

Interatomic Potentials for Structure Simulation of Alkaline-Earth Cuprates

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A specific potential model of interionic interactions was derived in which the crystal structures of alkaline-earth cuprates were satisfactorily described and some of their physical properties were predicted. It was found that a harmonic three-particle O–Cu–O potential and some Morse-type contributions to the simple Buckingham-type Cu–O repulsive potential enable one to improve essentially the results of crystal structure modelling for cuprates. The obtained potential set seems to be well transferable for different cuprates, despite the variety in linkages of the CuO₄ groups. In the present work this potential set model was applied in the crystal structure modelling for Ca₂CuO₃, CaCuO₂, SrCuO₃, (Sr_{1.19}Ca_{0.73})Cu₂O₄, and BaCuO₂. Some elastic and energetic properties of the compounds under question were predicted. © 2001 Academic Press

INTRODUCTION

The computer structural modelling and simulation of minerals and synthetic compounds based on the structural energy minimization for an atomic arrangement of a given stoichiometry has received wide acceptance during past two decades, as a direct response to the great progress in the power of modern computers. At present, the minimization procedure for the energy of interatomic interactions is successfully applied in the modelling of structure and properties for a large number of crystals, in calculations of defects in a crystal, in site localization of impurity ions, in predictions of thermodynamic stability and phase boundaries, in simulations of a crystal habit, in relaxation of a crystal surface, and in a series of other problems concerning crystalline objects (see, e.g., (1)).

The class of crystalline cuprates was widely investigated due to the high-temperature superconductivity discovered

in 1986. During the past decade a large amount of crystallographic and other data on these compounds was accumulated (see, e.g., (2)). However, the structural modelling of these compounds is still early in its development. To our knowledge, the computer modelling of the structure of high-*T_c* superconductors began in 1988, when the crystal structure of La₂CuO₄ was simulated (3, 4). The authors used empirical potentials from the relevant binary oxides, including also an angle-dependent three-body Cu–O–Cu term. Reference (5) is a brief communication on some preliminary results of the computer simulation of La₂CuO₄ and Nd₂CuO₄. This approach was used later in (6) for extensive theoretical study of the structures and defect chemistry of orthorhombic and tetragonal forms of La₂CuO₄ as well as a series of other cuprates such as Nd₂CuO₄, Y₂Cu₂O₅, Y₂BaCuO₅, Y₂CuO₄, YBa₂Cu₃O₆, YBa₂Cu₃O₇, YBa₂Cu₄O₈, YBa₂Cu₃O_{6.5}, La₂CaCuO₆, and La₂SrCu₂O₆. The short-range potentials used in this work were solely two-body and nonempirical, based on a modification of the Kim–Gordon model for interatomic forces. For all the binary oxides considered in this work a single O²⁻–O²⁻ repulsion potential and set of oxygen shell parameters were established. The resulting set of potentials and shell parameters was then used for more complex ternary and quaternary systems without modifications. It is worth noting that such different sets of potentials gave similar results for the basic bulk and defect properties of La₂CuO₄.

Only Sr₂CuO₄ has been considered among the alkaline-earth cuprates. In Ref. (6) it was concluded from the calculation of lattice parameters of this compound for different valence states of copper atom (Cu⁴⁺, Cu³⁺, Cu²⁺), together with the experimental values for Sr₂CuO_{3.9}, that the only acceptable valence state of Cu is that close to 3+ (and the corresponding charge of O is –1.75). In addition, it should be pointed out that no atomic coordinates and bond lengths were reported in (6). Such a gap in this field exists because the CuO₄ group, as is shown in the present work, cannot be described correctly by the interatomic potentials of central type using a conventional approach to the structural modelling of ionic compounds. In this connection, this work is an

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attempt to find the form of interatomic interaction potentials which could correctly reproduce and predict the crystal structures of cuprates.

DERIVATION OF THE FORM OF INTERATOMIC POTENTIALS

The theoretical structure modelling of the cuprates listed above was performed by using the General Utility Lattice Programs (GULP) code (7), running on a PC (Intel-Pentium-II processor, 128 MB RAM) under operation system Linux. This code was selected taking into account two important points:

(1) This allows one to calculate both the structural parameters and optimal values of the parameters in interatomic potentials. Forcing the potential parameters to fit the known crystal structure and its properties is usually a tedious procedure. Energy minimization with initially chosen potential parameters provides an apparent value of the minimized functional. After that, the difference between observed and calculated parameters is found and some expected changes of the interatomic potentials parameters are determined. The calculations are repeated until the sum of squared deviations between observed and calculated quantities gets to be minimal. Clearly the number of observable parameters should be larger than the number of optimized quantities.

(2) Though the code imposes severe conditions on a computer configuration, it provides an essential improvement in a high-speed operation as compared with analogous programs. This is an important aspect for the needed optimization procedure of pair and more complicated potentials.

According to the outlined code, the Madelung component of the interatomic interaction energy is summed up in a whole reciprocal space by the Ewald method, while the short-range potentials are summed up within the limits of space, where they are still significant (the radius of a sphere around an atom in its center usually not larger than 15 Å). As the short-range potentials, the Buckingham [1], Lennard-Jones [2], and Morse [3] types can be used:

$$V_{ij}(R_{ij}) = \lambda_{ij} \exp(-R_{ij}/\rho_{ij}) - C_{ij}/R_{ij}^6, \quad [1]$$

$$V_{ij}(R_{ij}) = A_{ij}/R_{ij}^6 - B_{ij}/R_{ij}^{12}, \quad [2]$$

$$V_M = D_{ij} \{1 - \exp[-\sigma_{ij}(R_{ij}^0 - R_{ij})]\}^2 - D_{ij}. \quad [3]$$

Here, λ_{ij} , A_{ij} , B_{ij} , and D_{ij} are fitting parameters of the pair potentials. D_{ij} can be determined as the cohesion energy for a single covalent bond. The quantity R_{ij}^0 is usually taken as the average interatomic distance (or as a sum of atomic radii) for the corresponding pair of atoms. The repulsion parameter of the Morse potential σ_{ij} and the softness parameter of the Buckingham potential ρ_{ij} are specific to the

interaction between the bonding atoms in question and can be refined in the fitting procedure. The terms C_{ij}/R_{ij}^6 and A_{ij}/R_{ij}^6 in Eqs. [1] and [2], respectively, describe the van der Waals dispersion interaction. The cohesion energy is expressed as the sum of the pair potentials. In a search for the energy minimum, the atomic coordinates and parameters of the unit cell are varied. The Newton-Raphson method is used as the minimization algorithm, in which the first and second derivatives of the energy with respect to the atomic coordinates are calculated.

The authors were making efforts to start from the simplest models of pair potentials possible. In this connection, in the initial modelling step the following potential model was accepted: in addition to the Coulomb interaction, the cation-oxygen and oxygen-oxygen repulsions in the Born-Mayer-Buckingham potentials were taken into account. The charges of ions were equal to the formal ones. As initial quantities of λ_{ij} and ρ_{ij} , the values of these potentials presented in (8) were used. The experimental parameters of the unit cells and coordinates of atoms were accepted as observable quantities for further optimization of the potential parameters.

However, it was realized that the parameters of potentials for interatomic interactions in the form [1], optimized in such a way, did not allow one to reproduce the structure of cuprates under consideration even with a satisfactory accuracy. In particular, the disagreement in the region of the copper atom site was especially pronounced: this was possibly related to a specific electronic structure of the Cu-O₄ complexes.

Replacement of the Buckingham potential for Cu-O interaction by the Morse or Lennard-Jones potentials also did not lead to a reasonable description of the crystal structures. It was found that a combined application of the Buckingham and conventional Morse potentials improved slightly the description of the Cu-O interaction. However, substituting a small contribution of the Morse potential with a negative value of the parameter D into the Born-Mayer-Buckingham potential for Cu-O improved essentially the description of the studied structures. It should be emphasized that in this case the Morse potential presented only a small correction for the Cu-O potential of the type [1]. Its parameters cannot be correlated to the real physical quantities such as the cohesion energy for the Cu-O bond (parameter D) or the sum of atomic radii of Cu and O atoms (parameter R_0), as is usually done.

In addition, in order to simulate the known intention of copper atoms to be surrounded by four oxygen atoms in the four-fold coordination, the harmonic angle-bending three-particle potential O-Cu-O of the following simple form was introduced:

$$V_{iji} = K(\alpha^0 - \alpha)^2, \quad [4]$$

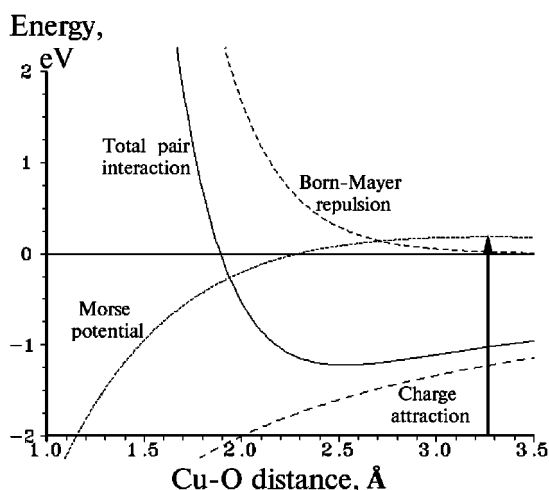


FIG. 1. Dependence of the energy of Cu-O interaction on the interatomic distance.

where α^0 is the bond angle with ideal value of 90° for a regular squared (or octahedral) coordination and K is the fitting stiffness parameter.

The dependence of the resulting energy of the Cu-O interaction (using the optimized parameters of the potential) on interatomic distance in the range from 1.0 to 3.5 Å is presented in Fig. 1. As can be seen, the additional Morse potential is attractive in the region of short Cu-O distances, becomes repulsive at 2.29 Å, and reaches the maximum value, equal to $-D$, at R_0 (3.27 Å). The resulting energy of the Cu-O pair interaction is minimal at 2.53 Å.

Despite the difference in the linkage type of the CuO_4 units, the obtained Cu-O potential was well transferable in the related structures. The potential was successfully applied for the modelling of significantly more complex compounds like $(\text{Sr}_{1.19}\text{Ca}_{0.73})\text{Cu}_2\text{O}_4$ and BaCuO_2 . The parameters of potentials used for the modelling of all these compounds are presented in Table 1.

The modelling of the structures of cuprates with additional account for the frequently used shell model for oxygen atoms (see, e.g., (8,9)) has been also performed. However, it did not lead to any improvement in the description of the geometrical features of structures. Therefore, we did not use it in further calculations.

It should be also noted that the values of pre-exponential factors λ of the potential [1] for Ca-O and Sr-O are considerably smaller than those known from the literature (8,9). In (8) these values were refined by fitting to the structures and properties of simple oxides. This comparison indicates that the role of ionic repulsion is smaller in cuprates than in oxides. It can be possibly related to a stronger role of the covalent component for the bonds Ca-O and Sr-O, which was not explicitly taken into account.

RESULTS OF MODELLING

The potentials thus optimized were tested on five compounds, Ca_2CuO_3 , CaCuO_2 , SrCuO_2 , $(\text{Sr}_{1.19}\text{Ca}_{0.73})\text{Cu}_2\text{O}_4$, and BaCuO_2 . The compounds were selected on the basis of the following considerations. The first three compounds are the members of polysomatic series in the group of alkaline-earth cuprates (Fig. 2 from (10)) and differ in the motives of CuO_4 groups. The modeling of the latter two structures presents some difficulties because of the deficiency in several positions, the presence of atoms with mixed valence, and CuO groups in nonsquared coordination. Therefore, the modeling of these structures was expected to show the limits of applicability for the proposed set of potentials.

Modelling of Ca_2CuO_3

The set of potentials was developed and applied first for Ca_2CuO_3 . The structure, which was studied in 1970 (11), is composed of two CuO_4 squares located on one plane and sharing corners (Fig. 3A). As is seen from Table 2, the

TABLE 1
Parameters of Potentials for Modelling of Cuprates

Buckingham potential	λ , eV	ρ , Å	C , eV*Å ⁶	Range of distances, Å	Method of derivation
Ca-O	852.64	0.3437	0.000	0-8	Fitting to Ca_2CuO_3 and CaCuO_2 structures
Sr-O	939.72	0.3484	0.000	0-8	Fitting to SrCuO_2 structure
Ba-O	1207.80	0.3500	0.000	0-8	Fitting to BaCuO_2 structure
Cu-O	1716.36	0.2884	0.000	0-8	Fitting to Ca_2CuO_3 structure (8)
O-O	22764.3	0.1490	27.880	0-8	
Morse potential	D , eV	β , Å ⁻¹	R_0 , Å		
Cu-O	-0.1822	0.7051	3.273	0-8	Fitting to Ca_2CuO_3 structure
Three-particle harmonic potential	K , eV/rad ²	α , deg			
O-Cu-O	4.933	90.0		0-2.0 (Cu-O) 0-3.2 (O-O)	Fitting to Ca_2CuO_3 structure

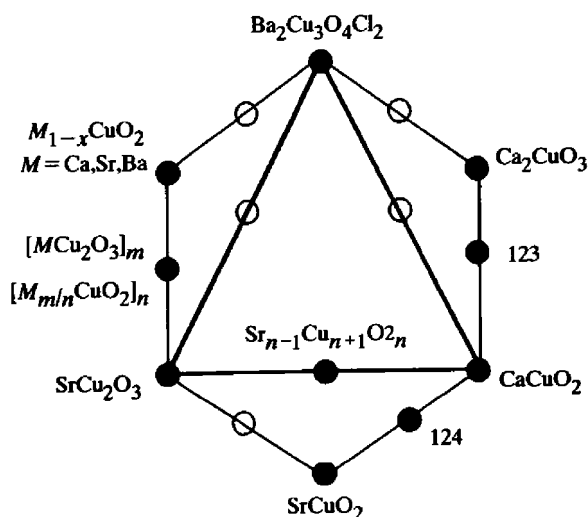


FIG. 2. Scheme of an alkaline-earth cuprates polysomatic series.

obtained potential set was able to reproduce the crystal structure of the compound with a high accuracy.

Modelling of CaCuO_2

The possibility to use the obtained potential set for the related cuprate structures was checked by the modelling of

TABLE 2
Modelling Results for Ca_2CuO_3

Parameter	Experiment (11)	Calculation	Difference
a , Å	12.230	12.230	0.000 (0.00%)
b , Å	3.770	3.763	-0.007 (-0.19%)
c , Å	3.250	3.252	0.002 (0.07%)
$\alpha = \beta = \gamma$, grad	90	90	0
Unit cell volume, Å ³	149.848	149.681	-0.167 (-0.11%)
Ca x	0.150	0.161	0.011
O1 x	0.345	0.339	0.006
Interatomic Distances, Å			
Bond	Experiment (11)	Calculation	
Ca-O	1*2.385, 4*2.490, 2* 2.451	1*2.186, 4*2.487, 2*2.551	
Cu-O	2*1.885, 2*1.896	2*1.882, 2*1.964	
O-O	4*2.673	4*2.720	
Predicted Properties			
Energy of interatomic interactions, eV	-109.878		
Elasticity coefficients, 10 ¹¹ dyn/cm ²	$C_{11} = 28.74$, $C_{33} = 21.16$, $C_{12} = 19.50$, $C_{13} = 3.64$, $C_{44} = -0.34$, $C_{66} = 18.97$		

CaCuO_2 . The CaCuO_2 structure is composed on the basis of the infinite Cu-O layer formed by the Cu_4O_{12} groups, i.e., four squares located on one plane and joined by one common apex (Fig. 3B) (12). The modelling results for CaCuO_2 are presented in Table 3.

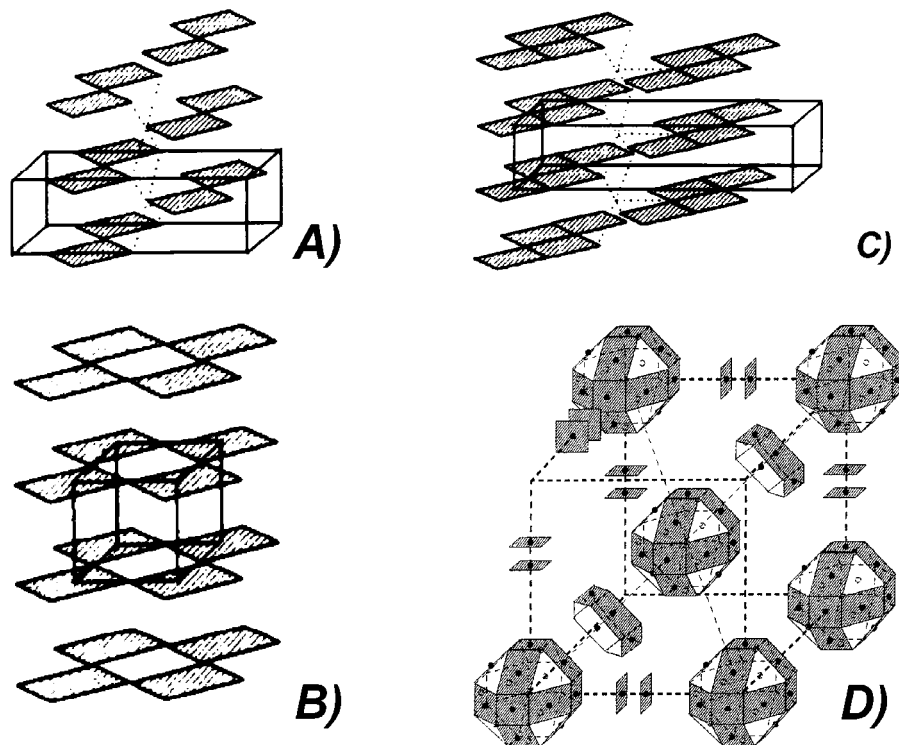


FIG. 3. Copper-oxygen motives (1) in the crystal structures of Ca_2CuO_3 (A), CaCuO_2 (B), SrCuO_2 and $\text{Sr}_{1.19}\text{Ca}_{0.73}\text{Cu}_2\text{O}_4$ (C), and BaCuO_2 (D).

TABLE 3
Modelling Results for CaCuO₂

Parameter	Experiment (12)	Calculation	Difference
a , Å	3.870	3.897	0.027 (0.70)
b , Å	3.870	3.897	0.027 (0.70)
c , Å	3.221	3.211	-0.010 (-0.32)
$\alpha = \beta = \gamma$, grad	90	90	0
Unit cell volume Å ³	48.241	48.761	0.520 (1.08%)
Interatomic Distances, Å			
Bond	Experiment (12)	Calculation	
Ca-O	8*2.518	8*2.525	
Cu-O	4*1.935	4*1.949	
O-O	4*2.737	4*2.756	
Predicted Properties			
Energy of interatomic interaction, eV	- 72.837		
Elasticity coefficients, 10 ¹¹ dyn/cm ²	$C_{11} = 33.81, C_{33} = 23.53, C_{12} = 22.87,$ $C_{13} = -0.86, C_{44} = -0.86, C_{66} = 29.35$		

Table 3 shows that the developed set of pair potentials reproduced this crystal structure with a high accuracy as well. This indicates the possibility to transfer the potential set for the modelling of similar structures.

Modeling of SrCuO₂

The Cu-O structural unit in SrCuO₂ is the infinite chain of Cu₂O₆ dimers, two squares joined by edges (Fig. 3C) (11). The potential for interatomic interaction Sr-O was obtained as the result of the structural modeling of SrCuO₂. The O-O and Cu-O interatomic potentials were derived from the above consideration of calcium cuprates and were not again fitted using the optimization process. The modelling results are presented in Table 4.

As can be seen from Table 4, the structural features of the compound were again very well reproduced. That indicates a stable character of interactions in the CuO₄ square, which is independent of the type of alkaline-earth cation and hence of the transfer of the parameters of interaction potentials to other related structures.

Modelling of (Sr_{1.19}Ca_{0.73})Cu₂O₄

The structure of Sr_{1.19}Ca_{0.73}Cu₂O₄ is akin to that of SrCuO₂ (13). The modelling results are presented in Table 5. In this case the reproducibility was slightly worse than for pure Sr compound. This is most probably related to the experimental error in the determination of the occupation of cation position leading to the necessity to increase insignificantly the Cu charge (in order to maintain the electrical neutrality of the unit cell). As can be seen from Table 5,

TABLE 4
Modelling Results for SrCuO₂

Parameter	Experiment (11)	Calculation	Difference
a , Å	3.560	3.572	0.012 (0.33%)
b , Å	16.320	16.319	-0.001 (-0.01%)
c , Å	3.920	3.884	-0.036 (-0.93%)
Unit cell volume, Å ³	227.749	226.361	-1.388 (-0.61%)
Sr y	0.331	0.320	0.011
Cu y	0.061	0.062	0.001
O1 y	0.945	0.942	0.003
O2 y	0.178	0.181	0.003
Interatomic Distances, Å			
Bond	Experiment (11)	Calculation	
Sr-O	1*2.497, 2*2.575,	1*2.259, 2*2.678,	
	4*2.652	4*2.638	
Cu-O	1*1.893, 1*1.909,	1*1.945, 1*1.960,	
	2*1.962	2*1.943	
O-O	2*2.658, 2*2.806	2*2.712, 2*2.796	
Predicted Properties			
Energy of interatomic interaction U , eV	-144.886		
Elasticity coefficients, 10 ¹¹ dyn/cm ²	$C_{11} = 12.01, C_{22} = 28.05, C_{33} = 29.37,$ $C_{12} = 3.53, C_{13} = 0.54, C_{23} = 16.48,$ $C_{44} = 17.21, C_{55} = -0.19, C_{66} = -0.08$		

the a parameter was most sensitive to the resulting disagreement between measured and calculated interatomic distances.

TABLE 5
Modeling Results for (Sr_{1.19}Ca_{0.73})Cu₂O₄

Parameter	Experiment (13)	Calculation	Difference
a , Å	3.453	3.545	0.092 (2.67%)
b , Å	16.110	16.066	-0.044 (-0.27%)
c , Å	3.868	3.881	0.013 (0.35%)
Unit cell volume, Å ³	215.168	221.083	5.915 (2.75%)
(Ca,Sr) y	0.330	0.318	0.012
Cu y	0.062	0.063	0.001
O1 y	0.944	0.942	0.002
O2 y	0.180	0.183	0.003
Interatomic Distances, Å			
Bond	Experiment (13)	Calculation	
(Ca,Sr)-O	1*2.415, 2*2.517,	1*2.160, 2*2.664,	
	4*2.597	4*2.629	
Cu-O	1*1.901, 1*1.907,	1*1.933, 1*1.951,	
	2*1.936	2*1.942	
O-O	2*2.656, 2*2.774	2*2.699, 2*2.794	
Predicted Properties			
Energy of interatomic interaction U , eV	-139.979		
Elasticity coefficients, 10 ¹¹ dyn/cm ²	$C_{11} = 11.10, C_{22} = 29.39, C_{33} = 29.02,$ $C_{12} = 3.12, C_{13} = 0.44, C_{23} = 16.74,$ $C_{44} = 16.95, C_{55} = -0.28, C_{66} = -0.78$		

Modelling of BaCuO₂

The structure of BaCuO₂ differs significantly from the structures of CaCuO₂ and SrCuO₂. The structure of this complex cuprate is schematically depicted in Fig. 3D. Two aspects cause a complexity of this crystal structure. First, the unit cell contains 360 atoms (parameter $a = 18.27 \text{ \AA}$). Sec-

TABLE 6
Modeling Results for BaCuO₂

Parameter	Experiment (14)	Calculation	Difference
a , \AA	18.27	18.261	-0.009 (-0.05%)
Unit cell volume, \AA^3	6098.396	6089.845	-8.551 (-0.14%)
Cu1 y	0.150	0.146	0.004
z	0.350	0.356	0.004
Cu2 x	0.125	0.135	0.010
z	0.125	0.135	0.010
Cu3 x	0.206	0.209	0.003
Cu4 x	0.430	0.413	0.017
O1 x	0.072	0.072	0.000
y	0.072	0.072	0.000
z	0.186	0.179	0.007
O2 x	0.144	0.145	0.001
y	0.144	0.145	0.001
z	0.343	0.335	0.008
O3 x	0.267	0.275	0.008
y	0.267	0.275	0.008
z	0.085	0.082	0.003
O5 x	0.338	0.314	0.024
O6 y	0.112	0.099	0.013
z	0.440	0.435	0.005
Ba1 y	0.151	0.149	0.002
z	0.310	0.311	0.001
Ba2 x	0.364	0.362	0.002
y	0.364	0.362	0.002
Ba3 x	0.177	0.169	0.008
y	0.177	0.169	0.008
z	0.177	0.169	0.008
Interatomic Distances, \AA			
Bond	Experiment (14)	Calculation	
Cu1-O	2*1.9439, 2*1.9510	2*1.9543 2*1.9130	
Cu2-O	4*1.9774	4*1.9261	
Cu3-O	4*1.8959 1*2.4116	4*1.9386 1*1.9338	
Cu4-O	1*1.6808 4*2.0544	1*1.8056 4*1.8545	
Ba1-O	2*2.9910 2*2.7021 2*2.7423 1*2.8058 1*2.4797	2*3.0835 2*2.6805 2*2.8263 1*2.7186 1*2.4404	
Ba2-O	2*2.8758 2*2.9484 4*2.7510	2*3.0224 2*2.6914 4*2.8818	
Ba3-O	3*2.7179 3*3.1504 3*2.8693	3*2.5166 3*3.0862 3*3.1600	
Ba4-O	24*3.870	24*3.867	
Predicted Properties			
Energy of interatomic interaction U , eV	-134.60		
Elasticity coefficients, 10^{11} dyn/cm^2	$C_{11} = 10.37$, $C_{12} = 6.06$, $C_{44} = 1.56$		

ond, several atomic positions (Cu4 and O6) are not fully occupied (14). The copper atoms are four-fold coordinated as well as located in the pentahedron. One Ba atom is situated in large structural voids and has 24 equidistant nearest anions. This leads to significant computational problems in the structural modelling of this compound. The modelling results are presented in Table 6. As can be seen from this table, the parameters and volume of the unit cell are well reproduced though atom coordinates and interatomic distances are reproduced not quite correctly. Significant differences between experimental and calculated interatomic distances for pentahedrons Cu3-O₅ and Cu4-O₅ are noticed, while the differences are reasonable for Cu atoms in a square coordination. The distortion of Cu polyhedra leads also to the difference between calculated and experimental Ba-O distances in some cases. However, the average experimental and calculated interatomic Ba-O distances are close each to another, indicating that the optimal Ba-O potential was found by the fitting procedure for this cuprate.

SUMMARY

As the result of the performed calculations, the following conclusions can be drawn.

(1) A set of interatomic potentials was developed which enables one to describe correctly the crystal structure of a series of Ca, Sr, and Ba cuprates.

(2) The structural modelling was performed for the following compounds: Ca₂CuO₃, CaCuO₂, SrCuO₃, (Sr_{1.19}Ca_{0.73})Cu₂O₄, and BaCuO₂. The previously unknown energetic and elastic properties were predicted. It should also be pointed out that the covalence effects for the bonds Sr-O and Ca-O seem to play a somewhat larger role in cuprates than in oxides.

(3) The developed set of interatomic potentials was well transferable for similar structures, despite the differences in the linkage of the CuO₄ groups. The set can be recommended for the structural modelling of more complex cuprates containing the CuO₄ groups, providing that the copper coordination is kept square.

(4) The derived potential set does not allow one to reproduce correctly the cuprate crystal structure in the case of the other copper atoms' coordination as well as in the presence of deficient occupation of positions in the structure.

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