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Simulation of Crystal Structures by Empirical Atom–Atom Potentials. 1. The Tetragonal-to-Orthorhombic Distortion in La_2CuO_4 and in the High-Temperature Superconductors $La_{2-x}M_xCuO_4$ (M = Ba, Sr)

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The high-temperature superconductors[1] $La_{2-x}M_xCuO_4$ (M = Ba, Sr; $x \simeq 0.1$–0.2; $T_c \simeq 30$–40 K) are closely related in structure to the oxide La_2CuO_4,[1h,2] which contains CuO_4 layers made up of corner-shared CuO_6 octahedra. The La^{3+} cations of La_2CuO_4 are located at the 9-coordination sites in between adjacent CuO_4 layers, and such 9-coordination sites are randomly occupied by the La^{3+} and M^{2+} cations in $La_{2-x}M_xCuO_4$. Above 533 K, the crystal structure of La_2CuO_4 is tetragonal, and its CuO_4 layers are flat.[2b] Below 533 K, however, La_2CuO_4 is orthorhombic, and its CuO_4 layers are buckled.[2a] When it was first observed that $La_{2-x}M_xCuO_4$ is tetragonal at room temperature,[1h] it was proposed[1h,3] that the tetragonal-to-orthorhombic ($T \rightarrow O$) distortion in La_2CuO_4 is a Peierls distortion,[4] and the important role the dopant M plays in $La_{2-x}M_xCuO_4$ is to suppress this distortion. However, this reasoning was found to be incorrect, since the $T \rightarrow O$ distortion (and hence the buckling of each CuO_4 layer) is not a Peierls distortion.[5] Furthermore, $La_{2-x}M_xCuO_4$ does become orthorhombic[6] well above its superconducting transition temperature (i.e., the $T \rightarrow O$ distortion at ~200–215 and ~180 K for $La_{2-x}Sr_xCuO_4$[6b–d] and $La_{2-x}Ba_xCuO_4$,[6a] respectively). The low-temperature properties of La_2CuO_4 depend sensitively upon the extent of lanthanum and oxygen vacancies.[7,8]

Table I. The Atom–Atom Potential Parameters of the $O^{2-}\cdots O^{2-}$, $Cu^{2+}\cdots Cu^{2+}$, and $La^{3+}\cdots La^{3+}$ Pairs

pair	B (eV)	ρ (Å)	C (eV Å^6)
$O^{2-}\cdots O^{2-}$	1387.7	0.375	63.31
$Cu^{2+}\cdots Cu^{2+}$	269.10	0.264	0.5586
$La^{3+}\cdots La^{3+}$	28855	0.250	325.0

Nonsuperconducting samples of La_2CuO_4 are susceptible to an antiferromagnetic (AFM) ordering,[8] and the electron localization associated with this AFM ordering is suppressed by the dopant M in $La_{2-x}M_xCuO_4$. Since the $T \rightarrow O$ distortion is not a Peierls distortion,[5] the buckling of an individual CuO_4 layer in La_2CuO_4 or $La_{2-x}M_xCuO_4$ does not stabilize the electronic energy.[5a] Therefore, the $T \rightarrow O$ distortion and the CuO_4 layer buckling in La_2CuO_4 must originate from the ionic interactions involving the La^{3+} cations.[5a] In the present work, we evaluate these interactions on the basis of empirical atom–atom potentials.[9]

For ions i and j separated by the distance r_{ij} with the charges q_i and q_j, respectively, their Coulomb (W_c), nonbonded repulsion (W_{nr}), and van der Waals attraction (W_v) energies are expressed by[9] $W_c = q_iq_j/r_{ij}$, $W_{nr} = B_{ij} \exp(-r_{ij}/\rho_{ij})$, and $W_v = -C_{ij}/r_{ij}^6$, where the constants B, ρ, and C are adjustable parameters to be determined on the basis of experimental data. We assume that the B, ρ, and C values between different ions are related to those between identical ions as[9d,10]

$$B_{ij} = \sqrt{B_{ii}B_{jj}}$$

$$1/\rho_{ij} = (1/\rho_{ii} + 1/\rho_{jj})/2 \qquad \text{and}$$

$$C_{ij} = \sqrt{C_{ii}C_{jj}} \tag{1}$$

The constant C_{ii} for a pair of identical ions i is approximated by[9c]

$$C_{ii} = 3I_iP_i^2/4 \tag{2}$$

where I_i and P_i are the ionization potential and the polarizability of the ion i, respectively. With eq 1, it is necessary to determine the B, ρ, and C values only for the $O^{2-}\cdots O^{2-}$, $Cu^{2+}\cdots Cu^{2+}$, and $La^{3+}\cdots La^{3+}$ pairs to define all the atom–atom potentials present in La_2CuO_4. Starting with the B, ρ, and C values of the $O^{2-}\cdots O^{2-}$ pair determined for the O–O distance range of 2.64–5.29 Å in MnO,[11,12] we use the WMIN program of Busing[13] to derive[14] the B, ρ, and C values for the $Cu^{2+}\cdots Cu^{2+}$, $La^{3+}\cdots La^{3+}$, and $O^{2-}\cdots O^{2-}$ pairs that reproduce the unit cell and atom positional parameters of CuO[15] and La_2O_3.[16] The B, ρ, and C parameters thus obtained are listed in Table I. As summarized in Table II, these B, ρ, and

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Table II. The Experimental and Calculated Values for the Unit Cell and Atom Positional Parameters of the CuO, La_2O_3, and La_2CuO_4 Crystals[a,b]

CuO[15] monoclinic (*C*2/*c*)	La_2O_3[16] trigonal (*P*$\bar{3}$*ml*)	La_2CuO_4[1h] orthorhombic (*Cmca*)	La_2CuO_4 tetragonal (*I*4/*mmm*)
a = 4.6837 (−0.0321)	a = 3.930 (−0.029)	a = 5.3562 (−0.0078)	a = 3.7945
b = 3.4226 (−0.0644)	c = 6.120 (0.196)	b = 13.1669 (0.1015)	c = 13.1205
c = 5.1288 (0.0233)	z(La) = 0.235 (0.012)	c = 5.3990 (0.0129)	z(La) = 0.3633
β = 99.54 (−1.82)	z(O) = 0.630 (0.032)	y(La) = 0.3613 (0.0011)	z(O2) = 0.1827
z(O) = 0.4184 (0.0065)		z(La) = 0.0061 (0.0018)	
		y(O1) = 0.0070 (0.0056)	
		y(O2) = 0.1842 (−0.0007)	
		z(O2) = −0.0336 (−0.0153)	

[a] Except for tetragonal La_2CuO_4, the experimental values are the numbers without parentheses. The numbers in the parentheses refer to the deviations of the calculated values from the corresponding experimental ones. [b] The cell parameters a, b, and c are in units of Å, and the angle β is in units of deg.

C values describe the crystal structures of CuO and La_2O_3 quite well.[19]

To evaluate the energetics associated with the T → O distortion in La_2CuO_4, we employ the WMIN program and calculate the crystal energy of La_2CuO_4 as a function of its unit cell and atom positional parameters on the basis of the atom–atom potentials generated by the *B*, *ρ*, and *C* values of Table I. As summarized in Table II, the crystal structure of orthorhombic La_2CuO_4 is very well reproduced by the present atom–atom potential calculations.[19] Under the space group *Cmca*,[1h] the crystal structure of La_2CuO_4 is calculated to remain orthorhombic [i.e., the z(La), y(O1), and z(O1) values are nonzero], although this space group does not prevent La_2CuO_4 from becoming tetragonal. Also listed in Table II are the optimum unit cell and atom positional parameters of tetragonal La_2CuO_4, calculated by imposing the space group *I*4/*mmm*, which are very close to the unit cell and atom positional parameters of tetragonal $La_{1.85}Ba_{0.15}CuO_4$ at room temperature.[1h] According to the optimum structures of orthorhombic and tetragonal La_2CuO_4 obtained by the present atom–atom potential calculations, La_2CuO_4 is more stable in the orthorhombic than in the tetragonal structure by 1.85 kcal/mol per formula unit La_2CuO_4. This small energy difference seems quite reasonable, given the small structural difference between the two structures. We now examine how the dopants M might affect the T → O distortion. The Sr^{2+} and Ba^{2+} cations are larger in ionic radius than the La^{3+} cation,[20] and, in average, the copper atoms of $La_{2-x}M_xCuO_4$ are in a higher oxidation state and hence are smaller in size than those of La_2CuO_4. In general, a larger cation gives rise to greater nonbonded repulsions and can be characterized by a larger *B* or *ρ* value in the nonbonded repulsion terms associated with the cation. To simulate the crystal structure of $La_{2-x}M_xCuO_4$, therefore, we perform the atom–atom potential calculations on orthorhombic La_2CuO_4 by increasing the *B* value for the $La^{3+}\cdots La^{3+}$ pair and decreasing that for the $Cu^{2+}\cdots Cu^{2+}$ pair. With such changes in the two values, La_2CuO_4 is calculated to be orthorhombic but "less orthorhombic" in that the z(La), y(O1), and z(O2) values become closer to zero. That is, the driving force for the T → O distortion is diminished in $La_{2-x}M_xCuO_4$, and thus the T → O distortion temperature would be lower in $La_{2-x}M_xCuO_4$ than in La_2CuO_4. Since the Ba^{2+} cation is larger in size than the Sr^{2+} cation,[20] the T → O distortion temperature would be lower in $La_{1.85}Ba_{0.15}CuO_4$ than in $La_{1.85}Sr_{0.15}CuO_4$. These predictions are all in agreement with experiments.[2b,6]

In summary, the T → O distortion in both La_2CuO_4 and $La_{2-x}M_xCuO_4$ is not driven by an electronic instability, such as a Peierls distortion but by the ionic interactions involving the La^{3+} ions (and the M^{2+} ions as well in the doped materials).

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A Regioselective Mechanism for Mutagenesis and Oncogenesis Caused by Alkylnitrosourea Sequence-Specific DNA Alkylation[1]

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In the standard mechanism for alkylnitrosourea (ANU) alkylation of DNA in vitro and in vivo,[2] reactive intermediates formed hydrolytically in cytosol by the sequence ANU ⇒ $\mathrm{RCH_2N{=}N{-}OH \rightarrow RCHN_2 \rightleftharpoons RCH_2N_2^+ \rightarrow}$ "$\mathrm{RCH_2^+}$" are thought to react with DNA nucleophiles by direct displacement, a process that should give a random distribution of products. Indeed, the "S_N2" reagents dimethylsulfate and 2-chloroethyl-(methylsulfonyl)methane sulfonate give random, nonsequence specific products at N_7-guanine (N_7-dG) in pBR-322 DNA.[3] Yet the powerful mutagenic[4] and oncogenic[5] properties of the ANUs 1-methyl-(MNU) and 1-ethyl-1-nitrosourea (ENU) are related to site- and sequence-specific alkylation of O^6-dG_2 in a 5′-dGdGdN-3′ DNA codon, where dN is any base; neither N_7-dG_1 nor O^6-dG_1 is alkylated.[3-5] Sequence-specific reactions of ANUs

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