PHYSICAL REVIEW B VOLUME 61, NUMBER 14 1 APRIL 2000-II

COMMENTS

Comments are short papers which criticize or correct papers of other authors previously published in **Physical Review B.** *Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Comment on "Structural and superconducting properties of $R_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ with $0.50\geqslant x\geqslant 0.00$"

J. L. Tallon and G. V. M. Williams
New Zealand Institute for Industrial Research, P.O. Box 31310, Lower Hutt, New Zealand

(Received 16 February 1999)

The interpretation of x-ray diffraction, resistivity, and susceptibility measurements on $R_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ by Sedky *et al.* [Phys. Rev. B **58**, 12 495 (1998)] in terms of different site preferences for oxygen vacancies and the compensation of Ca by the loss of oxygen is shown to be inconsistent with the wider body of experimental research.

The $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ superconducting cuprate has proved in recent years to be a powerfully instructive model system offering key insights based on transport, heat-capacity, neutron-diffraction, muon-spin-relaxation, nuclear-magnetic-resonance, and infrared studies.[1–9] Sedky *et al.*[10] have recently presented results from an x-ray-diffraction, resistivity, and ac susceptibility study of this system. They claim that the extra holes introduced by Ca substitution (Ca^{2+} for R^{3+}) are compensated for by a loss of oxygen in the samples and speculate that, for $R=$Er or Y, the oxygen loss occurs in the CuO_2 planes while for $R=$Sm or Nd the oxygen loss occurs in the CuO chains. They question the occurrence of overdoping in this system and criticize one of our publications which showed that the changes in T_c with Ca substitution are due to hole doping.[1] If correct, this would bring into question a large block of important conclusions we have drawn from this system. We show below that the conclusions reached by Sedky *et al.* are inconsistent with the wider body of experimental data. We believe that the inconsistencies arise from the sample preparation method used by Sedky *et al.* As we have often emphasized, considerable care must be taken in the synthesis of $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$.

First, Sedky *et al.* have misunderstood Fig. 2 in Ref. 1 where $T_c/T_{c,\max}$ is plotted against hole concentration for a variety of superconducting cuprates including $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$. This figure is reproduced here as Fig. 1. They suggest that the T_c data normalized to $T_{c,\max}$ (solid diamonds) for fully oxygenated $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ with a range of x values does not necessarily represent overdoping because $T_{c,\max}$ depends on x and one cannot therefore use a single value of $T_{c,\max}$. They failed to note that, indeed, we did not use a single value of $T_{c,\max}$ but a different value of $T_{c,\max}$ for each Ca concentration. The filled squares in Fig. 1 clearly show that the effect of Ca is primarily to introduce additional holes. It is not clear how any other interpretation would possibly be placed on these data especially as, for each value of x, deoxygenation initially raises T_c to an x-dependent $T_{c,\max}(x)$. It is also clear from thermopower,[1,2] bond valance sum calculations,[1] muon-spin-rotation,[3,4] neutron-diffraction,[5] heat-capacity,[6] and nuclear-magnetic-resonance measurements[7] that $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ can be overdoped. Furthermore, we note that pair-breaking studies on $Y_{1-x}Ca_x(Cu_{1-z}Zn_z)_3O_{7-\delta}$ are entirely consistent with holes being introduced by Ca and pair breaking by Zn.[8,9]

Secondly, their claim that the holes introduced by Ca are compensated for by a reduction in oxygen content is inconsistent with a number of other studies.[1–9] As noted above, all our Ca substituted samples can be fully oxygenated. Thermodynamic considerations make it clear that, with progressively increasing Ca content, samples must be annealed at progressively lower temperatures in order to fully oxygenate.

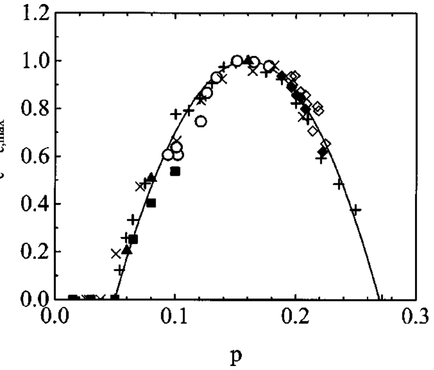

FIG. 1. T_c, normalized to $T_{c,\max}$ plotted as a function of hole concentration determined (i) from $p=x/2$ for $Y_{1-x}Ca_xBa_2Cu_3O_6$ (solid squares), (ii) from $p=V_-$ for $YBa_2Cu_3O_{7-\delta}$ with different δ (open circles), (iii) from $p=V_-$ for $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ with $\delta\approx 0.04$ and different x (solid diamonds), (iv) from V_- for $Y_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ and different δ (crosses), (v) from $p=V_-$ for the $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ data of Böttger *et al.* [open diamonds (Ref. 11)], (vi) from $p=x$ for $La_{2-x}Sr_xCuO_4$ (plus symbols), and (vii) from $p=x$ for $La_{2-x}Sr_xCaCu_2O_6$ (solid up triangles). The solid curve is $T_c/T_{c,\max}=1-82.6(p-0.16)^2$.

0163-1829/2000/61(14)/9820(3)/$15.00

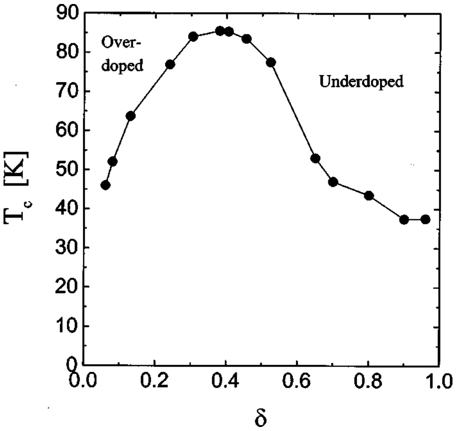

FIG. 2. Plot of T_c against δ for $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$.

Typically we anneal $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$ after slow cooling to temperatures as low as 320 °C for many days. This results in oxygenation as complete as is observed in pure $YBa_2Cu_3O_{7-\delta}$ with values of $\delta \leqslant 0.04$. Such low values were confirmed by neutron-diffraction structural refinements for the full range of Ca substitution investigated (solid diamonds plotted in Fig. 1). We show the full T_c variation with δ for $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$ in Fig. 2 where, again, it can be seen that δ may be reduced close to zero contrary to the claims of Sedky *et al.* who state that the minimum δ is 0.185 for $x = 0.2$.

Sedky *et al.* claim that our conclusion is incorrect because the deduced hole concentrations are different from those of Böttger *et al.*,[11] which were calculated in the same way using the bond valance sum V_- parameter, as defined by Tallon.[12] We note that V_- is constructed from the sum of excess copper and oxygen charge and proves to be a reasonable estimate of the hole concentration p. Thus,

$$p \approx V_- \equiv (V_{\mathrm{Cu}} - 2) + (2 - V_{\mathrm{O2}}) + (2 - V_{\mathrm{O3}}), \tag{1}$$

where $V_{\mathrm{O2}}, V_{\mathrm{O3}}$ are the bond valance sums from the O2 and O3 sites, respectively, and V_{Cu} is the effective bond valance sum for Cu in the CuO_2 plane. From their neutron refinement data, Böttger *et al.* obtained apparently underdoped V_- values of ~0.14 for the largest Ca concentration. This would appear to conflict with the overdoped V_- values of ~0.22 for $x = 0.2$ obtained by Tallon *et al.* also from neutron refinement data.[1] This apparent conflict is due to an error in the calculation of the bond valance sum parameter, V_-, by Böttger *et al.* In Fig. 1 we plot the data of Böttger *et al.* with the recalculated V_- values (open diamonds) where it can be seen that there is good agreement with the data of Tallon *et al.*

Finally, we believe that the claim of different types of oxygen vacancies in the larger rare-earth Sm and Nd based samples is incorrect. All these samples were sintered at a pressure of 1 bar O_2. However, it is known that $SmBa_2Cu_3O_7$ and $NdBa_2Cu_3O_{7-\delta}$ sintered under such conditions exhibit significant Nd and Sm substitution on the Ba site and a reduction in T_c by electron doping.[13] This is illustrated by the fact that T_c for the pure $NdBa_2Cu_3O_{6.92}$ sample of Sedky *et al.* is only 88 K rather than the 96 K achievable under proper synthesis. Phase-pure compounds can only be synthesised at much lower oxygen partial pressures. Consequently, one should expect the oxygenated Ca-substituted Sm and Nd compounds to be overdoped but not as much as the Ca-substituted Y and Er compounds. In fact the latter exhibit positive curvature in $\rho(T)$ typical of the overdoped high-temperature superconducting cuprates (HTSC's) while for the former any curvature is much weaker. Sedky *et al.* speculate that for $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ and $Er_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$, this curvature arises because oxygen vacancies reside in the CuO_2 planes. However, our neutron refinements showed only chain oxygen deficiencies. This is nicely confirmed by a thermopower study which show that the changes in δ are due to the removal of oxygen from the CuO chain sites.[2] The thermopower exhibits chain+plane thermopower for fully oxygenated $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$ changing to plane-only thermopower with progressive deoxygenation, thus indicating that the oxygen vacancies are on the CuO chains. The chain contributions to the thermopower are clearly recognizable by the positive slope in $S(T)$ while the plane contribution has a negative slope and its magnitude correlates closely with the doping state for all HTSO's.[14] The plane-contribution to the thermopower is identical to that found for a broad range of HTSC (Bi-2212, Bi-2223, Tl-1212, Tl-2223, Hg-1212, Hg-1223, etc.) for the same ratio of T_c to $T_{c,\max}$.[14] Finally, ^{89}Y NMR linewidths for $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$ and $Y_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ are found to be constant, independent of deoxygenation across a broad range of $\delta (0.04 \leqslant \delta \leqslant 0.7)$ corresponding to hole concentrations $0.11 \leqslant p \leqslant 0.23$.[7] This is very much contrary to expectations if the vacancies were to appear in the CuO_2 planes because an increasing concentration of vacancies should lead to increased disorder and hence an increased linewidth.

In conclusion, the claims made by Sedky *et al.* in relation to $R_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ are inconsistent with a wide body of experimental research. In particular, $R_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ can be overdoped with δ values close to zero and the oxygen vacancies are in the CuO chains and not the CuO_2 planes.

---

[1] J. L. Tallon, C. Bernhard, H. Shaked, R. L. Hitterman, and J. D. Jorgensen, Phys. Rev. B **51**, 12 911 (1996).

[2] C. Bernhard and J. L. Tallon, Phys. Rev. B **54**, 10 201 (1996).

[3] J. L. Tallon, C. Bernhard, U. Binninger, A. Hofer, G. V. M. Williams, E. J. Ansaldo, J. I. Budnick, and Ch. Niedermayer, Phys. Rev. Lett. **74**, 1008 (1995).

[4] C. Bernhard, Ch. Niedermayer, U. Binninger, A. Hofer, Ch. Wenger, J. L. Tallon, G. V. M. Williams, E. J. Ansaldo, J. I. Budnick, C. E. Stronach, D. R. Noakes, and M. A. Blankson-Mills, Phys. Rev. B **52**, 10 488 (1995).

[5] J. L. Tallon, C. Bernhard, H. Shaked, R. L. Hitterman, and J. D. Jorgensen (unpublished).

[6] J. W. Loram, K. A. Mirza, J. R. Cooper, and J. L. Tallon, Physica C **282-287**, 1405 (1997).

[7] G. V. M. Williams, J. L. Tallon, R. Michalak, and R. Dupree, Phys. Rev. B **57**, 8696 (1998).

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

[9] J. L. Tallon, C. Bernhard, G. V. M. Williams, and J. L. Loram, Phys. Rev. Lett. **79**, 5294 (1997).

[10] A. Sedky, Anuray Gupta, V. P. S. Awana, and A. V. Narlikar, Phys. Rev. B **58**, 12 495 (1998).

[11] G. Böttger, I. Magelschots, E. Kaldis, P. Fischer, Ch. Kruger, and F. Fauth, J. Phys.: Condens. Matter **8**, 8895 (1996).

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

[13] G. V. M. Williams and J. L. Tallon, Physica C **258**, 41 (1996).

[14] S. D. Obertelli, J. R. Cooper, and J. L. Tallon, Phys. Rev. B **46**, 14 928 (1992).