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Substitution of transition metals for Cu in $Bi_2(SrCa)_{n+2}Cu_{n+1}O_y$ whisker crystals: Fe and Pd

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We have measured the resistive superconducting transition temperature of single-crystal whiskers of $Bi_2(SrCa)_{n+2}(Cu_{1-x}M_x)_{n+1}O_y$ in which M represents the transition metals Fe and Pd that have been partially substituted for Cu. Combining these measurements with our earlier results for Co, Ni, and Zn substitutes, we derive a general relationship for the rate at which T_C is depressed by substitution of transition metals: $dT_C/dx \approx -780$ K for all these elements and both the 2212 ($n=1$) and 2223 ($n=2$) phases. Further, the normalized residual resistance is also a universal function of x. This is contrary to what others find for $YBa_2Cu_3O_{7-\delta}$ (YBCO), in which Zn and Ni substitutions act quite differently on dT_C/dx. The explanation of this effect in YBCO apparently does not involve the general behavior of the Cu-O planes. The magnitude of dT_C/dx is about half that predicted by the Abrikosov-Gorkov relation, as seen in other Cu-O superconductors.

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I. INTRODUCTION AND BACKGROUND

We report the final portion of a study of the physical, chemical, and structural effects brought about by partially substituting a transition or posttransition metal for Cu on the Cu-O planes in the high-T_C compound $Bi_2(SrCa)_{n+2}(Cu_{1-x}M_x)_{n+1}O_y$ (BSCCO). Since these planes are believed to carry the condensed electrons, numerous experimental and theoretical studies have been aimed at this problem. In addition to our own work, described previously[1–4] and concluded here, investigations have ranged over substitutions in BSCCO and $YBa_2Cu_3O_{7-\delta}$ (YBCO),[5–11] with a focus on the different effects of Ni and Zn substitutions in the latter compound. Experimental techniques have included transport phenomena,[12–18] NMR,[19–24] ESR,[25] Raman[26] muon spin,[27,28] and neutron scattering.[29]

We concluded early on that measurements on polycrystalline samples could not be definitive because there is no reliable way to determine conclusively how the substituent is divided between the crystal grains and the intergranular network. Growing monocrystalline phase-pure samples with masses in the milligram range or larger with known, uniform substitution for Cu in the Cu-O planes has proven thus far to be difficult, but we have found that it is relatively simple to grow microgram single-crystal whiskers of the Bi-based superconductors in which the substituent element is uniformly distributed along the whisker and the transitions are sharp. The growth habit of BSCCO whiskers, which is prone to the incorporation of stacking faults, tends to cause them to have coexisting filamentary 2212 and 2223 paths. We find no chemical inhomogeneities in sampling 5–10 areas as small as 25 μm^2 along the several millimeter length of the sample. Moreover, 2212 and 2223 transitions respond uniformly to compositional changes, so we believe there is equal substitution for Cu across the filamentary boundaries. This point will be discussed further.

The work reported here on Fe and Pd substitutions provides complementary findings to our previous study of Ni, Zn, and Co substitutions.[2–4] Like Ni and Co, Fe, and Pd substitutions can be expected to introduce bonding d electrons into the Cu-O lattice. However, Fe, mimicking Co with oxidation states of 2+ and 3+, is a strong oxide former, while Pd, the second long-period cogener of Ni, can be expected to show a single valence of 2+ and is a weak oxide former. From valence considerations we can expect their levels of substitution to differ.

If a magnetic perturbation of the spin-pairing mechanism is operative in the superconducting state, the effect of substitution should be expected to vary for these elements. We have made no measurements of the magnetic moments associated with the Fe, Co, Ni, and Pd sites when substituted on the Cu-O lattice and we are not aware of any other comparable single-crystal measurements. Lacking this information, we assign realistic bounds for the magnetic moment per substituted atom, based on low spin-state values reported in the literature for the pure oxides and their solid solutions. From Goodenough,[30] we estimate Fe^{3+}, $2.0\mu_B$; Co^{3+}, $1.7\mu_B$; Ni^{2+}, $0.6\mu_B$; Zn^{2+}, 0; Pd^{2+}, $0.3\mu_B$. We note that in doped powder samples of YBCO, Mendels *et al.*[31] found μ_{eff} for Ni to be $1.5\mu_B$ and μ_{eff} for Zn to be $0.36\mu_B$.

II. EXPERIMENTAL PROCEDURES

The whisker growth method was pioneered by Matsubara *et al.*[32] Details of our adaptation of their method have been given earlier and will not be repeated here. Quantitative compositional analysis of the whiskers with typical dimensions 2–10 mm (**a** axis), 10–100 μm (**b** axis), and 2–10 μm (**c** axis) was done by nondestructive electron-probe microanalysis using a Camica SX50 four-wavelength spectrometer electron probe. Our error analysis is reported elsewhere. The minimum detection limit is 0.025%. We found the composition to be uniform within 5% along the sample length for

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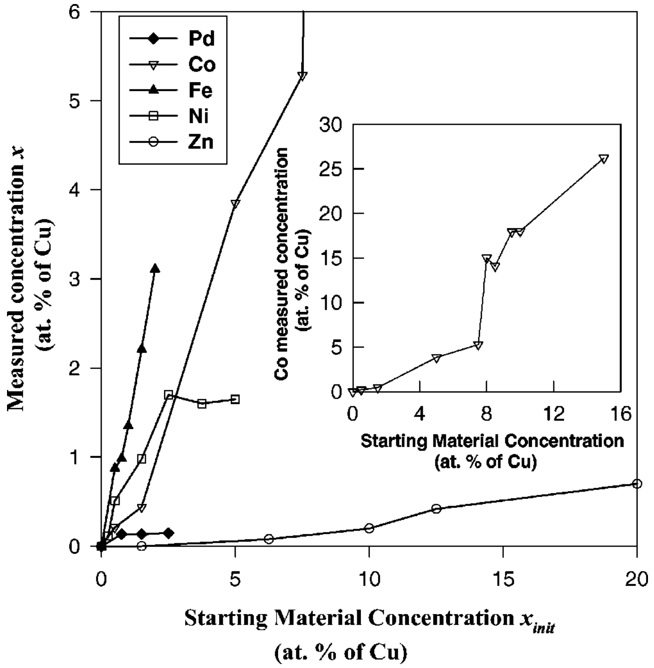

FIG. 1. Substituent concentration in BSCCO whiskers, measured by electron probe microanalysis. The inset shows the full concentration range for Co. Lines are a guide to the eye.

Zn, Ni, Co, Pd and a larger variation of 10% for Fe. vom Hedt *et al.*[33] report a similar inhomogeneous distribution of Fe in their larger single crystals. De Boeck, Ciurchea, and Duvigneaud[34] find that Fe concentrations over $x=0.05$ lead to the presence of the 2201 phase in ceramic samples, similar to what we find for Co substitutions over $x=0.06$ in whisker single crystals.[4] Fe-substituted whiskers are smaller with a more uneven morphology. We were unable to substitute measurable amounts of Cd in our samples.

Figure 1 shows the compositional details for Fe and Pd (filled symbols) and, from our previous work, for Co, Ni, and Zn (open symbols). We plot the measured concentration of substituent in the whisker x against the concentration in the starting material x_{init}. Fe and Co show high levels of substitution while the other substituents saturate at low levels. We infer that replacement is favored by a substituent having a 3+ oxidation state.

This study was limited to the determination of T_C by **a**-axis R vs T measurements by a standard four-probe dc technique with a typical excitation current $I=100\,\mu$A. Our adaptation of this technique has been previously described.[2–4]

III. RESULTS

We first show results for an unsubstituted sample: Fig. 2. The normalized resistance along the **a** axis is shown in the temperature range $4<T<300$ K for an as-grown whisker. R is linear in T in the normal state, but see Chen, Franck, and Jung[35] for the behavior of similar samples with different oxygen doping. The sharp drop in R at 108 K corresponds to T_C of the 2223 phase, while the second smaller drop at about 80 K is T_C for the 2212 phase. The transition width (10–90%) is about 1 K and there is a nearly zero residual resistance, indicating a high degree of perfection in the crystalline form. We have shown previously[1–4] that the major volume fraction is the 2212 phase, but filamentary paths of 2212 and 2223 coexist. So in a single sample under identical environmental conditions we can measure T_C for both phases. This is an advantageous materials venue provided that the substituent enters both phases at the same concentration. We believe we have shown this condition obtains by our observation that the changes in the residual resistance and in T_C with substituent concentration are essentially the same for the two phases.

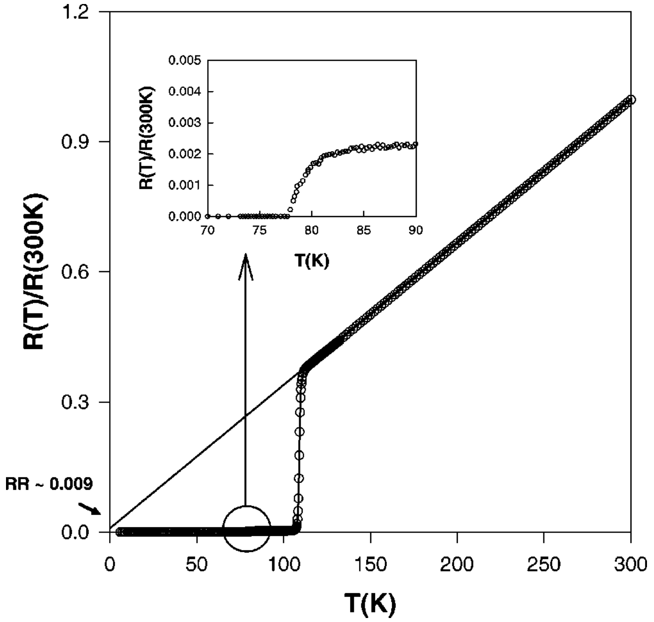

FIG. 2. Normalized resistance (at 300 K) vs temperature for an unsubstituted whisker. The inset shows a blowup plot near the 2212 transition.

Although in earlier work[2,3] we observed that the effect of substitution on T_C had no essential dependence on oxygen concentration, in the results reported here we have isolated the effect of substitution from the effect of oxygen doping by making all measurements on as-grown samples (1 atm oxygen pressure annealing) which is near their optimized transition temperatures.

In Fig. 3 we show our results for Fe and Pd substitutions. Increasing Fe substitution [Fig. 3(a)] produces a progressive decrease in T_C for the 2212 phase and a less orderly decrease for 2223. Unlike the narrow transitions usually observed for the other substituents, there is considerable broadening by Fe. This has been previously observed and attributed to an inhomogeneous distribution and clustering of the Fe atoms.[33] For Pd substitution [Fig. 3(b)] there is only a minor T_C depression because, as seen in Fig. 1, saturation occurs at a low concentration.

We now add these results to our earlier findings for Co, Ni, and Zn. In Fig. 4(a), T_C is taken as the temperature at the middle of the transition and we plot this value as a function of concentration for all substituents in both phases. Within

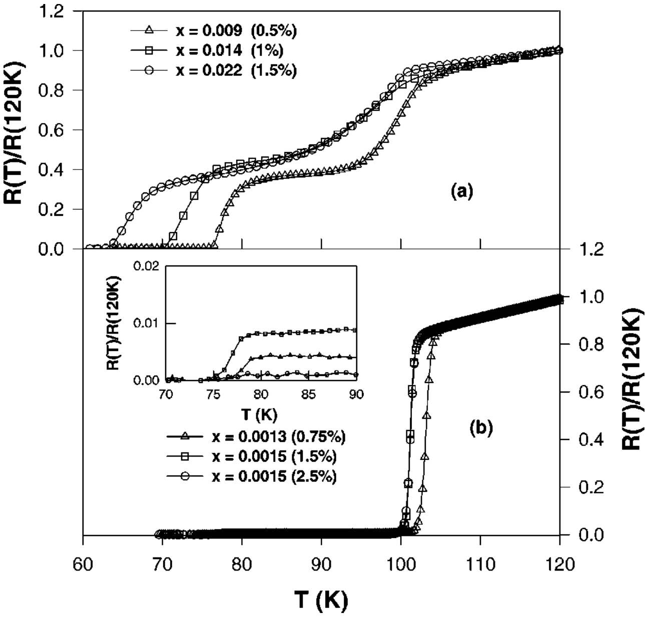

FIG. 3. Normalized resistance (at 120 K) vs temperature at measured concentrations shown. (a) Fe; (b) Pd.

the scatter of our data, the depression of T_C is linear in x with $dT_C/dx \approx -780\,\mathrm{K}$, independent of substituent. In Fig. 4(b) we plot the normalized residual resistance (NRR) $\equiv R(T \to 0)/R(120\,\mathrm{K})$ as a function of x, obtained by extrapolating the normalized normal-state resistance to $T=0$. Within our uncertainties NRR is also linear in x and again is quantitatively the same for all the substituents.

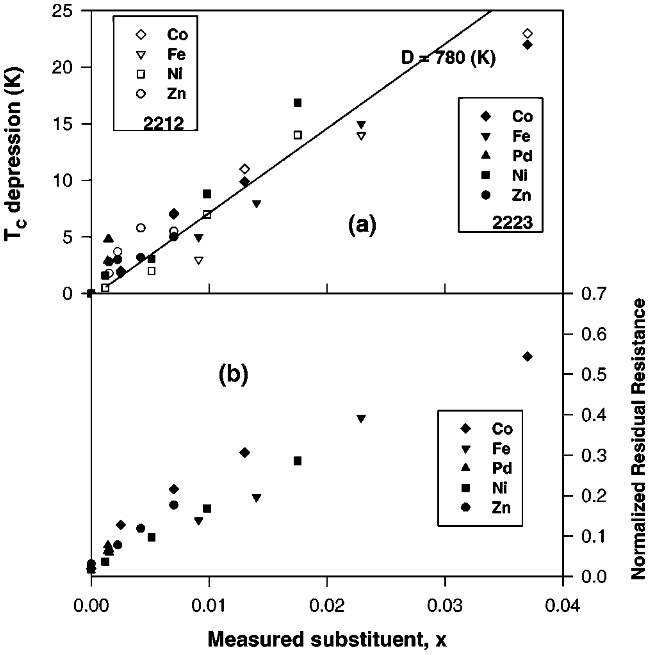

FIG. 4. (a) T_C depression (K) vs Fe, Co, Ni, Zn, and Pd measured concentrations (x) for 2212 and 2223 phases. dT_C/dx from least squares fit. (b) The normalized residual resistance NRR(x) vs measured substituent concentration x is approximately a linear function. Within our uncertainties, both dT_C/dx and NRR are quantitatively the same for all the substituents.

IV. DISCUSSION AND SUMMARY

The elements substituted for Cu in this study collectively introduce different valence states and a range of unpaired d-electron spin states into the Cu-O lattice of BSCCO crystals. Our significant finding is that in both superconducting phases 2212 and 2223, all the substituents have the same effect on NRR (a normal state property) and T_C (a superconducting property) independent of the electronic configuration of the substituting atom. This is contrary to the results on the $\mathrm{YBa_2(Cu_{1-x}M_x)O_7}$ system (where $T_C=91\,\mathrm{K}$ and M is Zn or Ni). Here dT_C/dx is found to be about −1200 K for Zn, but only about −350 K for Ni. This difference was taken to favor a magnetic mechanism of pairing and an asymmetric order parameter, such as for high-T_C superconductors,[36] or evidence of a van Hove singularity near the Fermi surface in cuprates,[8] or due to the differences in the anisotropy of scattering by different substituents or vacancies.[37] Our results, as well as those in LaSrCuO (Ref. 14) suggest that the differences between Ni and Zn substitutions for Cu are not universal in the Cu-O superconductors, but may be unique to the YBCO system. Pan *et al.*[38] have used scanning tunneling microscopy to measure tunneling spectra around Zn impurities in $\mathrm{Bi_2Sr_2CaCu_2O_{8+\delta}}$ and inferred a strong scattering potential for Zn substitutions. Further work by the same group[39] shows a much different scattering potential for Ni, which can be explained by a strong-potential scattering and a rather weak magnetic scattering, so that the potential scattering phase shifts for Ni and Zn are the same within 20%. Thus the similar effects that we find Ni and Zn substituents (as well as all other transition metals) to have on the NRR and T_C may be a result of similar nonmagnetic scattering.

In addition to the result that dT_C/dx is the same for all the substituents, the observed value of dT_C/dx is smaller by about a factor of two than the value predicted by the modified Abrikosov-Gorkov[40] relation for d-wave symmetry and isotropic scattering:

$$\ln\frac{T_{C_0}}{T_C}=a\Psi\left[\frac{1}{2}+b\,\frac{\Gamma}{T_c}\right]-\Psi\left[\frac{1}{2}\right].$$

Here Ψ is the digamma function, $T_{C_0}=T_C$ $(x=0)$, $\Gamma \equiv \rho_0/(d\rho/dT)$ is proportional to the isotropic component of the impurity scattering rate, a depends on the symmetry of the wave function,[41] usually assumed to be d-wave so that $a=1$ (for s-wave scattering $a=\frac{1}{4}$ and b proportional to $(1-g_l)$, where g_l is the ratio of anisotropic to isotropic scattering,[37,42,43] usually assumed to be isotropic so that $b=1$. Since the density of states at the Fermi surface is uncertain, and enters into b, there is a large uncertainty in the factor-of-2 difference. Further, as discussed in Haran and Nagi,[44] anisotropic scattering in which the scattering has maxima in the region of the nodes of the order parameter will decrease T_C much less than isotropic scattering. The factor-of-2 discrepancy between the observed and predicted

dT_c/dx is not only in our results, but in almost all Cu-O superconductors. Although it is possible to explain the discrepancy between experiments such as ours and the predictions of the Abrikosov-Gorkov equation by suitably adjusting the anisotropy of the scattering or the density of states at the Fermi surface (b) and/or the symmetry of the wave function (a) to fit the data, without a more detailed knowledge of the electronic structure to check such a fit we do not believe it to be profitable.

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[1] M. Chung, D. T. Verebelyi, C. W. Schneider, M. V. Nevitt, M. J. Skove, J. E. Payne, M. Marone, and P. Kostic, Physica C **265**, 301 (1996).

[2] Y. K. Kuo, C. W. Schneider, M. J. Skove, M. V. Nevitt, G. X. Tessema, and J. J. McGee, Phys. Rev. B **56**, 6201 (1997).

[3] C. W. Schneider, Ph.D. thesis, Clemson University, 1998.

[4] Y. K. Kuo, C. W. Schneinder, D. T. Verebelyi, M. V. Nevitt, M. J. Skove, G. X. Tessema, He Li, and J. M. Pond, Physica C **319**, 1 (1999).

[5] R. P. Gupta and M. Gupta, Physica C **305**, 179 (1998); Phys. Rev. B **59**, 3381 (1999).

[6] Y. Sun and K. Maki, Phys. Rev. B **51**, 6059 (1995).

[7] L. S. Borkowski and P. J. Hirschfield, Phys. Rev. B **49**, 15 404 (1994).

[8] R. Fehrenbacher, Phys. Rev. Lett. **77**, 1849 (1996).

[9] T. Hotta, J. Phys. Soc. Jpn. **62**, 274 (1993).

[10] R. J. Radke, K. Levin, H.-B. Schuttler, and M. R. Norman, Phys. Rev. B **48**, 653 (1993).

[11] M. Franz, C. Kallin, A. J. Berlinsky, and M. I. Salkola, Phys. Rev. B **56**, 7882 (1997).

[12] G. Xiao, F. H. Streitz, A. Garvin, Y. W. Du, and C. L. Chien, Phys. Rev. B **35**, 8782 (1987).

[13] A. Maeda, T. Yabe, S. Takebayashi, M. Hase, and K. Uchinokura, Phys. Rev. B **41**, 4112 (1990).

[14] G. Xiao, M. Z. Cieplak, J. Q. Xiao, and C. L. Chien, Phys. Rev. B **42**, 8752 (1990).

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

[16] T. R. Chien, Z. Z. Wang, and N. P. Ong, Phys. Rev. Lett. **67**, 2088 (1991).

[17] K. Muzihashi, K. Takenaka, Y. Fukuzumi, and S. Uchida, Phys. Rev. B **52**, 3884 (1995).

[18] Y. Fukuzumi, K. Muzihashi, K. Takenaka, and S. Uchida, Phys. Rev. Lett. **76**, 684 (1996).

[19] H. Alloul, P. Mendels, H. Casalta, J. F. Marucco, and J. Arabski, Phys. Rev. Lett. **67**, 3140 (1991).

[20] R. Dupree, A. Gencten, and D. M. Paul, Physica C **193**, 81 (1992).

[21] R. E. Walstedt, R. F. Bell, L. F. Schneemeyer, J. V. Waszczak, W. W. Warren, R. Dupree, and A. Gencten, Phys. Rev. B **48**, 10 646 (1993).

[22] K. Ishida, Y. Kitaoka, N. Ogata, T. Kamino, K. Asayama, J. R. Cooper, and N. Athanassopoulou, J. Phys. Soc. Jpn. **62**, 2803 (1993).

[23] G. V. M. Williams, J. L. Tallon, and R. Meinhold, Phys. Rev. B **52**, 7034 (1995).

[24] A. V. Mahajan, H. Alloul, G. Collin, and J. F. Marucco, Phys. Rev. Lett. **72**, 3100 (1994).

[25] A. Janossy, J. R. Cooper, L. C. Brunel, and A. Carrington, Phys. Rev. B **50**, 3442 (1994).

[26] M. Kall, A. P. Litvinchuk, L. Borjesson, P. Berastegui, and L. G. Johansson, Phys. Rev. B **53**, 3566 (1996).

[27] B. Nachumi, A. Keren, K. Kojima, M. Larkin, G. M. Luke, J. Merrin, O. Tchernyshov, Y. J. Uemura, N. Ichikawa, M. Goto, and S. Uchida, Phys. Rev. Lett. **77**, 5421 (1996).

[28] C. Bernhard, J. L. Tallon, C. Bucci, R. De Renzi, G. Guidi, G. V. M. Williams, and C. Niedermayer, Phys. Rev. Lett. **77**, 2304 (1996).

[29] Y. Sidis, P. Bourges, B. Hennion, L. P. Regnault, R. Villeneuve, G. Collin, and J. F. Marucco, Phys. Rev. B **53**, 6811 (1996).

[30] J. B. Goodenough, *Magnetism and the Chemical Bond* (Wiley, New York, 1963), p. 33.

[31] P. Mendels, H. Alloul, G. Collin, N. Blanchard, J. F. Marucco, and J. Bobroff, Physica C **235-240**, 1595 (1994).

[32] I. Matsubara, H. Kageyama, H. Tanigawa, T. Ogura, H. Yamashita, and T. Kawai, Jpn. J. Appl. Phys., Part 2 **28**, L1121 (1989).

[33] B. vom Hedt, W. Lisseck, K. Westerholt, and H. Bach, Phys. Rev. B **49**, 9898 (1994).

[34] C. De Boeck, D. Ciurchea, and P. H. Duvigneaud, J. Eur. Ceram. Soc. **19**, 1537 (1999).

[35] Weimin Chen, J. P. Franck, and J. Jung, Phys. Rev. B **60**, 3527 (1999).

[36] P. Monthoux and D. Pines, Phys. Rev. B **49**, 4261 (1994).

[37] J.-Y. Lin, S. J. Chen, S. Y. Chen, C. F. Chang, H. D. Yang, S. K. Tolpygo, M. Gurvitch, Y. Y. Hsu, and H. C. Ku, Phys. Rev. B **59**, 6047 (1999).

[38] S. H. Pan, E. W. Hudson, K. M. Lang, S. Uchida, and J. C. Davis, Nature (London) **403**, 746 (2000).

[39] E. W. Hudson, E. M. Lang, V. Madhavan, S. H. Pan, H. Eisaki, S. Uchida, and J. C. Davis (unpublished).

[40] A. A. Abrikosov and L. P. Gorkov, Zh. Eksp. Teor. Fiz. **39**, 1781 (1961) [Sov. Phys. JETP **12**, 1243 (1961)].

[41] R. Ferhenbacher and M. R. Norman, Phys. Rev. B **50**, 3495 (1994).

[42] A. J. Millis, S. Sachdev, and C. M. Varma, Phys. Rev. B **37**, 4975 (1988).

[43] G. Haran and A. D. S. Nagi, Phys. Rev. B **54**, 15 463 (1996).

[44] G. Haran and A. D. S. Nagi, Phys. Rev. B **58**, 12 441 (1998).