

Rigid-ion models for NiO and CoO: comparison between experimental and calculated thermal expansion

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys.: Condens. Matter 3 279

(<http://iopscience.iop.org/0953-8984/3/3/002>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 11/05/2010 at 07:04

Please note that [terms and conditions apply](#).

Rigid-ion potential models for NiO and CoO: comparison between experimental and calculated thermal expansion

Carlo Massobrio† and Madeleine Meyer‡

† Composés non Stoechiométriques, Unité de Recherche associée au CNRS 446,
Université de Paris Sud, 91405 Orsay Cédex, France

‡ Laboratoire de Physique des Matériaux, CNRS, 1 place Aristide Briand, 92195 Meudon
Cédex, France

Received 7 August 1990

Abstract. We developed rigid-ion interatomic potentials for NiO and CoO and we assess their reliability by calculating Schottky and Frenkel defect formation energies. Then we studied the variation with temperature in the lattice parameter at zero pressure via constant-temperature constant-pressure molecular dynamics simulations. The agreement obtained with experimental results is remarkably good.

Interatomic potentials for oxide materials have been developed over the years by using the ionic model mostly with formal charges and describing the short-range interactions in terms of pair potentials of the Born–Mayer and Buckingham form (Catlow *et al* 1988). Polarization effects are usually treated by adopting the shell model originally developed by Dick and Overhauser (1958). Interatomic potentials are either parametrized empirically by adjusting the potential parameters to achieve the best possible agreement between calculated and experimental properties (crystal structures, cohesive energies, dielectric and elastic constants) or determined theoretically via *ab initio* calculations (Kendrick and Mackrodt 1983, Harding and Harker 1985). The overwhelming majority of computer simulation results obtained for oxide materials consists of static simulations aimed at calculating point and extended defect energies for a relaxed crystalline configuration (see Jacobs (1990) and Duffy (1986) for a review) and therefore no inclusion of thermal motion is made. Calculations are usually performed within the Mott–Littleton (1938) two-region strategy, although recently the validity of the supercell approach has been proved (Leslie and Gillan 1985). On the other hand, only a few molecular dynamics (MD) simulations have been reported. Examples are the work by Sindzingre and Gillan (1988) on UO_2 and by Tarento and Harding (1988) on CoO. We believe this paucity stems from two main reasons: first the increase in computer requirements that would result from incorporating the shell model scheme for polarization in a molecular dynamics program; secondly the lack of simple rigid-ion potentials tested against high-temperature thermodynamic data and therefore suitable for MD simulations. Rigid-ion models are intrinsically limited to an inaccurate treatment of polarization (the dielectric constant ϵ_∞ at infinite frequency being equal to unity) but their use can be considered legitimate provided that the static dielectric constant and some basic defect energies are

Table 1. Parameters of the short-range rigid-ion potential for NiO and CoO (where the energy is in electronvolts and the length in ångströms). The minimum of $V_{--}(r)$ is at 2.75 Å. The potential and its first two derivatives are continuous at the spline points. We report also the parameters for the rigid-ion potential used by Tarento and Harding (1988) for CoO.

NiO	
$V_{++} = 0$	
$V_{+-} = A_{+-} \exp(-r/\rho_{+-}) = 556.43 \exp(-r/0.3553)$	
$V_{--} = A_{--} \exp(-r/\rho_{--}) = 22764.3 \exp(-r/0.149)$	$r < 1.5$
V_{--} is a fifth-degree polynomial	$1.5 < r < 2.75$
V_{--} is a third-degree polynomial	$2.75 < r < 2.9$
$V_{--} = C_{--}/r^6 = 154.715/r^6$	$2.9 < r$
CoO	
$V_{++} = 0$	
$V_{+-} = A_{+-} \exp(-r/\rho_{+-}) = 634.963 \exp(-r/0.346)$	
$V_{--} = A_{--} \exp(-r/\rho_{--}) = 22764.3 \exp(-r/0.149)$	$r < 1.5$
V_{--} is a fifth-degree polynomial	$1.5 < r < 2.75$
V_{--} is a third-degree polynomial	$2.75 < r < 2.9$
$V_{--} = C_{--}/r^6 = 83.446/r^6$	$2.9 < r$
CoO (Tarento and Harding 1988)	
$V_{++} = 0$	
$V_{+-} = A_{+-} \exp(-r/\rho_{+-}) = 825.5 \exp(-r/0.3262)$	
$V_{--} = A_{--} \exp(-r/\rho_{--}) - C_{--}/r^6 = 22764 \exp(-r/0.149) - 20.37/r^6$	

reproduced correctly, as well as the cohesive energy and the elastic constants of the perfect static lattice (Catlow 1983). This assertion has been confirmed by the quite realistic evidence of superionic conduction recorded in UO_2 by employing such a potential (Sindzingre and Gillan 1988). This result encourages using rigid-ion potentials for studying dynamical properties of oxides and supports the conjecture that in a largely ionic material the atomic movement can be highlighted without resorting to the more lengthy shell model scheme.

We present here MD simulation results for the thermal expansion of two transition-metal oxides (NiO and CoO) modelled by rigid-ion interatomic potentials. Upon testing their reliability against a set of defect energies we calculated the variation in the lattice parameter of our model crystal as a function of temperature at zero pressure. To this purpose we performed a series of MD simulations in the NPT ensemble at constant temperature and pressure. This approach enables a straightforward determination of the volume versus temperature change of a material at a given pressure.

Our rigid-ion calculations assume that NiO and CoO are fully ionic. The pair potentials are the sum of the short-range and Coulomb interactions. The short-range potential parameters are shown in table 1. For the anion-cation short-range potential we take a purely repulsive exponential form with no inclusion of van der Waals term while cation-cation non-coulombic interactions are ignored (Sangster and Stoneham 1981). Most workers adopted for the non-coulombic interaction between oxygen ions the potential elaborated by Catlow *et al* (1977) which is attractive over the entire range of interatomic separations encountered in defect simulations (Catlow *et al* 1977, Sangster and Stoneham 1981, Stoneham and Sangster 1985, Vempati and Jacobs 1983, Lewis and Catlow 1985). We modified the form of the potential by inserting two splines between the exponential repulsive part and the van der Waals inverse sixth-power function as done by Jackson *et al* (1986) for UO_2 . The parameters of the exponential part A_{--} and ρ_{--} are those commonly used in the literature (Catlow *et al* 1977), while the coefficient

Table 2. Calculated values of physical quantities for the static lattice at $T = 0$ K and comparison with published results obtained within the shell model and rigid-ion (for CoO) potential schemes: MM, results of the present work; ss, Sangster and Stoneham (1981); v1, Vempati and Jacobs (1983); LC, Lewis and Catlow (1985); CMNS Catlow *et al* (1977); TH, rigid-ion potential of Tarento and Harding (1988) (when employing this potential we used a lattice parameter optimized to zero pressure for a cut-off $r_c = 7$ Å). The experimental results at room temperature are those quoted by Sangster and Stoneham (1981). For our calculations the residual pressure on the static lattice amounts to a few kilobars at most and accounts for the small differences that we report for NiO between the elastic constants C_{12} and C_{44} . B is the bulk modulus. The value of the static dielectric constant of NiO is quoted by Stoneham and Sangster (1985).

Reference	E (eV)	a (Å)	B (10^{12} dyn cm $^{-2}$)	C_{11} (10^{12} dyn cm $^{-2}$)	C_{12} (10^{12} dyn cm $^{-2}$)	C_{44} (10^{12} dyn cm $^{-2}$)	ϵ_0	ϵ_s
				NiO				
MM	-40.28	2.08	1.82	2.70	1.37	1.38	11.9	1
SS	-41.9	2.084	2.62	4.59	1.64	1.64	11.9	5.7
V1	-43.82	2.09	2.0				12.7	5.4
LC	-40.5		2.08	2.63	1.80	1.80	11.9	5.7
CMNS	-41.01	2.08					11.8	6.1
Experimental	-42.3	2.084	1.73	2.7	1.25	1.05	11.9	5.7
				CoO				
MM	-39.8	2.127	1.83	2.56	1.47	1.47	12.9	1
SS	-41.0	2.133	2.41	4.22	1.50	1.50	12.9	5.3
VT	-42.88	2.13	1.89				13.4	5.3
LC	-40.0		1.98	2.59	1.68	1.68	12.9	5.3
CMNS	-40.0	2.13					12.8	5.7
Experimental	-41.54	2.133	1.81	2.56	1.44	0.80	12.9	5.3
TH	-40.13	2.129	2.01	2.81	1.60	1.61	12.2	1

Table 3. Calculated values of the formation energies of Frenkel and Schottky defects for NiO and CoO and comparison with published results obtained within the shell model and rigid-ion (for CoO) scheme: MM, results of the present work; SR, results of Sangster and Rowell (1981) which employed the potential of Sangster and Stoneham (1981); MU, results of Muxworthy (1977) (quoted by Sangster and Rowell (1981)) using the potential of Catlow *et al* (1977); VJ, Vempati and Jacobs (1983); TH, rigid-ion potential of Tarento and Harding (1988) with cut-off $r_c = 7 \text{ \AA}$.

Reference	Formation energy (eV)		
	Schottky defect	Frenkel anion	Frenkel cation
		NiO	
MM	6.58	13.63	10.94
SR	7.37	11.29	12.09
MU	6.86	11.16	
VJ	7.86	10.13	10.73
		CoO	
MM	4.78	8.97	8.69
SR	7.16	10.97	11.79
MU	6.39	10.55	
VJ	7.60	9.96	10.46
TH	5.29	8.69	9.0

C_{--} of the attractive interaction enters the fit together with A_{+-} and ρ_{+-} , the parameters of the cation-anion purely repulsive non-coulombic interaction. The fit that we performed consisted in varying the A_{+-} , ρ_{+-} and C_{--} potential parameters to achieve the best possible match between calculated and experimental dielectric constants at zero frequency ϵ_0 and elastic constant C_{11} . Minimization is carried out for a lattice parameter giving the best agreement *a posteriori* between the experimental lattice parameter and the MD value at room temperature. The latter is obtained by heating to $T = 300 \text{ K}$ the system relaxed at zero temperature and zero imposed pressure. This procedure necessitates a few iterations and accounts for the expansion of the MD lattice between 0 and 300 K. Throughout the computations we employed a system of 256 cations and 256 anions with periodic boundary conditions. In table 2 we display the values of the relevant physical quantities pertaining to the static lattice for both NiO and CoO. The cohesive energy and the elastic constant C_{12} do not enter the fit; nevertheless the overall agreement between experimental and calculated properties is quite satisfactory. In table 2 we also report data from previous computations within the shell model scheme for both NiO and CoO. The large disagreement between experimental and calculated values of the elastic constant C_{44} is due to the intrinsic limitation of the two-body approach that yields $C_{12} = C_{44}$. In the case of CoO we account also for the rigid-ion model proposed by Tarento and Harding (1988) with the same cut-off as ours for the short range forces and we display in table 2 the values that we calculated using their potential parameters (table 1).

Defect energies are obtained by introducing the defect in the system (either Schottky or Frenkel defects) which is allowed to relax to zero temperature via the 'quenched MD' method (Beeler and Kulcinski 1972). This procedure consist of running a standard MD program in the *NVE* microcanonical ensemble by setting the velocity of each ion to zero whenever the scalar product of its velocity and acceleration becomes negative. To implement MD simulations we used the Ewald summation method to cope with long-

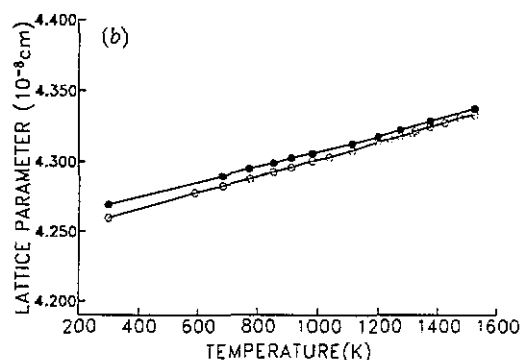
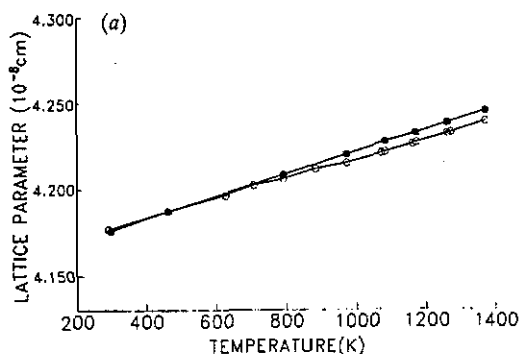


Figure 1. Experimental (Touzelin 1978) and calculated lattice parameter for (a) NiO and (b) CoO: \circ , experimental values; \bullet , calculated values.

range forces (Sangster and Dixon 1975), the calculated coulombic energy lying within 0.002 of the Madelung value. Short-range forces are calculated up to a cut-off radius $r_c = 7 \text{ \AA}$ and the direct space contributions in the Ewald summation up to half a box length. The value of the inverse Ewald length α was equal to $6/V^{1/3}$, V being the volume of the cubic simulation box. Summation in reciprocal space extended to all vectors n for which $|n^2| < 30$. In both defect computations the distances between vacancy and interstitial (Frenkel case) or vacancy of opposite charges (Schottky case) are taken to be the largest permitted by the size of the periodic system. The results are shown in table 3. The agreement with shell model computations is satisfactory, the most serious discrepancy being recorded in the case of the Schottky defect in CoO for both the Tarento-Harding potential and the one that we implemented.

Finally we intended to establish the reliability of our potential with respect to thermal expansion data obtained for NiO and CoO by Touzelin (1978) by performing MD simulations. The technique that we employed is a combination of the Nosé (1984) constant-temperature and the Andersen (1980) constant-pressure methods for studying systems at desired values of temperature and/or pressure. We integrated the equation of motion detailed by Sindzingre and Gillan (1988) by using a fifth-order Gear predictor corrector with a time step of 10^{-15} s. We did not include in the computation of the pressure a long-range correction to the van der Waals part of the anion-anion potential. For each state point we run 20 000 time steps at equilibrium and we take statistical averages of the lattice parameter over portions of the trajectory made of 2000 steps each. In figure 1 we show the variation in the lattice parameter with temperature. The agreement with the experimental values is excellent for both oxides. The statistical error on each point is of the order of 0.3% and therefore calculated and experimental values

coincide within the error bar. We also checked the behaviour of the rigid-ion potential devised by Tarento and Harding for CoO. This potential features an oxygen–oxygen short-range potential attractive at short distances. Despite this unphysical feature and the somewhat larger value of the bulk modulus (table 2) this potential performs well on thermal expansion and the related values of the lattice parameter up to $T = 1600$ K are essentially identical with those obtained by using the potential that we proposed above.

In conclusion we developed rigid-ion potentials for NiO and CoO that give defect energies in satisfactory agreement with potentials based on the shell model approach and display an excellent behaviour of the lattice parameter as a function of temperature. To our knowledge, no rigid-ion interatomic potentials have been so far implemented and used in the case of NiO. Work is in progress to study the high-temperature features of grain boundary structures in NiO by making use of the potential presented in this work. Grain boundaries have been studied extensively in NiO by static simulations (Duffy 1986). However, the temperature dependence of grain boundary structures has not been investigated and we believe that MD simulations are necessary to achieve a full understanding of these high-temperature properties.

Acknowledgments

Part of this work has been carried out during a stay of CM at the Laboratoire de Physique des Matériaux, CNRS, Meudon-Bellevue (France). Financial support from the MRES to CM is gratefully acknowledged.

References

- Andersen H C 1980 *J. Chem. Phys.* **72** 2384
 Beeler J R and Kulcinski G L 1972 *Interatomic Potentials and Simulation of Lattice Defects* ed P G Gehlen *et al* (New York: Plenum) p 735
 Catlow C R A 1983 *Solid State Ion.* **8** 89
 Catlow C R A, Freeman C M, Islam M S, Jackson R A, Leslie M and Tomlinson S M 1988 *Phil. Mag.* **A 58** 123
 Catlow C R A, Mackrodt W C, Norgett M J and Stoneham A M 1977 *Phil. Mag.* **35** 177
 Dick B G and Overhauser A W 1958 *Phys. Rev.* **B 112** 90
 Duffy D M 1986 *J. Phys. C: Solid State Phys.* **19** 4393
 Harding J H and Harker A H 1985 *Phil. Mag.* **B 51** 119
 Jackson R A, Murray A D, Harding J H and Catlow C R A 1986 *Phil. Mag.* **A 53** 27
 Jacobs P W M 1990 *Diffusion in Materials (NATO ASI Series)* ed A L Laskar, J L Bocquet, G Brebec and C Monty (Dordrecht: Kluwer) p 203
 Kendrick J and Mackrodt W C 1983 *Solid State Ion.* **8** 247
 Leslie M and Gillan M J 1985 *J. Phys. C: Solid State Phys.* **18** 973
 Lewis G V and Catlow C R A 1985 *J. Phys. C: Solid State Phys.* **18** 1149
 Mott N F and Littleton M J 1938 *Discuss. Faraday Soc.* **34** 485
 Muxworthy D G 1987 *Harwell Report* TP667
 Nosé S 1984 *Mol. Phys.* **52** 225
 Sangster M J L and Dixon D K 1975 *Adv. Phys.* **25** 247
 Sangster M J L and Rowell D K 1981 *Phil. Mag.* **A 44** 613
 Sangster M J L and Stoneham A M 1981 *Phil. Mag.* **B 43** 597
 Sindzingre P and Gillan M J 1988 *J. Phys. C: Solid State Phys.* **21** 4017
 Stoneham A M and Sangster M J L 1985 *Phil. Mag.* **B 52** 717
 Tarento R J and Harding J H 1988 *J. Phys. C: Solid State Phys.* **20** L677
 Touzelin B 1978 *Rev. Int. Hautes Temp. Réfr.* **15** 33
 Vempati C S and Jacobs P W M 1983 *Cryst. Latt. Defects Amorph. Mater.* **10** 19