

Monte Carlo and Hybrid Monte Carlo/Molecular Dynamics Approaches to Order–Disorder in Alloys, Oxides, and Silicates

John A. Purton,^{†‡} Gustavo D. Barrera,[†] Neil L. Allan,^{*,†} and Jon D. Blundy[‡]

School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, United Kingdom, and CETSEI, Department of Geology, University of Bristol, Wills Memorial Building, Bristol BS8 1RJ, United Kingdom

Received: December 10, 1997; In Final Form: April 6, 1998

Order–disorder in alloys, oxides, and silicates is studied by means of Monte Carlo methods. The key objective is to take explicit account of atom relaxation and cluster formation without resorting to the use of a parametrized Hamiltonian. We use a variety of Monte Carlo techniques, ranging from an Ising model to a hybrid Monte Carlo/molecular dynamics scheme. It is crucial to take account of relaxation of the local atomic environment and vibrational effects. We have investigated both convergent and nonconvergent ordering. Applications include (i) Cu/Au ordering in Cu–Au alloys, (ii) Mg/Mn ordering in olivine MgMnSiO_4 , and (iii) $\text{La}^{3+}/\text{M}^{2+}$ order–disorder in the quaternary cuprates $\text{La}_2\text{MCu}_2\text{O}_6$ ($\text{M} = \text{Ca}, \text{Sr}$). These examples include the interchange of atoms in a system where only short-range forces need to be considered, the interchange of isoivalent ions, and the interchange of heterovalent ions, respectively. The importance of relaxation effects increases in the order i–iii, i.e., as the size/charge mismatch between the interchanged atoms or ions increases.

Introduction

The continuing growth in computer power has led to a tremendous increase in the importance of computer simulation to the understanding and design of complex materials and minerals. Nevertheless most computational studies of oxides, silicates, and halides, for example, still assume perfect periodic ordering, which is a serious limitation since, for example, many ceramics and naturally occurring minerals are disordered. Disorder in polar solids has largely been investigated theoretically via *point*-defect calculations,¹ which refer only to the dilute limit, or using *periodic* arrays of defects (the so-called “super-cell” approach^{2,3}), in which only a few configurations can be considered. These methods are not readily extended to mixtures or disordered systems containing a finite impurity or defect content where it is necessary to take into account a large number of microscopically different configurations.

One traditional approach to the order–disorder problem, widely but not exclusively applied to metals,⁴ is the use of parametrized Hamiltonians. The parameters in such Hamiltonians are chosen so as to represent an average of first-, second-, and possibly third-neighbor interactions. In ionic and semiionic systems, however, there may be strong coupling between the atom distribution and the relaxation of the local atomic environment. This effect is particularly important when the disordered atoms carry different charges. We have discussed this coupling in detail previously for trace elements in the silicate minerals forsterite and diopside.⁵ In these systems, for example, relaxation energies for defect pairs may be as large as several hundred kilojoules per mole; they are not additive and cannot be predicted simply from the separate relaxations for the isolated defects. Also association energies between singly charged defects are large, reducing the formation energy of defect pairs by about typically 100 kJ mol^{-1} . The averaging of these *local*

effects when obtaining parametrized Hamiltonians may lead subsequently to a poor representation of ion clustering and association. Low-symmetry materials may also present problems. The key objective of the present work is to show explicitly how a number of modified Monte Carlo techniques may be used for taking explicit account of relaxation, thereby sampling efficiently a large number of different configurations and avoiding any averaging out of local effects. In this way we remove the major limitations of the existing methods which restrict considerably the contact between experiment and theory and extend the range of applications that can be tackled to include *real* rather than model systems.

The proposed techniques are tested using three different examples chosen to illustrate the versatility of our novel methodologies: first, Cu/Au ordering in Cu–Au alloys, where only short-range forces need be considered; second, Mn/Mg ordering in olivines as a function of temperature, involving long-range forces and the interchange of ions of the same charge; last, the ordering of La^{3+} and M^{2+} ions in the cuprate $\text{La}_2\text{MCu}_2\text{O}_6$ ($\text{M} = \text{Ca}, \text{Sr}$), where the ion disorder involves the interchange of ions with different charges. The first example involves convergent ordering, where the identity of the sites converges when they are randomly occupied, and the second and third examples, nonconvergent ordering, where the sites are crystallographically distinct even when randomly occupied. We compare the use of each of our modified Monte Carlo techniques for different types of problems. The results for realistic systems show that simulations beyond a simple Ising model are required. Calculations of the type presented here are now feasible for a wide range of materials and yield thermodynamic properties with acceptable precision. Our general approach turns out to be highly promising for the study of disordered systems previously thought intractable.

Computational Methods

The basis for all the methods we propose is the well-known Monte Carlo method but modified as described below. A key

* Corresponding author. E-mail: n.l.allan@bris.ac.uk. Fax: +44-117-925-1295.

[†] School of Chemistry.

[‡] Department of Geology.

feature of any simulation technique for the study of ordering effects is the sampling of many different configurations, allowing the exchange of those atoms or ions located at crystallographically nonequivalent positions. In our simulations this is achieved by explicitly interchanging the positions of these atoms or ions. Another important characteristic of the simulation is that it should provide an efficient procedure for the “relaxation” of the local environment around each atom or ion after every interchange. The three main methodologies we propose differ chiefly in the way this relaxation is achieved.

The first approach is a Monte Carlo simulation in which *both* the atomic configuration *and* the atomic coordinates of all of the atoms are changed. We refer to this as MCX. A related methodology has been proposed by Gordillo and Herrero,⁶ in their study of Al/Si ordering in albite except they did not consider long-range forces explicitly. Random moves of each atom are attempted as well as random exchanges between the atoms located at the sites of interest. The atomic coordinates are allowed to vary by making a random move of each atom in turn in the range $[-r_{\max}, +r_{\max}]$ as well as random exchanges between randomly chosen atoms or ions located at the sites of interest. To determine whether the displacement or exchange is accepted or rejected, the Metropolis algorithm⁷ is used. r_{\max} is chosen for each atomic species so that there are equal numbers of accepted and rejected trials.⁸ The efficiency of this scheme was found to be generally insensitive to the ratio of attempted exchanges to attempted displacements.

In the second approach (MC/MD) one of two options is chosen at random with equal probability. The first of these is a short NVE molecular dynamics (MD) simulation (typically 20–50 steps according to the application, with a time step of 1×10^{-15} s) in which the last configuration is accepted or rejected by comparing its energy with the energy of the starting configuration and using the standard Metropolis algorithm. In the second a short MD run follows a random exchange of atoms. Again, the difference in energy between the previous configuration and that immediately after the MD simulation is used in the Metropolis algorithm. If the exchange is rejected, the original configuration is included in the statistical averaging of thermodynamic properties. This second option allows us to sample efficiently different configurations, while the first mainly takes account of vibrations. At the start of each MD run, velocities are chosen anew at random from a Maxwellian distribution. The motivation for MC/MD has been the extensive use made of related techniques in the modeling of polymers and biomolecules.^{9–11}

In our last general technique, relaxation is achieved by determining, after each attempted swap, the configuration that minimizes the static contribution to the internal energy of the simulation cell,¹² using a conjugate gradients technique.¹³ We call this MC/SR (SR = static relaxation). The difference in energy between the relaxed configuration before the interchange and the new relaxed configuration is used in the Metropolis algorithm to decide if the interchange is accepted. If the exchange is rejected, the original configuration is included in the statistical averaging of thermodynamic properties and another swap then attempted. If accepted, the configuration is stored and subsequent interchanges attempted from it. This clearly introduces additional approximations not present in the other methods; for example, vibrations are neglected.

Applications

Cu–Au Alloys. Because of its relative simplicity, and the absence of long-range forces, our first example is CuAu, using

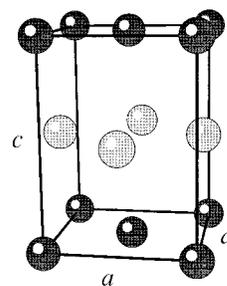


Figure 1. Structure of CuAu at low temperatures. Cu and Au atoms are dark and light, respectively. In the disordered phase at high temperature all sites are randomly occupied by Cu or Au atoms and $a = c$.

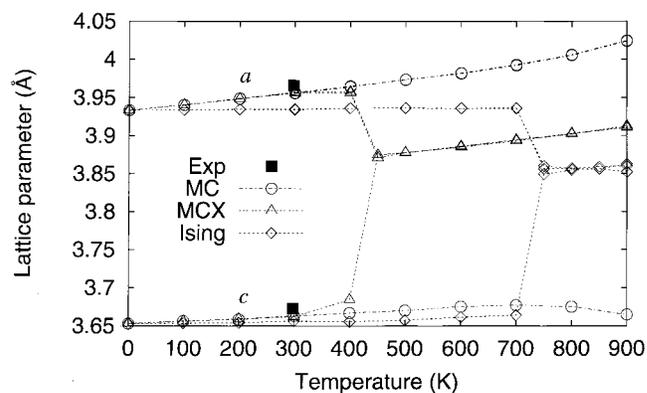


Figure 2. Lattice parameters (Å) of CuAu as a function of temperature (K), calculated using different approaches. Black squares denote experimental values. Open circles show the results of Monte Carlo calculations without explicit exchange of Cu and Au atoms. Triangles indicate values calculated using the MCX approach described in the text, which does include explicit exchanges. Diamonds are the results of the Ising-like calculations also described in the text.

the many-body potential proposed recently¹⁴ within the embedded atom method.¹⁵ At low temperatures CuAu has a tetragonal structure (Figure 1), with alternate layers of Cu and Au atoms. At higher temperature (683 K), it transforms to a face-centered cubic (fcc) structure where all crystallographic positions are occupied at random by Cu or Au atoms, in which the lattice parameters a and c are equal. This type of phase transition is important in metallurgy.

All simulations are carried out at constant temperature and pressure (*NPT*) using a unit cell containing 256 atoms, allowing anisotropic deformations of the unit cell.¹⁴ We first consider runs allowing atom displacements *without* explicit exchange of Cu and Au atoms. In these calculations the ordering of the alloy is maintained up to temperatures very close to the melting point. As shown by the open circles in Figure 2, no transition has taken place by 900 K. A much more efficient sampling of different atomic configurations is achieved in the MCX approach with explicit exchange of atoms as described earlier, and the resulting variation of the lattice parameters is also given in Figure 2 (open triangles). The transition temperature between the ordered and disordered phases, above which a and c are equal, now takes place at ≈ 430 K. This is lower than that observed experimentally (683 K), which appears to be due to the quality of the potentials.¹⁴

For comparison purposes, we have also carried out calculations in which vibrational contributions were neglected, by keeping the atoms at their crystallographic positions, although the cell was allowed to change shape in order to keep the pressure constant. The results of this Ising-type model are

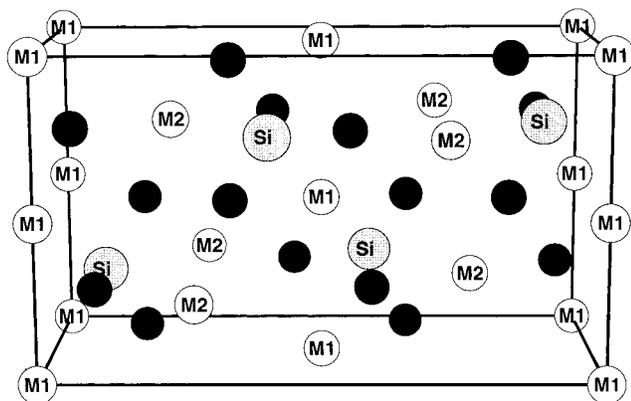


Figure 3. Structure of olivine showing the M1 and M2 sites.

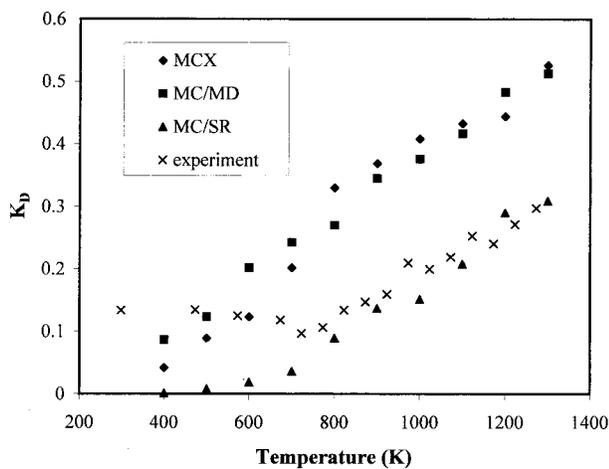


Figure 4. Calculated values of K_D for $(\text{Mg,Mn})_2\text{SiO}_4$ as a function of temperature.

shown in Figure 2 by open diamonds. It is clear that the transition temperature from this model is much larger than that from the MCX calculations (by 300 K),¹⁶ indicating the importance of vibrational contributions and relaxation effects.

Olivines. Our first application involving long-range forces is the olivine MgMnSiO_4 , where the two cations, Mg and Mn, involved in the disorder over the inequivalent octahedral M1 and M2 sites are isovalent. The structure of olivine is shown in Figure 3. Olivine is a major constituent of the Earth's upper mantle, and since the degree of order may alter significantly the thermodynamic stability and elastic properties of a mineral, knowledge of the ordering behavior of olivine is necessary for the interpretation of phase diagrams and seismic velocity data. Recent experiments^{17–19} using time-of-flight neutron diffraction have recorded the degree of order in the olivine minerals, MgMnSiO_4 , FeMgSiO_4 , and FeMnSiO_4 , as a function of temperature. All three minerals display similar ordering behavior, so we concentrate here only on MgMnSiO_4 . We define an equilibrium constant for the ordering, K_D , such that

$$K_D = X_{\text{M1}}^{\text{Mn}} X_{\text{M2}}^{\text{Mg}} / X_{\text{M1}}^{\text{Mg}} X_{\text{M2}}^{\text{Mn}} \quad (1)$$

where, for example, $X_{\text{M1}}^{\text{Mn}}$ denotes the fractional occupancy of the M1 site by Mn. In the experiment, on heating from room temperature a sample¹⁹ of MgMnSiO_4 which was previously quenched from a high T , no change in the degree of disorder was experimentally observed until ≈ 600 – 700 K (Figure 4); K_D now showed a slight decrease as the temperature was now sufficient to allow diffusion of the ions and the sample to approach equilibrium order. At low temperatures Mn prefers

TABLE 1: Short-Range Potential Parameters Derived for Olivine^a

interaction	A (eV)	ρ (Å)	C (eV Å ⁶)
O–O	1 388.73	0.3623	175.0
Si–O	18 003.76	0.2052	133.54
Mg–O	55 540.62	0.1655	10.0
Mn–O	12 507.99	0.2029	10.0

^a All potentials are of the Buckingham form (eq 2). In units of e , atomic charges q are as follows: $q_{\text{Mg}} = 1.2$, $q_{\text{Mn}} = 1.2$, $q_{\text{Si}} = 2.4$, and $q_{\text{O}} = -1.2$. The Si–O and O–O potentials were taken from reference 20 (see the text). All potential cutoffs are 12 Å.

TABLE 2: Calculated Lattice Parameters (Å) and Selected Elastic Constants (GPa) for Mg_2SiO_4 and Mn_2SiO_4

	Mg_2SiO_4		Mn_2SiO_4	
	calcd	obsd	calcd	obsd
a	10.166	10.225 ^a	10.596	10.596 ^a
b	5.961	5.994	6.232	6.257
c	4.823	4.762	4.976	4.902
C_{11}	322	328 ^b	244	258.4 ^c
C_{22}	181	200	140	165.6
C_{33}	226	235	178	206.8
C_{44}	55	66.7	32	45.3
C_{55}	65	81.3	51	55.6
C_{66}	65	80.9	57	57.8
C_{12}	67	69	59	87
C_{13}	77	69	65	95
C_{23}	76	73	61	92

^a Reference 30. ^b Reference 31. ^c Reference 32.

the larger M2 site so $K_D \ll 1$. Further increase in temperature led to further disordering of the Mg and Mn over the two sites and an increase in K_D . On subsequent cooling the degree of ordering increased until a “blocking temperature” was reached at which the cations can no longer diffuse through the structure. The faster the rate of cooling, the faster is the amount of disorder frozen into the crystal structure.

We started with the experimental structure^{18,19} and used an orthorhombic simulation box containing either 504 atoms ($2 \times 3 \times 3$ unit cells) or 896 atoms ($2 \times 4 \times 4$). To describe the short-range interactions between the atoms, we used two-body Buckingham potentials $V(r)$ of the form

$$V(r) = Ae^{-r/\rho} - \frac{C}{r^6} \quad (2)$$

with a cutoff of 12 Å. As our starting point, the SiO_2 potentials of Van Beest et al.,²⁰ successfully employed to describe the elastic properties of α -quartz,²¹ were used to describe interactions involving Si and O. Using this O–O potential, short-range potentials were then derived for Mg–O and Mn–O interactions by fitting to the lattice parameter and elastic data of MgO and MnO, respectively. These potentials, collected together in Table 1, were then used unchanged for MgMnSiO_4 , assuming all of the potentials for the binary oxides are transferable to the more complex mineral. Table 2 lists the calculated lattice parameters for Mg_2SiO_4 and Mn_2SiO_4 in the static limit together with available experimental data. Lattice parameters and elastic data are reproduced well for both compounds.

The MCX results presented here were all obtained within the NVT ensemble using the experimental volumes; for this example, test simulations indicate no observable variation of site occupancies with small changes in volume. Typically we carry out 20 000–100 000 cycles, following initial equilibration of 20 000 cycles; each cycle comprised 504 or 896 attempted

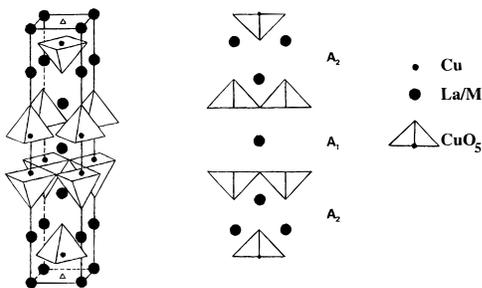


Figure 5. Crystal structure of $\text{La}_2\text{MCu}_2\text{O}_6$ ($M = \text{Ca}, \text{Sr}$). The distinct cation sites are labeled.

atom movements and one exchange of two atoms chosen at random. The site occupancies were monitored throughout to ensure that equilibrium values were reached.

Agreement between the calculated and experimental values of K_D is good above 700 K in the region of thermodynamic control. The MCX and MC/MD schemes give values for K_D close to each other, while the MC/SR scheme gives the same qualitative trends with a slightly lower value for the equilibrium constant; this difference is to be expected since the MC/SR scheme neglects lattice vibrations and hence the relative expansion of the two sites. The MC/SR values for K_D are somewhat closer to experiment; this is fortuitous, considering the very small energy differences associated with the exchange, and highlights the need of improved representations of the interionic interactions. The experimental value for the heat of exchange over the high-temperature range 700–1300 K is $15.7 \pm 0.9 \text{ kJ mol}^{-1}$, while that obtained theoretically from the three approaches is $11.5 \pm 0.7 \text{ kJ mol}^{-1}$, $12.2 \pm 0.5 \text{ kJ mol}^{-1}$ (MCX and MC/MD) and $19.5 \pm 0.8 \text{ kJ mol}^{-1}$ (MC/SR). The MCX results and MC/MD results are close to each other, and the MC/SR value differs appreciably from these. It should be emphasized that this exchange enthalpy is very small and so a stringent test of any theoretical approach and its implementation. Below the “blocking” temperature the experimental value for K_D is governed by kinetic factors and differs according to the thermal history of the sample, so it is not possible to compare our calculations with experiment. The results for simulation boxes containing 504 or 896 atoms were virtually identical.

We have found that the MC/MD approach is the most efficient at sampling phase space. At 1100 K, 28, 52, and 38% of attempted interchanges were successful for MCX, MC/MD, and MC/SR, respectively.

$\text{La}_2\text{MCu}_2\text{O}_6$ ($M = \text{Ca}, \text{Sr}$). Our final example concerns the crystal chemistry of $\text{La}_2\text{MCu}_2\text{O}_6$ ($M = \text{Ca}, \text{Sr}$). Although this structure possesses the double layer of CuO_5 pyramids present in all the cuprate systems with the highest T_C 's (e.g., $\text{YBa}_2\text{Cu}_3\text{O}_7$, $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$), *only* $M = \text{Ca}$ appears to give rise to a superconducting material on suitable doping ($\text{La}_{2-x}\text{Ca}_{1+x}\text{Cu}_2\text{O}_6$ ^{22,23} and $\text{La}_{2-x}\text{Sr}_x\text{CaCu}_2\text{O}_6$ ²⁴). The structure of $\text{La}_2\text{MCu}_2\text{O}_6$ is shown in Figure 5; the two distinct cation sites are A_1 , sandwiched between the CuO_2 planes, and A_2 , lying between the double layers of CuO_5 pyramids. Diffraction studies^{24–26} and calculations restricted to the static limit²⁷ have suggested that the cation ordering in $\text{La}_2\text{CaCu}_2\text{O}_6$ may be very different from that in $\text{La}_2\text{SrCu}_2\text{O}_6$, with Sr^{2+} ions, unlike Ca^{2+} , restricted to the A_2 sites. Together, these two compounds form an excellent test of our approach since any proposed method must be sufficiently robust to deal with the extensive relaxations accompanying the interchange of ions that not only are very different in size but which also do not possess the same charge.

TABLE 3: Short-Range Potential Parameters for $\text{La}_2\text{SrCu}_2\text{O}_6$ and $\text{La}_2\text{CaCu}_2\text{O}_6$ ^a

interaction	A (eV)	ρ (Å)
O–O	249.3764	0.3621
Sr–O	3 219.9547	0.3067
Sr–Sr	13 888.3973	0.2402
Sr–Cu	20 333.8861	0.2105
Sr–La	14 409.9348	0.2499
Cu–O	1 617.2373	0.2728
Cu–Cu	23 008.2205	0.1868
Cu–La	21 549.6495	0.2204
La–O	4 236.4294	0.3033
La–La	18 152.9102	0.2547

^a The parameters were derived from least-squares fitting to the electron-gas potentials used in ref 27. Charges of +3 for La, +2 for Sr, Ca, and Cu, and –2 for O were used. C is zero in all cases. All potential cutoffs are 6 Å.

Here we examine the distribution of La^{3+} and M^{2+} ions between the A_1 and A_2 sites. For this it is necessary to interchange the M^{2+} and La^{3+} ions. Since these have both different charges and sizes, the local distortion accompanying each exchange is much larger than in the previous example. In our earlier study of the static lattice properties²⁷ of these systems, we used nonempirical electron gas potentials in the form of tables. Here, for ease of use, we fitted these potentials to Buckingham forms, which give virtually identical results for all those properties obtained previously.²⁷ The potential parameters used in this work are collected together in Table 3. For $M = \text{Ca}$, it is worth noting that in this earlier work,²⁷ where only very small unit cells were considered and only the static contribution to the total energy was calculated, these potentials indicated a somewhat lower occupancy of the A_1 site than that observed experimentally.

We started the Monte Carlo studies from the structures obtained from a static minimization.²⁷ The MCX method fails completely, since it cannot accommodate the local relaxations to allow successful exchanges of the La and M ions. The resulting rate of exchanges is so small (much less than 1%) that this variant is impracticable given our available computational resources. Even at a temperature of 4000 K, virtually no exchanges take place.

Our results using MC/MD and MC/SR for a simulation cell containing 594 ions indicate marked differences in behavior between the superconductor $\text{La}_2\text{CaCu}_2\text{O}_6$ and the nonsuperconductor $\text{La}_2\text{SrCu}_2\text{O}_6$.

The calculated stacking sequence in $\text{La}_2\text{CaCu}_2\text{O}_6$ is mostly

A_1	La
A_2	La
A_2	Ca
A_1	La
A_2	La
A_2	Ca

where full lines denote superconducting planes. At a typical synthesis temperature of 1300 K, the MC/MD results indicate that $\approx 32\%$ of the Ca is in A_1 sites, sandwiched between the superconducting planes; the corresponding value for MC/SR is 20%. There is no direct experimental value for comparison; the observed occupancy²² of this site in the doped material $\text{La}_{1.9}\text{Ca}_{1.1}\text{Cu}_2\text{O}_6$ is 88% Ca. We have already commented²⁷ that even in static lattice minimizations the potentials used here

indicated a lower occupancy of the A₁ site than that observed experimentally. It is also worth noting that, in related static calculations,²⁷ structures where the A₁ sites are occupied by Ca²⁺ are made more favorable by hole-doping on the substitution of some La³⁺ by Ca²⁺ or Sr²⁺.

For La₂SrCu₂O₆ the corresponding calculated order is predominantly

A ₁	La
A ₂	Sr
A ₂	Sr
A ₁	La
A ₂	La
A ₂	La

with the La between the superconducting planes. MC/MD indicates a 11% occupancy of the A1 site by Sr, in good agreement with the corresponding experimental observations (16% at 1400 K).²⁶

Once more MC/SR, which neglects vibrational effects, predicts a result (<0.5% occupancy of the A1 site by Sr) which differs appreciably from MC/MD. In this context, it is worth noting that the relative magnitudes of the ionic radii of La³⁺, Ca²⁺, and Sr²⁺ are

$$r(\text{Sr}^{2+}) > r(\text{La}^{3+}) > r(\text{Ca}^{2+})$$

with the largest difference in size between Sr²⁺ and La³⁺, so the interchange of these ions involves the largest local distortions of all those considered in this paper.

A further interesting feature of our results for the Sr compound is that additional disorder is predicted to occur in La₂SrCu₂O₆ in the *a* and *b* directions between the Sr and La on the different A₂ sites. For example, neighboring cells are often aligned:

A ₁	La	La
A ₂	Sr	La
A ₂	Sr	La
A ₁	La	La
A ₂	La	Sr
A ₂	La	Sr

This leads to substantial local rumpling of the Cu–O planes, with a possible deleterious effect on the superconductivity.

Final Remarks

A very serious limitation of current simulation approaches is the difficulty of modeling disordered solids and hence of obtaining a systematic description of cation or anion ordering as a function of temperature, pressure, and composition. In this paper we have addressed this problem and shown that hybrid Monte Carlo simulations can be used to study disorder in materials such as ceramic oxides and minerals. We have examined both convergent and nonconvergent ordering problems. It is essential to take explicit account of ionic relaxation, without any averaging out of local effects.

We have presented results for a series of approaches of increasing complexity. These include an Ising-type model, which takes no account of molecular relaxation or vibration,

MC/SR, which takes some account of relaxation but not vibration and finally MCX and MC/MD, which include both relaxation and vibrational effects. The difference between the MCX and the MC/MD techniques is that MC/MD allows greater relaxation of the ions and hence more effective swapping of atoms and more efficient sampling of different configurations. When the relaxations are very large, as when La³⁺ and Sr²⁺ ions are interchanged in La₂SrCu₂O₆, MC/MD may well be the only viable approach.

Of course the success of any simulation depends on the accuracy of the interatomic potentials. Calculations such as those presented here are a severe test of the potential model as the energy differences involved are small (e.g., <20 kJ mol⁻¹ for MgMnSiO₄). There is clearly still a need for improved representations of interatomic interactions. For ionic compounds our methods can be readily extended to take account of polarization effects, by means of, for example, the well-known shell model.²⁸

Simulations of the type discussed in this paper are now feasible for a wide range of materials and yield thermodynamic properties with acceptable precision. Our general approach turns out to be highly promising for the study of disordered systems previously thought too complex for simulation; for example, we have shown elsewhere²⁹ that the MC/MD technique is readily applicable to the study of the thermodynamic properties of solid solutions.

Acknowledgment. This work was funded by NERC Grants GR3/09772 and GR9/02621. J.D.B. is also grateful for financial support through a research fellowship provided by the Royal Society (Grant 516002). G.D.B.'s contribution to this work was made possible by means of a grant from el Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina. We would like to thank Dr. Mark Taylor (Bristol) for useful discussions.

References and Notes

- (1) Catlow, C. R. A.; Mackrodt, W. C. In *Computer Simulation of Solids*; Catlow, C. R. A., Mackrodt, W. C., Eds.; Springer-Verlag: Berlin, 1982; Chapter 1.
- (2) Allan, N. L.; Mackrodt, W. C.; Leslie, M. *Adv. Ceram.* **1987**, *23*, 257.
- (3) Taylor, M. B.; Barrera, G. D.; Allan, N. L.; Barron, T. H. K.; Mackrodt, W. C. *Faraday Discuss.* **1997**, *106*, 377.
- (4) Wei, S. H.; Mbaye, A. A.; Ferreira, L. G.; Zunger, A. *Phys. Rev. B* **1987**, *36*, 4163.
- (5) Purton, J. A.; Allan, N. L.; Blundy, J. A. *Geochim. Cosmochim. Acta* **1997**, *61*, 3927.
- (6) Gordillo, M. C.; Herrero, C. P. *J. Phys. Chem.* **1996**, *100*, 9098.
- (7) Metropolis, N. L.; Rosenbluth, A. W.; Rosenbluth, M. N.; Teller, A. H.; Teller, E. *J. Chem. Phys.* **1953**, *21*, 1087. Frenkel, D.; Smit, B. *Understanding Molecular Simulation: From algorithms to applications*; Academic Press: San Diego, 1996.
- (8) Allen, M. P.; Tildesley, D. J. *Computer simulation of liquids*; Clarendon Press: Oxford, U.K., 1987.
- (9) Duane, S.; Kennedy, A. D.; Pendleton, B. J.; Roweth, D. *Phys. Lett. B* **1987**, *195*, 216.
- (10) Mehlig, B.; Heermann, D. W.; Forrest, B. M. *Phys. Rev. B* **1992**, *45*, 679.
- (11) Clamp, M. E.; Baker, P. G.; Stirling, C. J.; Brass, A. *J. Comput. Chem.* **1994**, *15*, 838.
- (12) Taylor, M. B.; Barrera, G. D.; Allan, N. L.; Barron, T. H. K. *Phys. Rev. B* **1997**, *56*, 14380.
- (13) Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. *Numerical recipes in Fortran; The Art of Scientific Computing*, 2nd ed.; Cambridge University Press: Cambridge, U.K., 1992.
- (14) Barrera, G. D.; de Tandler, R. H. Submitted for publication.
- (15) Daw, M. S.; Baskes, M. I. *Phys. Rev. B* **1986**, *33*, 7983.
- (16) The improved agreement with experiment is fortuitous.
- (17) Artioli, G.; Rinaldi, R.; Wilson, C. C.; Zanazzi, P. F. *Am. Mineral.* **1995**, *80*, 197.
- (18) Henderson, C. M. B.; Knight, K. S.; Redfern, S. A. T.; Wood, B. *J. Science* **1996**, *271*, 1713.

- (19) Redfern, S. A. T.; Henderson, C. M. B.; Wood, B. J.; Harrison, R. J.; Knight, K. S. *Nature* **1996**, *381*, 407.
- (20) Van Beest, B. W. H.; Kramer, G. J.; van Santen, R. A. *Phys. Rev. Lett.* **1990**, *64*, 1955.
- (21) Purton, J. A.; Jones, R.; Catlow C. R. A.; Leslie, M. *Phys. Chem. Miner.* **1993**, *19*, 392.
- (22) Ishii, T.; Watanabe, T.; Kinoshita, K.; Matsuda, A. *Physica C* **1991**, *179*, 39.
- (23) Cava, R. J.; Batlogg, B.; van Dover, R. B.; Krajewski, J. J.; Waszczak, J. V.; Fleming, R. M.; Peck, W. F., Jr.; Rupp, L. W., Jr.; Marsh, P.; James, A. C. W. P.; Scheemeyer, L. F. *Nature* **1990**, *345*, 602.
- (24) Cava, R. J.; Santoro, A.; Krajewski, J. J.; Fleming, R. M.; Waszczak, J. V.; Peck, W. F., Jr.; Marsh, P. *Physica C* **1990**, *172*, 138.
- (25) Izumi, F.; Takayama-Muromachi, E.; Nakai, Y.; Asano, H. *Physica C* **1989**, *157*, 89.
- (26) Caignaert, V.; Nguyen, N.; Raveau, B. *Mater. Res. Bull.* **1990**, *25*, 199.
- (27) Allan, N. L.; Baram, P. S.; Gormezano, A.; Mackrodt, W. C. *J. Mater. Chem.* **1994**, *4*, 817.
- (28) Mitchell, P.; Fincham D.; Mackrodt, W. C. *J. Phys. Condens. Matter* **1994**, *6*, 393.
- (29) Purton, J. A.; Blundy, J. D.; Taylor, M. B.; Barrera, G. D.; Allan, N. L. *Chem. Commun.* **1998**, 627.
- (30) Fugino, K.; Sasaki, S.; Takeuchi, Y.; Sadanaga, R. *Acta Crystallogr.* **1981**, *B37*, 513.
- (31) Herman, R. F. S. The elastic constants of crystals and other anisotropic materials. In *Landolt-Bornstein Tables*, III/11; Hellwege, K. H., Hellwege, A. M., Eds.; Springer-Verlag: Berlin, 1984; pp 1–244.
- (32) Sumino, Y. *J. Phys. Earth* **1979**, *27*, 209.