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An Ionic Model of the Crystal Chemistry in the Superconducting Copper Oxides of Stoichiometry $(RE)_2CuO_4$

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The mixed rare earth systems $La_{2-x}RE_xCuO_4$ (RE = Nd–Y) have been investigated in an effort to understand the crystal chemistry and phase stability of the related K_2NiF_4 (T)-, Nd_2CuO_4 (T')-, and hybrid T^*-type structures. The crystal chemistry of these $(RE)_2CuO_4$ phases is then discussed on the basis of a simple ionic model. A definitive correlation between the size of the RE cation and structure is found, and the stability limits of the T, T', and T^* phases are defined in terms of a perovskite-like tolerance factor (t). The T structure is found to exist for $0.87 \leq t \leq 0.99$, while the T' structure occurs for $0.83 \leq t \leq 0.86$. The smallest rare earths, or $t \leq 0.83$, do not form stable $(RE)_2CuO_4$ compounds. The T^* structure occurs in a very narrow region adjacent to the boundary of the T/T' stability field and is seen as resulting from a thermodynamic competition between the T and T' structures, due to a tendency toward T/T'-site ordering. Metastable T^* phases are observed for the larger rare earths Nd, Eu, and Gd, but the structure becomes quite stable for RE = Tb, Dy. Where both T' and T^* are of comparable thermodynamic stability, high oxygen activity is found to stabilize T^*, whereas low oxygen activity favors T'. The role of RE coordination preferences and the influence of the RE–O framework upon the structure and properties of these materials are discussed. © 1990 Academic Press, Inc.

Introduction

The rare earth copper oxides of stoichiometry $(RE)_2CuO_{4+\delta}$ (RE = rare earth) possess a richness of structural and physical properties as a consequence of the wide range in rare earth ion sizes, and the fact that some deviation in oxygen stoichiometry from its ideal value can be tolerated (*1–6*). There are three closely related structure types with stoichiometry $(RE)_2CuO_4$, each containing isolated sheets of fourfold (T' structure), fivefold (T^* structure), or sixfold (T structure) Cu–O coordination. For the largest rare earth cation (La), $(RE)_2CuO_4$ crystallizes in a slightly distorted K_2NiF_4 (*7, 8*) T structure (Fig. 1a). $La_2CuO_{4+\delta}$ contains perovskite-like sheets of elongated CuO_6 octahedra, sharing corners in the (001) planes and separated by rock-salt-like La–O layers in which La^{3+} is ninefold coordinated by oxide. The properties of $La_2CuO_{4+\delta}$ are extremely sensitive to changes in oxygen stoichiometry (*9, 10*). For a slightly negative value of δ ($-0.3 \leq \delta \leq 0.0$), $La_2CuO_{4+\delta}$ is an antiferromagnetic semiconductor with a Néel temperature of 257 K (*11*). Antiferromagnetism disappears with changes in oxygen stoichiometry as small as 1%. As δ becomes positive (i.e., as

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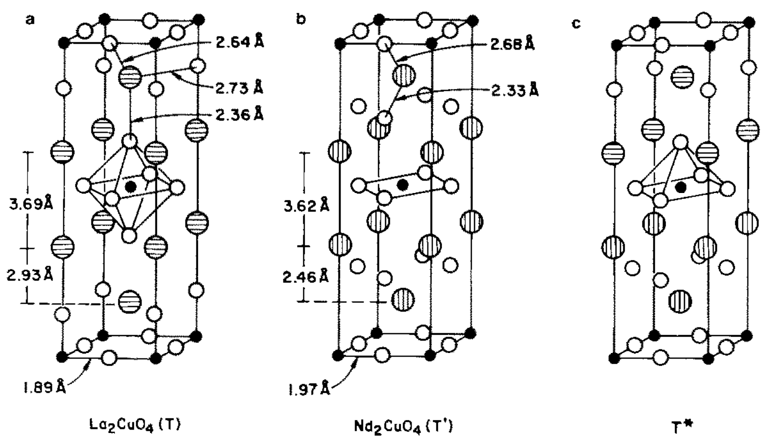

FIG. 1. Illustration of the *T*, *T*′, and *T** structures including some relevant bond and interplanar distances. Cu, solid circles; O, open circles; and Rare earth, shaded circles.

holes are introduced into the structure), a trend toward metallic behavior is observed. Finally, $La_2CuO_{4+\delta}$ becomes superconducting at temperatures as high as 40 K when doped with holes either by replacing some of the La with Ca, Sr, Ba, or Na (e.g., $La_{1.85}Sr_{0.15}CuO_4$, $T_c = 38$ K (*12*)) or by introducing excess oxygen into the structure (e.g., $La_2CuO_{4.13}$, $T_c = 38$ K (*9, 13*)).

The rare earth ions of intermediate size (Pr–Gd) assume the *T*′ structure of Nd_2CuO_4 (*5*) (Fig. 1b). In this structure (*14*), two-dimensional square-planar CuO_2 sheets share corners in the (001) planes and are separated by NdO_2 fluorite-type layers. The rare-earth ion is now eightfold coordinated by oxygen, and in contrast to $La_2CuO_{4+\delta}$, compounds with the *T*′ structure superconduct only when electron-doped, e.g., $Nd_{1.85}Ce_{0.15}CuO_4$, $T_c = 24$ K (*3*); $Nd_2CuO_{3.6}F_{0.4}$, $T_c = 27$ K (*15*). The properties of the *T*′ phases also depend strongly on oxygen stoichiometry. For example, superconductivity in $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ can be turned on (or off) by changes as small as 1% in oxygen content (*16, 17*). Band calculations (*18*) and muon spin rotation experiments (*19*) have shown that the electronic structures of La_2CuO_4 and Nd_2CuO_4 are very similar and that their physical properties may be symmetric with respect to hole and electron doping. Many authors have observed that the *T* structure (La_2CuO_4) can be easily doped with holes, but not with electrons, while the opposite is true for the *T*′ structure (*3, 20*).

A third RE_2CuO_4 structure, denoted *T**, is observed with certain *A*-site rare earth and alkaline earth cations (e.g., $LaGd_{0.8}Sr_{0.2}CuO_4$) (*4, 21*). Neutron diffraction studies have shown that the *T** structure consists of a hybrid of the *T* and *T*′ structures (*22, 23*). The *T** phase contains sheets of CuO_5 square-pyramids sharing corners in the (001) planes (Fig. 1c) and separated along (001) by alternating RE–O rock-salt and REO_2 fluorite layers. Thus, the structure contains two crystallographically independent rare earth ion sites: a ninefold-coordinated "*T* site," and an eightfold-coordinated "*T*′ site." The majority of known *T** phases require the presence of Sr^{2+} to stabilize the structure; only two "undoped" *T** phases have been reported: $La_{2-x}Tb_xCuO_4$; $x = 0.6$, 0.7 (*24*), and $La_{1.1}Dy_{0.9}CuO_4$ (*25*). Recently, it has been shown that the Sr-doped materials become superconducting ($T_c \approx 30$ K) after annealing in high-pressure oxygen (*26*). Although rare earth cation ordering is thought to play an important role in forming this phase, the precise factors governing T^* stability are not understood.

In an effort to understand the crystal chemistry, phase stability, and doping preferences of the T, T', and T^* phases, we have investigated the systems $La_{2-x}(RE)_x CuO_4$ (RE = Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb, and Y). The relative simplicity of these rare earth systems allows us to examine how structure and stability are related to ionic size effects and cation ordering. The results of these studies are explained within the framework of a simple ionic model, in which a perovskite-like tolerance factor (t) is found to be a remarkable predictor of T, T', and T^* stability limits. From this correlation, the T^* structure is seen to be the result of thermodynamic competition at the boundary between the T and T' stability fields due to the tendency toward T-/T'-site ordering. In addition, oxygen activity is found to have a very strong influence upon the crystal chemistry of these phases.

Experimental

All starting materials were high purity compounds (≥99.99%) purchased from AESAR. Lanthanum oxide was dried and CO_2 removed by firing the powder at 950°C prior to use; all other reactants were used as received. Powdered mixtures of rare-earth and copper oxides were heated in Pt crucibles for 24 hr, ground and pelletized, and reheated at temperatures ranging from 900 to 1150°C (48–72 hr). The samples were then cooled (100°C/hr) or quenched in air. In some cases it was necessary to refire the mixtures several times, with intermediate grindings and pressings, to achieve equilbrium phase assemblages. A coprecipitation technique was also used in attempts to prepare pure T^* phases. Stoichiometric amounts of the oxides were dissolved in concentrated HNO_3 by gentle heating and then diluted fivefold with deionized H_2O. Aqueous 6 *N* NaOH was then added with stirring until the solution became slightly basic (pH ≃ 10), and a gelatinous blue precipitate appeared. The precipitate was removed by filtration, washed with copious amounts of deionized H_2O, and then slowly decomposed by heating to the desired temperature at a rate of 50°C/hr under flowing O_2.

High-pressure oxygen reactions were performed in an externally heated René alloy vessel (LECO MRA-414) pressurized at room temperature with high purity gas (99.999%) from a standard laboratory cylinder. Reaction temperatures were measured with a chromel–alumel thermocouple inserted in a shallow recess in the reactor wall at the sample position, and pressures were measured with an uncalibrated gauge.

Powder X-ray diffraction data were obtained on a Seimens D500 diffractometer using Cu*Kα* radiation. Lattice parameters were refined by the least-squares method in which systematic errors associated with sample thickness, sample offset, and zero-angle calibration were corrected in the refinement program. Oxygen stoichiometry was measured by iodometric titration (*27*) using degassed solutions of 6 *N* $HCl_{(aq)}$ and distilled water. Experiments were repeated in duplicate or triplicate to ensure agreement in the stoichiometry to within ±0.5%. Superconducting critical temperatures were determined by the AC mutual inductance method.

Experimental Results

I. The $La_{2-x}Nd_xCuO_4$ *System*

A study of the mutal solid solubility of La_2CuO_4 (T) and Nd_2CuO_4 (T') provides a measure of the relative stabilities of these hole and electron superconductors. The lattice parameters and unit cell volumes of

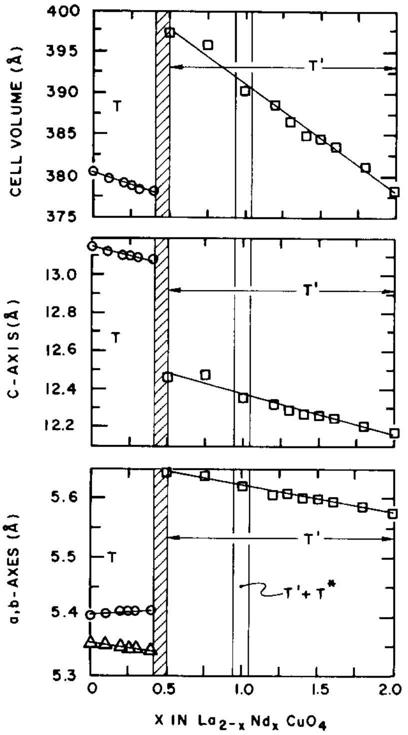

FIG. 2. La$_2$CuO$_4$/Nd$_2$CuO$_4$ phase diagram at 1050°C, including lattice parameters and unit-cell volume plotted as a function of x in La$_{2-x}$Nd$_x$CuO$_4$. The two phase region shown near $x = 1$ indicates nonequilibrium data (see text).

La$_{2-x}$Nd$_x$CuO$_4$ as a function of composition for samples quenched from 1050°C are plotted in Fig. 2. The T structure of La$_2$CuO$_4$ is found to occur for $0 \leq x \leq 0.4$. In this regime the orthorhombicity (b–a) increases with x, while the structure is simultaneously contracting along the c-axis. A narrow two phase region occurs for $0.4 \leq x \leq 0.5$, and the T' structure of Nd$_2$CuO$_4$, with its larger cell volume, dominates the system up to $x = 2$, provided that the system is quenched from equilibrium. In the transformation from T to T', the c-axis is reduced by 4.7%, which is more than compensated by a 5% elongation along the a-axis of the structure, resulting in a considerably larger cell volume in the T' phase.

Our results for La$_{2-x}$Nd$_x$CuO$_4$ indicate greater solubility of Nd in the T phase than reported by Singh *et al.* (*28*). More significant, however, is the observation of yet a third phase, whose X-ray powder pattern can be indexed with the T^*-type structure, appearing in phase assemblages near $x = 1$. In Fig. 3 is shown a portion of the X-ray powder diffraction profile for a sample of composition LaNdCuO$_4$ heated to 950°C for 36 hr in air. Reflections from the T' and T^* phases are clearly separated, and the indexed patterns give lattice parameters $a(T') = 3.967(3)$ Å, $c(T') = 12.323(4)$ Å; and $a(T^*) = 3.891(1)$ Å, $c\ (T^*) = 12.46(1)$ Å. As expected, the lattice parameters of the hybrid T^* phase fall between those of La$_2$CuO$_4$ and Nd$_2$CuO$_4$. Using Fig. 2, and the fact that $x = 1$, it is possible to infer a T' phase composition La$_{0.8}$Nd$_{1.2}$CuO$_4$. Assuming approximately equal amounts of T^* and T' phase on the basis of X-ray intensities, the composition of the T^* phase would be La$_{1.2}$Nd$_{.8}$CuO$_4$. The composition range $0.9 \leq x \leq 1.1$ in La$_{2-x}$Nd$_x$CuO$_4$ consistently showed T' and T^* phases; however, T^* could be eliminated and single phase LaNd CuO$_4$ obtained by prolonged heating of the samples (≥1 week) at 1100°C with repeated grindings. Since the effect of prolonged reaction even at lower temperatures is to appreciably reduce the amount of T^* phase

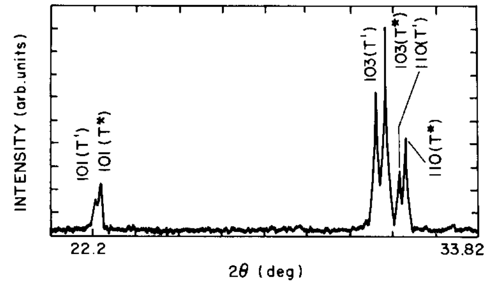

FIG. 3. A portion of the X-ray powder diffraction profile of LaNdCuO$_4$ with Miller indices indicating the contributions of both the T' and T^* phases.

present, it is concluded that T' is the thermodynamically more stable phase.

There have been several reports of superconductivity at temperatures of ~40 K $La_2CuO_{4+\delta}$ after treatment at high oxygen pressures (0.15–3 kbar) (*9*, *12*). Samples of orthorhombic, T-phase $La_{2-x}Nd_xCuO_4$ ($0.0 \le x \le 0.4$) annealed at 500°C (24 hr) and an oxygen pressure of 270 bar showed no evidence of superconductivity down to 4 K. As a check, superconductivity was observed in our $x = 0$ samples at 30 K. Even higher oxygen activities may be required to induce T phase superconductivity in the presence of Nd.

In order to assess the effect of oxygen stoichiometry upon $La_{2-x}Nd_xCuO_4$, the oxygen content was determined for samples cooled in air at 100°C/hr from 1050°C. In contrast to the results of Moran *et al.* (*29*), who observed excess oxygen in Ce-doped and undoped Nd_2CuO_4, we have found that the oxygen content per formula unit varies only slightly from 4.00 throughout the phase fields of T, T', and T^*. The values obtained ranged from 3.98 to 4.03 (±0.02).

II. La(RE)CuO$_4$ Systems

Observation of the T^* phase in $La_{2-x}Nd_xCuO_4$ led us to examine its possible occurrence in other $La_{2-x}(RE)_xCuO_4$ systems near $x = 1$; for RE = Sm, Eu, Gd, Dy, Ho, Er, Yb, and Y. The rare earth ions of intermediate ionic size, Sm and Eu, form two-phase T'/T^* mixtures (~70 : 30) when prepared from the coprecipitated hydroxides after heating at 950°C. However, on heating to 975°C, $LaSmCuO_4$ and $LaEuCuO_4$ become single phase T' after 48 hr at reaction temperature. Much longer times and higher temperatures were necessary to prepare single phase T' directly from the oxides. The T^* phase forms as a majority component in the system $La_{2-x}Gd_xCuO_4$ for $0.9 \le x \le 1.1$. This system nevertheless always contains a significant amount of T' phase even after prolonged heating (≥100 hr) at different temperatures. Repeated attempts to prepare single-phase T^* $LaGdCuO_4$ by reacting the coprecipitated hydroxides in air or oxygen at 800–950°C were not successful. However, we have found that both the percentage of T^* phase and the sharpness of its diffraction peaks are enhanced if synthesis is carried out at high oxygen pressures (270–350 bar), indicating that the T^* phase may be stabilized under high oxygen activity. Furthermore, heating $LaGdCuO_4$ at higher temperatures (1100°C) in air or at 1000°C in nitrogen atmosphere results in a single phase T' material.

$La_{2-x}Dy_xCuO_4$ can be prepared as single phase T^* for $0.8 \le x \le 1.0$. These materials were obtained by slow decomposition of the hydroxides (50°C/hr to 950°C/(24 hr)) followed by cooling (50°C/hr) under an oxygen flow. The X-ray powder diffraction pattern of $La_{1.2}Dy_{.8}CuO_4$ is shown in Fig. 4. The sample contains only the T^* phase with lattice parameters $a = 3.8604(3)$ Å and $c = 12.427(6)$ Å. Tao *et al.* (*25*) have prepared a T^* phase at 1050°C at the composition $La_{1.1}Dy_{.9}CuO_4$ using oxide precursors, but no homogeneity range is reported.

No evidence was found for T^* phases in the $La_{2-x}RE_xCuO_4$ systems at $x = 1$ for the smallest ions Ho, Er, Yb, and Y. Instead, three-phase equilibria involving La_2CuO_4 (T), $RE_2Cu_2O_5$ (*30*), and CuO were observed, with the T phases containing a small amount of RE in solid–solution.

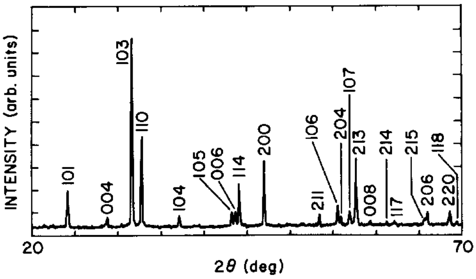

FIG. 4. X-ray powder diffraction profile of the T^* phase $La_{1.2}Dy_{.8}CuO_4$ with Miller indices indicated.

The difficulty in obtaining single phase materials seems to be quite general for compounds with the T^* structure (*4, 23, 26*), suggesting that the free energies of formation of T, T', and T^* are all very similar. This is not surprising in view of the relationship between the structure types. Synthesis of the T^* phase via the hydroxide route offers some distinct advantages over the direct oxide method, since mixing is easily obtained on a submicron (and possibly smaller) scale. This results in an enhancement of kinetics at significantly lower temperatures. The lower temperatures are particularly important for T^* phase synthesis, since T^* tends to be unstable relative to T' at the higher temperatures necessary to get the oxides to react. It is interesting that only for the smaller rare earth ions Tb (*24*) and Dy can relatively pure $(La,RE)CuO_4$ T^* phase be isolated. As the RE ionic size increases toward that of lanthanum, the T^* phase becomes metastable. The reasons for this behavior can be understood by examining the stabilities of the RE–O coordinations in the T, T', and T^* structures.

Discussion

I. General Considerations

The commonality of features in perovskite and K_2NiF_4 structures suggests that the rules governing the former should also apply to T-phase stability. Indeed, a "tolerance factor" derived from perovskite has been used to rationalize the wide occurrence of a T lattice among mixed metal oxides of A_2BO_4 stoichiometry (*2, 31*). It will be shown here that this approach provides a simple yet complete framework to explain the stability fields of the T, T', and T^* phases. In terms of A–O and B–O ionic bonding and coordination requirements, the tolerance factor for perovskite can be defined as $t = (r_A + r_O)/\sqrt{2}(r_B + r_O)$, where the radii are those of the A-site, B-site, and oxide ions in the cubic perovskite cell. In comparing the relative stabilities of T, T', and T^*, the RE–O coordination of the T structure is the most suitable reference state, for which $t = 1$ represents the "ideal" arrangement with perfect fitting of the RE cation into the A site. Therefore, tolerance factors were calculated using ionic radii appropriate to ninefold RE–O coordination.

The solid–solution limit of the T structure in the $La_{2-x}Nd_xCuO_4$ system occurs at $x = 0.4$; the average rare earth cation radius at this composition is 1.205 Å. In other $La_{2-x}RE_xCuO_4$ systems, T-phase solid–solution limits and average rare earth cation sizes at these extrema are Sm: $x = 0.2$, 1.208 Å; Eu: $x = 0.3$, 1.202 Å; and Gd: $x = 0.3$, 1.200 Å (*32*). From these values, the $T \rightarrow T'$ transition takes place sharply at an average RE cation radius of 1.204(4) Å. This corresponds to a tolerance factor $t = 0.865$, defining the lower stability limit of the K_2NiF_4 structure. The tolerance factors calculated for a number of cuprates and other ternary metal oxides exhibiting the K_2NiF_4 and Nd_2CuO_4 structures are listed in Table I. (Tolerance factors have been calculated for all the observed T and T' compounds and their solid–solutions; however, for brevity only a few representative systems are included here.) From this tabulation, it can be concluded that the K_2NiF_4 structure is stable for $0.87 \leq t \leq 0.99$. Further, the T structure is orthorhombically distorted at the lower boundary of its range, $0.87 \leq t \leq 0.88$. The T' phase observed below the transition point appears to occur only in the cuprates. In this ionic model, it would be expected to occur in all A_2BO_4 compounds for which $t < 0.865$, provided they contain B-site cations stable in square-planar coordination. We will return to this point in the subsequent discussion. Remarkably, the $T \rightarrow T'$ transition occurs at $t = 0.865$ for all the cuprate systems studied to date. The T' structure itself exists only in

TABLE I

TOLERANCE FACTORS (t) FOR OXIDES WITH THE K_2NiF_4(T) AND Nd_2CuO_4(T') STRUCTURES

T phases

Compound	t^a	Ref.	Compound	t	Ref.
Sr_2TiO_4	0.956	(*33*)	$Pr_2NiO_4{}^d$	0.873	(*2*)
$LaSrVO_4$	0.923	(*2*)	$Nd_2NiO_4{}^d$	0.867	(*2*)
$LaSrCrO_4$	0.935	(*34*)	$GdSrNiO_4$	0.941	(*2*)
$NdSrCrO_4$	0.925	(*34*)	$La_2CuO_4{}^d$	0.868	(*6*)
$GdSrCrO_4$	0.915	(*34*)	$LaSrCuO_4$	0.971	(*37*)
Ca_2MnO_4	0.945	(*33*)	$La_{1.9}Sr_{.1}CuO_4$	0.879	(*37*)
Sr_2MnO_4	0.993	(*33*)	$LaSrAlO_4$	0.973	(*2*)
$LaSrMnO_4$	0.976	(*34*)	$LaSrGaO_4$	0.932	(*34*)
$PrSrFeO_4{}^b$	0.914	(*2*)	Sr_2MoO_4	0.917	(*33*)
$GdSrFeO_4$	0.902	(*2*)	Sr_2RuO_4	0.921	(*33*)
$LaSrCoO_4$	0.968	(*34*)	Sr_2IrO_4	0.921	(*33*)
$La_2CoO_4{}^{c,d}$	0.865	(*35*)	Ba_2PbO_4	0.933	(*33*)
La_2NiO_4	0.885	(*36*)	Sr_2SnO_4	0.917	(*33*)

T' phases

Compound	t	Ref.	Compound	t	Ref.
$La_{1.5}Nd_{.5}CuO_4$	0.864	(*39*)	Eu_2CuO_4	0.837	(*38*)
Pr_2CuO_4	0.856	(*38*)	Gd_2CuO_4	0.832	(*38*)
Nd_2CuO_4	0.851	(*38*)	$LaNdCuO_4$	0.860	(*39*)
Sm_2CuO_4	0.841	(*38*)	$LaSmCuO_4$	0.855	(*39*)
$LaEuCuO_4$	0.853	(*39*)	$Nd_{1.85}Ce_{.15}CuO_4$	0.847	(*3*)

[a] Shannon's ionic radii (*Acta Crystallogr. A* **32**, 751, 1976) are used with the transition metal and oxygen in sixfold coordination. For the sake of consistency, all data are calculated for rare earth ions in ninefold coordination geometry.

[b] All Pr ions are assumed to be in a 3^+ oxidation state.

[c] High-spin Co^{2+}, all others in lower spin state.

[d] Orthorhombically distorted K_2NiF_4 structure.

the narrow range $0.83 \leq t \leq 0.86$. Rare earth–copper oxide systems with $t < 0.83$ do not form RE_2CuO_4 phases at ambient pressures; only $RE_2Cu_2O_5$ compounds (*30*) with sixfold-coordinated RE sites are known for these smaller rare earths (Ho–Lu, Y).

A complete summary of the results of the present work has been collected in Fig. 5, where compound and solid–solution compositions are plotted vs the tolerance factor, calculated using the average value for the mixed rare earth systems. Shown in Fig. 5 are points for T^* phases observed in this work and several previous studies, including those we have observed to be metastable. For clarity, previously published Sr-doped T^* phases have not been included; nevertheless, we find that without exception all the data place T^* into a very narrow region adjacent to the T/T' boundary. This result will be examined subsequently in greater detail. T-type structure data for noncuprate systems included in Fig. 5 show the full range of the correlation.

A. The tetragonal to orthorhombic distortion. The first indication of T-phase instability in the copper oxide systems is the occurrence of orthorhombic La_2CuO_4 at the T/T' boundary of Fig. 5. In the context of the present ionic model, La_2CuO_4 is orthorhombic because the structure must "pucker" to accommodate La in the ninefold site, i.e., lanthanum itself is of borderline stability in the ninefold coordinate structure. As even smaller rare earth cations replace La in $La_{2-x}RE_xCuO_4$, the degree of orthorhombicity increases with increasing x until a transformation to the tetragonal Nd_2CuO_4 structure occurs at $t = 0.865$ (cf., Fig. 2). The orthorhombic structure can therefore be thought of as distortion originating in the RE–O layers, signaling the onset of the instability which eventually leads to the T' phase. Electronic factors may also be involved in the transition, for the energy of the Cu^{2+}-like x^2–y^2 antibonding states can be lowered by such a distortion (*40*). In addition, since it involves a cooperative displacement of the LaO rock-salt (*8*), the La–O bond strength may increase as well. This would be consistent with band structure calculations, which show that the driving force for the tetragonal to orthorhombic distortion originates from La–O interactions (*41*). Thus, several factors may combine to produce the distortion. When the average RE radius becomes too small, the orthorhombic phase itself becomes unstable and a major transformation to the T' structure occurs. Our results reveal a critical point for the transition in the cuprates at an average RE radius corresponding to $t \approx 0.865$.

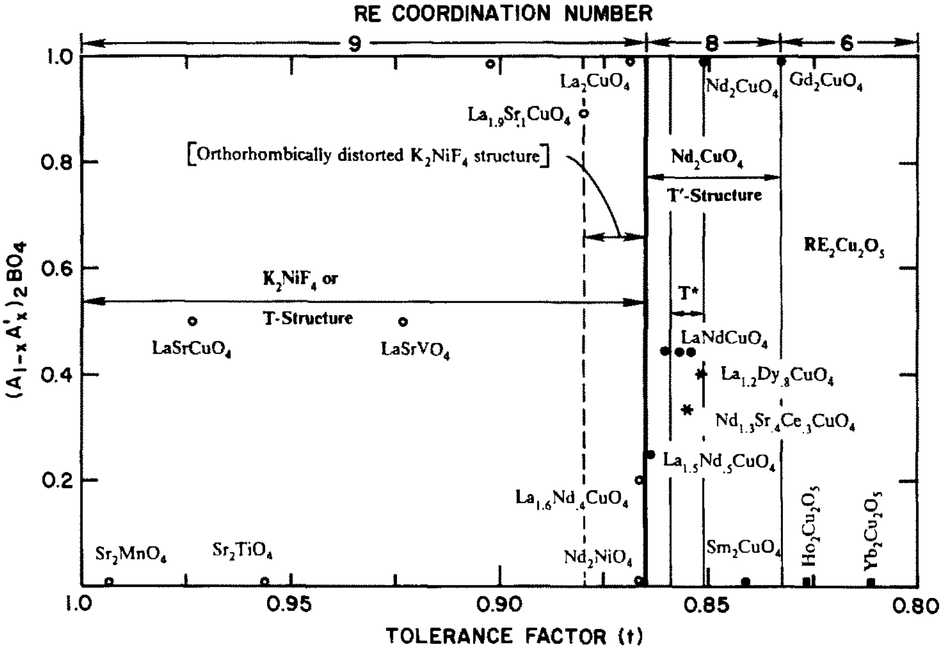

FIG. 5. Compositions of discrete phases and solid–solutions exhibiting the T, T', and T^* structures found in (La,RE)$_2$CuO$_4$. The boundaries are based on the results of this study; for clarity only a few points are represented. Some metastable T^* phases are included but not labeled for clarity. Several noncuprates are also tabulated. The rare earth coordination number in the discrete phases is indicated at the top of the figure.

B. The T to T' transition. As mentioned above, La^{3+} is of borderline stability in the ninefold site of the K$_2$NiF$_4$ (T) cuprates. It is not surprising then that, as La^{3+} is replaced by the smaller Nd^{3+} ion, we observe a transition to the lower density, lower coordinate Nd$_2$CuO$_4$ (T') structure. The transition from the La$_2$CuO$_4$ to the Nd$_2$CuO$_4$ structure also creates, on average, considerably shorter RE–O distances. The average La–O distance in La$_2$CuO$_4$ (*8*) is already quite long (2.65 Å) compared, for example, to La$_2$O$_3$ (2.54 Å) (*43*). The average Nd–O bond distance in Nd$_2$CuO$_4$ is 2.50 Å (*14*). In addition, while La$_2$CuO$_4$ contains one very short La–O contact at 2.36 Å, the Nd$_2$CuO$_4$ structure is able to provide four RE–O contacts at approximately this distance (cf., Fig. 1). Thus, the $T \rightarrow T'$ transition apparently occurs to optimize RE–O distances.

One of the most striking features of the transition from the T to the T' structure is the dramatic increase in cell volume observed (cf., Fig. 2). This would not be expected based upon rare earth size alone, since La^{3+} is larger than Nd^{3+} and the other RE cations with which lanthanum forms a T'-phase solid–solution. Furthermore, this effect is not manifested uniformly throughout the structure as the a-axes are elongated, but the c-axis is compressed in the T' structure. The structural deformations on traversing the $T \rightarrow T'$ transition can clearly be understood as the result of the different RE–O arrangements (rock-salt-like vs fluorite-like) in the T and T' phases.

The transformation from rock-salt to fluorite-like RE–O layers results in much shorter O–O contacts in the (001) plane of the T' compounds. For example, anion–anion spacing in the RE–O layers is equal to the a-parameter in the T phases, but is related by $a/\sqrt{2}$ in the T' phases. Indeed, the O–O distance in Nd_2CuO_4 is 2.79 Å, about equal to the sum of ionic radii (2.80 Å), and is even smaller in the T' compounds of Gd and Eu (*8*). The result is that the fluorite layers must expand along the a-axes to diminish O–O repulsions. This has a profound effect upon the Cu–O planes in Nd_2CuO_4, as the in-plane Cu–O bond distance (1.97 vs 1.89 Å in La_2CuO_4) must then elongate to match the periodicity of the fluorite layers. Thus, it is the rock-salt and fluorite RE–O layers that determine the bond lengths in the Cu–O sheets of the T and T' structures. These factors further emphasize the dominant role of the RE–O layers in determining the crystal chemistry of $(RE)_2CuO_4$ compounds.

Ganguly and Rao (*2*) have interpreted the $T \rightarrow T'$ transition in terms of a competition between RE and Cu ions for bonding with the apical oxygens of La_2CuO_4, asserting that the smaller rare earths destabilize the structure by elongating the Cu–O bond in this competition. The much shorter Nd–O distances and longer Cu–O distances in Nd_2CuO_4 clearly show that the transition occurs at the expense of Cu–O bonding, and is consistent with our view that the primary driving force originates in the RE–O layer. The optimum way to improve bonding upon introducing smaller RE cations into the T structure would be through compression of the Cu–O sheets. However, the in-plane Cu–O bond distances in La_2CuO_4 are already very short (1.89 Å), the shortest of all the cuprates, and such a compression would further destabilize the antibonding x^2–y^2 band. Under these circumstances, lower coordination is favored and a major transformation occurs to T', where on the average shorter RE–O distances are realized.

It is interesting that the T' structure appears to occur only in cuprate crystal chemistry. Tolerance factor considerations would predict that RE_2NiO_4 phases should adopt the T' structure for the smaller rare earths, e.g., Gd, Eu, Dy. However, Gd_2NiO_4 has been reported to crystallize in the T form (*43*) and the others are not known. We could not synthesize Gd_2NiO_4 using the published procedure (*43*), finding instead only the starting oxide mixtures upon reaction under a variety of conditions. A similar result was obtained for the Sm–Ni–O and Dy–Ni–O systems. Our results are consistent with the report of Dubois *et al.* (*44*), who found that the system Gd_2O_3–NiO contained only the component oxides up to 2200°C. Electronic factors may be involved in stabilizing the T' phase in the cuprates, since the ionic model based on tolerance factors alone would predict that these phases exist.

II. The T Phase*

The T^* phase can be considered a hybrid of the T and T' structures (*22, 23*). Therefore, one might expect that it would display physical properties characteristic of both the T and T' phases. That is to say, given appropriate doping conditions, the T^* phase could be either an electron or hole superconductor. Published reports show that both Ce^{4+} (an electron dopant) and Sr^{2+} (a hole dopant) can be substituted into the T^* structure. However, thus far, the T^* phase is found to occur (*4*) only for samples which have a net concentration of holes (e.g., $Nd_{1.32}Sr_{.41}Ce_{.27}CuO_4$).

The results of our investigation of $La_{2-x}(RE)_xCuO_4$ systems near $x = 1$, for RE = Sm, Eu, Gd, Dy, Ho, Er, Yb, and Y, provide information concerning the role of A-site cation ordering and the importance of alkaline-earth doping on T^*-phase stabil-

TABLE II

SOME T^* PHASES, AVERAGE IONIC RADII, NINEFOLD- AND EIGHTFOLD-COORDINATED RARE EARTH IONS, AND OVERALL TOLERANCE FACTORS (t)

T^* phase	r_T(Å)	$r_{T'}$(Å)	$r_T/r_{T'}$	t^a	Ref.
$La_{.9}Y_{.8}Sr_{.3}CuO_4$	1.244	1.047	1.188	0.855	(*22*)
$LaDy_{.8}Sr_{.2}CuO_4$	1.235	1.054	1.172	0.854	(*22*)
$LaGd_{.8}Sr_{.2}CuO_4$	1.235	1.074	1.149	0.857	(*22*)
$La_{.8}EuSr_{.2}CuO_4$	1.235	1.066	1.158	0.856	(*22*)
$La_{.8}SmSr_{.2}CuO_4$	1.235	1.079	1.145	0.858	(*22*)
$La_{1.3}Tb_{.7}CuO_4$	1.216	1.076	1.130	0.855	(*23*)
$La_{1.4}Tb_{.6}CuO_4$	1.216	1.088	1.118	0.856	(*23*)
$Sm_{1.0}La_{.75}Sr_{.25}CuO_4$	1.240	1.079	1.149	0.858	(*25*)
$La_{1.2}Dy_{.8}CuO_4$	1.216	1.065	1.142	0.851	(*39*)
$La_{.82}Sm_{1.0}Sr_{.18}CuO_4$	1.233	1.079	1.143	0.857	(*25*)
$La_{1.1}Eu_{.8}Sr_{.1}CuO_4$	1.225	1.085	1.129	0.857	(*25*)
$LaEu_{.9}Sr_{.1}CuO_4$	1.225	1.075	1.139	0.855	(*25*)
$La_{.9}Eu_{.9}Sr_{.2}CuO_4$	1.235	1.075	1.149	0.857	(*20*)
$La_{.85}Eu_{.9}Sr_{.25}CuO_4$	1.240	1.075	1.153	0.859	(*25*)

[a] For the sake of consistency with Table I, tolerance factors are calculated from the reference state of ninefold RE coordination. Cu and oxygen are in sixfold coordination.

ity. These findings lead to the following general observations concerning T^*-phase formation. The structure is observed for RE = Nd–Dy, but its thermodynamic stability depends strongly on the size of the rare earth. The structure is metastable for the larger rare earths, competing for existence with T', but the latter phase clearly begins to dominate as equilibrium is approached. Only for the smaller rare earths (Tb (*24*) and Dy) can single phase "undoped" T^* be prepared, while the intermediate rare earths (Nd–Gd) require some strontium doping to stabilize the structure (*21*). T^* phases are not observed for the smallest rare earths, Ho–Yb and Y. These results can be understood in the context of the ionic model presented for the T and T' compounds.

The majority of the known T^* phases along with the average ionic radii of their ninefold (r_T) and eightfold ($r_{T'}$) cations, the $r_T/r_{T'}$ ratios, and their overall tolerance factors are tabulated in Table II. In order to calculate the average size of the rare earth ions in the two different A sites of the T^* structure, preferential occupancy of T sites with Sr > La > RE was assumed. The opposite order was taken for the T' sites. These assumptions appear valid given the very specific doping preferences of the T and T' phases, and are consistent with neutron diffraction results which show an ordering of Sr^{2+} into the T sites and Ce^{4+} into the T' sites of $Nd_{1.32}Sr_{0.41}Ce_{0.27}CuO_4$ (*23*). The following picture of T^*-phase stability emerges from the tabulation in Table II and from Fig. 5. The T^* structure occurs in a very narrow region adjacent to the boundary of the T/T' stability fields (cf., Fig. 5) because the tendency toward T-/T'-site ordering makes it thermodynamically competitive. The very narrow range of its occurrence, $0.85 \leq t \leq 0.86$ (Table II), may arise from the periodicities imposed by the two different RE–O layers in the T^* structure (i.e., their periodicities must be commensurate). Furthermore, relatively pure T^* phases occur only when the disparity in size between La^{3+} and its counter rare earth cation becomes sufficient ($1.12 \leq r_T/r_{T'} \leq 1.19$). This disparity in the sizes of the two cations can be viewed as the driving force for the formation of the T^* phase. Nevertheless, it is apparent from Table II that the majority of known T^* phases still require Sr^{2+} to stabilize the structure. This is due to the very specific preference of Sr^{2+} for the T site, which induces the cation-ordering required for T^*-phase formation.

The smaller rare earths Tb–Yb do not form the T' structure at the composition $(RE)_2CuO_4$. Instead, these adopt the unrelated $Y_2Cu_2O_5$ structure (*30*). However, since the T^* phase forms in $La_{2-x}RE_xCuO_4$ for RE = Tb, Dy, it is apparent that the T' structure need not be stable in a particular system for the rare earth to form the hybrid

T^* phase with La. On the other hand, our results show a cut-off at Dy. Below this point the RE-cation is too small to form a T^* phase with lanthanum, despite the fact that the computed tolerance factor may fall in the T^* field. Clearly, the value of the t factor is a necessary but not sufficient predictor of the existence of T^*.

Summary and Conclusions

The ionic model of RE_2CuO_4 crystal chemistry based on a perovskite-like tolerance factor appears to be a remarkable predictor of the T, T', and T^* stability fields. Indeed, even when all the known K_2NiF_4-type metallates are included, few exceptions are found (*45*). However, it should be noted that while all the metallates possessing the T structure exhibit $t > 0.865$, only the cuprates are known to form all three structures. This must, in part, be attributed to the paucity of metals stable in multiple coordination geometries; in particular, square-planar (T') and square-pyramidal (T^*). Copper is somewhat unique in its ability to adopt many different coordination geometries, although planar-coordinated Ni, Pd, Pt, and Au compounds are also known (*5*). In addition, of course, "electronic factors" must also play a role in determining the stability of the T' and T^* phases. This is made evident by our inability to synthesize T' phases with Ni on the B sites, since tolerance factor arguments alone would predict that these phases exist. Nevertheless, the ionic model presents a useful tool with which to understand the crystal chemistry of the RE_2CuO_4 phases. A similar model has been independently proposed by Manthiram and Goodenough (*49*).

The segregation of T, T', and T^* cuprate phases into discrete regions, according to their tolerance factors, can be attributed to the breakdown of RE–O coordination number as the rare earth size decreases. This instability is reflected by the different rare earth coordinations observed (cf., Fig. 5); RE coordination is ninefold in T, eightfold in T', and, finally, sixfold in $RE_2Cu_2O_5$. Within the context of the present model, the structural transformations which occur in the cuprates as the RE coordination number is lowered are a consequence of electrostatic requirements, which serve to optimize the Madelung energy of the RE–O framework. This effect is well-known in the crystal chemistry of a host of rare-earth structures, including alloys, intermetallics, and borides (*46*) and perovskites (*47*).

The ionic description clearly reveals the dominant role of the RE–O framework in determining the crystal chemistry and therefore the physical properties of the RE_2CuO_4 phases. Indeed, an important conclusion from this work is that the RE–O layers impose the observed spacings upon the Cu–O polyhedra in RE_2CuO_4 (i.e., they determine the in-plane Cu–O bond distances). This has important implications concerning the superconducting critical temperatures (T_c) of the RE_2CuO_4 phases, since T_c may be correlated with the in-plane Cu–O bond distances (*48*). The ionic bonding requirements of the rock-salt layers result in a compression of the Cu–O sheets in T, while the fluorite-type layer in T' expands them. The influence of these factors, and the possible role of electrostatic factors in determining the doping preferences of the T, T', and T^* phases, is presently being investigated.

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