Thermal conductivity of $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$: Relation between x and δ

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The effect of oxygen stoichiometry content δ and zinc doping x on the thermal conductivity κ of $YBa_2Cu_3O_{7-\delta}$ compounds is investigated. Various experimental results for $0 \leq x \leq 0.017$ and $0 \leq \delta \leq 0.5$ are analyzed by using a theoretical model for the electronic contribution to the thermal conductivity in the case of a two-dimensional d-wave superconductor with Van Hove singularities (VHS) in the density of states. It is shown that the data can be quite well reproduced by considering the effect of the position of these VHS from the Fermi level on the thermal conductivity peak observed below T_c. From this analysis, a simple relation between x and δ can be extracted. We argue that this relation is correlated to the variation of the Cu(2) valence with oxygen content and Zn concentration, and that the Cu(2) valence controls the critical temperature of such cuprates, further strengthening the Van Hove scenario of high-T_c superconductivity. [S0163-1829(97)00534-1]

I. INTRODUCTION

The thermal conductivity κ of high-T_c superconductors presents a characteristic peak below the superconducting transition. It is now widely accepted that this peak is mostly due to the contribution of electrons located in the CuO_2 planes.[1–6] Besides, it has been recently shown that the thermal conductivity of high-T_c superconductors is consistent with an anisotropic superconducting energy gap parameter of the $d_{x^2-y^2}$-wave type.[5–8]

On the other hand, there is experimental[9,10] and theoretical[11,12] evidence that the Fermi surface of high-T_c superconductors presents saddle points close to the Fermi level ε_F. These saddle points lead to logarithmic singularities in the electronic density of states, the so-called Van Hove singularities (VHS). The occurrence of these VHS has led to the so-called Van Hove scenario of high-T_c superconductivity.[11–14]

In this work, we consider the effect of the position of these VHS with respect to the Fermi level on the thermal conductivity of a two-dimensional $d_{x^2-y^2}$-wave superconductor. A chemical way to modify the Fermi energy of a metallic compound is to dope it by impurities. Within the Van Hove scenario of high-T_c superconductivity, it is believed that the Fermi level of optimally doped materials (i.e., materials with the highest critical temperature) coincides with the energy of the VHS. When the material is under- or overdoped, its Fermi level is shifted from the VHS, leading to a reduction of the critical temperature (and the superconducting energy gap).[12–15]

In this respect, various experimental results on the thermal conductivity κ of $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ compounds[6,16–18] for $0 \leq x \leq 0.017$ and $0 \leq \delta \leq 0.5$ are analyzed. It is shown that these data can be quite well explained by our theoretical model. Moreover, a simple relation between x and δ can be extracted from this analysis. We also show that this latter relation is correlated to the density of charge carriers and the average in-plane Cu(2) valence as a function of oxygen content and Zn concentration.

The theoretical model is briefly described in Sec. II. In Sec. III, the theoretical results are discussed and compared with various experimental results in $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ compounds. Conclusions are finally drawn in Sec. IV.

II. MODEL

The electronic contribution κ_e to the thermal conductivity can be calculated using the theoretical model described in Refs. 5 and 19. We use a variational expression for the electronic contribution to the thermal conductivity

$$\kappa_e^{\mu\mu} = \frac{1}{T}\left[\sum_{ij} U_i^{\mu\mu} Q_{ij}^{\mu\mu} U_j^{\mu\mu} - \frac{(\Sigma_{ij} J_i^{\mu\mu} Q_{ij}^{\mu\mu} U_j^{\mu\mu})^2}{\Sigma_{ij} J_i^{\mu\mu} Q_{ij}^{\mu\mu} J_j^{\mu\mu}}\right], \quad (1)$$

where $\mu = (x,y)$. In Eq. (1), $J_i^{\mu\mu}$ and $U_i^{\mu\mu}$ are the trial currents and $Q_{ij}^{\mu\mu} = (P^{-1})_{ij}^{\mu\mu}$ with $P_{ij}^{\mu\mu}$ the elements of the scattering matrix. Their expressions are explicitly given in Refs. 5 and 19.

We consider a strictly two-dimensional electronic spectrum given by[20,21]

$$\varepsilon(\mathbf{k}) - \varepsilon_F(1-\beta) = \frac{\hbar^2}{2m_{ab}^*} k_x k_y, \quad (2)$$

where m_{ab}^* is the effective mass in the ab (CuO_2) plane. The spectrum described by Eq. (1) gives logarithmic singularities in the density of states at $\varepsilon_{VHS} = \varepsilon_F(1-\beta)$. The parameter β allows one to control the position of the VHS with respect to the Fermi level. We stress that the spectrum given by Eq. (1) has been shown to be in qualitative agreement with angle-resolved photoemission spectra experiments in high-T_c superconductors[20] and seems satisfactory for describing the main electronic properties when the ab-plane contributions are dominant, see for example Ref. 21.

On the other hand, various experimental and theoretical investigations[22,23] have revealed that the symmetry of the superconducting energy gap parameter $\delta(\mathbf{k},T)$ of high-T_c superconductors is anisotropic and most probably of the d-wave type. We thus consider such a symmetry for $\Delta(\mathbf{k},T)$, which can be well approximated by[24]

$$\Delta_{d_{x^2-y^2}}(\mathbf{k},T) = \Delta_{\max}(0)[\hat{k}_x^2 - \hat{k}_y^2]\tanh(\alpha\sqrt{(T_c-T)/T}), \tag{3}$$

where $\Delta_{\max}(0)$ is the maximum of the zero-temperature energy gap, $\hat{k}_\mu$ is a normalized wave vector along the $\mu = (x,y)$ direction, and $\alpha = 2.2$.

Scattering of electrons by point defects and acoustic phonons are both considered to be the most important heat carrier dissipation mechanisms here. The scattering probabilities, calculated in the Born approximation, are explicitly given in Ref. 5. In the next section, we discuss our theoretical results and compare them with experimental data on the thermal conductivity of $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ materials[6,16-18] for $0 \le x \le 0.017$ and $0 \le \delta \le 0.5$.

III. RESULTS

The temperature dependence of the normalized electronic contribution $\kappa_e/\kappa_e(T_c)$ to the thermal conductivity obtained by using the above formulas is shown in Fig. 1(a) for different values of then normalized shift between the VHS and the Fermi level, i.e., $\beta = (\varepsilon_F - \varepsilon_{VHS})/\varepsilon_F$. For illustration purposes, we have fixed the values of the point defect fraction $N = 0.05$ and the electron-phonon transport coupling constant $\lambda = 0.3$.[5] One can see (Fig. 1) that κ_e presents a peak near $0.6T_c$ for $\beta = 0$, a peak which results from the interplay between inelastic scattering of electrons by acoustic phonons and elastic scattering by point defects. Besides, the height of the peak is lowered and shifted towards higher temperatures when the Fermi level is shifted from the energy of the VHS, i.e., when β is increased. We interpret this behavior as being mainly due to a decrease of the quasiparticle density of states at the Fermi level as β increases, resulting in a weaker enhancement of the electronic contribution to the thermal conductivity in the superconducting state.

In Fig. 1(b), we show the normalized value $\kappa_e(T_{\max})/\kappa_e(T_c)$ of the maximum electron contribution to the thermal conductivity vs the β parameter. The height of the maximum decreases symmetrically with respect to β. This is strictly due to the fact that we have assumed a symmetrical decrease of T_c and $\Delta_{\max}(0)$ with β (Refs. 15 and 25) in our model calculations.

The thermal conductivity maximum of various $YBa_2Cu_3O_{7-\delta}$ samples is shown as a function of oxygen stoichiometry δ (Refs. 16-18) and Zn content x,[6] respectively, in Figs. 2(a) and 2(b). For $\delta \approx 0.1$ and $x = 0$, the maximum in κ_e reaches the highest value. These latter values for δ and x thus correspond to optimally doped samples. As the oxygen or zinc content are shifted from these values, the maximum value of κ_e decreases, in agreement with our theoretical predictions if we assume that $\beta = 0$ at optimal doping.

The solid lines in Figs. 2(a) and 2(b) are fits from our model calculations obtained by considering that $(\delta - \delta_{opt})$
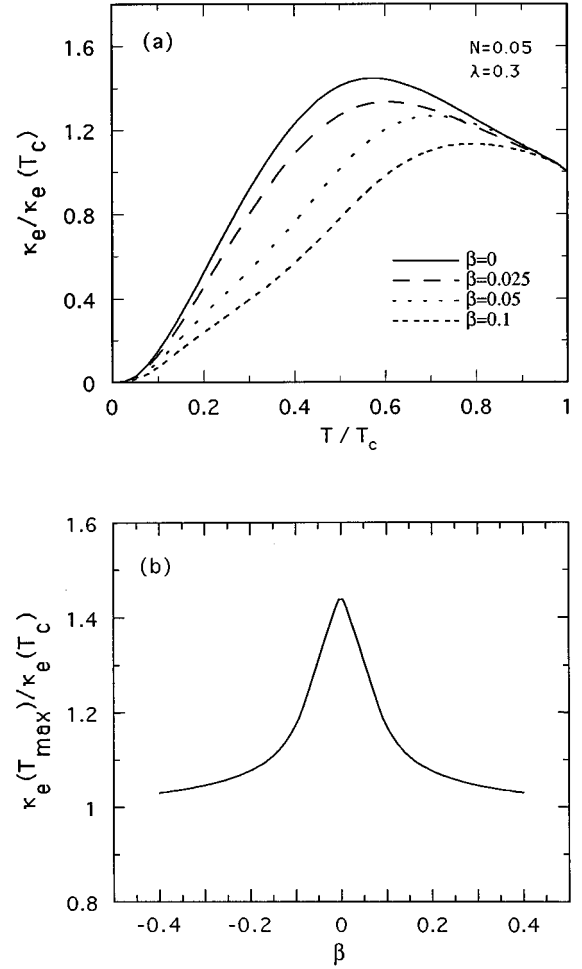

FIG. 1. (a) Normalized electronic contribution to the thermal conductivity $\kappa_e/\kappa_e(T_c)$ vs reduced temperature T/T_c as a function of the relative position β of the Fermi level with respect to the Van Hove singularities. (b) Normalized maximum value $\kappa_e(T_{\max})/\kappa_e(T_c)$ of the electronic thermal conductivity vs β.

$= |\beta|$ and $x = \gamma\beta^2$, with $\delta_{opt} = 0.11$ and $\gamma = 0.52$, respectively. The experimental results are well recovered through our theoretical curves, for reasonable values of the free parameters, i.e., $\lambda = 0.32$ and $N = 0.05$. From these fits, we obtain the empirical relation between x and δ

$$(\delta - \delta_{opt}) = \sqrt{x/\gamma}, \tag{4}$$

where δ_{opt} and γ have been given above.

We show below that this latter relation can be correlated to the variation of the Cu(2) valence of $YBa_2Cu_3O_{7-\delta}$ with oxygen stoichiometry and zinc content. The valence of Cu(2) can be calculated using the equation[26]

$$V_{Cu(2)} = \sum_i \exp[(R_0 - R_i)/B], \tag{5}$$

where the R_i parameters are the Cu-O bond lengths in the crystal, R_0 and B are constant values tabulated for many bond types.[27] In the case of the Cu-O bond, $R_0 = 1.679$ Å and $B = 0.37$ Å. We stress that Eq. (5) indicates that the oxidation state of copper comes from the length of the Cu-O bonds, since higher oxidation states result in shorter bonds.
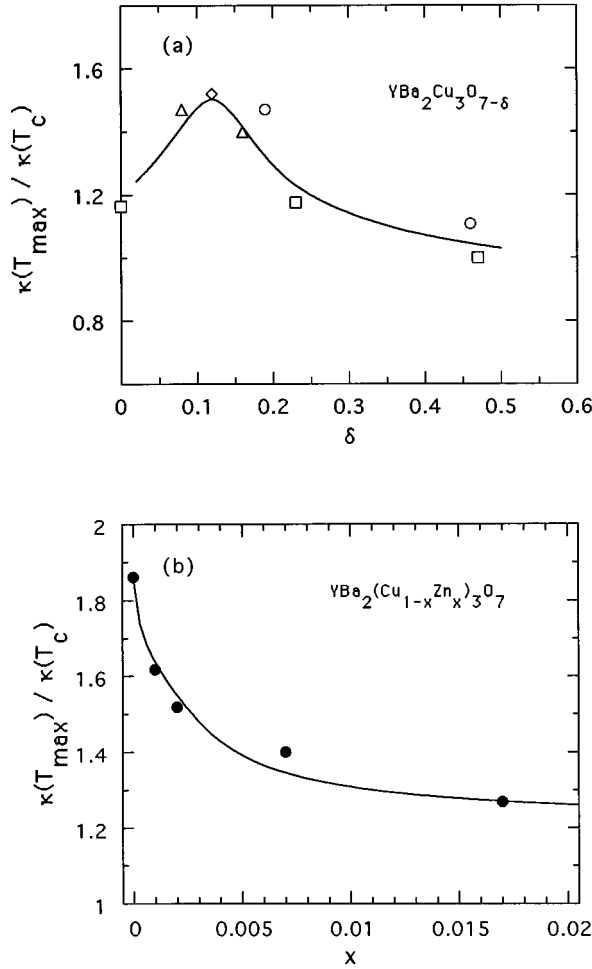
FIG. 2. Normalized maximum value of the thermal conductivity of (a) various $YBa_2Cu_3O_{7-\delta}$ samples (Refs. 16–18) as a function of oxygen stoichiometry δ and (b) of $YBa_2(Cu_{1-x}Zn_x)_3O_7$ compounds (Ref. 6) vs Zn doping x. The solid lines are fits obtained within our theoretical model (see text).

Bond valence sums on copper in the planes have been calculated from Eq. (5) for undoped $YBa_2Cu_3O_{7-\delta}$ compounds as a function of the oxygen concentration δ.[28,29] These calculations lead to a ''two-plateau'' curve quite similar to the famous relationship between T_c and δ (Ref. 30) as shown in Figs. 3(a) and 3(b). From these results, Cava et al.[28] have concluded that the decrease of T_c in underdoped samples is due to a transfer of negative charges to the CuO_2 planes.

The same calculations can be made for the zinc-doped $YBa_2Cu_3O_{7-\delta}$ compounds. The Cu-O bond lengths in the crystals can be deduced from the crystallographic data reported for the a, b, and c lattice parameters if we consider that the oxygen concentration is not altered by zinc doping. In fact, we can expect that the oxygen concentration of the different zinc-doped compounds does not change very much with x due to the constancy of the reported crystallographic c-axis values, cf. Ref. 31 and Table I. The valence of Cu(2) has been calculated using the crystallographic data reported by Xiao et al.[31] (see Table I) on $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ compounds.

The Cu(2) valence as a function of Zn concentration as obtained from Eq. (5) is given in Table I and is also shown in

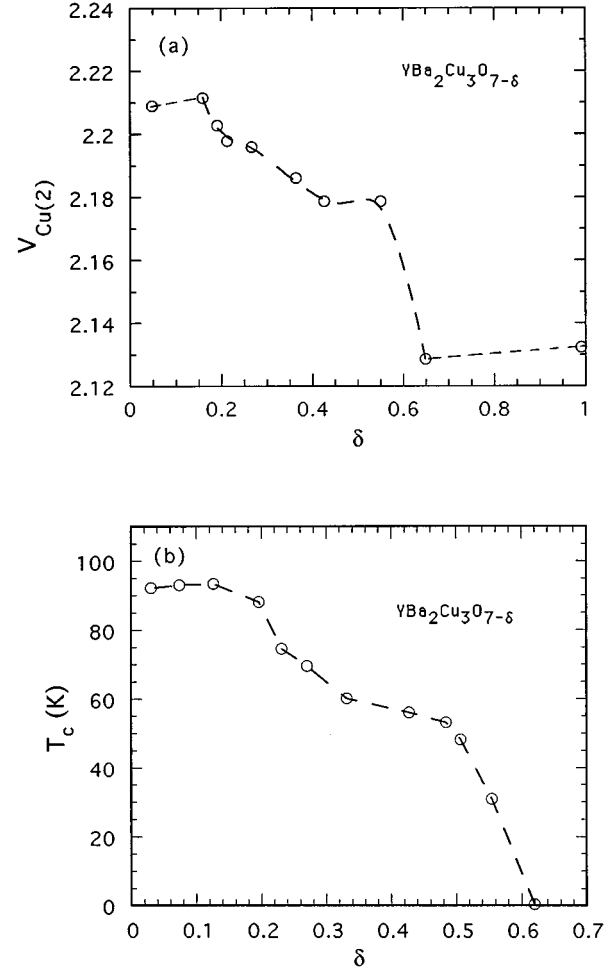FIG. 3. (a) In-plane copper valence $V_{Cu(2)}$ of $YBa_2Cu_3O_{7-\delta}$ vs oxygen content δ from Ref. 28. (b) Behavior of the critical temperature T_c of $YBa_2Cu_3O_{7-\delta}$ as a function of δ from Ref. 29.

Fig. 4(a). One observes that $V_{Cu(2)}$ decreases linearly with Zn content. This behavior is again quite similar to the observed (linear) decrease of T_c with Zn content in $YBa_2(Cu_{1-x}Zn_x)_3O_7$ materials[32] as shown in Fig. 4(b). This leads us to conclude that the suppression of the critical temperature with Zn content is also related to a negative charge transfer to the CuO_2 planes. This charge transfer modifies the Fermi level which does not coincide anymore with the energy of the VHS, leading to a suppression of the critical

TABLE I. Crystallographic parameters (a,b,c) of $YBa_2(Cu_{1-x}Zn_x)_3O_7$ materials from Ref. 31. $V_{Cu(2)}$ are the values of the in-plane copper Cu(2) valence as calculated from Eq. (5).

Zn content	a (Å)	b (Å)	c (Å)	$V_{Cu(2)}$
0	3.8204	3.8946	3.8750	2.229
0.950	3.8256	3.8900	3.8750	2.228
1.965	3.8270	3.8900	3.8750	2.226
2.979	3.8279	3.8899	3.8749	2.224
5.001	3.8311	3.8899	3.8750	2.220
5.952	3.8216	3.8899	3.8749	2.219
6.459	3.8311	3.8922	3.8749	2.217

FIG. 5. Relation between Zn content x and oxygen stoichiometry δ of $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ obtained from the $T_c(\delta)$ and $T_c(x)$ curves as shown in Figs. 3(b) and 4(b), respectively.
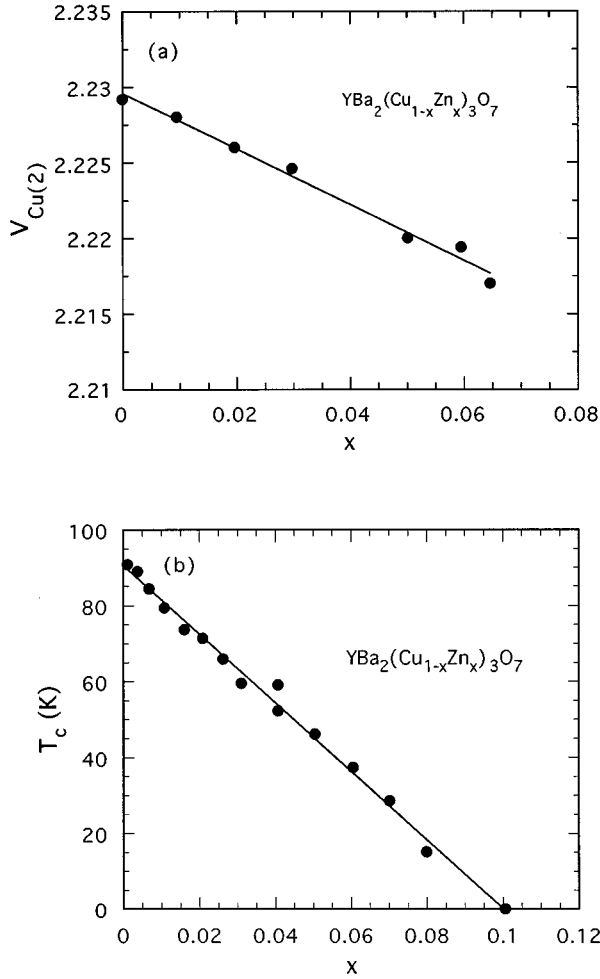
FIG. 4. (a) In-plane copper valence $V_{Cu(2)}$ of $YBa_2(Cu_{1-x}Zn_x)_3O_7$ vs Zn content x calculated from Eq. (5). (b) Behavior of the critical temperature T_c of $YBa_2(Cu_{1-x}Zn_x)_3O_7$ as a function of x from Ref. 32.

lyzed by using an electronic model which considers the effect of the position of the Fermi level with respect to the energy of Van Hove singularities in the density of states. The behavior of the thermal conductivity peak of $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ samples with $0 \leq x \leq 0.017$ and $0 \leq \delta \leq 0.5$ could be quite well reproduced by the model with realistic values of the physical parameters. Besides, a simple relation between x and δ could be obtained from these fits.

We have next shown that the effect of Zn content x on the in-plane copper valence $V_{Cu(2)}$ is quite similar to the behavior of the critical temperature of $YBa_2(Cu_{1-x}Zn_x)_3O_7$ vs Zn doping, like in the case of oxygen-depleted $YBa_2Cu_3O_{7-\delta}$ compounds.[28] This has allowed us to conclude that the Cu(2) valence (whence the charge density in the planes) is closely related to the critical temperature of the cuprates, which concurs with the Van Hove scenario of high-T_c superconductivity. From the $T_c(\delta)$ and $T_c(x)$ curves, we obtained a relation between x and δ in very good agreement with the $\delta(x)$ expression obtained from our fits to the thermal conductivity peak in various $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ samples.

Finally, it is worth pointing out that we have neglected the phonon contribution to the thermal conductivity in our model. Hirschfeld and Putikka[6] have recently shown that the thermal conductivity peak observed below T_c in $YBa_2Cu_3O_{7-\delta}$ is essentially due to the electronic contribution, the phonon contribution presenting a small peak near 20 K. Since we are mainly concerned here by the thermal conductivity peak near $T_c/2$, we believe that our conclusions should not be altered (at least qualitatively) by accounting for a phonon contribution.

temperature for finite x values. Besides, from the $T_c(\delta)$ and $T_c(x)$ curves shown in Figs. 3(b) and 4(b), respectively, an empirical relation between x and δ can be again deduced (Fig. 5). One can see from this latter figure that the $\delta(x)$ relation obtained from the T_c curves is in good agreement with Eq. (4) deduced from our fits to the thermal conductivity peak in the superconducting state. These observations give strong support for the above analysis of the thermal conductivity peak of $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ within the Van Hove scenario of high-T_c superconductivity.

IV. CONCLUSIONS

In this work, we have investigated the effect of oxygen doping and Zn content on the thermal conductivity of $YBa_2Cu_3O_{7-\delta}$. Several experimental results have been ana-
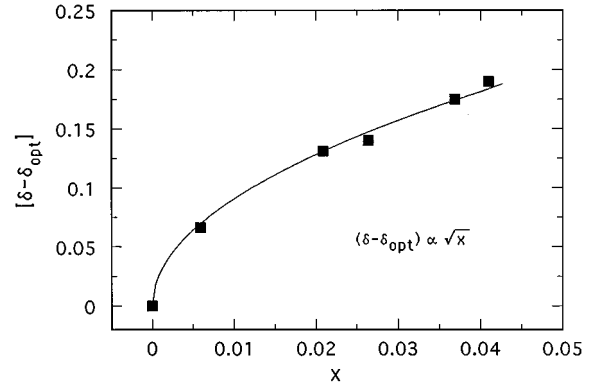
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[1] R. C. Yu, M. B. Salamon, J. P. Lu, and W. C. Lee, Phys. Rev. Lett. **69**, 1431 (1992).

[2] P. B. Allen, X. Du, L. Mihaly, and L. Forro, Phys. Rev. B **49**, 9073 (1994).

[3] M. Houssa and M. Ausloos, Phys. Rev. B **51**, 9372 (1995).

[4] M. Houssa, M. Ausloos, and S. Sergeenkov, J. Phys.: Condens. Matter **8**, 2043 (1996).

[5] M. Houssa and M. Ausloos, Physica C **265**, 258 (1996).

[6] P. J. Hirschfeld and W. O. Putikka, Phys. Rev. Lett. **77**, 3909 (1996).

[7] M. Houssa and M. Ausloos, Europhys. Lett. **33**, 695 (1996).

[8] M. Houssa and M. Ausloos, J. Phys.: Condens. Matter **9**, 201 (1997).

[9] K. Gofron, J. C. Campuzano, A. A. Abrikosov, M. Lindroos, A. Bansil, H. Ding, D. Koelling, and B. Dabrowski, Phys. Rev. Lett. **73**, 3302 (1994).

[10] J. Ma, C. Quitmann, R. J. Kelley, P. Alméras, H. Berger, G. Margaritondo, and M. Onellion, Phys. Rev. B **51**, 3832 (1995).

[11] E. Dagotto, A. Nazarenko, and A. Moreo, Phys. Rev. Lett. **74**, 310 (1995).

[12] D. M. Newns, C. C. Tsuei, and P. C. Pattnaik, Phys. Rev. B **52**, 13 611 (1996).

[13] J. Labbe and J. Bok, Europhys. Lett. **3**, 1225 (1987).

[14] L. Force and J. Bok, Solid State Commun. **85**, 975 (1993).

[15] C. C. Tsuei, D. M. Newns, C. C. Chi, and P. C. Pattnaik, Phys. Rev. Lett. **65**, 2724 (1990).

[16] N. V. Zavaritskii, A. V. Samoilov, and A. A. Yurgens, JETP Lett. **48**, 242 (1988).

[17] A. Jezowski, J. Klamut, R. Horyn, and K. Rogacki, Supercond. Sci. Technol. **1**, 296 (1989).

[18] J. L. Cohn, S. A. Wolf, T. A. Vanderah, V. Selvamanickam, and K. Salama, Physica C **192**, 435 (1992).

[19] M. Houssa and M. Ausloos, Physica C **257**, 321 (1996).

[20] D. M. Newns, C. C. Tsuei, P. C. Pattnaik, and C. L. Kane, Comments Condens. Matter Phys. **15**, 273 (1992).

[21] D. M. Newns, C. C. Tsuei, R. P. Huebener, P. J. M. van Bentum, P. C. Pattnaik, and C. C. Chi, Phys. Rev. Lett. **73**, 1695 (1994).

[22] D. J. Scalapino, Phys. Rep. **250**, 329 (1995).

[23] D. J. Van Harlingen, Rev. Mod. Phys. **67**, 515 (1995).

[24] J. H. Xu, J. L. Shen, J. H. Miller, and C. S. Ting, Phys. Rev. Lett. **73**, 2492 (1994).

[25] A. Gama Goicochea, Phys. Rev. B **49**, 6864 (1994).

[26] I. D. Brown, J. Solid State Chem. **82**, 122 (1989).

[27] I. D. Brown and D. Altermatt, Acta Crystallogr. Sec. B **41**, 244 (1985).

[28] R. J. Cava, A. W. Hewat, E. A. Hewat, B. Batlogg, M. Marezio, K. M. Rabe, J. J. Krajewski, W. F. Peck, and L. W. Rupp, Physica C **165**, 419 (1990).

[29] J. L. Tallon, Physica C **168**, 85 (1990).

[30] J. L. Tallon, C. Bernhard, H. Shaked, R. L. Hitterman, and J. D. Jorgensen, Phys. Rev. B **51**, 12 911 (1995).

[31] G. Xiao, M. Z. Cieplak, A. Gavrin, F. H. Streitz, A. Bakhshai, and C. L. Chien, Phys. Rev. Lett. **60**, 1446 (1988).

[32] S. Zagoulaev, P. Monod, and J. Jégoudez, Phys. Rev. B **52**, 10 474 (1995).