

LETTERS TO THE EDITOR

Factors Governing the Structural Phase Transition Temperatures of Doped La_2CuO_4 Systems

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We examined the doping dependence of Ishibashi's free energy function for $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$, which describes the successive $\text{HTT} \rightarrow \text{LTO} \rightarrow \text{LTT}$ phase transitions of this doped La_2CuO_4 system, in terms of the tolerance factor and the local steric pressure effect of the dopant. On the basis of these microscopic considerations, we explained the general trends in the doping dependence of the $\text{HTT} \rightarrow \text{LTO}$ and the $\text{LTO} \rightarrow \text{LTT}$ transition temperatures in other doped La_2CuO_4 systems. © 1992 Academic Press, Inc.

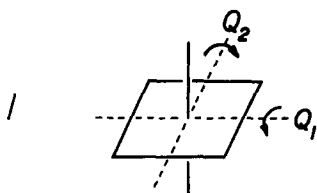
1. Introduction

The structure of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ can be high-temperature tetragonal (HTT), low-temperature orthorhombic (LTO), or low-temperature tetragonal (LTT) depending upon the doping level x and temperature (T). As observed for $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ (1, 2) and $\text{La}_{1.6-x}\text{Nd}_{0.4}\text{Sr}_x\text{CuO}_4$ (3), an LTT structure generally lowers the superconducting transition temperature T_c . When a doped La_2CuO_4 system with the hole density $n_H = \frac{1}{8}$ has an LTT structure (e.g., $\text{La}_{1.875}\text{Ba}_{0.125}\text{CuO}_4$ (1), $\text{La}_{1.845}\text{Th}_{0.02}\text{Ba}_{0.145}\text{CuO}_4$ (4), and $\text{La}_{1.475}\text{Nd}_{0.4}\text{Sr}_{0.125}\text{CuO}_4$ (3)), the T_c lowering is particularly strong. Thus it is important to understand what factors govern the structural phase transitions of doped La_2CuO_4 systems. On the basis of the Landau phenomenological theory, several free energy functions have been proposed for doped La_2CuO_4 systems (1, 3, 5). In particular, the function formulated by Ishibashi (5) suc-

cessfully reproduces the essential features of the $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ phase diagram. So far, however, why certain terms of this function depend upon x as proposed has not been explained on the basis of microscopic considerations. In the present work, we discuss possible microscopic reasons for the doping dependence of Ishibashi's function. In terms of these considerations, we then examine the doping dependence of the $\text{HTT} \rightarrow \text{LTO}$ and $\text{LTO} \rightarrow \text{LTT}$ phase transition temperatures in other doped La_2CuO_4 systems.

2. Free Energy Function

As depicted in Diagram 1, the HTT, LTO, and LTT structures of a doped La_2CuO_4 system are conveniently described in terms of two tilting parameters Q_1 and Q_2 of an axially elongated CuO_6 octahedron: An HTT structure is characterized by $Q_1^2 = Q_2^2 = 0$, an LTO structure by $Q_1^2 \neq 0$ and $Q_2^2 = 0$,



and an LTT structure by $Q_1^2 = Q_2^2 \neq 0$. Under stress-free conditions, Ishibashi's function for $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ can be rewritten as

$$F = \frac{A}{2}(Q_1^2 + Q_2^2) + \frac{\beta}{4}(Q_1^2 + Q_2^2)^2 + \frac{\delta}{2}Q_1^2Q_2^2 - \frac{\varepsilon}{4}(Q_1^2 - Q_2^2) + \frac{\eta}{6}(Q_1^2 - Q_2^2)^2(Q_1^2 + Q_2^2), \quad (1)$$

where β , ε , and η are positive constants. Equation (1) predicts (5) successive $\text{HTT} \rightarrow \text{LTO} \rightarrow \text{LTT}$ transitions when $\delta + \varepsilon > 2\beta - \varepsilon > 0$ and a direct $\text{HTT} \rightarrow \text{LTT}$ transition when $2\beta - \varepsilon > \varepsilon + \delta > 0$. The doping dependence of the structural phase transitions of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ is reproduced by assuming (5) that the coefficients A and ε depend upon x as

$$A = \alpha - \left(1 - \frac{x}{0.21}\right) \quad (2)$$

$$\varepsilon = \left[-2 + \kappa\left(1 - \frac{x}{0.18}\right)\right]\varepsilon, \quad (3)$$

where $\kappa > 0$. In Eq. (2), α represents a reduced temperature. The $\text{HTT} \rightarrow \text{LTO}$ transition temperature T_{d1} is given by the α value for which the coefficient A vanishes (5), so that $T_{d1} = 1 - x/0.21$. ($T_{d1} = 1$ corresponds to 533 K, i.e., the T_{d1} of La_2CuO_4 .) The $\delta Q_1^2 Q_2^2/2$ term of Eq. (1) changes the relative energy between LTO and LTT structures. As the coefficient δ decreases with increasing x , this term preferentially lowers the energy of an LTT structure. The

phase diagram predicted for $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ by Ishibashi (5) is shown in Fig. 1.

3. Microscopic Considerations

The structure of a K_2NiF_4 -type oxide A_2BO_4 can be regarded as an intergrowth of AO rock-salt and BO_2 perovskite layers (6). For each BO_6 octahedron of A_2BO_4 , the four equatorial oxygen atoms (O_{eq}) belong to the BO_2 layers and the two axial oxygen atoms (O_{ax}) belong to the AO layers. The occurrence of an LTO structure in A_2BO_4 is explained in terms of the mismatch between the rock-salt and the perovskite layers (7, 8). In an HTT structure, the A-O bond length $r_{\text{A-O}}$ is related to the B-O bond length $r_{\text{B-O}}$ by $r_{\text{A-O}} = \sqrt{2} r_{\text{B-O}}$. This A-O bond length is larger than the distance predicted by the ionic radii sum, i.e., $r_{\text{A}} + r_{\text{O}}$. Therefore, the A-O bonds of the rock-salt layer tend to shorten, thereby leading to chain- and island-like distortion patterns (6). The formation of chain- and island-like distortion patterns in the AO rock-salt layer induces the tilting of the BO_6 octahedra as found for LTO and LTT structures, respectively (6). The extent of the rock-salt and perovskite layer mismatch may be measured by the tolerance factor τ (7, 8),

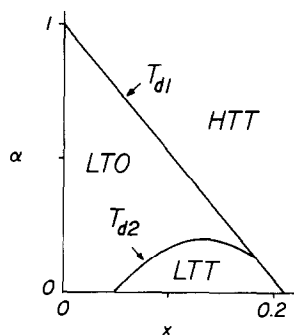


FIG. 1. Phase diagram of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ predicted by Ishibashi's free energy function for $\eta = 1$, $\beta = 0.8$, $\varepsilon = 0.5$, and $\kappa = 3$; α is a reduced temperature and $\alpha = 1$ corresponds to 533 K.

$$\tau = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}, \quad (4)$$

where the ‘‘optimum’’ A–O and B–O bond lengths are approximated by the ionic radii sums $r_A + r_O$ and $r_B + r_O$, respectively. Here the extent of the mismatch increases as τ decreases from 1. In $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ (i.e., $A = \text{La}$, Ba ; $B = \text{Cu}$), the in-plane Cu–O bond length (i.e., r_{B-O}) decreases with increasing x (6), which therefore increases τ with x . In addition, the average A-cation size [i.e., $(1 - x/2)r_{\text{La}}^{3+} + (x/2)r_{\text{Ba}}^{2+}$] increases with increasing x because Ba^{2+} is larger than La^{3+} (9), which also increases τ with x . As a result, the tolerance factor of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ increases from that of La_2CuO_4 as x increases. Thus the tendency for the rock-salt layer A–O bond shortening is reduced with increasing x , so that the T_{d1} of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ is lowered with increasing x (1, 10). For the same reason, the T_{d1} of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ is lowered (10) with increasing x because Sr^{2+} is larger than La^{3+} . The tolerance factor of $\text{La}_{1.875}\text{Ba}_{0.125-x}\text{Sr}_x\text{CuO}_4$ should decrease with increasing x because Sr^{2+} is smaller than Ba^{2+} , so that the T_{d1} of $\text{La}_{1.875}\text{Ba}_{0.125-x}\text{Sr}_x\text{CuO}_4$ is predicted to increase with increasing x in agreement with experiment (11). According to the same reasoning, the T_{d1} of $\text{La}_{1.88-x}\text{Nd}_x\text{Sr}_{0.12}\text{CuO}_4$ should increase with x because Nd^{3+} is smaller than La^{3+} . Likewise, the T_{d1} of $\text{La}_{1.6-x}\text{Nd}_{0.4}\text{Sr}_x\text{CuO}_4$ should decrease with increasing x , as in the case of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.

The tolerance factor discussed above is an ‘‘average’’ effect. As a function of x , the LTO \rightarrow LTT transition temperature T_{d2} of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ has a dome shape (see Fig. 1). This is not explained in terms of the tolerance factor, so that we consider a ‘‘local’’ effect associated with Ba^{2+} . As noted earlier, a decrease in the $\delta Q_1^2 Q_2^2/2$ term preferentially stabilizes an LTT structure thereby raising the T_{d2} . Since Ba^{2+} is much larger than La^{3+} in size, a dopant Ba^{2+} in the LaO rock-salt layer would push away the sur-

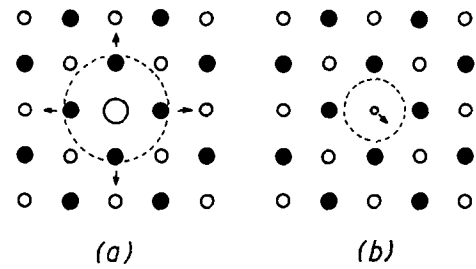


FIG. 2. Local distortion induced by a dopant in the LaO rock-salt layer of La_2CuO_4 : (a) isotropic expansion around a large dopant-like Ba^{2+} and (b) anisotropic movement of a small dopant such as Th^{4+} . The shaded circles represent the O^{2-} anions and the unshaded circles represent the La^{3+} and dopant cations. The dashed circle around each dopant cation represents the optimum distance between the dopant and the O^{2-} anion.

rounding oxygen atoms isotropically within the rock-salt layer as depicted in Fig. 2a. This local ‘‘steric pressure’’ reinforces the tendency for all the La–O bonds surrounding Ba^{2+} to shorten. An LTO structure of $A_2\text{BO}_4$ is characterized by an anisotropic shortening of the A–O bands (i.e., the formation of a chain-like distortion pattern), and an LTT structure by an isotropic shortening of the A–O bonds (i.e., formation of an island-like distortion pattern) (6). Consequently, the local steric pressure of Ba^{2+} is compatible with the formation of an LTT structure. Thus the $\delta Q_1^2 Q_2^2/2$ term should decrease with increasing x , which supports the doping dependence of the coefficient δ in Eq. (3).

The T_{d2} of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (3, 12) is much lower than that of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ (1). It means that Sr^{2+} is not large enough to cause a strong local steric pressure necessary for inducing an LTO \rightarrow LTT transition at a high temperature. This explains why the T_{d2} of $\text{La}_{1.875}\text{Ba}_{0.125-x}\text{Sr}_x\text{CuO}_4$ decreases with increasing x (11). When a very small cation such as Th^{4+} is doped into the rock-salt layer of La_2CuO_4 , it is not likely to induce an isotropic contraction of the Th–O contacts because such a contraction will stretch the

adjacent La–O bonds. An energetically favorable distortion in this case would be an anisotropic movement of the small cation, as depicted in Fig. 2b, which is incompatible with the formation of an LTT structure and hence destabilizes an LTT structure thereby lowering T_{d2} . This explains why the T_{d2} of $\text{La}_{1.98-x}\text{Th}_{0.02}\text{Ba}_x\text{CuO}_4$ is lower than that of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ (1, 4).

An LTT structure is observed to occur in $\text{La}_{2-x-y}\text{Nd}_y\text{Sr}_x\text{CuO}_4$ for y greater than a critical value y_c (e.g., $y_c \cong 0.20$ for $x = 0.12$) (3). Although Nd^{3+} is smaller than La^{3+} , the two cations are comparable in size (9) so that the Nd^{3+} ions in the rock-salt layer may not undergo such an anisotropic distortion as depicted for a very small cation in Fig. 2b. Then, Nd^{3+} ions, being smaller than La^{3+} ions, would help accentuate the local steric pressure of Sr^{2+} in the rock-salt layer, thereby allowing $\text{La}_{2-x-y}\text{Nd}_y\text{Sr}_x\text{CuO}_4$ to have an LTT structure for $y \geq y_c$ at temperatures much higher than T_{d2} of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_y$. Furthermore, the T_{d2} of $\text{La}_{2-x-y}\text{Nd}_y\text{Sr}_x\text{CuO}_4$ is expected to increase either with increasing x for a fixed y or with increasing y for a fixed x . In general, these predictions are in agreement with experiment (3).

4. Concluding Remarks

We examined the doping dependence of Ishibashi's free energy function for $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ in terms of the tolerance factor and the local steric pressure of the dopant. The T_{d1} of a doped La_2CuO_4 system is lowered when the doping increases the tolerance factor. A doped La_2CuO_4 system can adopt an LTT structure only when the dopant is large enough to exert a strong local steric pressure. For such a system, the T_{d2} generally increases with increasing the doping level.

An LTT structure occurs in La_2NiO_4 (13, 14) and La_2CoO_4 (15) without any doping. The most noticeable structural feature of

these $A_2\text{BO}_4$ oxides is that the $B\text{--O}_{ax}$ to the $B\text{--O}_{eq}$ bond length ratio is considerably smaller for La_2NiO_4 and La_2CoO_4 than for La_2CuO_4 . Thus, for a given O_{ax} atom displacement in the rock-salt layer, the tilting angle of the BO_6 octahedra is larger for La_2NiO_4 and La_2CoO_4 than for La_2CuO_4 . In a doped La_2CuO_4 system with large dopant, an important consequence of the local steric pressure would be an increase in the tilting angles of the CuO_6 octahedra around each dopant. For undoped $A_2\text{BO}_4$ oxides, the $\delta Q_1^2 Q_2^2/2$ term of Ishibashi's free energy function should decrease with decreasing the $B\text{--O}_{ax}$ to the $B\text{--O}_{eq}$ bond length ratio.

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References

1. J. D. AXE, A. H. MOUDDEN, D. HOHLWEIN, D. E. COX, M. K. MOHANTY, A. R. MOODENBAUGH, AND Y. XU, *Phys. Rev. Lett.* **62**, 2751 (1989).
2. A. R. MOODENBAUGH, Y. XU, M. SUENAGA, T. J. FOLKERTS, AND R. N. SHELTON, *Phys. Rev. B* **38**, 4596 (1988).
3. M. K. CRAWFORD, R. L. HARLOW, E. M. MCCARRON, W. E. FARNETH, J. D. AXE, H. CHOU, AND Q. HUANG, *Phys. Rev. B* **44**, 7749 (1991).
4. Y. MAENO, N. KAKEHI, M. KATO, AND T. FUJITA, *Phys. Rev. B* **44**, 7753 (1991).
5. Y. ISHIBASHI, *J. Phys. Soc. Jpn.* **59**, 800 (1990).
6. M. -H. WHANGBO AND C. C. TORARDI, *Acc. Chem. Res.* **24**, 127 (1991).
7. J. F. BRINGLEY, S. S. TRAIL, AND B. A. SCOTT, *J. Solid State Chem.* **86**, 310 (1990).
8. P. GANGULY AND C. N. R. RAO, *J. Solid State Chem.* **53**, 193 (1984).
9. R. D. SHANNON, *Acta Crystallogr. Sect. A: Cryst. Phys. Diffr. Theor. Gen. Crystallogr.* **32**, 751 (1976).
10. M. KATO, Y. MAENO, AND T. FUJITA, *Physica C* **152**, 116 (1988).

11. Y. MAENO, A. ODAGAWA, N. KAKEHI, T. SUZUKI, AND T. FUJITA, *Physica C* **173**, 322 (1991).
12. T. FUKASE, T. NOMOTO, T. HANAGURI, T. GOTO, AND Y. KOIKE, *Physica B* **165** and **166**, 70 (1990).
13. H. MÜLLER-BUSCHBAUM AND U. LEHMANN, *Z. Anorg. Allg. Chem.* **447**, 47 (1978).
14. G. H. LANDER, P. J. BROWN, J. SPALEK, AND J. M. HONIG, *Phys. Rev. B* **40**, 4463 (1989).
15. K. YAMADA, M. MATSUDA, Y. ENDOH, B. KEIMER, R. J. BIRGENEAU, S. ONODERA, J. MIZUSAKI, T. MATSUURA, AND G. SHIRANE, *Phys. Rev. B* **39**, 2336 (1989).