Superconducting order parameter in partially substituted $Bi_2Sr_2CaCu_2O_{8+x}$ single crystals as measured by the tunneling effect

H. Hancotte and R. Deltour
Université Libre de Bruxelles, Service de Physique des Solides, CP233, Boulevard du Triomphe, B-1050 Brussels, Belgium

D. N. Davydov,* A. G. M. Jansen, and P. Wyder
Grenoble High Magnetic Field Laboratory, Max-Planck-Institut für Festkörperforschung and Centre National de la Recherche Scientifique, Boîte Postale 166, F38042 Grenoble Cedex 9, France
(Received 18 June 1996; revised manuscript received 13 November 1996)

Tunneling-spectroscopy measurements have been performed on pure and Ni- and Zn-substituted $Bi_2Sr_2CaCu_2O_{8+x}$ single crystals using a scanning tunneling microscope and a break-junction setup. The superconducting energy gap for the Ni-doped samples was found to be larger with respect to the pure samples. Anomalies have also been found in the temperature dependence of the gap for the Ni-substituted samples. [S0163-1829(97)50110-X]

One of the important questions in high-T_c superconductivity is the relation between the superconducting order parameter Δ and the critical temperature T_c of the superconducting transition. In experiments on various high-T_c superconductors, the ratios $2\Delta/k_BT_c=6-8$ are anomalously large compared to the BCS value 3.5.[1] The study of the variation of Δ with respect to T_c by substitution and/or oxygen doping in these compounds is of interest for further investigations of this phenomenon in view of the understanding of the mechanism of superconductivity.

The energy gap in high-T_c superconductors with lower critical temperatures due to oxygen deficiency was studied by different techniques, such as high-resolution electron-energy-loss spectroscopy (HREELS)[2] and tunneling spectroscopy.[3,4] The energy gap is found to be nearly T_c independent, yielding an increasing $2\Delta/k_BT_c$ ratio with decreasing T_c. This increase of the ratio $2\Delta/k_BT_c$ was attributed to an enhanced strong coupling mechanism due to quasiparticle scattering from spin fluctuations.[5,6]

Many studies of the substitution of Zn, Ni, and Fe for Cu reveal an effective substitution at the Cu sites leading to significant changes in the transport properties and a reduction of T_c.[7] Only a few energy-gap studies are reported on partially substituted high-T_c compounds.[8,9] On tunneling measurements on Co-substituted $Bi_2Sr_2CaCu_2O_{8+x}$ single crystals, Boekholt *et al.* report a stronger decrease of the order parameter compared to the decrease of T_c, yielding a decrease of the $2\Delta/k_BT_c$ ratio.[8] In the far-infrared reflectance experiments of Seider *et al.*, a strong reduction of the energy gap was found for Fe-doped $YBa_2Cu_3O_x$.[9]

In this paper we report on the tunneling spectroscopy study of the superconducting order parameter 2Δ in pure and Zn- and Ni-substituted $Bi_2Sr_2CaCu_2O_{8+x}$ single crystals.[10] The absolute values of 2Δ obtained on the Ni-substituted $Bi_2Sr_2CaCu_2O_{8+x}$ samples are found to be significantly higher than on the pure material. The change from $2\Delta/k_BT_c\sim6-8$ to $2\Delta/k_BT_c\sim10-12$ gives evidence that the order parameter is not uniquely related to T_c upon doping. This increase of the reduced gap value, due to a decrease of T_c together with an increase of the absolute magnitude of the gap, could be an indication for the influence of the magnetic substituants at the Cu sites as could be expected if a magnetic mechanism is responsible for the superconductivity in the high-T_c compounds.

Pure and substituted $Bi_2Sr_2CaCu_2O_{8+x}$ single crystals were prepared by the self-flux method and mechanically separated from the flux in the Al_2O_3 or ZrO_2 crucibles.[11] The dimensions of the samples are typically $3.5\times1\times0.2$ mm^3. The chemical composition of the BSCCO 2:2:1:2 phase corresponds to the formula $Bi_2Sr_{1.9}CaCu_{1.8}O_{8+x}$ in the undoped crystals and to $Bi_2Sr_{1.95}Ca_{0.95}(CuNi)_{2.05}O_{8+x}$ for the substituted crystals as measured by energy dispersive x-ray fluorescence (EDX). The Ni content (1.3−1.8 %) varied from sample to sample, but was homogeneous inside a sample. The T_c of each crystal was determined by dc-magnetization measurements giving the values of 85−88 K and 67−80 K for, respectively, the different pure and Ni-substituted samples. The tunneling spectroscopy data were obtained for a large number of pure and Ni-substituted samples, and the presented results are believed to represent typical features of these materials. We also performed a few experiments on Zn-substituted $Bi_2Sr_2CaCu_2O_{8+x}$.

We performed tunneling measurements using both the scanning tunneling microscopy (STM) technique, and the break-junction technique (B-J). No appreciable differences were observed in the results obtained by means of the two techniques. The STM experiments were performed on the *in situ* cleaved samples with Pt/Ir tips at 4.2 K.[12,13] The tunnel-junction resistances ranged from 10 to 100 MΩ. For the break junctions, the samples were glued by epoxy on a flexible insulating substrate and broken by bending the substrate at $T\leq20$ K. The break-junction resistances varied from 0.2 to 10 kΩ. The current-voltage (I-V) characteristics and $dI/dV(V)$ curves were measured by the four-terminal method using a standard lock-in modulation technique. The electrical contacts ($1-100$ Ω) were obtained by attaching gold wires with silver paint.

Figure 1 shows a typical conductance curve $dI/dV(V)$ of a S-I-S tunnel junction obtained by breaking a pure

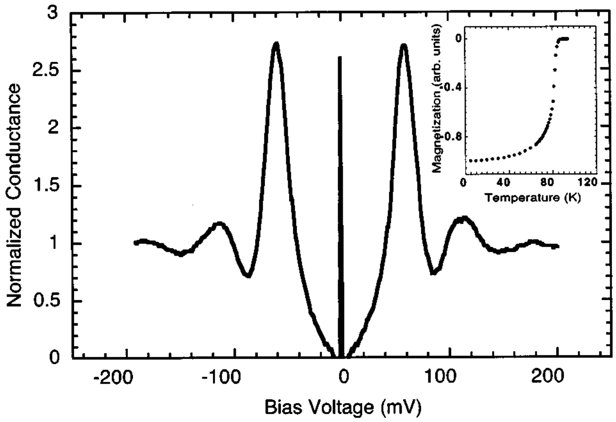

FIG. 1. Normalized conductance dI/dV obtained at 4.2 K by the break-junction technique on a pure $Bi_2Sr_2CaCu_2O_{8+x}$ single crystal. The inset shows the magnetization measurement for the same sample.

(T_c=87 K) $Bi_2Sr_2CaCu_2O_{8+x}$ sample. The curve reveals the characteristic features for a superconducting tunnel junction with a reduced conductance at low voltages and with two well-defined peaks at the gap value. All dI/dV curves reveal the presence of a peak structure around zero-bias voltage due to the Josephson effect, a nearly constant conductance outside the gap, and a dip at energy values higher than the gap (as observed previously in tunneling and photoemission experiments[14–17]). The apparent negative signals close to the zero-bias Josephson-effect peak are an experimental artifact due to the finite response time of the ac-measurement setup which is not adequate for a correct measurement of the Josephson effect around zero-bias voltage. To obtain the normal-state normalized conductance curves, the conductance data have been normalized by a sufficiently broadened conductance in order to smooth the gap-related structures.[17] In the inset of Fig. 1, the result of the dc-magnetization measurement is presented from which the T_c of this sample can be deduced. We defined T_c as the onset value for the decrease of magnetization as this parameter is independent of the applied field and of the sample shape. The energy gap $2\Delta_{p-p}$ was taken from the peak-to-peak separation V_{p-p} in the experimental conductance curves, i.e., $V_{p-p}/2$ for B-J and V_{p-p} for STM experiments.

Figure 2(a) shows a comparison between conductances measured by STM on pure ($2\Delta_{p-p}$ = 46 meV) and Ni-substituted ($2\Delta_{p-p}$ = 90 meV) $Bi_2Sr_2CaCu_2O_{8+x}$ crystals while Fig. 2(b) shows similar results for the break-junction technique on pure ($2\Delta_{p-p}$ = 60 meV) and Ni-substituted ($2\Delta_{p-p}$ = 86 meV) $Bi_2Sr_2CaCu_2O_{8+x}$ crystals. These characteristics are representative for the average values of the gap parameters obtained in the two systems. In view of the difference in V_{p-p} values between the pure and Ni-substituted sample in Fig. 2(a), we may suspect that some part of the superconducting sample could be attached to the tip leading to a S-I-S junction rather than a S-I-N junction which would explain the difference by more or less a factor of two. This argumentation motivated us to investigate break junctions where the tunneling junction is always of the S-I-S type. Also the break-junction experiments in Fig. 2(b) show the larger energy gap in the Ni-substituted sample.

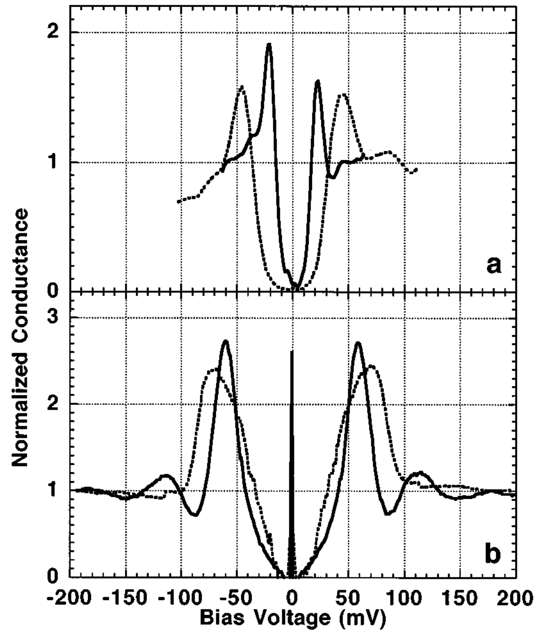

FIG. 2. Comparison between conductance curves obtained on pure (full line) and Ni-substituted (dotted line) $Bi_2Sr_2CaCu_2O_{8+x}$ single crystals by the STM (a) and break-junction (b) techniques at 4.2 K.

Figure 3 shows the distribution of the energy gap 2Δ obtained in a number of independent break-junction and STM experiments for the pure [Fig. 3(a)] and partially Ni-substituted [Fig. 3(b)] samples. These histograms clearly give evidence for a higher 2Δ value observed in the Ni-substituted samples, although the spreading in the 2Δ values is much larger for the substituted samples. The observation

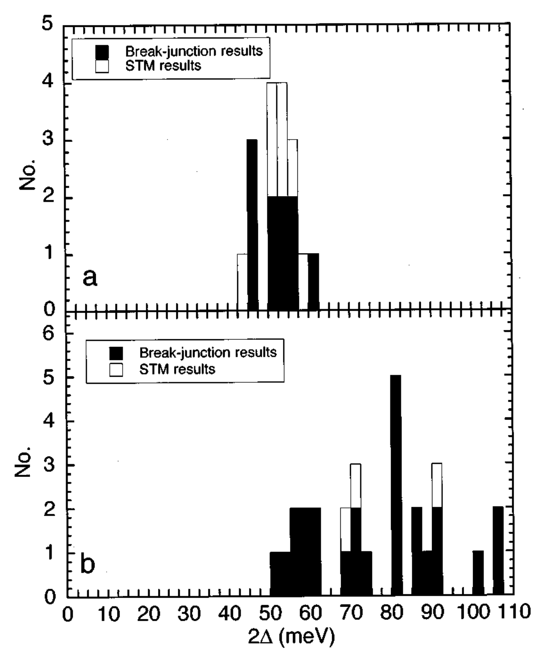

FIG. 3. Histograms of the measured gap-value distribution by the STM (open columns) and break-junction (filled columns) techniques on pure (a) and partially Ni-substituted (b) $Bi_2Sr_2CaCu_2O_{8+x}$ crystals.

TABLE I. Average values for T_c, 2Δ, and $2\Delta/k_BT_c$ for pure and Ni-substituted samples.

Sample	T_c (K)	2Δ (meV)	$2\Delta/k_BT_c$
BiSrCaCuO (2212) pure	85	52 ± 5	7.0 ± 1
BiSrCaCuO (2212) 2% Ni	75	77 ± 20	11.9 ± 3

of this effect by two independent techniques (STM and B-J) makes an explanation in terms of experimental artifacts less probable. The average values of 2Δ determined from a number of independent experiments are given in Table I.

In view of the large spreading in the energy-gap data for Ni-substituted crystals, one should note that tunneling spectroscopy is a local technique probing the density of states on a scale of the coherence length (only a few angstroms for the high-T_c superconductors) while the T_c is a parameter measured for the whole sample. Although the substituant element distribution and the tunnel-junction geometry are not exactly known, one cannot exclude the situation where the average distance between Ni impurities is larger or comparable to the coherence length (for a homogeneous distribution of 2% of Ni atoms, the distance between two Ni ions in the CuO_2 plane is 35 Å). Therefore, for different junctions, the tunneling current can result from regions at different distances from the Ni atoms which could explain the relative scattering of the data for the substituted samples. However, in many tunnel junctions with the Ni-substituted samples we have found larger gap values than for the pure samples.

Another perturbing factor is the possibility of a voltage drop across normal parts close to the superconducting tunneling contact, leading to an enlarged voltage compared to the voltage over the tunneling part of the contact. A nonhomogeneous impurity distribution could lead to the presence of normal phases with high resistivity (the resistivity in Ni-doped $Bi_2Sr_2CaCu_2O_{8+x}$ in the normal state is much higher compared to pure samples). However, the high 2Δ values for Ni-doped samples were found in a wide range of tunnel-junction resistances ranging from a few 100 Ω to 100 MΩ in the break junction and the STM measurements. The latter makes an additional voltage drop close to the tunneling contact rather improbable as an explanation for the observed difference of 2Δ between pure and doped samples.

Some measurements have also been performed on Zn-substituted $Bi_2Sr_2CaCu_2O_{8+x}$ crystals. Figure 4 gives an example of $dI/dV(V)$ for a Zn-substituted ($2\Delta_{p-p}$ = 50 meV) sample with $T_c=79$ K in comparison with a pure sample. The concentration of Zn in this sample is around 1%. A slight decrease of the energy gap is observed in this particular case but its value is still within the range of gap values usually measured on pure crystals [see Fig. 3(a)] and no increase of this value was observed on the relatively small number of measured Zn-substituted samples. Unlike the case for Ni substitution, the zero-bias conductance increases for the Zn-substituted samples. This increase, corresponding to a residual normalized density of states of around 0.4, is in good agreement with the results of Ishida *et al.* and Hodges *et al.* obtained from, respectively, NMR-NQR and Mössbauer experiments.[18,19]

The temperature dependences of 2Δ obtained by means of the break-junction experiments reveal an anomalous behavior in the Ni-substituted samples. Figures 5(a) and 5(b) show examples of the temperature dependences of the normalized gap $\Delta(T)/\Delta(T_{\rm min})$ as a function of T/T_c for, respectively, pure and Ni-substituted samples, presented in each case for two break junctions on two different crystals. $\Delta T_{\rm min}$ is the measured gap at the lowest temperature reached. The increased value for 2Δ in the temperature range T/T_c from 0.3 to 0.5 was nearly always observed in the Ni-substituted $Bi_2Sr_2CaCu_2O_{8+x}$.

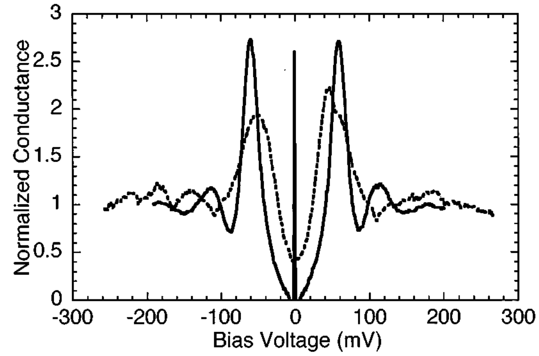

FIG. 4. Comparison between conductance curves obtained on pure (full line) and Zn-substituted (dotted line) $Bi_2Sr_2CaCu_2O_{8+x}$ single crystals by the break-junction technique at 4.2 K.

Already in an early stage of the high-T_c investigations it was found that magnetic substituants like Ni and Fe in the YBaCuO compound yield a smaller T_c suppression compared to Zn.[20] More recently, it has been shown theoretically that the interaction between quasiparticles induced by the exchange of antiferromagnetic paramagnons leads to the transition to a superconducting state and in this framework, Monthoux *et al.* have shown that Zn, by disturbing the local magnetic order, exerts a much larger influence on T_c than Ni.[21] Within this model the difference in the influence on T_c between magnetic and nonmagnetic substituants is explained.[5,6,22]

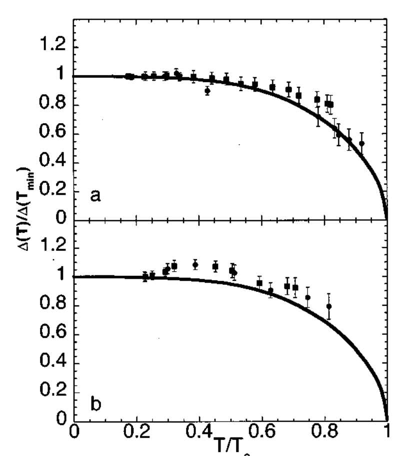

FIG. 5. Temperature dependence of the reduced gap $\Delta(T)/\Delta(T_{\rm min})$ as determined by break-junction measurements on two pure (a) and two Ni-substituted (b) $Bi_2Sr_2CaCu_2O_{8+x}$ single crystals. The different symbols correspond to the tunneling data of different break junctions. The full curve represents the BCS dependence $\Delta(T)$.

Ishida *et al.*[18] have shown, in their NMR-NQR experiments, that the substitution of Cu by Zn or Ni, in $YBa_2Cu_3O_7$, leads to other differences besides the one in T_c. Zn drastically influences T_c, induces a finite density of states (DOS) at the Fermi level and leads to a local collapse of the antiferromagnetic correlation. On the other hand, Ni only slightly reduces T_c, induces no finite DOS and behaves as a local moment. A prominent feature is that nonmagnetic Zn doping causes a marked modification of the electronic states in the CuO_2 plane in the normal state, whereas the magnetic Ni doping does not. A slight enhancement of the spin susceptibility upon doping by Ni is even observed.

Zn and Ni seem therefore to influence differently the electronic properties of high-T_c superconductors, as confirmed by our results. Moreover, from our results, one can deduce that the doping with Ni enhances the coupling strength of the superconducting pairing as the order parameter is increased with the substitution of Cu by Ni.

In conclusion, we performed tunneling spectroscopy studies on pure, Zn- and Ni-substituted single crystals of the $Bi_2Sr_2CaCu_2O_{8+x}$ superconductors. We have observed an increase of the gap and a decrease of T_c for the Ni-substituted samples yielding an increase of the reduced gap ratio $2\Delta/k_BT_c$. The temperature dependence of the gap also shows an anomaly for the Ni-substituted samples, not observed in the pure samples. As these two features are not observed on Zn-substituted samples, we interpret these phenomena as related to the magnetic character of Ni.

This work was partially supported by the Belgian SSTS program SUPRANAT SU02/009. H.H. acknowledges support of his work by F.R.I.A.

---

*Present address: Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, M5S 1A1, Canada.

[1] For a review, see T. Hasegawa, H. Ikuta, and K. Kitasawa, in *Physical Properties of High Temperature Superconductors III*, edited by D. M. Ginzberg (World Scientific, Singapore, 1992).
[2] Y. Li, J. Liu, and C. M. Lieber, Phys. Rev. Lett. **70**, 3494 (1993).
[3] J. Liu, Y. Li, and C. Lieber, Phys. Rev. B **49**, 6234 (1994).
[4] L. Buschmann, M. Boekholt, and G. Güntherodt, Physica C **203**, 68 (1992).
[5] P. Monthoux and D. Pines, Phys. Rev. Lett. **69**, 961 (1992).
[6] P. Monthoux, A. V. Balatsky, and D. Pines, Phys. Rev. Lett. **67**, 3448 (1991).
[7] See, for example, B. vom Hedt, W. Lisseck, K. Westerholt, and H. Bach, Phys. Rev. B **49**, 9898 (1994).
[8] M. Boekholt, Th. Bollmeier, L. Buschmann, M. Fleuster, and G. Güntherodt, Physica C **198**, 33 (1992).
[9] E. Seider, M. Bauer, L. Genzel, P. Wyder, A. G. M. Jansen, and C. Richter, Solid State Commun. **72**, 85 (1989).
[10] In this article the two terms ''energy gap'' and ''order parameter'' will be used without distinction and directly related to the peak-to-peak distance in the conductance curves.
[11] D. N. Davydov, A. Quivy, P. Diko, R. Deltour, M. Mehbod, and M. Ye, Solid State Commun. **86**, 267 (1993).
[12] D. N. Davydov, N. Horii, V. A. Timofeev, A. S. Grokholski, and R. Deltour, Rev. Sci. Instrum. **64**, 3153 (1993).
[13] H. Hancotte, D. N. Davydov, M. Ye, and R. Deltour, Physica B **204**, 206 (1995).
[14] H. Ding, A. F. Bellman, J. C. Campuzano, M. Randeria, M. R. Norman, T. Yokoya, T. Takahashi, H. Katayama-Yoshida, T. Mochiku, K. Kadowaki, G. Jennings, and G. P. Brivio, Phys. Rev. Lett. **76**, 1533 (1996).
[15] Ch. Renner and Ø. Fischer, Phys. Rev. B **51**, 9208 (1995).
[16] D. Mandrus, J. Hartge, C. Kenziora, L. Mihaly, and L. Forro, Europhys. Lett. **22**, 199 (1993).
[17] S. I. Vedeneev, A. G. M. Jansen, P. Samuely, V. A. Stepanov, A. A. Tsvetkov, and P. Wyder, Phys. Rev. B **49**, 9823 (1994).
[18] K. Ishida, Y. Kitaoka, N. Ogata, T. Kamino, K. Asayama, J. R. Cooper, and N. Athanassopoulou, J. Phys. Soc. Jpn. **62**, 2803 (1993).
[19] J. A. Hodges, P. Bonville, P. Imbert, and A. Pinatel-Phillipot, Physica C **146**, 323 (1995).
[20] J. Clayhold, N. P. Ong, P. H. Har, and C. W. Chu, Phys. Rev. B **38**, 7016 (1988).
[21] P. Monthoux and D. Pines, Phys. Rev. B **49**, 4261 (1994).
[22] D. J. Scalapino, Phys. Rep. **250**, 329 (1995) and references therein.