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Hydrostatic-pressure effects on the *a*-axis resistance of monocrystalline $Bi_{2.2}(Sr,Ca)_{2.8}Cu_2O_{8+y}$

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Measurements of the effects of hydrostatic pressure up to 1 GPa on the *a*-axis resistance R_a of monocrystalline $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ high-T_c superconductor are reported. The superconducting transition temperature T_c increases linearly under pressure with dT_c/dP equal to 1.3±0.2, 2.4±0.2, and 1.9±0.2 ($K\,GPa^{-1}$) at the onset, midpoint, and offset of the resistance-temperature curve, respectively. $d\ln T_c/d\ln V$ has been calculated thermodynamically using the bulk modulus determined for $Bi_2Sr_2CaCu_2O_{8+y}$ single crystals. A value of -1.5 is obtained and it is noted that some previous estimates for $Bi_2Sr_2CaCu_2O_{8+y}$ using the bulk modulus determined for $YBa_2Cu_3O_{7-x}$ are inappropriately large. This value of -1.5 falls in the range between those estimated from the 3-*d* BCS theory and the resonating-valence-bond theory. The pressure derivative $d\ln\rho_a/dP$ of the *a*-axis electrical resistivity remains almost constant between 116 and 296 K in the pressure range of the experiments, having a value of $-25.5\pm0.2\%\ GPa^{-1}$ at 296 K, which is larger than those reported previously for $Bi_2Sr_2CaCu_2O_{8+y}$ high-T_c superconductors. An empirical equation used for the temperature dependence of the electrical resistivity ρ in oxygen-deficient superconductors has been adapted to describe both temperature and pressure dependences of the in-plane resistance of $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$. Application of the conventional theory of the electrical resistivity of metals shows that the pressure dependence of the normal-state electrical resistance of high-T_c superconductors is dominated by pressure dependence of the mobile charge-carrier density and that the effect of pressure on lattice vibrational scattering plays only a minor role.

I. INTRODUCTION

Pressure has played an important role in the investigation of high transition temperature superconductors since the observation by Chu *et al.*[1] of a large pressure dependence of T_c in the La-Ba-Cu-O system. There have been many studies (see Refs. 2 and 3) of the pressure dependences of T_c and the normal-state resistivity ρ of high-T_c superconductors. Some of these investigations, for instance that of Chu *et al.*, have been performed to assist in the optimization of composition, whilst many others have had the objective of obtaining fundamental information about the nature of high-temperature superconductivity. In the nontransition metallic, low-T_c, superconductors both the normal-state resistivity and T_c decrease with pressure. This behavior is fundamental because both the normal-state resistivity and the superconducting electron coupling are functions of the electron-phonon interaction, which decreases with the lattice stiffening caused by an applied pressure. The magnitude of the change in T_c, dT_c/dP, is small and negative, e.g., in aluminum $dT_c/dP=-0.29\ K\,GPa^{-1}$.[4] For the high-$T_c$ superconductors, however, dT_c/dP appears to be much larger and in most cases positive. For the original La-Ba-Cu-O compound a value of $+10\ K\,GPa^{-1}$ has been reported and in samples of $YBa_2Cu_3O_{7-x}$ dT_c/dP ranges between -0.3 and $+14\ K\,GPa^{-1}$. However, there are reasons[3] to consider the very large values of dT_c/dP in these two compounds to be anomalous and not to be an intrinsic characteristic of high-temperature superconductivity.

Superconductivity in the lanthanum compounds occurs at temperatures close to that of a low-temperature structural phase transition which is also affected by pressure. Although the relationship between the superconducting transition and the structural transition is not fully understood, it is reasonable to suspect that at least a part of the large dT_c/dP is caused indirectly by the effect of pressure on the structural transition and its consequent influence on T_c.

The superconducting transition in $YBa_2Cu_3O_{7-x}$ is known to be critically dependent on oxygen content and on the ordered states that may be adopted by oxygen vacancies. Applied pressure produces a reduction in lattice volume which promotes ordering and this appears to lead to an artificially high values of dT_c/dP for some values of oxygen content. By contrast, the less studied bismuth compounds offer much "cleaner" systems for the investigation of the intrinsic pressure dependence of the high-temperature superconducting transition. Detailed mea-

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surements of the pressure dependences of transition temperature and the normal-state a-axis resistance R_a of high quality monocrystalline samples of $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ high-T_c superconductor are reported in this paper. The results show similarities and significant differences with other studies of this compound. A comparison is made between the effects observed and those predicted by competing theories.

II. EXPERIMENTAL PROCEDURES

A. The structural characteristics of the samples of monocrystalline $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$

The samples, whose properties have been measured, are cleavage products of an ingot of $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ which was grown by the traveling solvent floating-zone method.[5] The ingot, with a diameter of about 11 mm, was cut with a diamond wire saw into a piece about 14 mm in length along the growth direction, which was the a axis. The ingot consisted of $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ crystallites with dimensions ranging from hundreds micrometers to a few millimeters; it cleaved readily in the ab plane. The boundaries of the crystallites were clearly visible on the sides of the ingot. A cylinder with a thickness of 6.2 mm was cut off the ingot and polished. The structural characteristics of this crystalline $Bi_{2.2}(Sr,Ca)_{1.8}Cu_{2.0}O_{8+y}$ cylinder were investigated by x-ray diffractometry, using a Phillips 1730 4-kW x-ray generator in conjunction with Philips PC-APD software for data collection. The intensities of the x-ray-diffraction peaks are plotted as a function of the diffraction angle 2θ in Fig. 1(a). For x rays incident on the top face of the cylinder (dotted line) the strongest reflection peak corresponds to the (200) planes and the next strongest from the (400) planes. The x rays incident on the side wall were reflected strongly from the planes perpendicular to the c axis; the strongest peak is that reflected from the $(00\underline{20})$ planes. The intensity curves for x rays incident on the different faces are completely distinctive and show that the axis of the cylinder lies along the a-axis direction, while the side wall of the cylinder is largely perpendicular to the c axis. An x-ray powder-diffraction study has been made on a powdered piece of cleaved sheet from the ingot [Fig. 1(b)]. Analysis of the powder-diffraction pattern gave the lattice parameters of the $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ ingot as $a = 5.397$ Å, $b = 5.390$ Å, and $c = 30.643$ Å. In Sec. IV A an analysis of the measured resistance-versus-temperature curve shows that the sample is slightly underdoped.

The cleaved crystal used in the resistance measurements had dimensions of $5.5 \times 2.5 \times 0.09$ mm^3, and it had a smooth and shining ab-plane cleavage face. Its largest dimension was that along the axis of the cylinder, i.e., along the a axis, and the large faces were perpendicular to the c axis. The crystal structure of the cleaved crystal was also studied using the Laue back-reflection technique. The direction of the incident beam was along the c axis of the crystal. The Laue photograph showed the Bragg diffraction spots to distribute on different hyperbolas, which are associated with a lattice row of different order of diffraction. The photograph, which was similar to the one presented by Zhou *et al.*,[6] showed the structure of the single crystal $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ to be modulated along the b axis: the condensed spots in hyperbolas indicate the coexistence of a "lattice" with a different period along b axis. The high-resolution electron microscope images[7] show that Bi_2O_2 layers consist of the alternate "Bi-concentrated bands" and "Bi-deficient bands" repeating along the direction of the b axis. The Bi-concentrated bands extend along the a axis, while having a width of about 1.5 nm along the b axis. The arrangement of the bands forms a body-centered-orthorhombic superlattice.

B. The configuration of the electrical contacts and the measurement techniques

The electrical resistance of the crystals was measured using a conventional four-point configuration. The four contact points were aligned along the a axis. Hence, the electrical resistance measured is that of the a axis, R_a. The electrical contacts were made by a newly devised method using a mixture of silver and gold. The procedure used was as follows. The sample was placed in an evaporator which was pumped down to a base pressure below 7.5×10^{-6} torr. The electrical contact areas on the sample surface were sputter etched in an argon discharge at a pressure of about 10^{-2} torr. Then, the evaporator was re-evacuated and four silver contact pads of 1–2 μm thickness were immediately evaporated onto the sample. After this stage a gold layer of 0.2–0.25 μm thick was evaporated onto the top of the four silver pads. The sample was then annealed at 400 °C in air; this annealing process caused the gold and silver to interdiffuse. The contact pads for current were circular, diameter 0.5 mm, and those for voltage probes were semicircular. The distance between two voltage contacts was 1.0 mm. Gold wires with a diameter of 0.05 mm were attached to the contact pads by ultrasonic bonding. The contact resistance was below 0.5 Ω at room temperature.

The a-axis electrical resistance was measured in a BeCu pressure cell as a function of pressure up to 1 GPa at room temperature (296 K), and as a function of temperature between 300 and 77 K under different hydrostatic pressures. The pressure-transmitting medium was a mixture of 50% n-pentane and 50% isoamylalcohol. The pressure in this type of cell changes considerably on cooling down; for example if the initial pressure is set at 1 GPa at room temperature then it has reduced to about 0.67 GPa. Therefore it is necessary to monitor the pressure throughout the entire temperature-pressure range in any experiment; this was carried out using a manganin pressure gauge, which had been precalibrated against an InSb pressure gauge. The manganin pressure gauge was wound noninductively on a former designed to avoid any uniaxial strain in the wire. The temperature was measured by a calibrated K-type thermocouple situated next to the sample. The sample was not stuck on the substrate to avoid stresses caused by the differences in thermal expansion and compressibility of the substrate and the sample.

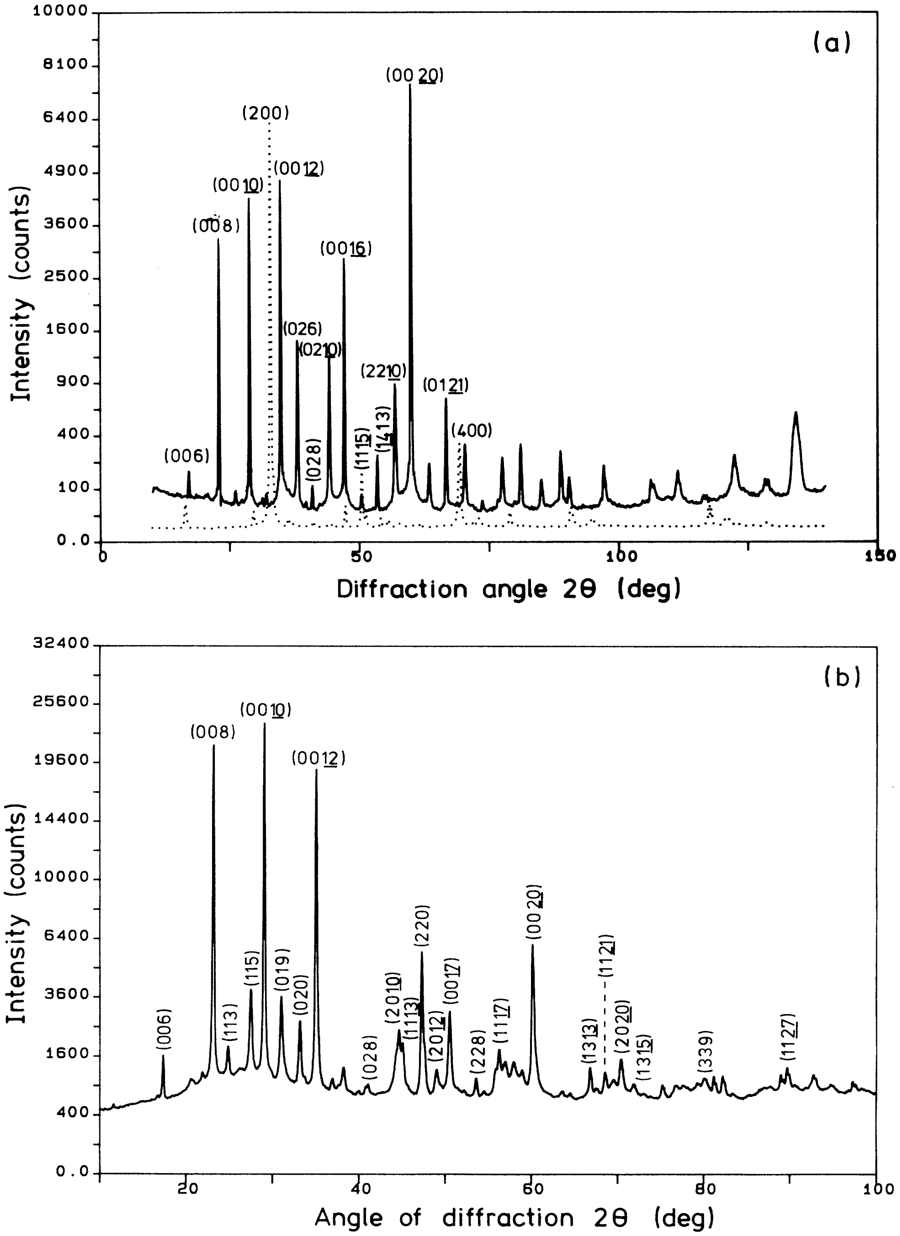

FIG. 1. X-ray-diffraction patterns of a $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ ingot grown by the traveling solvent floating-zone method. (a) Performed on a polished cylindrical sample: the dotted and full lines correspond to the spectrum for x-rays incident along and perpendicular to the cylinder axis, respectively. (b) Powder-diffraction pattern.

III. EXPERIMENTAL RESULTS

The measured temperature dependence of the electrical resistance R_a under different pressures is shown in Fig. 2. There was excellent agreement between the data obtained whilst decreasing and increasing temperature. For clarity, the data measured under some pressures have been omitted. After all of the temperature cyclings had been completed, the resistance R_a at 296 K at atmospheric pressure had increased by $2.0\pm0.2\%$. The data (lines) shown in Fig. 2 have been corrected to be isobaric (at constant pressure). To establish the accuracy of the correction, the data picked up from other temperature cycles, under the same pressure as the isobaric lines, are given (open circles) together in Fig. 2. It can be seen that there is excellent correlation. Figure 3 shows in detail the results obtained between 170 and 300 K. In this region the normal-state resistance R_a is a linear function of temperature.

The results show a positive effect of pressure on T_c. Figure 4 shows the pressure dependences of T_c (onset), T_c (mid), and T_c (offset), the lines being least-squares fits. The transition width ΔT_c is usually defined as the temperature at 90% of the normal-state resistance R_N linearly extrapolated to the transition region minus the temperature at 10% of R_N. The values of T_c and ΔT_c under different pressures are given in Table I. ΔT_c is almost constant under hydrostatic pressure. In Table II, the data for dT_c/dP, determined by the least-squares fit, are listed and compared with those given by other authors for Bi-2:2:1:2 superconductors. Within the pressure range of 2 GPa there are no large differences in dT_c/dP

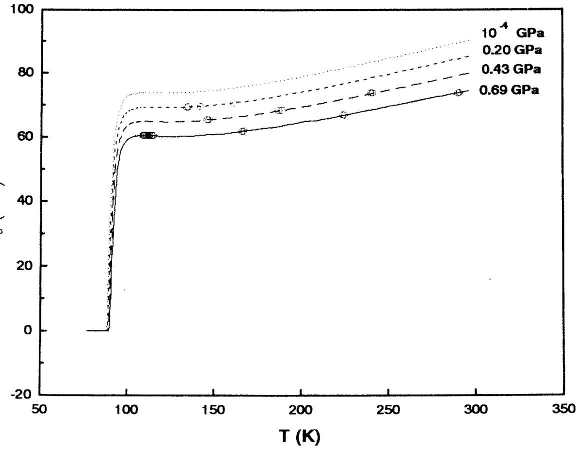

FIG. 2. Temperature dependences of the a-axis electrical resistance R_a of a $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ single crystal under constant pressure (isobaric lines). The open circles are the data picked up from other temperature cycles, at the points that have the same pressure as the corrected isobaric curves.

despite the data coming from a range of different sample types and the use of different experimental methods.

The pressure dependence of the a-axis resistance R_a at room temperature (296 K) is shown in Fig. 5. At room temperature (296 K) the a-axis resistance R_a decreased under hydrostatic pressure. R_a changed nonlinearly with pressure: the pressure derivative dR_a/dP is pressure dependent. Increasing pressure from 0 up to 1 GPa caused a decrease in R_a by $\Delta R_a/R_a(P=0)$ equal to $-22.5\pm0.2\%$. The resistance was measured during two pressure cycles. In the first cycle there was a small hys-

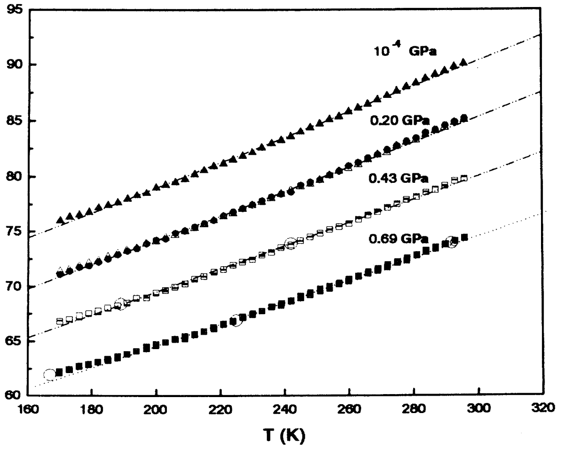

FIG. 3. Temperature dependences of the a-axis electrical resistance R_a of a $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ single crystal under constant pressure from 170 to 296 K. The lines are for guiding. Symbols: solid triangles: cooling under 10^{-4} GPa; open triangles: cooling under 0.2 GPa; solid circles: warming under 0.2 GPa; open squares: cooling under 0.43 GPa; bars: warming under 0.43 GPa; solid squares: warming or cooling under 0.69 GPa; open circles, data picked up from other temperature cycles as indicated in Fig. 2.

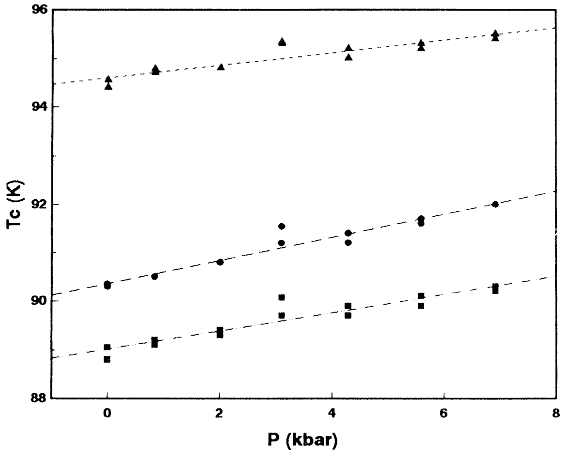

FIG. 4. The pressure dependence of T_c of a $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ single crystal: solid triangle T_c (onset), solid-circle T_c (mid), solid square T_c (offset), with the least-squares fit lines.

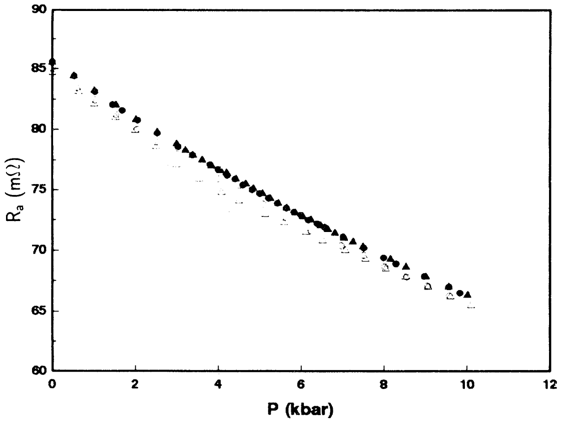

FIG. 5. Pressure dependence of the a-axis resistance R_a of a $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ single crystal at 296 K. Open (or solid) triangles: increasing pressure for the cycle 1 (or 2); open (or solid) circles: decreasing pressure for the cycle 1 (or 2).

TABLE I. T_c and ΔT_c (in the unit of K) of $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ single crystal under different pressures.

Measurements	T_c (onset)	T_c (mid)	T_c (offset)	ΔT_c
1-bar cooling	94.5±0.2	90.3±0.2	89.0±0.2	5.5±0.2
1-bar warming	94.4±0.2	90.3±0.2	89.0±0.2	5.4±0.2
0.84-kbar cooling	94.7±0.2	90.5±0.2	89.2±0.2	5.5±0.2
0.84-kbar warming	94.7±0.2	90.5±0.2	89.1±0.2	5.6±0.2
2.0-kbar cooling	94.8±0.2	90.8±0.2	89.3±0.2	5.5±0.2
2.0-kbar warming	94.8±0.2	90.8±0.2	89.4±0.2	5.4±0.2
3.1-kbar cooling	95.3±0.2	91.5±0.2	90.1±0.2	5.2±0.2
3.1-kbar warming	95.3±0.2	91.2±0.2	89.7±0.2	5.6±0.2
4.3-kbar cooling	95.0±0.2	91.2±0.2	89.7±0.2	5.3±0.2
4.3-kbar warming	95.2±0.2	91.4±0.2	89.9±0.2	5.3±0.2
5.6-kbar cooling	95.2±0.2	91.6±0.2	89.9±0.2	5.3±0.2
5.6-kbar warming	95.3±0.2	91.7±0.2	90.1±0.2	5.2±0.2
6.9-kbar cooling	95.4±0.2	92.0±0.2	90.2±0.2	5.2±0.2
6.9-kbar warming	95.5±0.2	92.0±0.2	90.3±0.2	5.2±0.2

teresis, presumably induced by relaxation of the sample. When pressure was reduced back to atmospheric pressure, it was found that R_a had increased by 0.41±0.2% after the first cycle. However, there was good coincidence between the data obtained by increasing and decreasing pressure in the second pressure cycle. The R_a increased by only 0.12±0.2% after the pressure was released.

ln R_a decreases linearly with increasing pressure (Fig. 6) and can be fitted by

$$\ln R_a = -0.255P + 4.4437 \;, \tag{1}$$

where P is in units of GPa. Hence $d\ln R_a/dP$ is constant in the pressure range of the experiments. The relationship between resistance R and resistivity ρ is

$$R = \frac{L}{A}\rho \;, \tag{2}$$

where L and A are the length and the area of the cross section of the sample respectively, hence,

$$\frac{d\ln R}{dP} = \frac{d\ln L}{dP} - \frac{d\ln A}{dP} + \frac{d\ln\rho}{dP} \;. \tag{3}$$

If L is chosen to be along the a axis then $d\ln L/dP = d\ln a/dP$ and

$$\begin{aligned} d\ln A/dP &= d\ln b/dP + d\ln c/dP \\ &\approx d\ln a/dP + d\ln c/dP \;. \end{aligned} \tag{4}$$

For $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ single crystals, $d\ln a/dP = -3.5\times10^{-3}$ GPa^{-1} and $d\ln c/dP = -6.2\times10^{-3}$ GPa^{-1} (Takahashi and Môri, quoted in Ref. 8). Equation (3) can be written as

$$\frac{d\ln\rho_a}{dP} = \frac{d\ln R_a}{dP} + \frac{d\ln c}{dP} \;. \tag{5}$$

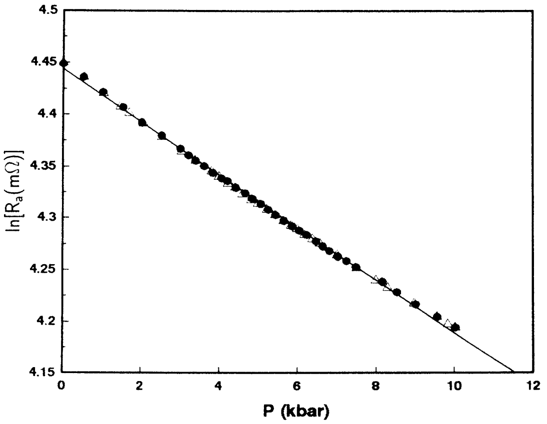

FIG. 6. Pressure dependence of lnR_a of a $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ single crystal at 296 K, with a line of least-squares fit. Solid dots: increasing pressure; open triangles: decreasing pressure.

Since for $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ single crystals $d\ln c/dP$ is two orders smaller in magnitude than $d\ln R_a/dP$, it can be neglected, so that $d\ln\rho_a/dP$ is almost equal to $d\ln R_a/dP$. From the present measurements, we find $d\ln\rho_a/dP \approx d\ln R_a/dP = -25.5\pm0.2\%$ GPa^{-1} and 296 K. This result is compared in Table III with other reported data, together with $d\ln\rho_{ab}/dP$ and $d\ln\rho/dP$ of some $YBa_2Cu_3O_{7-x}$ compounds. The value obtained here is rather larger than those given by other authors for Bi-2:2:1:2 single crystals. For $YBa_2Cu_3O_{7-x}$ the values for pressure derivatives of the electrical conductivity are around −12% irrespective of the sample type, while for $Bi_2Sr_2CaCu_2O_{8+y}$ the values are sample dependent, even for single crystals.

TABLE II. Comparison of dT_c/dP (K GPa^{-1}) of some Bi-2:2:1:2 superconductors with their T_c. P_m is the upper limit of the pressure range for the dT_c/dP listed in the table.

Source	T_c (K)	dT_c/dP (onset)	dT_c/dP (mid)	dT_c/dP (offset)	P_m (GPa)	Sample type
This work	90.3[c]	1.3±0.2	2.4±0.2	1.9±0.2	0.69	Single crystal
8	83.6[b]			2.4	2.0	Single crystal
8	81.3[b]			2.0	2.0	Single crystal
8	82.3[b,e]			2.0	2.0	Single crystal
9	80[a]		2		1.42	Plateletlike single crystal
10	90.2[d]	1.5±0.2			0.6	Sintered
11		1.5±0.2	1.5±0.2	1.5±0.2	2.0	Single crystal
12	80.6[d]	1.3±0.3			0.56	Single crystal
12	92.4[c]		−1.6		8.0	Polycrystalline
13	93[d]	−2			5.0	Sintered
14	88[a]	1.2			1.5	Single crystal
15	80[c]		1.7		0.42	Single crystal

[a] Zero resistance.

[b] Offset.

[c] Midpoint.

[d] Onset.

[e] Measured along the *c* axis.

TABLE III. Comparison of $d\ln\rho_a/dP$ of $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ single crystal and $d\ln\rho_{ab}/dP$ (% K GPa^{-1}) of some Bi-2:2:1:2 single crystals with $d\ln\rho_{ab}/dP$ and $d\ln\rho/dP$ of Y-1:2:3 compounds at room temperature. The upper limit of the pressure range for the measurements are listed under the references quoted.

Single crystal	This work 1.0 GPa	Ref. 9 1.42 GPa	Ref. 11 2.0 GPa	Ref. 8 2.0 GPa	Ref. 8 2.0 GPa
Bi-2:2:1:2	−25.5±0.2	−15.0	−7.5	−12.0	−8.4
Compound	Ref. 16 1.6 GPa	Ref. 17 2.0 GPa	Ref. 18 2.0 GPa	Ref. 19 1.5 GPa	Ref. 20 1.2 GPa
Y-1:2:3	−12.0[a]	−12.0[b]	−10.0[a]	−13.0[b]	−12±2[c]

[a] Single crystal.
[b] Sintered ceramic.
[c] Sinter-forged ceramic.

To discuss the pressure dependence of the a-axis resistance R_a at different temperatures, the data of R_a were picked up from temperature cycles under different pressures, which are the same sets of data as those given in Fig. 2. The pressure dependence of the a-axis resistance R_a is plotted in Fig. 7 at selected temperatures 116, 146, 176, 206, 236, 266, 296 K. The pressure dependences of $\ln R_a$ at different temperatures in the range 116 to 296 K are linear (Fig. 8): $d\ln R_a/dP$ is independent of pressure in this temperature range. The least-squares fit of $\ln R_a$ as a function of pressure for each temperature takes the form

$$\ln R_a=\left[\frac{d\ln R_a}{dP}\right]_0 P+(\ln R_a)_0 \qquad (6)$$

with the coefficients given in Table IV; $d\ln R_a/dP = -26.9\pm2.2\%$ at 296 K and $-28.4\pm2.2\%$ GPa^{-1} at 116 K, that is, from 116 to 296 K $d\ln R_a/dP$ changes by only $1.5\pm2.2\%$. (In this set of data, $d\ln R_a/dP$ at 296 K is larger than that ($25.5\pm0.2\%$) obtained directly from the pressure cycle. This is because the effect of the temperature cycling on the sample causes R_a to increase by $2.0\pm0.2\%$ under atmospheric pressure at 296 K.) Hence in the normal state, $d\ln R_a/dP$ for $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ does not depend markedly on temperature. Forró, Ilakovac, and Keszei[11] measured both the in-plane and out-of-plane resistivity of some $Bi_2Sr_2CaCu_2O_8$ single crystals up to 2 GPa. They found that below 140 K the pressure dependence of ρ_{ab} increases with decreasing temperature. However from their results (see Fig. 5 in Ref. 11) it can be seen that above 100 K there is no pronounced temperature dependence of $\rho_{ab}(P)/\rho_{ab}(0)$ at pressures below 1 GPa, which is the pressure range used in this work. Similar results have been obtained on other types of high-T_c superconductors. For example, Kamarád *et al.*[21] found, in two polycrystalline Pb-doped Bi-Sr-Ca-Cu-O samples, that $d\ln\rho/dP(=-0.11\ \text{GPa}^{-1})$ does not change with temperature at pressures up to 1 GPa. In addition, Ilakovac *et al.*[18] found the ratio $\rho_{ab}(P)/\rho_{ab}(0)$ to be temperature independent in a $YBa_2Cu_3O_{7-\delta}$ single crystal at pressures up to 2 GPa.

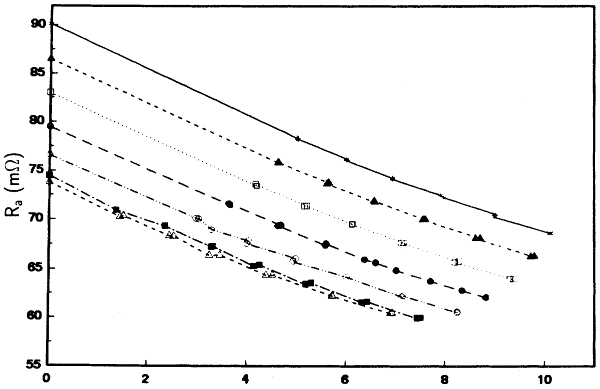

FIG. 7. Pressure dependence of R_a of a $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ single crystal at different temperatures. The lines in the figure are for the guidance of eye. Stars: 296 K; solid triangles: 266 K; open squares: 236 K; solid circles: 206 K; open circles: 176 K; solid squares: 146 K; open triangles: 116 K.

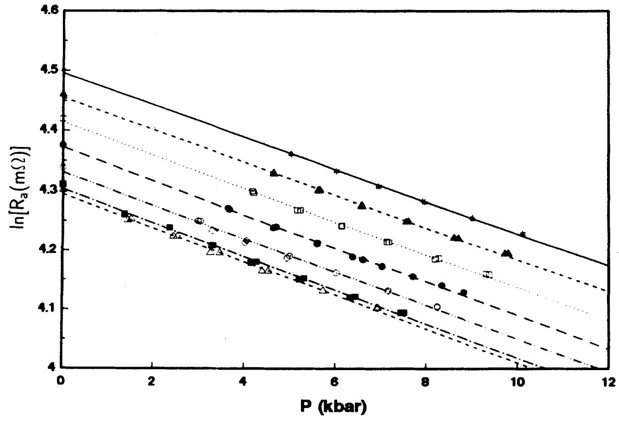

FIG. 8. Pressure dependence of $\ln R_a$ of a $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ single crystal at different temperatures, with the least-squares fitting lines. Symbols are same as in Fig. 7.

TABLE IV. The temperature dependence of the coefficients $(d\ln R_a/dP)_0$ (in units of GPa^{-1}) and $(\ln R_a)_0$ [in units of $\ln(\mathrm{m}\,\Omega)$] of the least-squares fit [Eq. (6)] to the pressure dependence of $\ln R_a$ of $\mathrm{Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}}$ single crystal. The data of R_a for the fitting were picked up from temperature cycles under different pressures as explained in the text. FR is the relative coefficient of the least-squares fit.

T (K)	FR	$(d\ln R_a/dP)_0$	$(\ln R_a)_0$
296	0.998	−0.269	4.496
266	0.999	−0.271	4.456
236	0.999	−0.277	4.414
206	0.998	−0.282	4.372
176	0.996	−0.281	4.331
146	0.997	−0.285	4.303
116	0.996	−0.284	4.294

IV. DISCUSSION OF THE EFFECT OF HYDROSTATIC PRESSURE AND TEMPERATURE ON THE NORMAL STATE OF *a*-AXIS ELECTRICAL RESISTANCE

A. Temperature dependence and oxygen underdoping

Transport properties such as electrical conductivity, resistivity, Hall coefficients, and thermal conductivity of single crystal Bi-2:2:1:2 are highly anisotropic. A well-known anisotropic feature observed in $\mathrm{YBa_2Cu_3O_{7-x}}$ single crystals[22,23] is that while the in-plane electrical resistivity ρ_{ab} shows metallic characteristics with a deviation from linear behavior near T_c, the out-of-plane ρ_c shows a semiconductorlike upturn at temperatures close to T_c; similar behavior has also been reported for $\mathrm{Bi_2Sr_2CaCu_2O_8}$ single crystals.[11,24] The *a*-axis resistance R_a of monocrystalline $\mathrm{Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}}$ measured here does not show such a clear distinction between metallic and semiconductorlike behavior: R_a decreases linearly with temperature down to about 200 K and below that temperature the rate of decrease of R_a gradually reduces until R_a bends slightly upwards before dropping down at T_c (Fig. 2). This behavior is not a result of any inaccuracy in sample orientation with respect to the *c* axis because this has been definitively defined by x-ray orientation with reference to the cleavage faces. An explanation of the particular features of R_a observed in this work may lie in the dependence of physical properties of high-T_c cuprate superconductors on defect concentration. It has been known that the Bi-Sr-Ca-Cu-O system contains various amounts of excess oxygen,[25] which depend on the condition and procedure of sample preparation. Both superconducting properties and structural characteristics of the system change with oxygen content.[14,25] Not only the superconducting properties but also the normal-state properties of the high-T_c materials vary remarkably with doped allovalent cations and oxygen concentration.[26] The phase research by Xu *et al.*[27] on ceramic $\mathrm{Bi_2Sr_2Ca_2Cu_3O_y}$ doped with Sb and Pb revealed that the temperature dependence of the normal-state resistivity changed from metallic to semiconducting behavior when the concentration of dopants Sb and Pb was altered. The normal-state static susceptibility χ_{DC} of $\mathrm{Bi_2Sr_2CaCu_2O_y}$ decreased[28] and the resistivity changed gradually from a metallic to a more semiconductorlike behavior[29] when the quenching temperature T_q was increased (which leads to a decrease of oxygen content). The results of Groen, deLeeuw, and Feiner[30] showed that in the whole temperature range above T_c the magnitude of electrical resistance of $\mathrm{Bi_2Sr_2CaCu_2O_{8+\delta}}$ changed when the sample was annealed at different partial oxygen pressures. The oxygen nonstoichiometric study of $\mathrm{Bi_{2.00}Sr_{1.88}Ca_{1.00}Cu_{2.14}O_y}$ by Idemoto and Fueki[26] showed that following annealing under partial oxygen pressures, the temperature dependence of the electrical resistivity was metallic when the annealing temperature T_a was higher than 600 °C, while it was semiconductorlike when T_a was lower than 600 °C. The investigations of Crommie and his co-workers[31–33] on the normal transport properties of $\mathrm{Bi_2Sr_2CaCu_2O_{8-x}}$ single crystals revealed that the resistivity, thermoelectric power, and Hall coefficients in the *ab* plane are oxygen sensitive and their temperature dependences varied dramatically with change of oxygen content. The in-plane resistivity of $\mathrm{Bi_2Sr_2CaCu_2O_{8-x}}$ single crystals follows an empirical equation[32]

$$\rho(T)=\rho_0 T^{\alpha} e^{\Delta/k_B T} , \tag{7}$$

where $\alpha=0.7$ and Δ is a small characteristic "activation" energy that increases from 0 to 23 meV as oxygen underdoping is enhanced.[32] Equation (7) has same form as the equation in the conventional theory for the electrical conductivity σ of semiconductors[34]

$$\frac{1}{\sigma}=\frac{1}{\sigma_0} e^{\varepsilon/k_B T} , \tag{8}$$

where σ_0 varies slowly with temperature and ε is the activation energy (equal to half of the work required to raise an electron from an impurity center into the conduction band). When oxygen concentration is decreased, the in-plane resistivity and the thermal transport properties of $\mathrm{Bi_2Sr_2CaCu_2O_{8-x}}$ single crystals approach the behavior of the out-of-plane properties with full oxygen content;[32] Eq. (7) accounts well for the resistivity along the *c* axis with $\rho_0=3.32\times10^{-2}\ \Omega\,\mathrm{cm\,K^{-0.7}}$, $\alpha=0.7$ and $\Delta=8.77$ meV.[33] The *a*-axis resistance measured here for monocrystalline $\mathrm{Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}}$ fits Eq. (7) very well, with $\alpha=0.7$ and $\Delta=7.25$ meV for the data measured at atmospheric pressure. On the basis of the work of Crommie *et al.*,[32] this value (7.25) for Δ indicates that our material was slightly underdoped. It has been suggested that in a quasi-two-dimensional model[35,36] the insulating $\mathrm{(BiO)_2}$ layers and the superconducting $\mathrm{(CuO_2)_2}$ layers are alternately stacked and weakly connected through Josephson coupling. In an atomic site tunneling spectroscopy study of bulk single crystal of $\mathrm{Bi_2Sr_2CaCu_2O_y}$, Hasegawa *et al.*[36] showed that the BiO layer is semiconducting with an energy gap of 0.1 eV and that the $\mathrm{CuO_2}$ layer is responsible for the quasi-two-dimensional superconductivity. From the scanning tunneling spectroscopy study on the cleaved face of single crystalline $\mathrm{Bi_2Sr_2CaCu_2O_y}$ Wei *et al.*[37] concluded that the BiO layer with less oxygen content is semiconducting but tends to become metallic when an excess amount of oxygen is incorporated. This property of the BiO layer seems to be responsible for the change from metallic to semiconducting behavior of the in-plane resistivity of $Bi_2Sr_2CaCu_2O_{8+y}$.

B. Combined effect of pressure and temperature on electrical resistance

Application of pressure decreases the electrical resistance of monocrystalline $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ (Fig. 5). An empirical expression for the combined effects of pressure and temperature on the normal-state a-axis resistance R_a can be obtained using Eq. (7) and Eq. (5):

$$R_a=\frac{R_0T^{\alpha}}{(1+\alpha_{33}T)}e^{[\Delta/k_BT+\zeta P]} . \tag{9}$$

Here α_{33} is the c-axis thermal-expansion tensor component and $\zeta=d\ln R_a/dP$ which is a function of temperature. For monocrystalline $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ the parameter ζ is found to be almost independent of temperature; the data given in Table IV gives

$$\zeta=-0.278-1.1\times10^{-4}T+4.894\times10^{-7}T^2 . \tag{10}$$

Pressure has only a very small effect on the activation energy Δ for $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ single crystals: a value for $d\Delta/dP\approx2.83\times10^{-2}$ meV GPa^{-1} was obtained over the range of pressures used in this work.

C. Theoretical models

For most metals and materials that show high-T_c superconductivity the electrical resistance decreases with increasing pressure. In the conventional theory of lattice vibrational scattering (e.g., Mott and Jones[38]) the particle vibrational amplitude X decreases under pressure; the resistance of metal is proportional to the mean square amplitude $\overline{X}^2$, and hence is proportional to the reciprocal of the Debye temperature Θ. The main part of the pressure effects on the resistivity ρ may be attributed to the change in Θ with volume V.[39] For $T>\Theta$, the resistivity $\rho\propto\Theta^{-2}$; for $T\ll\Theta$, $\rho\propto\Theta^{-6}$.[39] For the electrical resistance in the ab plane, using Eq. (2), it can be shown that

$$\frac{d\ln R}{d\ln V}=\frac{d\ln\rho}{d\ln V}-\left[\frac{d\ln c}{dP}\right]\left[\frac{d\ln V}{dP}\right]^{-1} \tag{11}$$

or, for $T>\Theta$,

$$\frac{d\ln R}{d\ln V}=-2\frac{d\ln\Theta}{d\ln V}-\left[\frac{d\ln c}{dP}\right]\left[\frac{d\ln V}{dP}\right]^{-1} \tag{12}$$

and, for $T\ll\Theta$,

$$\frac{d\ln R}{d\ln V}=-6\frac{d\ln\Theta}{d\ln V}-\left[\frac{d\ln c}{dP}\right]\left[\frac{d\ln V}{dP}\right]^{-1} . \tag{13}$$

Since $-d\ln\Theta/d\ln V$ is the Grüneisen parameter γ and for high-T_c superconductors $(d\ln c/dP)(d\ln V/dP)^{-1}$ is about one third of γ, the second terms in Eqs. (11) and (12) can be neglected. Equations (11) and (12) can then be replaced by

$$\frac{d\ln R}{d\ln V}\approx2\gamma\quad(T>\Theta) \tag{14}$$

and

$$\frac{d\ln R}{d\ln V}\approx6\gamma\quad(T\ll\Theta) . \tag{15}$$

$d\ln R/d\ln V$ can be obtained from measurements of the resistance or resistivity under high pressures using

$$\frac{d\ln R}{d\ln V}=-B^T\frac{d\ln R}{dP} \tag{16}$$

where B^T is the isothermal bulk modulus. For $Bi_2Sr_2CaCu_2O_y$ the elastic Debye temperature Θ^{el} has been found equal to 275±6 K (Ref. 40) and for $YBa_2Cu_3O_{7-\delta}$ single crystals a value of 430 K (Ref. 41) has been obtained from specific-heat measurements. The Grüneisen parameter γ for $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ single crystals has been calculated to be 1.56 from the equation

$$\gamma=\frac{\beta B^S}{C_Pd} \tag{17}$$

taking 51×10^{-6} K^{-1} to be the volume thermal-expansion coefficient β obtained for $Bi_2Sr_2CaCu_2O_{8-x}$ single crystals,[42] $C_P=354$ J K^{-1}kg^{-1} at 300 K for $Bi_2Sr_2CaCu_2O_y$ single crystals,[43] and the x-ray density $d(=6724$ kg m$^{-3})$. Yoneda *et al.*[44] obtained a value of 61 GPa for the bulk modulus B^T of $Bi_2Sr_2CaCu_2O_{8-x}$ using very high-pressure x-ray-diffraction measurements of lattice parameters in a diamond cell; a value of 62.5 GPa was obtained by Olsen *et al.*[45] from similar high-pressure measurements. Tajima *et al.*[8] reported that the bulk modulus B^T for a $Bi_{2.2}Sr_{2.8}CaCu_2O_{8+y}$ single crystal had been obtained as 73 GPa by Takahashi and Môri using x-ray analysis under high pressure. This value is in good agreement with that for the adiabatic bulk modulus $B^S(=70$ GPa) (Ref. 40) obtained from the elastic constants of $Bi_2Sr_2CaCu_2O_{8-x}$ single crystals determined by Brillouin-scattering experiments[46] and ultrasonic measurements,[47] assuming that $C_{23}=C_{13}$ and $C_{55}=C_{44}$. All of these values are rather small compared with those of other high-T_c superconductors, such as La_2CuO_4, $YBa_2Cu_3O_{7-x}$, $YBa_2Cu_4O_8$, $La_{1.85}Sr_{0.15}CuO_4$, and $Tl_2Ba_2Ca_2Cu_3O_{10}$. For the comparison of normal-state experimental results with the conventional theory of lattice vibrational scattering the condition $(T\ll\Theta)$ is not satisfied. If it is assumed that $T>\Theta$, Eq. (14) predicts for $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ single crystals $d\ln R_a/d\ln V=3.1$, while using Eq. (16) with $B^T=73$ GPa (Ref. 8) and the measured data $d\ln R_a/dP=-0.255$ GPa^{-1} a value of 18.61 has been obtained for $d\ln R_a/d\ln V$ at 296 K. For $Bi_2Sr_2CaCu_2O_y$ single crystals, using Eq. (16) with the same value of B^T, the results of Forró, Ilakovac, and Keszei[11] give $d\ln R_{ab}/d\ln V=5.47$ and the results of Beille *et al.*[9] give $d\ln R_{ab}/d\ln V=10.95$ at room temperatures. From recent high-pressure neutron-diffraction studies on $YBa_2Cu_3O_{6.93}$ single crystals Jorgensen *et al.*[48] found that $B^T=123$ GPa. Taking this value for

$YBa_2Cu_3O_{7-\delta}$ single crystals, the results obtained by Ilakovac *et al.*[18] ($d\ln\rho_{ab}/dP = -10.0\%\ \mathrm{GPa}^{-1}$) and by Konczykowski, Rullier-Albenque, and Collin[16] ($d\ln\rho_{ab}/dP = -12\%\ \mathrm{GPa}^{-1}$) give $d\ln R_{ab}/d\ln V \approx 12.3$ and 14.8, respectively, when Eq. (16) is used, while Eqs. (14) gives $d\ln R_{ab}/d\ln V = 3.5$ for $T > \Theta$ [with $\gamma = 1.75$ (Ref. 3)]. These comparisons between the values of $d\ln R/d\ln V$ obtained from the measurements and the conventional theory of lattice vibrational scattering show that the conventional theory of lattice vibrational scattering cannot provide a satisfactory explanation for the large pressure effects on the electrical resistance of high-T_c superconductors and indicates that the behavior of the in-plane resistance of high-T_c superconductors cannot be accounted for by phonon scattering alone.

One of the striking features of most high-T_c superconductors is that their Hall coefficient R_H has a significant pressure dependence in the normal state, which indicates that the number of mobile charge carrier in these materials is a function of pressure. From the Hall-effect studies it follows that, except for $La_{1-x}Sr_xCuO_4$, the mobile charge carrier density δ of hole-doped high-T_c materials increases at a rate of $d\ln\delta/dP \approx 10\%\ \mathrm{GPa}^{-1}$ (Ref. 3) with applied pressure. The electrical resistance therefore decreases under pressure as δ increases. Hence it is necessary to consider the pressure effects on the mobile charge-carrier density δ in the study of the normal-state electrical resistance of these materials. In the classical theory, the electrical resistivity of a metal can be considered to be a function of both the mean free path l of the electrons and the effective number n of mobile charge carrier,[49]

$$\rho \propto \frac{m}{nl} . \tag{18}$$

Here m is the effective mass of an electron. From Eq. (18) the volume derivative of the resistivity ρ can be written, assuming that the effective mass m does not change with volume, as

$$\frac{d\ln\rho}{d\ln V} = -\frac{d\ln l}{d\ln V} - \frac{d\ln n}{d\ln V} . \tag{19}$$

The mean free path l is proportional to the reciprocal of the mean square $\overline{X}^2$ of the particle vibrational amplitude and the effective number n of the mobile charge carriers is proportional to its density δ. Considering the Eqs. (11)–(14), the volume derivative of the resistance for $T > \Theta$ can be written as

$$\frac{d\ln R}{d\ln V} \approx 2\gamma + B^T \frac{d\ln\delta}{dP} . \tag{20}$$

From the Hall-effect studies the derivative $d\ln\delta/dP$ can be estimated[50] equal to $12\%\ \mathrm{GPa}^{-1}$ for $Bi_2Sr_2CaCu_2O_y$ and $9.0\%\ \mathrm{GPa}^{-1}$ for $YBa_2Cu_3O_{7-\delta}$. For $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ single crystals, with $B^T = 73$ GPa and $\gamma = 1.56$, Eq. (20) gives $d\ln R_{ab}/d\ln V \approx 11.88$ when $T > \Theta$. This is closer to the large values calculated from the experimental data using Eq. (16) for $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ (18.6 from this work) and $Bi_2Sr_2CaCu_2O_y$ (10.9 by using the data of Beille *et al.*[9]). The higher value found in the $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ single crystal measured in this work may be caused by its oxygen underdoping, i.e., the pressure derivative $d\ln\delta/dP$ of this sample might be higher than the one with optimum oxygen concentration. For $YBa_2Cu_3O_{7-\delta}$ single crystals, with $B^T = 123$ GPa (Ref. 48) and $\gamma = 1.75$,[3] Eq. (20) gives $d\ln R_{ab}/d\ln V \approx 14.6$ when $T > \Theta$. This value is very close to those calculated using Eq. (16) and the experimental data (12.3 by using the data of Ilakovac *et al.*[18] and 14.8 by using the data of Konczykowski, Rullier-Albenque, and Collins[15]). In Eq. (20) the second term contributes 74% to that of $d\ln R_{ab}/d\ln V$ for $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ and 76% for $YBa_2Cu_3O_{7-\delta}$. This discussion leads to the conclusion that the pressure dependence of the normal-state electrical resistance of high-T_c superconductors is dominated by the pressure dependence of the mobile charge-carrier density δ and that the effect of pressure on lattice vibrational scattering plays only a minor role.

V. DISCUSSION OF THE EFFECTS OF HYDROSTATIC PRESSURE ON SUPERCONDUCTING PROPERTIES OF Bi-2:2:1:2

A. Volume dependence of the superconducting transition temperature T_c

Theoretical models for the mechanism of high-T_c superconductivity lead to different predictions for the volume dependence $d\ln T_c/d\ln V$ of T_c. Hence it is necessary to determine $d\ln T_c/d\ln V$ from the experimental results to provide a basis for comparison with theory. The thermodynamic relationship between the measured pressure dependence dT_c/dP and $d\ln T_c/d\ln V$ is

$$\frac{d\ln T_c}{d\ln V} = -\frac{B^T}{T_c}\frac{dT_c}{dP} . \tag{21}$$

By substituting into Eq. (21) the values of $B^T (= 73$ GPa), $T_c (= 90$ K), and $dT_c/dP (= 1.9\ \mathrm{K\,GPa}^{-1})$ for the single crystal $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$, the value of -1.5 has been obtained for $d\ln T_c/d\ln V$. This is considerably smaller than those of many other high-T_c materials[2,3] (e.g., -122 for $La_{1.885}Ba_{0.115}CuO_4$ and -8.1 for $YBa_2Cu_4O_8$). It is also smaller than the values given for $Bi_2Sr_2CaCu_2O_8$ single crystals by some authors (e.g., -3 by Forró, Ilakovac, and Keszei,[11] -4 by Beille *et al.*[9]). The difference arises from the use of different values for the bulk modulus in estimating $d\ln T_c/d\ln V$: inspection of Eq. (21) shows that $d\ln T_c/d\ln V$ is linearly proportional to the bulk modulus. In some earlier studies[9,12,21] of the high-pressure effects on materials belonging to the Bi-Sr-Ca-Cu-O system, the value of $B (= 170$ GPa) obtained for $YBa_2Cu_3O_7$ was used because no other values of bulk modulus were available. This leads to an estimate of $d\ln T_c/d\ln V$ about twice as large as that obtained now using the more reliable value of 73 GPa for B^T.

B. Consideration within the framework of some theoretical models

Many theoretical models have been developed to explain the mechanism of the high-T_c superconductivity and some of them have been used to predict or to interpret the behavior under pressure. By simplifying the work of Allen and Dynes,[51] Griessen[2] concluded that the standard BCS model predicts $d\ln T_c/d\ln V \approx -1$ for superconductors. This value is much smaller than those observed in some of the high-T_c superconducting materials[2,3] but it is close to the value (-1.5) of $d\ln T_c/d\ln V$ found here for single crystal $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ and to that (-1.1) for $Bi_2Sr_2CaCu_2O_{8+y}$ obtained by Sieburger, Múller, and Schilling.[10] On the basis of the BCS model Griessen[2] obtained a simplified expression for $d\ln T_c/d\ln V$:

$$\frac{d\ln T_c}{d\ln V}=-\gamma+g\frac{d\ln\lambda}{d\ln V}\ , \tag{22}$$

where γ is the Grüneisen parameter, g is a function of the electron-phonon enhancement parameter λ and the effective Coulomb pseudopotential μ^* whose value was chosen as 0.13 and was assumed to be volume independent.[2] The volume dependence of the electron-phonon enhancement parameter λ is related to that of the electronic electron-phonon interaction parameter η by[2]

$$\frac{d\ln\lambda}{d\ln V}=\frac{d\ln\eta}{d\ln V}+2\gamma\ . \tag{23}$$

Hence Eq. (22) can be rewritten in terms of $d\ln\eta/d\ln V$ as

$$\frac{d\ln T_c}{d\ln V}=\gamma(2g-1)+g\frac{d\ln\eta}{d\ln V} \tag{24}$$

For a strong electron-phonon interaction g is equal to 0.5.[2] Inserting the value of $d\ln T_c/d\ln V(=-1.5)$ obtained for $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ single crystals, it is found that $d\ln\eta/d\ln V$ is -3.0. If a weak electron-phonon interaction is assumed, g is 1.1 and this leads to a value for $d\ln\eta/d\ln V$ of -3.1. Hence, in the context of the BCS theory there seems to be almost no difference between the effects of either strong or weak electron-phonon interactions on the behavior of T_c under pressure for $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ single crystals. The volume dependence of the electronic electron-phonon interaction parameter η for $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ is stronger than that predicted by the BCS theory for conventional superconductors (-2).[2] Substituting 1.56 for γ and -3.1 for $d\ln\eta/d\ln V$ into Eq. (23) gives 0.02 for $d\ln\lambda/d\ln V$ for $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$. Therefore the volume dependence of λ, which is calculated by this method and required to match with the experimental determined dT_c/dP for $Bi_{2.2}(Sr,Ca)_{1.8}Cu_{2.0}O_{8+y}$, is almost equal to zero. There is a huge range of values estimated for $d\ln\lambda/d\ln V$ from the experimental data:[52] for materials in the YBCO system $d\ln\lambda/d\ln V$ is about 2.8, while for Ba-La-Cu-O it is about -39.

A value of about -2 for $d\ln T_c/d\ln V$ has been obtained by Griessen[2] for the Anderson's resonating-valence-bond model[53] (RVB) strong-coupling limit model for high-T_c superconductors. However, Schilling and Klotz[3] have estimated for this model that $d\ln T_c/d\ln V\approx -8.4$ for $Bi_2Sr_2CaCu_2O_{8.15}$. They used expressions given in Ref. 54 for the intraplanar and interplanar integrals, with the assumptions that the carrier concentration δ is proportional to the inverse Hall constant R_H^{-1} and that the pressure dependence of the effective masses of the both intraplanar and interplanar electrons can be neglected. The equation used by Griessen[2] for calculation for the volume dependence of T_c is

$$\frac{d\ln T_c}{d\ln V}=2\frac{d\ln W_b}{d\ln V}-\frac{d\ln U}{d\ln V}\ , \tag{25}$$

where W_b is the width of the electron band for a two-dimensional square lattice and U is the local electron-electron repulsion for electrons of opposite spins in the same atomic orbital. Assuming $d\ln U/d\ln V\approx 0$ and using $d\ln T_c/d\ln V\approx -1.5$ for $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_y$, we find that $d\ln W_b/d\ln V\approx -0.75$, which lies between the values for pure d-band structures $(-5/3)$ and for free electrons $(-2/3)$ (Ref. 2) but closer to the latter. The value determined experimentally here of -0.75 for $d\ln W_b/d\ln V$ is quite close to that of -1 assumed for high-T_c superconductors by Griessen.[2]

Although estimations made by using the BCS and RVB theoretical models give values of $d\ln T_c/d\ln V$ which are close to that measured here for $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$, it is not clear that either estimation is more satisfactory than the other or that the measurement of $d\ln T_c/d\ln V$ is capable of deciding between the models. The value obtained for $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ is close to the theoretical predictions of both models, in contrast to the values obtained for several other high-temperature superconductors, which can only be explained by the insertion of unlikely parameters due to presence ancillary physical phenomena, such as soft modes in the Ba-La-Cu-O compound. However, if we compare our results obtained from the above discussion with those of the conventional superconductors, some light can be shed on the argument of the role of the BCS theory in the explanation of the superconductivity of high transition temperature superconductors. Within the frame of the BCS theory,[55] the transition temperature T_c is related to the electron-phonon interaction parameter g by

$$T_c=1.14\Theta_D e^{-1/g}\ , \tag{26}$$

where Θ_D is the Debye temperature. Using $T_c=89.0\pm0.2$ determined in this work and 275 ± 6 K for Θ_D,[40] a value $g=0.79$ is estimated for the $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ single crystal, an intermediate value rather closer to that (0.5) predicted for a strong electron-phonon interaction.[2] The volume derivative of Eq. (26) can be written as

$$\frac{d\ln T_c}{d\ln V}=-\gamma+\frac{1}{g}\frac{d\ln g}{d\ln V}\ . \tag{27}$$

Here the Grüneisen parameter has been set as $\gamma=-d\ln\Theta_D/d\ln V$. From Eq. (27) the volume derivative of the electron-phonon interaction parameter is estimated as $d\ln g/d\ln V = 0.049$ for $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ single crystal. Using the results of Neumeier and Zimmermann[56] obtained from a study of the pressure dependence of T_c for $YBa_2Cu_3O_{7-\delta}$, Neumeier[57] has estimated that for $YBa_2Cu_3O_{7-\delta}$ $g = 0.60$ and $d\ln g/d\ln V = 0.185$. If the effective Coulomb-repulsion parameter μ^* is set to zero, the parameter g is related to the electron-phonon enhancement parameter λ by $g \cong \lambda/(1+\lambda)$.[57] Using this relation, it can be estimated that for $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ single crystals, $\lambda = 3.76$ and $d\ln\lambda/d\ln V = 0.23$, while for $YBa_2Cu_3O_{7-\delta}$ it has been estimated[57] that $\lambda = 1.7$ and $d\ln\lambda/d\ln V = 0.46$. Inserting the value $d\ln\lambda/d\ln V = 0.23$ and that of $\gamma(1.56)$ into Eq. (23), it is found that $d\ln\eta/d\ln V$ is -2.89 for $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ single crystals, which is close to the values (-3.0 or -3.1) obtained in the above discussion. In his work, Neummeier[57] compared the values of $d\ln T_c/d\ln V$ and $d\ln g/d\ln V$ for $YBa_2Cu_3O_{7-\delta}$ with those of conventional elemental superconductors and found that the results for $YBa_2Cu_3O_{7-\delta}$ are comparable to those of the conventional superconductors (see Fig. 1 of Ref. 32). It is also found that our results of $d\ln T_c/d\ln V$ and $d\ln g/d\ln V$ for $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ single crystals fall on the line formed by the results for the conventional elemental superconductors and those for $YBa_2Cu_3O_{7-\delta}$ obtained by Neummeier.[57] This leads us to share with other people a belief that the mechanism of the superconductivity for the layered high-temperature superconductors could also be described by the BCS theory with electron-phonon coupling.

Recently, Neumeier and Zimmermann[56] have proposed a model, based on the fact that T_c is dependent on the hole concentration, that the pressure effects on T_c can be separated into an "intrinsic" contribution dT_c^i/dP and a part arising from the pressure-induced change in hole carrier concentration n

$$\frac{dT_c}{dP} = \frac{dT_c^i}{dP} + \frac{\partial T_c}{\partial n}\frac{\partial n}{\partial P} . \tag{28}$$

The first term is the part of dT_c/dP not influenced by the pressure effects on the carrier concentration. However, referring to the results of the study of the dependence of T_c on oxygen content y for $Bi_2Sr_2CaCu_2O_{8+y}$ crystals by Sieburger, Múller, and Schilling[10] casts some doubts on the applicability of this model to $Bi_2Sr_2CaCu_2O_{8+y}$ crystals. The results of Sieburger, Múller, and Schilling[10] show that although the value of T_c of $Bi_2Sr_2CaCu_2O_{8+y}$ crystals depends significantly on carrier concentration ($\partial T_c/\partial n$ changes sign when oxygen doping passes the optimal value) the pressure derivative $\partial T_c/\partial P$ keeps almost constant with changing the carrier concentration. This fact suggests that Eq. (28) is not adequate for $Bi_2Sr_2CaCu_2O_{8+y}$ crystals.

VI. CONCLUSIONS

The bismuth cuprates appear to provide particularly "clean" high-temperature superconducting compounds having properties that are genuinely characteristic of high-temperature superconductivity. In this study, measurements of the pressure dependence of the transition temperature of a single-crystal sample of $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ have been used to obtain an estimate of the normalized volume dependence of T_c, $d\ln T_c/d\ln V$. The value obtained, $d\ln T_c/d\ln V = -1.5$, is in good agreement with results obtained in studies of both single-crystal and sintered polycrystalline samples of Bi-2212. This general agreement across samples contrasts with the very significant differences found in other families of superconductors, notably $YBa_2Cu_3O_{7-\delta}$. A reason for this is that $d\ln T_c/d\ln V$ has been found to be relatively independent of oxygen content in the bismuth cuprates.[3] It is suggested here that the value -1.5 is indicative of the characteristic volume dependence of T_c in a high-temperature superconductor. When compared with the much larger values reported for other high-T_c compounds, which are now taken to be caused by extrinsic factors, the value -1.5 appears to be very small. It is also small compared with the normalized volume dependence of T_c for the simple metallic superconductors.[3] Recently, Klehe *et al.*[58] have estimated a value of -1.25 for $d\ln T_c/d\ln V$, using the bulk modulus $B^T = 123$ GPa determined by Jorgensen *et al.*[48] for optimally doped $YBa_2Cu_3O_{7-\delta}$. This value is close to our result for $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ crystals. In a recent study of hydrostatic pressure dependence of T_c of Hg-Ba-Ca-Cu-O systems, Klehe *et al.*[58] have estimated the values of -1.22 ± 0.05, -1.19 ± 0.06, and -1.20 ± 0.05 for optimally doped ceramic compounds $HgBa_2CuO_{4+\delta}$, $HgBa_2CaCu_2O_{6+\delta}$, and $HgBa_2Ca_2Cu_3O_{6+\delta}$, respectively. They also suggest that the value of around -1.5 for $d\ln T_c/d\ln V$ is a common characteristic of optimally doped layered cuprate superconductors.

The effect of pressure on the normal-state resistance of single crystal $Bi_{2.2}(Sr,Ca)_{2.8}Cu_{2.0}O_{8+y}$ has been found to produce a reduction in *a*-axis resistivity $d\ln\rho_a/dP = -25.5\%$ GPa^{-1}. This is larger than the values reported in other studies of Bi-2212 samples but it is to be noted that there is considerable variation in the reported magnitudes of the effects of pressure on the normal-state properties of the bismuth cuprates. This contrasts with $YBa_2Cu_3O_{7-\delta}$ in which there is strong consistency in measurements of the pressure dependence of the normal-state resistivity, $d\ln\rho/dP \approx -12\%$ GPa^{-1}. However, the curvature in the temperature dependence of the resistivity in our sample indicates it to be oxygen underdoped. The authors are not aware of any studies of the influence of oxygen content on $d\ln\rho/dP$ in the bismuth cuprates. In general, the magnitude of $d\ln\rho/dP$ is much larger in high-T_c superconductors than in simple metals having similar elastic properties (e.g., $d\ln\rho/dP$ for copper is only -1.9% GPa^{-1}).[59] The conventional theory of the electrical resistivity of a metal suggests that the pressure effect on the mobile charge carrier density δ contributes much more than the lattice vibrational scattering to the pressure effects on the normal-state electrical resistance of high-T_c superconductors $Bi_2Sr_2CaCu_2O_{8+y}$ and $YBa_2Cu_3O_{7-\delta}$.

We conclude that a small negative value of $d \ln T_c / d \ln V$ and a value of $d \ln\rho / dP$ that is about an order magnitude larger than found in metals are characteristics of high-temperature superconductors. There is no clear correlation between the influence of pressure on the normal and superconducting state properties. This is particularly evident in the bismuth cuprates where very similar values of $d \ln T_c / d \ln V$ are found for samples having very different $d \ln\rho / dP$. This indicates the superconductivity in these materials to be less dependent on the nature of the normal-state properties than suggested by many theories. The very small value of the lattice volume dependence of T_c, $d \ln T_c / d \ln V$, also seems to be in conflict with those theoretical models that explain high-temperature superconductivity by a form of Josephson coupling between the electrons in the conduction planes.

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