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Structural basis for enhanced T_c in $YBa_2Cu_3O_yF_x$

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The optimum empirical formula and a model for the ordered crystalline motif for the high-T_c (155 K), fluoride-substituted ceramic, $YBa_2Cu_3O_6F_2$ are deduced based on simple structural considerations. The average Cu-atom oxidation state (2.33) is predicted to be the same as in the oxygenated material ($T_c \sim 95$ K), $YBa_2Cu_3O_7$.

Recently, it has been reported that fluoride-substituted Y-Ba-Cu oxides with the nominal formulation $YBa_2Cu_3O_yF_x$ can yield substantially increased superconducting transition temperatures (T_c).[1] In particular, with a preparation scheme designed to optimize the $x=2$ phase, a zero-resistance state was achieved near 155 K.[1] It is suggested here that a simple structural basis for enhanced T_c in these fluoride containing ceramics can be envisioned, and, moreover, optimal enhancement is anticipated for the substitution of two fluoride (F^-) anions for one oxide (O^{2-}) anion ($y=6$, $x=2$).

To illuminate this point of view, the triple perovskite structure of $YBa_2Cu_3O_y$ (in space group *Pmmm*, following closely the determination of Siegrist *et al.*[2]) is briefly outlined. First, the triple periodicity ($a \simeq b \simeq c/3$) is ensured by the ordered arrangement of Y and Ba atoms employing Wyckoff sites $1h(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and $2t(\frac{1}{2},\frac{1}{2},0.19)$. Second, the three Cu atoms per cell are placed in positions $1a(0,0,0)$ and $2q(0,0,0.36)$. Third, placement of the oxygen atoms is, for emphasis, accomplished in two steps: (1) six oxygen atoms occupy Wyckoff sites $2q(0,0,0.15)$, $2s(\frac{1}{2},0,0.38)$, and $2r(0,\frac{1}{2},0.38)$; and (2) two further oxygen atom sites $1e(0,\frac{1}{2},0)$ and $1b(\frac{1}{2},0,0)$ are identified.

It is these latter two oxygen atoms sites that lie at the focal point of the arguments presented here (and at the nucleus of an alternative description of the crystalline structure of $YBa_2Cu_3O_y$).[3-7] If both sites are fully occupied (and assuming full occupation of all other atomic locations), the empirical formula would be $YBa_2Cu_3O_8$, and the average Cu-atom oxidation state would be three [in a formal sense, 3Cu(III)]. In the model of Siegrist *et al.*,[2] each of these two sites is half occupied to give $YBa_2Cu_3O_7$ and an average Cu-atom oxidation state of 2.33 [in a formal sense, 2Cu(II) and 1Cu(III)]. Others[3-7] (based on x-ray, neutron, or electron diffraction and electron microscopy) have argued for a preferential (full occupancy, in the limit) of the $1e(0,\frac{1}{2},0)$ oxygen atom site, to yield an identical chemical formulation and average Cu-atom oxidation state. It is possible that different sample preparation (annealing) schemes or twinning may partially account for the alternative descriptions of the crystal chemistry of $YBa_2Cu_3O_7$ cited above.

Consider now the possible substitution of F^- anions for O^{2-} anions. Such a proposal is facilitated by the very similar ionic radii[8] for the two anions ($r_I = 1.29$ Å for F^- and $r_I = 1.35$ Å for O^{2-}), with their ionic charges being the most obvious difference. It is further considered probable, based on the structural properties of the triple perovskite cell, that the two oxygen atom sites $1e$ and $1b$ are the most likely candidates for substitution. Incorporation of one F^- anion can be accomplished by utilizing, say, site $1e$, leaving site $1b$ for an O^{2-} anion (or more likely sites $1e$ and $1b$ would be randomly occupied by F^- and O^{2-} anions leading to positional disorder). One site incorporation yields the empirical formula $YBa_2Cu_3O_7F$ and an average Cu-atom oxidation state of 2.67 [in a formal sense, 1Cu(II) and 2Cu(III)]. Most interestingly, the substitution of two F^- anions (using both sites $1e$ and $1b$ to the exclusion of any oxygen occupancy) gives the ideal formula $YBa_2Cu_3O_6F_2$ and *preserves* the same (perhaps ideal)[9] average Cu-atom oxidation state (2.33) as in the oxygenated ceramic, $YBa_2Cu_3O_7$. Moreover, in $YBa_2Cu_3O_6F_2$, atomic disorder between anion sites $1e$ and $1b$ would clearly be absent (in contrast to the oxygen atom positional disorder of Ref. 2 or the likely F^--O^{2-} disorder of the monofluorinated material). In addition, the (perhaps detrimental)[10] 1D columns of square planar CuO_4 coordination polyhedra (Refs. 3-7) in the alternative model for the structure of $YBa_2Cu_3O_7$ would be replaced by 2D planes of ordered, square bipyramidal, CuO_2F_4 coordination polyhedra in $YBa_2Cu_3O_6F_2$. Finally, it is suggested that the crystalline motif for $YBa_2Cu_3O_6F_2$ would likely display tetragonal (possible space group *P4/mmm*) symmetry as opposed to the orthorhombic (*Pmmm*) symmetry of $YBa_2Cu_3O_7$.

In summary, the optimum empirical formula and ordered crystalline structure of the high-T_c, fluoride-substituted, ceramic $YBa_2Cu_3O_6F_2$ can be formulated based on simple structural arguments. The absence in the proposed crystalline motif of atomic positional disorder or potentially unstable 1D columns of CuO_4 coordination polyhedra, but the retention of an average Cu-atom oxidation state[9] of 2.33, may well account for the enhanced superconducting properties of this fluorinated ceramic.[1]

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[9] The model presented here relies in part on the presence of mixed valency at the Cu ion sites in both $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6F_2$. Experimental studies are certainly mixed on this issue. (a) Interpretations of photoemission (x-ray photoemission spectrocopy and ultraviolet photoemission spectroscopy) results on $YBa_2Cu_3O_y$ [perhaps owing to differences in surface oxygen content (y)] have ranged from inconclusive [R. L. Kurtz, R. L. Stockbauer, D. Mueller, A. Shih, L. E. Toth, M. Osofsky, and S. A. Wolf, Phys. Rev. B **35**, 8818 (1987); M. Onellion, Y. Chang, D. W. Niles, R. Joynt, G. Margaritando, N. G. Stoffel, and J. M. Tarascon, *ibid.* **36**, 819 (1987)], to a definite absence [N. Fukushima, H. Yoshino, H. Nui, M. Hayashi, H. Sasaki, Y. Yamada, and S. Murase, Jpn. J. Appl. Phys. **26**, L719 (1987); A. Fujimori, E. Takayama-Muromachi, Y. Uchida, and B. Okai, Phys. Rev. B **35**, 8814 (1987); Ji Mingrong, He Zhenghui, Wu Jianxin, Zhang Han, Pan Guogiang, Cheng Zhuyao, Qian Yitai, Zhao Yong, Hu Liping, Xia Jiansen, and Zhang Qinui, Solid State Commun. **63**, 511 (1987)], to a definite presence [H. Ihara, M. Hirabayashi, N. Terada, Y. Kimura, K. Senzaki, M. Akimoto, K. Bushida, F. Kawashima, and R. Uzuka, Jpn. J. Appl. Phys. **26**, L460 (1987); F. Garcia-Alvarado, E. Moran, J. M. Gonzalez-Frias, J. L. Vincent, S. Ferrier, E. Garcia-Michel, and M. C. Asensio, Solid State Commun. **63**, 507 (1987)] of Cu(III); (b) extended x-ray-absorption fine structure data [H. Oyanagi, H. Ihara, T. Matsusshita, M. Tokumoto, M. Hirabayashi, N. Terada, K. Senzaki, Y. Kimura, and T. Yao, Jpn. J. Appl. Phys. **26**, L638 (1987)] and crystal chemical arguments (Ref. 6) have been put forth to suggest the presence of Cu(III) in $YBa_2Cu_3O_y$; and, finally (c) Mössbauer data [M. Eibschutz, D. W. Murphy, S. Sunshine, L. G. Van Uitert, S. M. Zahurak, and W. H. Grodiewicz, Phys. Rev. B **35**, 8714 (1987)] have been unambiguously interpreted as favoring Eu^{3+} (and indirectly Cu^{3+}) ions in $EuBa_2Cu_3O_y$.

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