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Effect of substitutional impurities (Al,Co,Fe,Ga) on the orthorhombic phase of $YBa_2Cu_3O_{7-\delta}$

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Structural changes in $YBa_2Cu_3O_{7-\delta}$ resulting from alloying with Al, Co, Fe, and Ga are studied theoretically. A bond model for the various interatomic interactions yields results indicating that the tetragonal phase seemingly observed by x-ray diffraction experiments for $YBa_2(Cu_{1-x}M_x)_3O_{7+y}$ (M = Al,Co,Fe; $x > 0.03$) consists of differently oriented orthorhombic domains. Doping with Al,Co,Fe and domain formation causes uptake of excess oxygen.

I. INTRODUCTION

At room temperature, $YBa_2Cu_3O_{7-\delta}$ is orthorhombic. The orthorhombic distortion of the lattice is induced by ordering of oxygen ions and vacancies in the Cu(1) planes, where Cu-O chains are formed.[1] X-ray diffraction experiments[2,3] yielded, as shown in Fig. 1(a), that the orthorhombic distortion decreases continuously in $YBa_2(Cu_{1-x}M_x)_3O_{7+y}$ as a function of x (M=Al,Co,Fe). Investigation by electron microscopy[4-6] indicates that the seemingly tetragonal phase with equal lattice parameters a and b consists of differently oriented orthorhombic domains, [see Fig. 1(b)].

At the impurity content $x = x_0$ where the lattice parameters a and b become equal in x-ray diffraction experiments, $YBa_2(Cu_{1-x}M_x)_3O_{7+y}$ still has a high superconducting transition temperature[2,3] ($T_c > 60$ K). This led to the conclusion that the Cu-O chains are not important for superconductivity,[7] since it seemed that even a tetragonal 1:2:3 compound can be a high-T_c superconductor. Yet, if the phase with $a = b$ consists of small orthorhombic domains, short Cu-O chains are still present in $YBa_2(Cu_{1-x}M_x)_3O_{7+y}$ for $x > x_0$.

Since the impurities occupy mainly Cu(1) sites,[5,8] we shall study in the following at $T = 0$ the redistribution of oxygen atoms in the Cu(1) planes as a consequence of alloying using a bond model for the interatomic interactions between the oxygen and metal atoms. In our model four different interaction energies are introduced (see Fig. 2). However, we will show that our results only depend on a few features of these parameters. We require a strong attractive bond energy between the impurities and the oxygen atoms. Thus, the impurities attract additional oxygen atoms to increase their oxygen coordination, as is observed in experiment. At a given impurity content x the difference in energy between various oxygen configurations with highly coordinated impurities depends then only on the difference between the nearest- and the next-nearest-neighbor oxygen-oxygen repulsion. Accordingly, the number of parameters necessary to calculate the difference in energy between the various physically relevant oxygen configurations is reduced to one.

Within this model, we obtain results indicating that no tetragonal phase occurs due to doping. Instead, the formation of small orthorhombic domains becomes energetically favorable at $x \simeq x_0$. For $x < x_0$ the number of nearest oxygen neighbors around the impurities is increased due to a local oxygen redistribution in the neighborhood of the impurities, but apart from this, the Cu-O

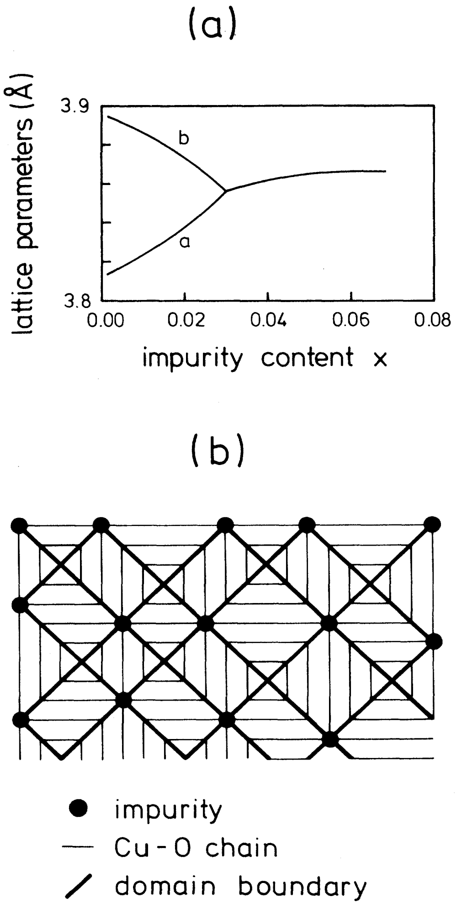

FIG. 1. Illustration of the x-ray results (Ref. 2) for the change of the lattice parameters a and b caused by Al, Co, or Fe impurities in $YBa_2(Cu_{1-x}M_x)O_{7+y}$ [part (a)] and of the domain structure (Ref. 4) induced by Fe impurities [part (b)].

chains remain intact. Furthermore, the formation of domains gives rise to oxygen configurations in the Cu(1) plane that involve the observed uptake of excess oxygen. Thus, our model shows how impurities induce oxygen redistribution and uptake of excess oxygen in the Cu(1) plane. This may be the basis for an understanding of $T_c(x)$ in $YBa_2(Cu_{1-x}M_x)_3O_{7+y}$, for M=Al,Co,Fe,Ga.

II. THEORY

We introduce the (attractive) bond energies ε_{CuO} and ε_{MO} and the (repulsive) direct nearest-neighbor and next-nearest-neighbor interaction energies ε_{OO} and ε'_{OO} (see Fig. 2) to find out which oxygen configuration in the Cu(1) plane is energetically favorable at a given impurity content x.[9] Note that the bond energies ε_{CuO} and ε_{MO} depend on the oxygen coordination of the cation because they include the indirect interactions between its nearest oxygen neighbors, which are mediated by the cation. And ε_{OO} gives the (coordination-independent) increase of the oxygen-oxygen repulsion in the nearest-neighbor oxygen configuration around a cation due to removing a nearest-neighbor oxygen of a cation in a cation-oxygen chain from its O(1) site within the chain and placing it at a nearest-neighbor O(5) site, for example. Apparently, at fixed coordination k, the energies of the different nearest-neighbor oxygen configurations around a cation can be completely described by the cation-oxygen bond energy at this coordination and the nearest-neighbor repulsion of the oxygen ions, ε_{OO}. For the dependence of the cation-oxygen bond energies on the oxygen coordination of the cation we make some simplifying assumptions in the following.

The driving force behind the oxygen rearrangement in the Cu(1) plane of $YBa_2(Cu_{1-x}M_x)_3O_{7+y}$ is the impurities which prefer a higher oxygen coordination than copper. In fact, Mössbauer spectroscopy reveals that the trivalent and fourvalent dopands may acquire a fivefold or sixfold oxygen coordination (see Ref. 3 and references therein). Assuming the valencies[2,8,10] Cu^{2+} and M^{3+} or M^{4+} (M=Al,Co,Fe,Ga) for the ions in the Cu(1) plane, we determine the oxygen coordination of the impurities from the strength s of the various cation-oxygen bonds (see the Appendix). We then find that Co^{3+}, Fe^{3+}, and Ga^{3+} impurities have a fivefold coordination ($k=5$), whereas Al^{3+}, Co^{4+}, and Fe^{4+} ions should have six nearest oxygen neighbors ($k=6$). The copper atoms in the Cu-O chains have a fourfold coordination. They are

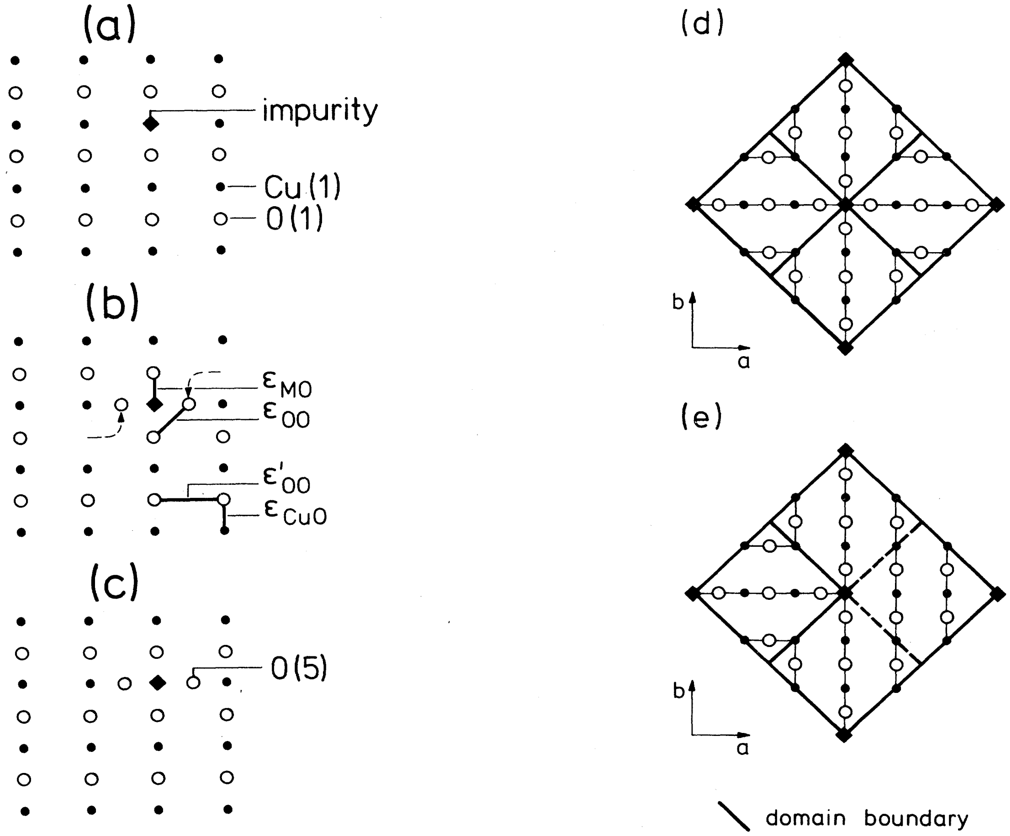

FIG. 2. Illustration of the various oxygen configurations around an impurity with a sixfold coordination ($k=6$). (a) refers to impurity substitution without redistribution of oxygen atoms, (b) refers to impurity substitution inducing O(1)→O(5) redistribution, and (c) refers to impurities surrounded by excess oxygen. Parts (d) and (e) show domain formation for impurities having $k=6$ and $k=5$, respectively.

surrounded by two nearest oxygen neighbors on O(1) sites within the chains [Fig. 2(a)] and two nearest oxygen neighbors on O(4) sites. The O(4) sites lie in the Ba planes above and below the chains. Thus if we substitute Al, Co, Fe, or Ga for Cu, these impurities tend to attract additional oxygen to increase the number of their nearest oxygen neighbors in the Cu(1) plane to three (Co^{3+},Fe^{3+},Ga^{3+}) or four (Al^{3+},Co^{4+},Fe^{4+}). Actually, this tendency of the trivalent and fourvalent dopands to acquire a square-pyramidal or an octahedral environment is in accord with their appearance in other compounds.

If the coordination number of the impurities is increased, either copper loses a nearest-neighbor oxygen or extra oxygen atoms have to be put from the gas phase into the Cu(1) plane of the 1:2:3 compound [see Figs. 2(b) and 2(c)]. The energy change resulting from these local changes in the oxygen configuration is given by

$$\Delta E_l = \varepsilon_{MO} - \varepsilon_{\mathrm{CuO}} + 3\varepsilon_{\mathrm{OO}} - 2\varepsilon'_{\mathrm{OO}} + \Delta\varepsilon \ , \tag{1}$$

in the case (i), where one copper atom loses a nearest-neighbor oxygen, that is transferred into the neighborhood of an impurity, or by

$$\Delta E_l = \varepsilon_{MO} + \varepsilon_{\mathrm{CuO}} + 4\varepsilon_{\mathrm{OO}} + \tfrac{1}{2}E_d + \Delta\varepsilon \ , \tag{2}$$

in case (ii), where an extra oxygen is put around the impurity.

Here, E_d is the dissociation energy of O_2, and the ε_{AB} are the bond energies in case of a normal coordination, for example, $k(\mathrm{Cu}^{2+})=4$, etc. With $\Delta\varepsilon$ we denote corrections due to deviations from these coordination numbers. Using empirical values for the bond energies,[11,12] and neglecting the $\Delta\varepsilon$, we find case (ii) described by Eq. (2) to be energetically favorable. However, the increase in the number of nearest-neighbor oxygen atoms to five around a copper atom that occurs in case (ii) has not been observed experimentally. This increase in the oxygen coordination of a copper atom probably leads to a significant decrease in the Cu—O bond energies. For example, if this energy decrease for the Cu—O bonds is about 5–10 %, then the inclusion of the term $\Delta\varepsilon$ in Eqs. (1) and (2) makes the case (i) energetically favorable. Note that in the following we shall consider only oxygen configurations where a cation does not exceed its normal coordination, i.e., $k(\mathrm{Cu}^{2+}) \leq 4$, etc. For such configurations we neglect the correction $\Delta\varepsilon$.

If the local redistribution of oxygen atoms described in Eq. (1) shall be energetically possible, we must have $\Delta E_l < 0$ or $|\varepsilon_{MO} - \varepsilon_{\mathrm{CuO}}| > (3\varepsilon_{\mathrm{OO}} - 2\varepsilon'_{\mathrm{OO}})$. Here, $(\varepsilon_{MO} - \varepsilon_{\mathrm{CuO}})$ is the energy gained due to replacing one Cu—O bond by an M—O bond. According to our empirical estimates of the cation-oxygen bond energies, this energy gain outweighs the energy loss $(3\varepsilon_{\mathrm{OO}} - 2\varepsilon'_{\mathrm{OO}})$ due to the formation of nearest-neighbor oxygen pairs in the neighborhood of Al, Co, Fe, and Ga impurities. It is the purpose of our bond model to establish whether this energy loss can be reduced by an additional oxygen rearrangement in the Cu(1) plane leading to an ensemble of small orthorhombic domains or a tetragonal phase with highly coordinated impurities.

To determine now the energy change resulting from the various (global) oxygen rearrangements in the Cu(1) plane, which are induced by the local oxygen redistribution around an impurity, we use the energy expression ($E = \sum_b \varepsilon_b$, ε_b denotes interaction energy):

$$E(p) = \sum_{i=1}^{2N} t_i [2(1-p)\varepsilon_{\mathrm{CuO}} + 2p\varepsilon_{MO}] + \sum_{\langle ij \rangle}^{\mathrm{nn}} t_i t_j \varepsilon_{\mathrm{OO}} + \sum_{\langle ij \rangle}^{\mathrm{nnn}} t_i t_j \varepsilon'_{\mathrm{OO}} \ . \tag{3}$$

Here, $\sum_{i=1}^{2N}$ is a sum over all oxygen sites in the Cu(1) plane, $\sum_{\langle ij \rangle}^{\mathrm{nn}}$ runs over all nearest-neighbor pairs of oxygen sites, and $\sum_{\langle ij \rangle}^{\mathrm{nnn}}$ runs over all next-nearest-neighbor pairs. t_i is equal to 1, if the oxygen site i is occupied, and $t_i = 0$ otherwise. p is the concentration of impurities with respect to the Cu(1) sites, and is given by $p \equiv 3rx$, where x is the impurity content in $\mathrm{YBa}_2(\mathrm{Cu}_{1-x}M_x)_3\mathrm{O}_{7+y}$ and r is the number of impurities which occupy Cu(1) sites divided by the total number of impurities. In the following we consider substitutional impurities with $k=6$, i.e., Al^{3+}, Co^{4+}, and Fe^{4+}.

First, we assume that the chain structure remains intact upon substituting the impurities for copper (phase A). Second, we assume that in the neighborhood of an impurity two copper atoms have lost one nearest-neighbor oxygen and that the impurity has six nearest oxygen neighbors (phase B). Note that in phase B the impurities interrupt the chains, but the Cu(1) planes remain orthorhombic. If two impurities occupy neighboring Cu(1) sites, they attract an oxygen atom from the surroundings of the 1:2:3 compound to increase their coordination number. Third, we assume the same nearest-neighbor oxygen structure around the impurities as in phase B, but allow random occupation of the O(1) and O(5) sites by oxygen atoms, which are not nearest neighbors of an impurity (phase C). Fourth, we assume that domains consisting of Cu-O chains along the a or b axis are formed (phase D). The impurities are placed at the corners of the domains in such a way that they have four nearest oxygen neighbors in the Cu(1) plane [see Fig. 2(d)]. The formation energy of the domains is determined by the nearest-neighbor repulsion of oxygen atoms on the domain surface. In our bond model the domain boundaries are oriented in the (110) and $(1\bar{1}0)$ directions for energetical reasons, since this minimizes the number of nearest-neighbor oxygen pairs arising as a consequence of domain formation. This configuration agrees with electron microscopy experiments.[4] For simplicity we suppose that the impurities are distributed on lines in the (110) direction in such a way that adjacent domains always have different orientations of the Cu-O chains [see Fig. 1(b)].

The domains that exist in phase D can be divided into two classes. Let (m_1,n_1) and (m_2,n_2) be the coordinates of the two impurities on the corners of a domain, and $\Delta m = m_1 - m_2$, $\Delta n = n1 - n2$. Then, if $(|\Delta m| + |\Delta n|)$ is an uneven number, one additional oxygen atom is brought into the Cu(1) plane as a consequence of the formation of two of such domains. In that case the surface energy of a domain is given by

$$E_D=2(\varepsilon_{OO}-\varepsilon'_{oo})l+\Delta\varepsilon \ , \tag{4}$$

where $l\equiv\max\{\Delta m,\Delta n\}$, and

$$\Delta\varepsilon\equiv2\varepsilon_{\mathrm{CuO}}+\tfrac{1}{2}E_d+2\varepsilon_{OO}+3\varepsilon'_{OO}$$

is the energy correction due to the additional oxygen. In the case where $(|\Delta m|+|\Delta n|)$ is an even number, the system cannot incorporate an additional oxygen as a consequence of the formation of such domains. In contrast to the former case, one Cu would then have the coordination $k=5$. The surface energy of this domain type is

$$E_D=2(\varepsilon_{OO}-\varepsilon'_{OO})l \ . \tag{5}$$

Note that in order to determine the total surface energy of the domain phase (D), we sum over the surface energies of half the domains existing in this phase to avoid double counting of domain surfaces. Equivalently, we could define a formation energy per domain E'_D, given by $E'_D=\frac{1}{2}E_D$.

The phenomenological model presented here can be extended to an electronic theory by using the Hubbard Hamiltonian and calculating the local density of states, the charge distribution, and finally expressing $E(p)$ within such a theory. However, in this paper we use empirical interaction energies for the numerical analysis determining which of the phases A,B,C,D is energetically the most favorable one.

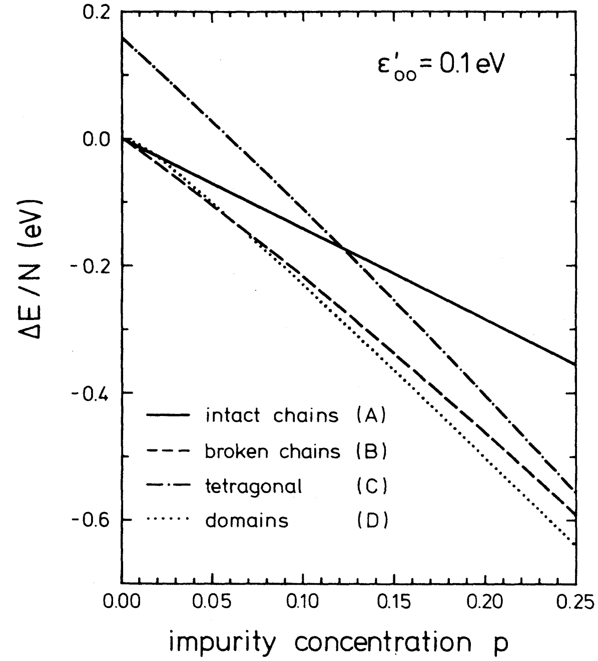

FIG. 3. Energy difference with respect to the undoped orthorhombic phase per Cu(1) site ($\Delta E/N$) for various phases as a function of the impurity concentration p in the Cu(1) planes. Note that we chose 0.1 eV for the direct next-nearest-neighbor oxygen pair repulsion ε'_{OO}.

III. RESULTS AND DISCUSSION

In Fig. 3 results are shown for the change in energy $\Delta E(p)=[E(p)-E_0(0)]$ for various phases. Here, $E_0(0)$ refers to the undoped orthorhombic phase. The calculations are performed for $M=\mathrm{Al}^{3+}$, with $\varepsilon_{\mathrm{CuO}}=-1.83$ eV, $\varepsilon_{MO}=-2.54$ eV (Refs. 11–13), and $\varepsilon_{OO}=0.21$ eV.[14,15] For ε'_{OO} we take 0.1 eV. It can be seen that for $\varepsilon'_{OO}=0.1$ eV the domain phase D is the lowest in energy for $p>0.06$, whereas the broken chain phase B has the lowest energy for lower impurity concentrations. In general, one obtains for Al^{3+}, Co^{4+}, and Fe^{4+} impurities with a coordination number $k=6$ and a bond energy with oxygen, ε_{MO}, which makes the local rearrangement of oxygen energetically favorable that phase B is lower in energy than phase A. In order to see whether the phases C or D are even lower in energy than phase B, we have to consider only the repulsive energies ε_{OO} and ε'_{OO}, since the number of Cu—O and M—O bonds is the same in the phases B, C, and D if we neglect the corrections due to the uptake of excess oxygen. For these phases an impurity always has four nearest oxygen neighbors in the Cu(1) plane. We then find from Eqs. (1) and (5) that the domain phase is lower in energy than phase B if

$$\left[\frac{1}{\sqrt{p}}-2\right]\frac{\varepsilon_{OO}-\varepsilon'_{OO}}{\varepsilon_{OO}}<1 \ . \tag{6}$$

It follows from Eq. (6) that the impurity concentration p_c, where the transition into the domain phase occurs, depends only on the parameter $q\equiv(\varepsilon_{OO}-\varepsilon'_{OO})/\varepsilon_{OO}$. In Fig. 4 we plotted p_c as a function of q. Note that allowing excess oxygen will change p_c only slightly (less than 10%). Furthermore, for impurity concentrations p, where the transition to a phase with equal lattice parameters a and b is observed, we obtain from our calculations that the tetragonal phase is much higher in energy than phases B and D if $q>0$. In conclusion, our calculations at $T=0$ suggest that no tetragonal phase occurs due to doping. This behavior is in contrast to the order-disorder transition in the undoped oxygen-deficient 1:2:3 compound, which is driven by entropy.[14–20] Note that at very high impurity concentrations ($p>0.3$) phases B, C, and D become equivalent because all oxygen atoms in the Cu(1) plane are then fixed in the neighborhood of the impurities.

It is of interest to compare our results for the critical concentration p_c with experiment. It has been previously reported[4] that the tetragonal structure suggested by x-ray diffraction may result from an averaging procedure over adjacent domains. The transition to the phase with $a=b$ was observed[2] in x-ray experiments for $\mathrm{YBa_2(Cu}_{1-x}M_x)_3\mathrm{O}_{7+y}$ ($M=$Al, Co, Fe) at an impurity content x between 2.5% and 3%. Assuming that at least 75% of the impurities[2,5] occupy Cu(1) sites, this corresponds to impurity concentrations p in the Cu(1) plane with $0.06\le p\le0.09$. This agrees with our results for p_c, if ε'_{OO} is between 0.05 and 0.11 eV, i.e., if $\frac{1}{2}\le q\le\frac{3}{4}$. Actually, this relation between nearest- and next-nearest-

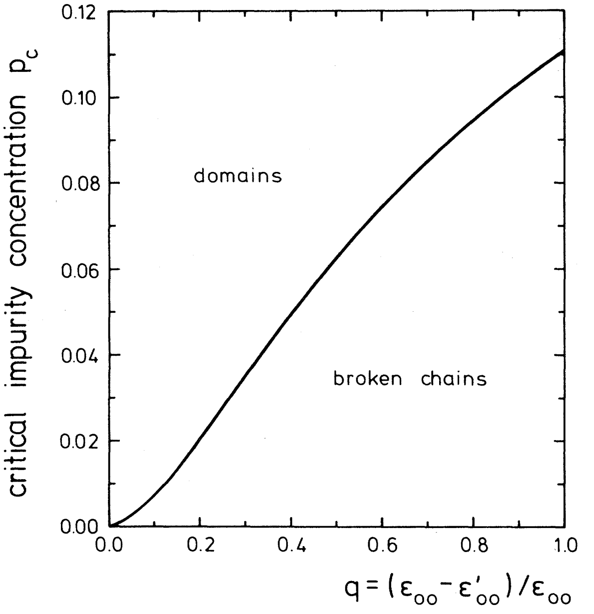

FIG. 4. Critical concentration of impurities, p_c, at which the transition from the broken chain phase B to the domain phase D occurs, as a function of q. q is a measure for the difference in repulsive energy between nearest- and next-nearest-neighbor oxygen pairs. Note that in general our curve for p_c may not coincide with the curve for p_0, at which one observes $a = b$ experimentally. In particular, for impurities with $k = 5$ the domains can be too large at p_c to give $a = b$ as a result of the averaging procedure in x-ray experiments.

neighbor oxygen pair repulsion was also proposed by other authors.[17,19] Therefore, assuming the formation of orthorhombic domains as a consequence of doping we can explain why the transition into the phase with $a = b$ is observed in x-ray experiments at such low impurity concentrations.

Furthermore, x-ray and neutron experiments[2,3,7] observed a continuous transition from the $a \neq b$ to the $a = b$ phase. In order to understand this we suppose that the impurities are randomly distributed on the Cu(1) sites, and that it depends on the environment of an impurity, whether together with other impurities domains are formed or whether only a local redistribution of oxygen atoms in the neighborhood of the impurity occurs. Domain formation results when two impurities are located on Cu(1) sites of such a distance that the formation energy of a domain [see Eqs. (4), and (5)] with the two impurities on opposite domain corners [see Fig. 2(d)] is smaller than the energy required to redistribute the oxygen atoms only locally around the two impurities. Generally, for small distances l between the two impurities new domains are formed, while for distances larger than a certain critical one, l_0, oxygen is only rearranged locally around the impurities. Consequently, for increasing impurity concentration p, the density of domains[21] increases, and the average domain size[22] decreases continuously. Thus, averaging the lattice parameters over a certain area, corresponding to the averaging procedure of x-ray experiments, one obtains[23] a continuous change $a \rightarrow b$ for the lattice parameters.

Regarding the presence of excess oxygen, we observe the following. In the pure domain phase D each impurity is involved in the formation of four domains, and each domain has two impurities on opposite corners. Thus, the number of domains exceeds the number of impurities by a factor of 2. For half of these domains we expect $(|\Delta m| + |\Delta n|)$ to be uneven. According to our preceding discussion in Sec. II the formation of two of such domains will cause the uptake of one additional oxygen atom from the gas phase. It follows that two impurities involved in the formation of domains bring one additional oxygen into the system. This uptake of excess oxygen has already been observed experimentally[2,3,24]

Up to now we have considered only impurities with a sixfold coordination. For Ga^{3+} we found $k = 5$, i.e., gallium has only three nearest oxygen neighbors in the Cu(1) plane. This means that one of the four domains surrounding a Ga^{3+} must be oriented in such a way that it has no oxygen which is a nearest neighbor to Ga [see Fig. 2(e)]. Thus, there is a great number of neighboring domains having Cu-O chains with the same orientation, and consequently they form larger domains with parallel Cu-O chains. The density of differently oriented domains decreases, implying an increase of p_c. For example, if we assume that the impurity concentration p_c(Al) corresponds to domain sizes which give a few domains within the region over which x-ray diffraction averages so that $a = b$ in these experiments, then we estimate that we need about two to three times as many impurities to observe $a = b$ in the case of gallium. This may explain the x-ray experiments by Xiao *et al.*,[7] who observed the transition from $a \neq b$ to $a = b$ for a gallium content $x_c = 0.06$, whereas[2] $x_c = 0.03$ for Al, which has $k = 6$. These considerations might also be relevant for Co and Fe impurities[25] with mixed valencies M^{3+} or M^{4+}, and $k = 5$ or $k = 6$, respectively. However, Mössbauer spectroscopy indicates[8] that dominantly Fe^{4+} and Co^{4+} are present in 1:2:3 compounds. In particular, Fe impurities were found to be octahedrally coordinated in a recent extended x-ray-absorption fine-structure spectroscopy study.[26] Thus, for these impurities one expects the same results for p_c as for Al. This is confirmed by the experiments of Tarascon *et al.*[2]

Summarizing, our calculations based on bond theory suggest that the phase with lattice parameters $a = b$ consists of an ensemble of differently oriented orthorhombic domains. No tetragonal phase occurs, since it is energetically less favorable than other phases. The calculated critical impurity concentration p_c, at which a becomes equal to b, is determined to be the same for Al, Co, and Fe impurities, which agrees well with experiment. The observed uptake of excess oxygen as a consequence of doping with Al, Co, and Fe is also explained.

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APPENDIX

In order to determine the oxygen coordination of the impurities from the strength s of the various cation-oxygen bonds, we proceed as follows. First the bond strengths are estimated from the empirical relations[27]

$$s_i = (R_i/R_0)^{-N} \tag{A1}$$

or

$$s_i = \exp[-(R_i - R_c)/B] \ . \tag{A2}$$

Here, B, N, R_0, and R_c are parameters depending on the cation. For the distance R_i between a cation on a Cu(1) site and its nearest oxygen neighbor $O^{(i)}$ we take the values reported by David *et al.*[28] and Bordet *et al.*[24] We confirm the results for the bond strengths in an independent second calculation, where we use a bond-strength–bond-length relation[11,12] of Coulombic form. We insert the calculated bond strengths into the equation[29]

$$\sum_{i=1}^{k} s_i = z \ . \tag{A3}$$

Here, $\sum_{i=1}^{k}$ is a sum over all nearest oxygen neighbors of a cation and z is its valency. We then consider the value of k which best fulfills this relation for a given cation as the coordination number of the cation.

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[9] The cation-oxygen bond energies in oxide crystals, ε^0_{AO} (Refs. 11 and 12), are defined by $E_t = \sum_i \varepsilon^0_{AO}(i)$, where E_t is the total energy of the A_mO_n crystal (A = Al, Cu, Fe, etc.) and i runs over all A—O bonds in the crystal. Thus, the ε^0_{AO} include all the oxygen-oxygen interactions. To be able to distinguish the energies of different oxygen configurations we introduce new cation-oxygen bond energies, ε_{AO}, that are defined by $E_t = \sum_{i,j,k}[\varepsilon_{AO}(i) + \varepsilon_{OO}(j) + \varepsilon'_{OO}(k)]$, where j and k run over all nearest- and next-nearest-neighbor O-O pairs in the crystal, respectively. For the calculations we take $\varepsilon_{OO} = 0.21$ eV (Refs. 14 and 15) and treat the direct next-nearest-neighbor oxygen-oxygen interaction ε'_{OO} as a parameter.

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