Substitutional disorder, random dipoles and the binding energy of orthorhombic $La_{2-x}Sr_xCuO_4$

Mario Birkholz[1], Rainer Rudert[2,*]

[1] Ingenieurbüro für Solartechnik, Offenbacher Strasse 7, D-14197 Berlin, Germany
[2] Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Rudower Chaussee 5, D-12489 Berlin, Germany

Abstract. This study investigates the effect of heterovalent, substitutional disorder on the binding energy of $La_{2-x}Sr_xCuO_4$. First, disorder has been found to create crystal electric fields that fluctuate over different lattice sites and induce ionic dipole moments of varying strength and orientation. The strength of these random dipoles will be presented for increasing x. Second, disorder may slightly displace the ions from their average lattice sites. The large thermal parameters obtained from diffraction experiments are discussed in this context. Finally, the polarization energy related to random dipoles was calculated to be on the order of eV and favourizes the positive charge carriers introduced by Sr doping to be associated with the copper ions. It is concluded that the solid exists in a state containing mixed copper valencies (Cu^{2+}/Cu^{3+}).

PACS: 61.50.Lt; 61.70. $-r$; 74.70.Vy

Introduction

$La_{2-x}Sr_xCuO_4$ is regarded by many research groups as a model system for investigating high-temperature superconductivity in cuprates. The compound still has a relatively simple structure, and high-precision structural data have been determined for many points in the phase diagram, see [1–6] for example.

In a previous study [7], referred to as I in the following, we calculated the electrostatic interaction energy of $La_{2-x}Sr_xCuO_4$ (LSCO). For this purpose we assumed that the holes supplied by Sr doping were related to either 1. copper ions, $Cu^{2+} \rightarrow Cu^{3+}$, 2. apex oxygens, $O(A)^{2-} \rightarrow O(A)^-$, or 3. in-plane oxygens, $O(P)^{2-} \rightarrow O(P)^-$. For the first time we calculated the five second-order electrostatic moments that may occur in the low-temperature orthor-

hombic phase (LTO). By minimization of the binding energy, the charge assignment according to model 1 was determined to be the one actually taken by the system. This result was obtained independent of whether dipolar contributions were considered or neglected. However, we only calculated so-called regular dipoles in I, which are linked to certain ions whenever they occupy crystallographic lattices sites of certain symmetries. Essentially, there is characteristically an absence of a center of inversion at these sites, which causes a crystal electrical field to arise and polarize the ion. The latter then has to be accounted for by a charge and a dipole moment if electrostatic considerations were applied.

Another work [8] has pointed to the fact that, for such heterovalently disordered compounds as $La_{2-x}Sr_xCuO_4$, so-called random dipoles may arise in addition to regular ones. Random dipoles are a direct consequence of disorder at (La, Sr) sites, where $3+$ and $2+$ electrical charges become randomly distributed for $x > 0$. This leads to crystal electric fields of varying strengths at all lattice sites. In this work we will present the randomly induced dipoles for the three valency models and incorporate an associated polarization energy into the binding energy E_B. Again, the state actually taken by the system is found by minimizing E_B.

We think that the concept of randomly induced dipoles as applied in this work should be of interest for many other compounds in which heterovalent disorder occurs. We mention the case of Fe_3O_4, in which octahedral lattice sites are randomly occupied by Fe^{2+} and Fe^{3+} ions and numerous other compounds crystallizing in the inverse spinel structure [9]. The concept should also be usable for compounds of the chalcopyrite class ABC_2. In some of them, an order-disorder phase transition which causes an irregular distribution of A^I and B^{III} ions on equivalent lattice sites can be observed [10]. In all of these compounds, heterovalent substitution is related to a modification of the electronic, optical, mechanical and elastic properties of the solid. Often, these parameters may even be adjusted by the degree of introduced disorder. We expect that these effects can be better understood with the help of the concept of randomly induced dipoles. To our

knowledge, this work is the first study where the concept is applied.

Randomly induced dipoles

The starting point of the following considerations is the binding energy E_B of a crystalline solid, which is mainly the sum of ionization energies E_I, Coulomb interactions E_C and polarization energy E_{pol}

$$E_B = E_I + E_C + E_{pol} + E_r + E_{vdW} + E_{tv} \tag{1}$$

with less important shares due to core-core repulsion E_r, van der Waals attraction E_{vdW} and thermal vibrations of the lattice constituents E_{tv}. As will be shown, the polarization energy is broken down into two parts, one due to regular dipoles, i.e. those restricted to certain site symmetries, the other due to randomly induced dipoles

$$E_{pol} = E_{p,reg} + E_{p,ran}. \tag{2}$$

E_I, E_C and $E_{p,reg}$ at $T \approx 16\,\mathrm{K}$ for orthorhombic $La_{2-x}Sr_xCuO_4$ were previously determined in I. In this work the term $E_{p,ran}$ will be considered. For this purpose, we will investigate three different valency models that can occur with the substitution of La by Sr ions and which can account for the oxidation of different species in the lattice to maintain charge neutrality of the whole crystal. With increasing Sr content x it will be assumed that the average valencies of the ions are accounted for by 1.) $(2 + x)$ for copper 2.) $(-2 + x/2)$ by in-plane oxygen and 3.) $(-2 + x/2)$ for apex oxygen ions in models 1-3, respectively.

The physical background of randomly induced dipoles and the associated energy $E_{p,ran}$ may be understood from the following arguments. The incorporation of Sr ions on La sites in La_2CuO_4 occurs by chance, as was revealed by diffraction experiments [1]. According to probability theory the occupation of an La site is governed by a Bernoullian distribution or two-point distribution [11] with weights $w_1 = (1 - x/2)$ and $w_2 = x/2$ describing the probability of finding an La or an Sr ion of charge $3 +$ or $2 +$. Strictly speaking, all symmetry elements as mirror planes, axes of rotation etc. vanish at each lattice site, causing the point symmetry group of every ion to become $C_1(1)$. Because of disorder, the crystal electrical field F_i at every lattice site will become a statistically varying function. Of course, the strength of fluctuating crystal fields will vanish on the average. However, because the F_i enter quadratically the polarization energy formula, we have to consider the average of the square, $\overline{F_i^2}$. Applying this concept we obtain for the energy of a set of induced dipole moment

$$E_{pol} = -\sum_{i=1}^{4} \frac{K_i}{Z} \frac{4\pi\varepsilon_0 \kappa_i \overline{F_i^2}}{2}$$
$$= -\sum_{i=1}^{4} \frac{K_i}{Z} \frac{4\pi\varepsilon_0 \kappa_i}{2} \{\overline{F_i}^2 + \sigma^2(F_i)\} \tag{3}$$

where use has been made of the definition of the statistical variance σ^2. From the first summand in the last line the

regular polarization energy is derived, see I, while the second term leads to randomly induced dipoles. The index $i = 1, 2, 3, 4$ stands for the ions on LS, Cu, O(A) and O(P) sites (LS abbreviates La or Sr). κ accounts for dipole polarizability, and K_i is the frequency of the i-th ion in the unit cell, with $K_i = 4, 8, 8, 8$ for $i = 1, \ldots, 4$, that contains $Z = 4$ formula units LSCO. The other symbols have their usual meaning.

The varying crystal electric fields may induce dipole moments which were named random dipoles [8] to distinguish them from regular dipoles that only occur for certain lattice sites under special symmetry conditions. In contrast to the regular dipoles, the random ones are not symmetry restricted, but depend only on the degree of disorder caused by heterovalent substitution in the crystal lattice. $E_{p,ran}$ may be compared to the van der Waals attractive energy, E_{vdW}. Whereas E_{vdW} accounts for the mean polarization energies in time [12], $E_{p,ran}$ considers the spatial average of polarization energies. Both averaging procedures actually account for relaxation of the solid and an increase of crystal binding. In fact, the energy gain due to random polarization is most probably the driving force for the irregular distribution of Sr and La ions over LS lattice sites.

It has been shown [8] that the variance of random crystal fields at the i-th lattice site, $\sigma^2(F_i)$, may be formulated as

$$\sigma^2(F_i) = \frac{E_0^2}{w^2 e^2} \sum_{j=1}^{4} D^2(z_j) R_{ij}^4. \tag{4}$$

E_0 is an energy unit that equals $2\,Ryd\,a_0/\sqrt[3]{V}$, with a_0 for Bohr's radius and V being the volume of the crystallographic unit cell. The cube root of the latter is abbreviated by w and its volume will be symbolized by w^3. R_{ij}^4 accounts for a set of infinite lattice sums over all inverse distances to the fourth power between an ion i and all other ions (index l) of the j-th sort

$$R_{ij}^4 = \sum_{l}^{\infty} (\rho_i - \rho_l(j))^{-4}. \tag{5}$$

Distances are given in fractions of the unit length w and the power of 4 in (5) is understood from the fact the squares of electrical monopole fields enter (3) and (4). There occur 4×4 such lattice sums in LSCO for each Sr concentration.

The main ingredient for the occurrence of random dipoles, however, is the statistical scatter or dispersion of charges, symbolized by $D^2(z_j)$. As usual in probability theory, D^2 is the difference between the mean square and the square mean charge of an ion

$$D^2(z_j) = \overline{z_j^2} - (\overline{z_j})^2. \tag{6}$$

Both quantities $\overline{z_j^2}$ and $\overline{z_j}$ can be calculated with probability weights of charges distributed over the j-th lattice site. For the case of the LS site, $j = 2$, one find

$$D^2(z_2) = \left(1 - \frac{x}{2}\right) z_{La}^2 + \frac{x}{2} z_{Sr}^2 - \left[\left(1 - \frac{x}{2}\right) z_{La} + \frac{x}{2} z_{Sr}\right]^2. \tag{7}$$

The dispersion of z_2 is the same x-dependent function in all valency models. We make an important assumption

Table 1. Mean ionic charges as a function of the doping rate x for different valency models and statistical parameters calculated therefrom. The numbering of ions Cu, LS, O(A) and O(P) is accounted for in ascending order by index j

Model	Ion j	$\bar{z}_j$	$\overline{z_j^2}$	$\overline{z_j^2} - (\bar{z}_j)^2$
1	1	$2+x$	$4+5x$	$x - x^2$
	2	$3-\dfrac{x}{2}$	$9-5\dfrac{x}{2}$	$\dfrac{x}{2} - \dfrac{x^2}{4}$
	3	-2	4	0
	4	-2	4	0
2	1	2	4	0
	2	$3-\dfrac{x}{2}$	$9-5\dfrac{x}{2}$	$\dfrac{x}{2} - \dfrac{x^2}{4}$
	3	$-2+\dfrac{x}{2}$	$4-3\dfrac{x}{2}$	$\dfrac{x}{2} - \dfrac{x^2}{4}$
	4	-2	4	0
3	1	2	4	0
	2	$3-\dfrac{x}{2}$	$9-5\dfrac{x}{2}$	$\dfrac{x}{2} - \dfrac{x^2}{4}$
	3	-2	4	0
	4	$-2+\dfrac{x}{2}$	$4-3\dfrac{x}{2}$	$\dfrac{x}{2} - \dfrac{x^2}{4}$

regarding the dispersion of charges on other lattice sites. In model 1, for instance, Cu^{2+} and Cu^{3+} occur with statistical weights $(1-x)$ and x. We will also assume that $2+$ and $3+$ charges are randomly distributed over Cu sites in this model, whereas the O(A) and O(P) valencies remain constant. Comparable assumptions are made in model 2 and 3. The $D^2(z_j)$ for the three models are all given in Table 1. Of course, they all vanish for $x = 0$, indicating that neither random dipoles nor a related stabilization energy occurs for La_2CuO_4.

It finally is obtained for the random polarization energy

$$E_{p,\text{ran}} = -\frac{E_0}{2} \sum_{i,j}^{4} \frac{K_i}{Z} \frac{\kappa_i}{w^3} D^2(z_j) R_{ij}^4. \tag{8}$$

As it was proceeded in I, we will calculate energy parameters E for all valency models, which is the binding energy E_B of the solid except for E_r, E_{vdW} and E_{tv}

$$E = E_B - E_r - E_{vdW} - E_{tv} = E_I + E_C + E_{\text{pol}}. \tag{9}$$

Whereas $E_{p,\text{ran}}$ as a part of E_{pol} was neglected in I, we will include it in our considerations here. The charge distribution actually taken by LSCO is then assumed to be the one with the smallest E parameter.

In the forthcoming section we will present the results for R_{ij}^4 coefficients and the deduced quantities for all three valency models. Structural parameters as determined for $x = 0$ and $x = 0.13$ by Jorgensen et al. [2] and Braden et al. [5] for $T = 10$ and 22 K, respectively, and as extrapolated in I to $x = 0.21$ will be used. For the latter Sr content the phase transition from the low-temperature orthorhombic phase (LTO) to the high-temperature tetragonal phase (HTT) occurs at low temperatures according to

Takagi et al. [13]. All data are valid for temperatures of about 10–22 K.

Results and discussion

In Table 2 R_{ij}^4 coefficients for the stoichiometry coordinates $x = 0$, 0.13 and 0.21 are given. They are precise to the fifth digit and have been calculated according to the same procedure and computer code [14] as mentioned in I. R_{ij}^4 can be seen to become very large compared to other electrostatic lattice coefficients. This is due to the fact that they do not account for alternating sums – as do α^m, α^d, β^m and β^d coefficients, but sum up always positive entities, see (5). As was expected, R_{ij}^4 matrices were found to be invariant for transpositions when the components were weighted by the frequency of the ions in the lattice, $K_i R_{ij}^4 = K_j R_{ji}^4$.

In Fig. 1 we present a plot of the mean random dipole strength in model 1, which was calculated with the ansatz $\bar{p}_i = 4\pi\varepsilon_0 \kappa_i \sigma(F_i)$. For this purpose R_{ij}^4 coefficients have been interpolated by a quadratic function in the x-range under investigation. Polarizabilities of La^{3+}, Sr^{2+} and O^{2-} were inserted as given in I, while $\kappa(Cu^{2+}) = 0.36$ Å^3 and $\kappa(Cu^{3+}) = 0.21$ Å^3 was used according to [15]. The random distribution of charges $3+$ and $2+$ on LS and Cu lattice sites induces dipole moments on the average as presented in the plot. If a certain ion is considered, however, its random dipole strength may differ from the mean due to statistical variations

Compared with regular dipoles (Fig. 4 in I), some random dipoles are found to become ten-times stronger for large values of x, i.e. for large disorder. Random dipoles are also induced for Cu ions, which was forbidden in La_2CuO_4 because of their site symmetry C_{2h} (2/m). Nevertheless, random moments are much smaller for metal ions than for oxygen ions, which is simply understood from the higher polarizabilities of the latter. Interestingly, substitutional disorder causes stronger random dipoles to occur on in-plane oxygens than on apex oxygens. This effect is due to the large R_{41}^4 coefficient, which is

Table 2. Electrostatic lattice sums R_{ij}^4 in LSCO calculated as explained in the text. For each index pair, ij, three R_{ij}^4 values are given, thereby accounting for the different Sr contents x of 0.0, 0.13 and 0.21 from top to the bottom

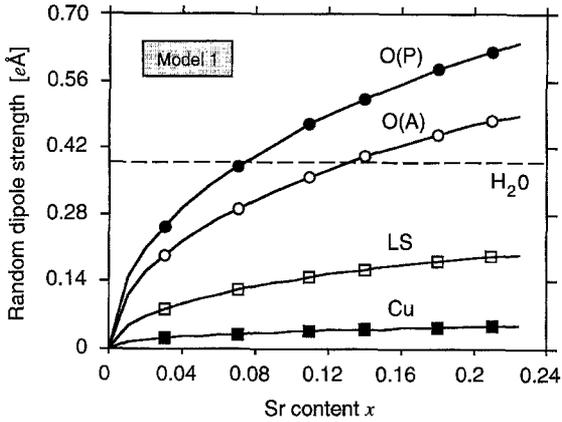| Ion j	Cu $i = 1$	LS 2	O(A) 3	O(P) 4
1	124.71	176.90	188.08	516.99
	125.68	176.12	189.20	526.69
	126.38	175.63	189.69	533.30
2	353.79	261.86	471.69	423.05
	352.24	261.96	467.74	418.70
	351.25	262.08	465.54	415.74
3	376.16	471.69	308.18	317.74
	378.39	467.74	305.73	318.91
	379.37	465.54	303.62	319.52
4	1,033.98	425.05	317.74	405.98
	1,053.38	418.70	318.91	411.58
	1,066.60	415.74	319.52	415.53

Fig. 1. Average strengths of random dipoles $\bar{\rho}_i$ as induced for the different ions of LSCO in model 1. For comparison, the dashed line indicates the dipole moment of the water molecule

found to surmount R^4_{31}, as can be seen in Table 2. This is mainly due to the shorter Cu-O(P) distance as compared to that of Cu-O(A).

The occurrence of random dipoles in heterovalently substituted compounds was derived from the fact that certain lattice sites are occupied by varying charges z_j having a non-vanishing statistical dispersion, $D^2(z_j) \neq 0$. Infinite lattice sums of electrical fields of charges

$$F_{ij} = \frac{E_0}{ew} \sum_l^\infty z_j (\rho_i - \rho_l(j))^{-2} \qquad (10)$$

became normally distributed quantities for the disordered compound and random dipole moments were induced at all lattice sites. Regarding (10) carefully, one may speculate that the varying displacement of charges from their average lattice sites may also cause the occurrence of random crystal fields. Accordingly, the phenomenon of random dipoles would not be limited to disorder of the hetero-valent-substitutional type, with $D^2(z_j) \neq 0$, but may also be related to displacements of the ions from their equilibrium lattice sites, with $\sigma^2(\rho_{ij}) \neq 0$.

It is precisely this effect that might have been observed in a recent X-ray absorption fine structure (XAFS) study by Frenkel et al. [16,17]. The authors investigated the mixed alkali halides $Rb_{1-x}K_xBr$ and $RbBr_yCl_{1-y}$, which were disordered on either cation or anion lattice sites. In contrast to $La_{2-x}Sr_xCuO_4$ these compounds are homovalently substituted, with $D^2(z_j) = 0$. The study revealed small displacements of the ions from their mean lattice sites, leading to a buckled crystalline structure. In this work any two adjacent distorted bonds were associated with an effective dipole. Also, the orientation of dipole vectors was argued to be randomly distributed and frozen at low temperature. The system was named a dipole glass, in accordance with spin glass [17]. The expression seems to be appropriate to describe the situation in $La_{2-x}Sr_xCuO_4$ as well. In contrast to a spin glass, however, the dipole glass in LSCO is not characterized by a random distribution of orientations alone, but also by a random distribution of strengths of moment vectors. These considerations imply that randomly induced

dipoles may be related to both types of disorder, first, of the heterovalent type and, second, of the displacive type.

In this context it is of some interest to pose the question of whether the valency disorder in LSCO may be accompanied by displacive disorder. If this is case, random displacements should become normally distributed, as were the crystal electrical fields. It is easily derived from the theory of diffraction that Gaussian distributed displacements should artificially enhance thermal parameters or Debeye-Waller temperatures as determined by diffraction studies [18]. Indeed, anomalously large thermal parameters were found in diffraction experiments for many HTSC cuprates, see [19] for a discussion of this point and the citations given therein. Moreover, for the case of $La_{2-x}Sr_xCuO_4$, thermal parameters have actually been measured to increase with increasing Sr content x, see the profound study of Braden et al. on the relation between structure and doping in LSCO [5]. One may conclude that structural analyses do confirm the suggestion that substitutional disorder in LSCO causes random displacement of the ions from their average lattice sites. Frenkel et al. pointed out that, for a thorough description of disorder, new structural parameters that are distinguishable from the usual average structure parameters are needed to account for the local distortion of ionic coordinations [16]. Methods for the determination of the local structure as XAFS should be more appropriate for this purpose than diffraction procedures that average structural informations over large spatial extensions of the solid. See [20] for a recent description of the capabilities of the XAFS technique and [19, 21] for its application on some HTSC compounds.

In Fig. 2 we have plotted the polarization energy $E_{p,\mathrm{ran}}$ associated with the random dipoles for all three valency models. For reasons of comparison, the energy due to regular dipoles, $E_{p,\mathrm{reg}}$, has also been presented, but the scale is twice as large as the scale used in $E_{p,\mathrm{ran}}$. The random polarization energy vanishes at $x = 0$, since no valency disorder occurs in the La_2CuO_4 lattice. As the Sr content increases $E_{p,\mathrm{ran}}$ grows to large values of some eV. At $x = 0.21$ $E_{p,\mathrm{ran}}$ is found to be larger than $E_{p,\mathrm{reg}}$ approximately by a factor of ten. The energy gain due to random dipoles clearly favours model 1. For this model the
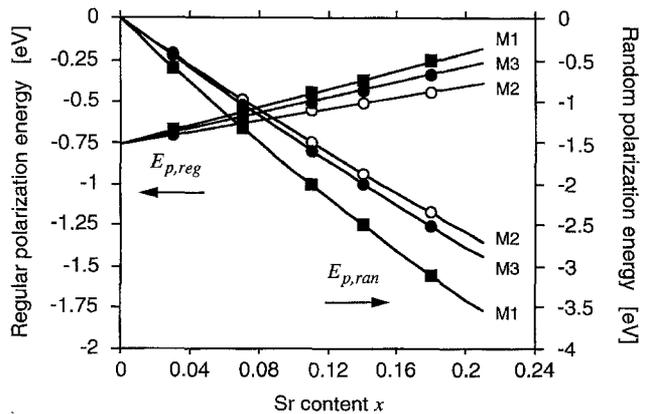

Fig. 2. Polarization energies due to random and regular dipoles, $E_{p,\mathrm{ran}}$ and $E_{p,\mathrm{reg}}$, for all three valency models (M1-M3)

disorder polarization amounts to $-3.5\,\mathrm{eV}$ at $x = 0.21$ which is a significant enhancement of crystal binding. First, the effect of favouring model 1 can be explained by differences in polarizability which is larger for oxygen ions than for copper ions, $\kappa(O^{2-}) - \kappa(O^{-}) = 0.81\,\text{Å}^3 > \kappa(Cu^{2+}) - \kappa(Cu^{3+}) = 0.15\,\text{Å}^3$. According to (3) $E_{p,\mathrm{ran}}$ is proportional to the dipole polarizability of the individual ions. Consequently, the strength of $E_{p,\mathrm{ran}}$ is more enhanced if the oxygen ions maintain a 2- charge as assumed in model 1 as compared to models 2 and 3. The latter models assume that electrons are partially depleted from oxygen ions, and that their polarizability is reduced. Second, model 1 is favoured because of the crystal structure, i.e. the selective choice of large R_{ij}^4 in combination with model 1. This can be demonstrated by successively inserting the values of the different models given for $D^2(z_j)$ and R_{ij}^4 in Table 1 and 2 into (8).

We emphasize again that we made use of a non-vanishing statistical dispersion for the copper charge, $D^2(z_1)$, for the calculation of $E_{p,\mathrm{ran}}$ in model 1 (or $D^2(z_3) \neq 0$ in model 2 or $D^2(z_4) \neq 0$ in model 3). We thereby implicitely assumed that 2 + and 3 + charges are randomly distributed on Cu lattice sites (or 2 − and 1 − on oxygen sites). Strictly speaking, we do not have experimental evidence that this is case as it was demonstrated for LS sites. For the latter the difference of scattering form factors is large enough to be detected by diffraction procedures. If we renounce to assume the doped holes to be randomly distributed, the maximum effect will be that all dispersions of charges would vanish except for $D^2(z_2)$. The random polarization energy would accordingly become equal for all models, being less than 1.5 eV in the whole x-range investigated. However, we argue the opposite way, i.e. from the large energy gain of the system associated with $D^2(z_1) \neq 0$, we derive that holes are randomly distributed on copper lattice sites.

We now proceed to a discussion of binding energy or of E parameters in the different models, see (8). As in I we will assume that the terms E_r, E_{vdW} and E_{tv} are almost equal for all models. Therefore, they are insignificant for deciding which state is taken by the compound. Except for $E_{p,\mathrm{ran}}$ the E parameters have already been calculated. Model 1, which is associated with mixed copper valencies, was found to yield the smallest E values, see Fig. 3 in I.

In Fig. 3 we present a plot of E parameters as a function of Sr content by inclusion of the random polarization energy (straight lines). For all models the binding energy of the system can be seen to relax significantly when effects due to random dipoles are considered in addition to regular dipole shares. Again, the smallest E parameters are found in model 1, which assumes a share x of all copper ions to be oxidized with increasing Sr content. We conclude that by also considering randomly induced dipoles, $La_{2-x}Sr_xCuO_4$ is found to be in the state of model 1. The occurrence of Cu^{3+} ions would mainly be caused (i) by the disorder in the lattice and (ii) by the larger polarizability of oxygen ions as compared to copper ions.

Figure 3 also displays E parameters as they would be obtained by neglecting the share of the binding energy due to randomly induced dipoles (dashed lines). As can be seen, the set of E does not only differ from the latter by an
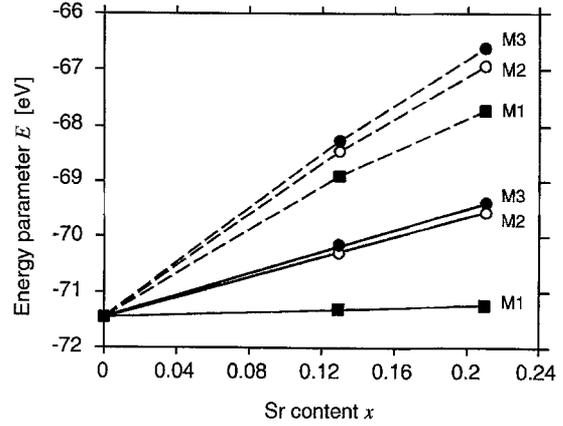

Fig. 3. E parameter for one formula unit $La_{2-x}Sr_xCuO_4$ calculated for the different models M1-M3 according to (9). Dashed lines: by neglecting, and straight lines: by including shares due to random dipoles. The binding energy of model 1 (mixed copper valencies) is always found to be less than that of the other models

enhanced binding energy, but the differences in E parameters between the different models are altered. This is most relevant for E in model 1, which becomes significantly smaller than the E parameters of models 2 and 3 when random dipoles are taken into account. In I, fluctuations of the solid were considered as they may occur among the different valency models. This now appears to be refuted by the large and increased differences in binding energy.

Last, we want to consider the possible errors in the calculated quantities. A first source a ambiguity is the ionic polarizability, the value of which depends greatly upon the surrounding in different solids. We therefore have varied the set of κ_i by $\pm 20\%$ and have done the same calculations as given above. No significant deviations from the presented results were thereby obtained, i.e. the hierarchy of the strengths of random dipoles was not changed, and the charge assignments according to model 1 remained the one with lowest E parameter.

Another possible source of error is related to the small displacements of the ions from their average lattice sites in $La_{2-x}Sr_xCuO_4$ as pointed out above. This might be of relevance because the mean random dipoles as presented in Fig. 1 have simply been calculated by R_{ij}^4 coefficients as obtained with mean distances $\bar{\rho}_{ij}$, between the ions. According to the displacive type of disorder the random dipole strength and the associated polarization energy may be erroneous to a certain degree. For precise determination of the related error one will need more parameters that account for local structural distortions. We roughly estimated the variations of distances and found them to be too small to affect the large random dipole moments solely due to valency disorder.

Conclusions

We investigated the consequences of disorder caused by heterovalent substitution upon the binding energy of orthorhombic $La_{2-x}Sr_xCuO_4$ at low temperature. Disorder was found to generate crystal electrical fields that vary in

54

strength and orientation. These varying fields induce random dipole moments for all ions in the LSCO lattice. The overall configuration may be named dipole glass, as was done in a comparable study of disordered solids. The valency disorder at metal lattice sites is accompanied by displacive disorder, which is derived from the large thermal parameters as revealed by diffraction experiments. The polarization energy related to randomly induced dipoles leads to considerable relaxation of the binding energy (-3.5 eV at $x = 0.21$). This definitely suggests the charge assignments with mixed copper valencies (Cu^{2+}/Cu^{3+}) to be the one actually taken by the system. This can be explained by the higher polarizability of oxygen ions as compared to that of copper ions. Considering the random polarization energy has proven its value in deciding which charge distribution should be assigned to a disordered compound. The concept should be of general relevance for HTSC cuprates and many other heterovalently substituted compounds.

References

1. Cava, R.J., Santoro, A., Johnson, D.W., Rhodes, W.W.: Phys. Rev. B **35**, 6716 (1987)
2. Jorgensen, J.D., Dabrowski, B., Pei, S., Hinks, D.G., Soderholm, L., Morosin, B., Schirber, J.E., Venturini, E.L., Ginley, D.S.: Phys. Rev. B **38**, 11337 (1988)
3. Kamiyama, T. et al.: Physica C **172**, 120 (1990)
4. Braden, M., Schweiss, P., Heger, G., Schwarz, W., Wohlleben, D., Fisk, Z., Rumiantsev, A., Tanaka, I., Kojima, H.: Physica C **185–189**, 549 (1991)
5. Braden, M., Schweiss, P., Heger, G., Reichardt, W., Fisk, Z., Gamayunov, K., Tanaka, I., Kojima, H.: Physica C **223**, 396 (1994)
6. Takahashi, H., Shaked, H., Hunter, B.A., Radaelli, P.G., Hitterman, R.L., Hinks, D.G., Jorgensen, J.D.: Phys. Rev. B **50**, 3221 (1994)
7. Birkholz, M., Rudert, R.: Z. Phys. B **97**, 7 (1995)
8. Birkholz, M.: Z. Phys. B **96**, 333 (1995)
9. Weiss, A., Witte, H.: Kristallstruktur und chemische Bindung, pp 133–140. Weinheim: Verlag Chemie 1983
10. Zunger, A.: Appl. Phys. Lett. **50**, 164 (1986)
11. Fisz, M.: Wahrscheinlichkeitsrechnung und mathematische Statistik, p. 160, Chap. 6. Berlin: VEB Deutscher Verlag der Wissenschaften 1980
12. Ashcroft, N.W., Mermin, N.D.: Solid state physics, p. 390. Tokyo: CBS Publishing Japan 1981
13. Takagi, H., Cava, R.J., Marezio, M., Batlogg, B., Krajewski, J.J., Peck, W.F., Bordet, P., Cox, D.E.: Phys. Rev. Lett. **68**, 3777 (1992)
14. Rudert, R., Birkholz, M.: ELC – a computer program for the calculation of electrostatic lattice coefficients (1994)
15. Fraga, S., Karwowski, J., Saxena, K.M.S.: Handbook of atomic data, Table VI (1). Amsterdam: Elsevier 1976
16. Frenkel, A., Stern, E.A., Voronel, A., Qian, M., Newville, M.: Phys. Rev. Lett. **71**, 3485 (1993)
17. Frenkel, A., Voronel, A., Katzir, A., Newville, M., Stern, E.A.: In: 8th International Conference on X-ray Absorption Fine Structure, Babersche, K., Arvanitis, D. (eds.). Berlin 1994, p. WeM-C4
18. Warren, B.E.: X-Ray Diffraction, p. 36–37. Reading, Mass.: Addison-Wesley 1969
19. Egami, T., Billinge, S.J.L.: In: Advances in superconductivity V, p. 67 Bando, Y., Yamauchi, H. (eds.). Berlin Heidelberg New York: Springer 1993
20. Tröger, L., Yokoyama, T., Arvanitis, D., Lederer, T., Tischer, M., Baberschke, K.: Phys. Rev. B **49**, 888 (1994)
21. Yamaguchi, H., Nakajima, S., Kuwahara, Y., Oyanagi, H., Syono, Y.: In: Advances in superconductivity V, p. 73. Bando, Y., Yamauchi, H. (eds.). Berlin: Springer 1993