-doped Bi2201 systems, we find that the NS excitation spectrum is intimately related to the crystal microstructure characteristic and a strong incommensurate modulation can suppress the opening of a NS gap.

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[1] B. Bucher *et al.*, Phys. Rev. Lett. **70**, 2012 (1993).
[2] H. Alloul *et al.*, Phys. Rev. Lett. **63**, 1700 (1989).
[3] J. Rossat-Mignod *et al.*, Physica (Amsterdam) **169B**, 58 (1991).
[4] J. W. Loram *et al.*, Phys. Rev. Lett. **71**, 1740 (1993).
[5] J. L. Tallon *et al.*, Phys. Rev. Lett. **75**, 4114 (1995).
[6] T. Machi *et al.*, Physica C **185-189**, 1147 (1991).
[7] Y. Kitaoka *et al.*, Physica (Amsterdam) **185-189C**, 98 (1991).
[8] R. E. Walstedt *et al.*, Phys. Rev. B **44**, 7760 (1991).
[9] Y. Ruan *et al.*, Chin. J. Low Temp. Phys. **10**, 161 (1988).
[10] K. Q. Wang *et al.*, Chin. J. Low Temp. Phys. **18**, 339 (1996).
[11] M. R. Presland *et al.*, Physica C **176**, 95 (1991).
[12] W. A. Groen *et al.*, Solid State Commun. **72**, 697 (1989).
[13] P. J. Ouseph and M. Ray O'Bryan, Phys. Rev. B **41**, 4123 (1990).
[14] S. D. Obertelli *et al.*, Phys. Rev. B **46**, 14 928 (1992).
[15] M. Onoda and M. Sato, Solid State Commun. **67**, 799 (1988).
[16] O. Eibl, Physica C **168**, 215 (1990).
[17] M. Sera *et al.*, Solid State Commun. **81**, 415 (1992).
[18] F. Devaux *et al.*, Phys. Rev. B **41**, 8723 (1990).