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Deviation from Vegard's law: Changes in the c-axis parameter in $La_{2-x}Sr_xCuO_{4-d}$ in relation to the insulator-superconductor-metal transition

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The deviation from Vegard's law for the changes in the c parameter of the solid solutions $La_{2-x}A'_xCuO_{4-d}$ (A'=Ba,Sr,Ca) is examined. When $d=0$, the changes in the c parameter are controlled in a linear manner (Vegard's law) by two factors: the size effects associated with the difference in ionic radius between the A' ion and La cations, as well as the number of holes created. These two effects are isolated by fixing the number of holes and varying the average size of the A' cations. Surprisingly, there is a linear dependence of the c-parameter expansion on the hole concentration for $x \leq 0.15$. The significance of these results in terms of the insulator-superconductor-metal transition in $La_{2-x}Sr_xCuO_4$, $0<x<0.3$ is briefly discussed.

I. INTRODUCTION

The phenomenon of high-temperature superconductivity in layered perovskite multinary copper oxide systems[1-3] has revealed several important aspects which are yet to be satisfactorily understood. One of the most fascinating of these is the behavior of $La_{2-x}Sr_xCuO_4$ with the layered perovskite K_2NiF_4 structure (Fig. 1). In these compounds the superconducting transition temperature T_c goes through a maximum at $x \sim 0.15$–0.20 and then decreases with increasing hole concentration,[4-6] becoming zero at $x \sim 0.30$. At this value of x, the system still remains metallic and the basic crystal structure remains the same. Little is understood about the origin of this behavior.

Systematics of the changes in the structural parameters could be of importance in obtaining an insight. Extraction of such chemical insights depends strongly on structure-property correlations, and the most basic of these is the changes in lattice parameters. The quality of a solid solution is usually examined from the composition-dependent lattice parameter changes in terms of the empirical Végard law.[9] This law states that in the absence of strong electronic effects the variation of lattice parameters is linear with composition in a true *three-dimensional* solid solution. The Végard law is a consequence of the way a solid solution reduces strain by an expansion (or compression) when species of different sizes are involved. In *two-dimensional* systems, the non-Vegard law behavior (nonlinear changes in lattice parameter with composition) has been well documented[10-13] especially in $A_{1-x}A'_xL$ systems where the solid solution involves the A or A' ions of different size intercalated between L layers. The c parameters of $La_{2-x}Sr_xCuO_4$ changes in a markedly nonlinear fashion[4,6,14] with x. Two typical cases reported in the literature[4,14] are given in Fig. 2. We note a marked deviation from Vegard's law

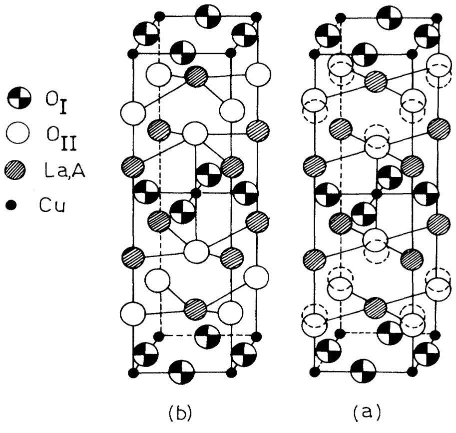

FIG. 1. The K_2NiF_4 structure in A_2BO_4 oxides such as $La_{2-x}A_xCuO_4$ compounds showing different axial (O_{II}) and basal (O_I) oxygens. (a) The idealized structure with regular BO_6 octahedra and the A-O_{II} distance being 2B-O_I distance. (b) The actual structure in La_2CuO_4c. The a parameter is the same in both (a) and (b). The distortion in (b) is mainly achieved by the displacement of the O_{II} ions.

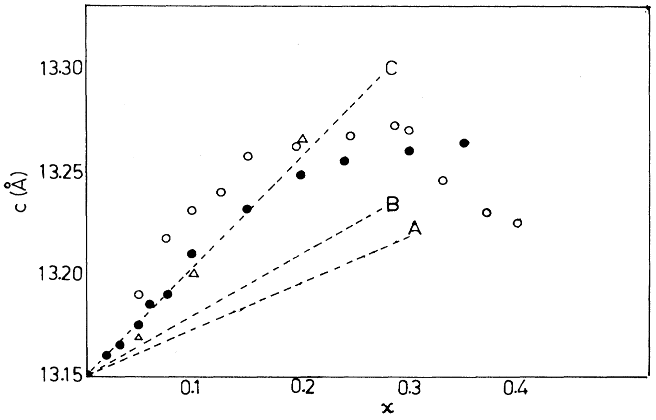

FIG. 2. Variation in the c parameter in $La_{2-x}Sr_xCuO_{4-d}$ for $x<0.3$ (from Ref. 4, open circles, $d=0$; partially filled circles, $d=0$; Ref. 14, filled circles). The triangles are obtained from this study. The dashed lines A and B correspond, respectively, to the expected values of the c parameter from Eq. (1) (see text) for different sizes and from Eq. (3) for increasing hole concentration; the line C is the sum of the two lines A and B.

in the two cases, the deviation becoming prominent around $x = 0.15$–0.20 in the $La_2CuO_{4.00}$ system. It is at this value of x that T_c is a maximum. The question then arises whether the non-Végard law behavior is similar to that in other two-dimensional systems and arises from the intercalation of larger[15] Sr^{2+} ions in place of La^{3+} ions between rigid CuO_2 layers or whether it is a reflection of new electronic effects being introduced with increasing x. The latter may be important in understanding the superconductor-metal transition with increasing x.

We have examined the changes in lattice parameters as we vary both the average size[15] of the A' ions (maintaining a fixed hole concentration) as well as the effect of deviations from oxygen stoichiometry. The results of our investigation are reported below. The changes in the c parameter, for small values of x, consist of effects due to the introduction of holes as well as those due to size effects due to the difference in size between the A' ion and the La ion. The changes in the c-axis parameter obeys Végard's law when the size of the A' ion is changed for a *fixed hole* concentration or when the hole concentration is changed for a *fixed average size* of the A' ion. The deviation from Végard's law for large values of x is due to the diminishing influence of the holes in increasing the c parameter.

II. EXPERIMENTAL

The compounds were prepared by standard ceramic methods[16,17] using La_2O_3 (prefired at 1000 °C just before use), $BaCO_3$, $SrCO_3$, $CaCO_3$, and CuO as starting material. Required stoichiometric amounts of the starting material were weighed out and ground under alcohol for several hours. The dried mixture was then prefired in air at 900 °C for 24 h. The partially decomposed product was then pelletized and fired in air at temperatures ranging between 950 and 1100 °C for 48 h with intermittent grinding and repellitizing. After a single-phase product was obtained, the samples were given various treatments in oxygen so as to obtain various values of d. Low temperatures of firing were required to obtain good oxygen stoichiometry when $A' = \mathrm{Ca}$.

The oxygen stoichiometry was determined by iodometric titration methods using saturated KI solutions. Powder x-ray diffraction parameters were obtained using a powder diffractometer. The lattice parameters were obtained for the material using an internal standard for calibration.

III. RESULTS

The lattice parameters and the values of d for all the compounds studied in this investigation are given in Table I. The changes in the lattice c parameter as a function of x in the system $La_{2-x}Sr_xCuO_{4-d}$ as obtained by us in this investigation ($d \sim 0$) and as reported in the literature[4,14] for $x < 0.3$ is shown[4,6,16] in Fig. 2. The non-Végard law behavior of the c parameter with x for $x \lesssim 0.3$ is apparent from Fig. 2. We note in Fig. 2 that in the data of Torrance *et al.*[4] the c parameter is larger than those of Takagi *et al.*[14] Torrance *et al.*[4] report a larger oxygen content ($d < 0$) while Takagi *et al.* reported a nearly exact stoichiometry[14] ($d \sim 0$). This indicates that either the excess oxygen or the excess holes are causing an increase in the lattice parameter.

In Fig. 3 we show the changes in the c parameter as a

TABLE I. Lattice parameters and oxygen content of various $La_{2-x}A_xCuO_{4-d}$ compounds.

Composition		Lattice parameters (Å) (±0.005 Å)		
A	x	a	c	d(±0.005)
Sr	0.0	3.807[a]	13.158	−0.012
	0.05	3.799[a]	13.166	−0.012
	0.10	3.793	13.201	−0.050
	0.20	3.77	13.267	−0.085
Ca	0.05	3.811[a]	13.150	0.043
	0.10	3.799	13.156	0.068
	0.15	3.796	13.166	0.076
	0.20	3.793	13.161	0.080
$Ca_{0.66}Sr_{0.33}$	0.05	3.799[a]	13.178	0.001
	0.10	3.790	13.180	0.008
	0.15	3.789	13.191	0.016
	0.20	3.786	13.208	0.020
$Ca_{0.5}Ba_{0.5}$	0.10	3.796	13.184	0.014
$Ca_{0.15}Ba_{0.85}$	0.10	3.790	13.168	0.010
$Ca_{0.5}Sr_{0.5}$	0.10	3.790	13.180	0.011
$Ba_{0.5}Sr_{0.5}$	0.10	3.794	13.210	0.016

[a] Pseudotetragonal values from an orthorhombic cell.

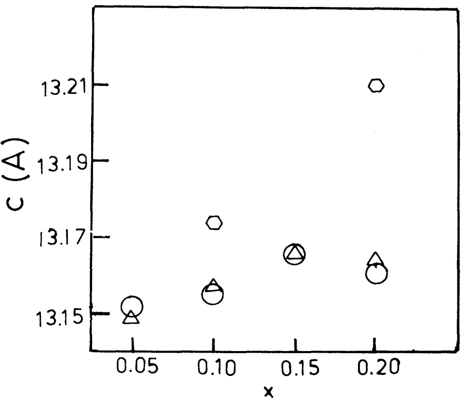

FIG. 3. Variation in the *c* parameter for the $La_{2-x}A_xCuO_{4-d}$ compounds (A=Ca); triangles: this work; hexagons: from Ref. 16; circles: from Ref. 17.

function of x in the system $La_{2-x}A'_xCuO_{4-d}$ when A'=Ca and for $d \sim x/2$ as well as for $d \sim 0$. We have compared our results with those available in the literature.[17,18]

In Fig. 4 we show the changes in the *c* parameter for $d=0$ and $x=0.1$ for various proportions of different A' ions. We have plotted the changes as a function of the average difference in radius[15] of x A' ions compared to that of the corresponding number of La ions, $\delta r_{A',\mathrm{La}} = x\delta r_{A'} = x(r_{A'} - r_{\mathrm{La}})$. We find that we obtain a linear dependence of the *c* parameter on $\delta r_{A',\mathrm{La}}$. We also find that the extrapolated value when $\delta r_{A',\mathrm{La}}=0$ is nearly 13.18 Å, which is considerably larger than that for the $x=0$ composition La_2CuO_4 (13.15 Å, Refs. 14, 18, 19, and 20). This suggests the important point that the effect of introducing holes is to increase the *c* parameter.

We have replotted in Fig. 4 the changes in the *c* parameter as reported by Kishio *et al.*[19] for $La_{1.8}A'_{0.2}CuO_4$ (A'=various ratios of Ba, Sr, and Ca) as a function of $\delta r_{A',\mathrm{La}}$. We find again a linear dependence on $\delta r_{A',\mathrm{La}}$ and the extrapolated value of the *c* parameter when $\delta r_{A',\mathrm{La}}=0$ is 13.21 Å indicating once again that the effect of holes themselves is to introduce an increase in the *c* parameter.

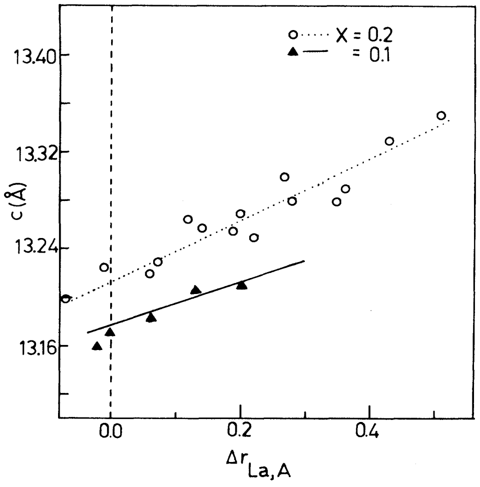

FIG. 4. Changes in the *c* parameter in $La_{1.9}(Ba_{1-y-z}Sr_yCa_z)_{0.1}CuO_4$ as obtained in this work (filled triangles). We have also replotted the results of Kishio *et al.* (Ref. 19) for the $La_{1.8}A_{0.2}CuO_4$ compounds (open circles).

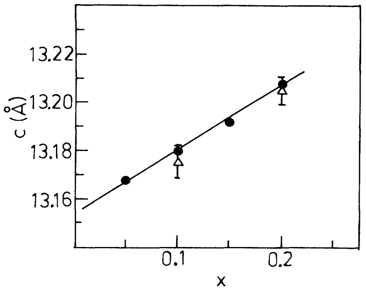

FIG. 5. Changes in the *c* parameter in the $La_{2-x}(Ca_{0.66}Sr_{0.33})_xCuO_4$ compounds as a function of x (filled circle). The extrapolated values of the *c* parameter when $\delta r_{A',\mathrm{La}}=0$ as obtained in Fig. 4 is also shown (triangles).

The average radius of Ca^{2+} and Sr^{2+} ions taken in the ratio of 2:1 is the same as that of La^{3+} according to the ionic radii tables of Shannon.[15] We have determined the lattice parameter of the solid solutions $La_{2-x}(Ca_{0.66}Sr_{0.33})_xCuO_4$ so that we may evaluate the changes in the lattice parameter as a function of the hole concentration x, keeping the average size of the A' ions to be the same as that of the La^{3+} ions. A plot of *c* parameter vs x again shows a linear Vegard law behavior (Fig. 5). The extrapolated values for the *c* parameter when $\delta r_{A',\mathrm{La}}=0$ from Fig. 4 also falls on the same line. We thus obtain two linear relationships for the dependence of the *c* parameter on the size difference: δr_A for a fixed hole concentration as well as on the hole concentration x for a fixed δr_A. Interestingly, the rate of increase in the *c* axis is the same when holes are introduced by intercalated oxygen[20,21] in La_2CuO_{4-d} taking $x=0$ and d to be negative.

IV. DISCUSSIONS

From the slope of the plots of *c* vs $\delta r_{A',\mathrm{La}}$ for a fixed value of x, we obtain the dependence of *c* on $\delta r_{A',\mathrm{La}}$ alone to be

$$\begin{aligned} c &= c_0 + S\delta r_{A',\mathrm{La}} \\ &= c_0 + Sx\delta r_A , \end{aligned} \tag{1}$$

with the proportionality constant $S = 2.5 \pm 0.25$ and c_0 is the lattice *c* parameter of La_2CuO_4. From Fig. 1(a) the *c*-axis parameter is given by Eq. (2a)

$$c = 4d_{\mathrm{Cu\text{-}O(II)}} + 2d_{A\text{-}\mathrm{O(II)}} \tag{2a}$$

$$= 4.82d_{A\text{-}\mathrm{O(II)}} = 4.82(r_A + r_{\mathrm{O}}) , \tag{2b}$$

where $d_{\mathrm{Cu\text{-}O(II)}}$ and $d_{A\text{-}\mathrm{O(II)}}$ are the axial Cu-O(II) and A-O(II) distances, respectively. In the close-packing model[22] for the perovskites, the B-O distances are not independent of the A-O distances. The A and O ions, which are of similar size, may be considered to form a close-packed array and the B ions occupy the octahedral

O_6 sites. The size of the A ions determines the size of the octahedral sites and hence the B-O distances. In an ideal perovskite structure $d_{A\text{-O}}=\sqrt{2}d_{B\text{-O}}$ so that we obtain Eq. (2b). r_A and r_O are the radii of the A and O ions, respectively. The change c in the c parameter from Eq. (2) is thus due to changes $\delta r_{A'}=[(r_{A'}-r_{La})]$ and δr_O in the average radius of the A and O ions. We show below that the changes in the c parameter may be understood as arising from the two contributions by the A and O ions as in Eq. (2b).

Writing the formula of $La_{2-x}A'_xCuO_{4-d}$ as $(La_{1-y}A'_y)_2CuO_{4-d}$ with $x=2y$, the change δc in the c parameter as a function of the size of the A ion should then be $\sim 4.82y\delta r_A=2.41x\delta r_A$. This is what is experimentally observed in Eq. (1). This implies that for a fixed hole concentration the solid solutions involving various A' ions obey Végard's law.

The most interesting aspect of our investigation is the observation (Fig. 5) that there is a linear relation between the hole concentration and the increase in the c parameter for small values of x. The dependence of the c parameter on the hole concentration, x, is experimentally found to be

$$c=c_0+Hx\ , \tag{3}$$

with $H\sim 0.3$. As can be seen in Fig. 2, the experimentally observed increase in the c parameter with x is just that expected from the combined effect of the holes and the size of the A' ions on the c parameter. The average Cu-O distances[23–25] in La_2CuO_4 of ~ 2.078 Å is about 0.052 Å smaller per Cu-O linkage as compared to ionic Cu^{2+}-O^{2-} distance (2.13 Å) using the ionic radii of Shannon[15] for Cu^{2+} ions in sixfold coordination. The reduction in the average Cu-O distance in La_2CuO_4 can be understood in terms of constraints imposed by the lattice compatibility condition on the intercalated species. This aspect has not been addressed in the model of Lee *et al.*[13] When a compatibility constraint is imposed on the intercalating A or A' species in the $A_{1-x}A'_xL$ compounds, the matching of the actual spatial sizes in the L as well as in the A, A' plane is important. Such constraints lead to local strains and are important in the area of strained superlattices.[26] There could be effects which affect the valence forces due to, for example, a "constituent strain"[27] which is the energy of the epitaxial strained superlattice relative to the energy of the bulk states. Hybertsen[28] has shown from first-principles total energy minimum calculations that in the nominally lattice-matched $In_{0.53}Ga_{0.47}As/InP(001)$ heterostructures interface strain is reduced by anion mixing. This compatibility constraint is expressed in perovskites in terms of a tolerance factor.[29,30]

In the ABO_3 perovskites or the layered A_2BO_4 perovskites a matching of A-O and B-O distances is expressed in terms of the classical tolerance factor[29,30]

$$t=d_{A\text{-O}}/\sqrt{2}d_{B\text{-O}}\ . \tag{4}$$

The perovskite or layered perovskite structure is stable[29] only in the limit $0.86\le t\le 1.02$. The low tolerance factor of La_2CuO_4 accounts[29,30] for the substantially larger c/a value (~ 1.25) of the CuO_6 octahedra compared to that[31] of the NiF_6 octahedra in K_2NiF_4 itself ($c/a\sim 1$, $t\sim 1$). The internal compression due to low t makes the average Cu-O distance in La_2CuO_4 (2.078 Å) less than that calculated from ionic radii (2.13 Å).

Since the negatively charged oxygen anion is the more compressible, the decrease in the average Cu-O distance as a result of a low tolerance factor is expected to be predominantly due to the compression of the oxygen ion. It is in this sense that the radius r_O of the oxygen ion in Eq. 2(b) plays a role in determining the changes in the c parameter. The value of the parameter H in Eq. (3) is obtained from $H=4.82x(\delta t/\delta x)(\delta r_O/\delta t)$. The rate of change of tolerance factor (calculated from the tabulated radii of Shannon[15]) with $x, \delta t/\delta x\approx 0.1$. When $H\sim 0.3$, we should obtain $\delta r_O/\delta t\sim 0.7$ Å. The decrease of the average Cu-O distance to 2.078 Å in La_2CuO_4 ($t=0.868$) from the ionic radii value of 2.13 Å implies that $\delta d_{Cu\text{-}O}/\delta t\sim\delta r_O/\delta t\sim 0.40$ Å. The discrepancy in the observed and estimated values could be attributed to the anisotropic nature of compression.

The deviation from Végard's law at $x=0.15$ may be understood as well if we attribute the changes in the c parameter to the changes in the axial Cu-O_{II} distances. We examine the empirical constraint obtained from ionic radii[15] for the average Cu^{2+}-O^{2-} ([Cu-O]) distance of 2.13 Å, the ionic radius of the O^{2-} ion being assumed to be the same (1.40 Å) in all cases. For such an average ionic Cu-O distance, the axial [Cu-O_{II}] distance should be 2.61–2.59 Å, for the basal [Cu-O_I] distance in La_2CuO_4 of 1.89–1.90 Å. The experimentally observed [Cu-O_{II}] distance of ~ 2.43 Å is then due to a low t. The increase in the t due to the introduction of holes reduces the internal pressure and is thus expected to increase the Cu-O_{II} distance. On the other hand, on the introduction of holes, the axial $[Cu\text{-}O_{II}]^+$ distance is expected to be reduced to ~ 2.04 Å only for an *ab* plane distance of ~ 1.89 Å assuming an average $[Cu\text{-}O]^+$ distance[15] of 1.94 Å. The changes in the Cu-O_{II} distance is thus a combined effect of the above factors, which act in opposite directions. We expect the changes to be proportional to $[(2.59-2.43)(1-x)-(2.43-2.04)x]x$. The maximum increase is thus expected when $x=0.15$. The increase in the tolerance factor could therefore be important in accounting for the observed non-Végard law behavior at high hole concentration in the $La_{2-x}Sr_xCuO_4$ series for $x\ge 0.15$.

The average [Cu-O] distance calculated from the *ab initio* potential induced breathing ionic model by Cohen *et al.*[32] is 2.113 Å, which is close to the value of 2.13 Å used by us. Cohen *et al.* showed from their calculations that the CuO_6 octahedra were actually elongated. They thus suggested that in the case of these oxides the simple ionic description is sufficient to describe structural features and that many-body effects are not important. The drawback in the calculation of Cohen *et al.*[32] is that they overestimate the average Cu-O distance in La_2CuO_4 by a sizable amount. In this paper, we have attributed this difference to an internal pressure brought about by lattice compatibility or tolerance factor arguments. Our findings show that the effects due to low tolerance factors are important in reducing the Cu-O distance below that obtained from ionic radii considerations. Low tolerance factors should elongate the octahedra[29,30] in layered perovskites. In this case the lattice matching constraints or the "constituent strain"[27,28] is the important many-body effect determining the stability of valence states. As argued earlier, at low tolerance factors a dynamic double valence fluctuating[33,34] disproportionated Cu^{1+} and Cu^{3+} ($S=0$) states could be admixed into the ground state and thus could favor superconductivity. Such an admixture is possible when there is a pre-existing antiferromagnetic coupling[34] between the precursor Cu^{2+} ions that would be involved in the charge disproportionation.

The tolerance factor arguments emphasize "elastic factors" since it takes into account the mismatch between steric aspects such as ionic radii. Ferreira *et al.*[35] have emphasized that the inclusion of such elastic terms along with the chemical interaction energy terms give much better results in describing alloy stability. We suggest that such elastic factors could be related to the existence of superconductivity in the sense that valence changes due to the "constituent strain" could be important.

The composition at which there seems to be a deviation from Végard's law in Fig. 1 for $A'=\mathrm{Sr}$ is coincident with the maximum in T_c. As discussed by us, the deviation from Végard's law is to be attributed to the absence of a contribution from holes to the elongation of the c axis at larger values of x. Crystal-field effects which lift the degeneracy of the e_g orbitals are thus reduced. There is then the possibility of the degeneracy of the $e_g(d_{x^2-y^2}$ and $d_{z^2})$ orbitals being reintroduced at high values of x. An increasing admixture of the d_{z^2} orbitals into the $d_{x^2-y^2}$ orbitals makes the interlayer exchange interactions possible. The system thus becomes effectively three-dimensional[6] at higher values of x. These results then suggest that two-dimensional character is an important constraint for high T_c in these compounds.

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