

# Applicability of a quantum mechanical ‘virtual crystal approximation’ to study Al/Si-disorder

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## Abstract

We show that a quantum mechanical version of the virtual crystal approximation can be used to study Al/Si-disorder in silicates. Full geometry optimizations show that this approach reproduces disordered crystal structures with an accuracy equal to that of density functional calculations for fully ordered structures. As this approach is based on density functional theory in conjunction with a plane wave basis set and ultrasoft pseudopotentials, it is possible to study large and complex crystal structures. As first examples we present calculations for hollandite-type  $\text{KAlSi}_3\text{O}_8$ , where Si is octahedrally coordinated, and gehlenite,  $\text{Ca}_2\text{Al}_2\text{SiO}_7$ , with tetrahedrally coordinated Al and Si-atoms. © 2002 Elsevier Science B.V. All rights reserved.

## 1. Introduction

An important application of atomistic model calculations in silicate chemistry is the understanding of Al/Si order-disorder and the related problem of ordering in solid solutions [1–3]. In those methods which are based on the modelling of three-dimensional periodic crystals two fundamentally different approaches are used. In the first, supercells which have specific Al/Si distributions are employed. This ‘configurational approach’

typically requires the calculation of many configurations to deduce structural parameters, physical properties and the energetics of the ordering process. The main advantage of the configurational approach is that it allows the modelling of the local distortions which occur around a specific site as a function of the occupation by either Al or Si. The main shortcoming of this approach is that the use of supercells necessarily imposes an unwanted long-range order. In addition, the accuracy of the statistical sampling based on a finite number of configurations is often difficult to quantify and, furthermore, in cases of nearly full ordering or of solid solutions with compositions close to the end members enormously large supercells are required. Hence, it would be extremely advantageous to

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have a reliable alternative to the configurational approach which mimics the statistical distribution of different atomic species on each site.

To be truly useful, this method must be compatible with state-of-the-art modelling approaches for complex, low-symmetry inorganic crystal structures. Currently, the most widely used method in the study of complex solids is based on density functional theory (DFT) [4–8]. While DFT itself is exact [4], practical calculations require an approximation for the treatment of the exchange-correlation energies. Here we use the ‘generalized gradient approximation’ (GGA) for exchange-correlation effects in the form suggested by Perdew, Burke and Ernzerhof, GGA–PBE [9]. Results based on this GGA are generally in better agreement with experiment than those obtained with the local density approximation, LDA [10–13]. The computational efficiency and the accuracy of DFT calculations depends to a large extent on the basis set used, and computational schemes in which the charge density and electronic wavefunctions are expanded in a basis set of plane waves are currently widely used. However, as it is impractical to consider tightly bound core electrons explicitly when using a plane wave basis set, pseudopotentials have to be introduced to mimic the screening of the Coulomb potential of the nucleus by the core electrons. A number of approaches for the construction of pseudopotentials have been presented in the literature [14,15]. The state-of-the-art are the efficient ‘ultrasoft’ pseudopotentials, which require a comparatively small number of plane waves [16,17].

Within the ultrasoft pseudopotential method it is possible to formulate a virtual crystal approximation (VCA) which can be used to study order/disorder and solid solutions [18]. In the conceptually most straightforward variant two or more pseudoatoms are placed at a given site and an average potential is obtained. Pseudoatoms occupying the same site do not interact with each other. This approach is complementary to the configurational approach in that it does not require the use of supercells. It is easier to implement than perturbation theory-based methods [19,20] and probably can be applied to a wider range of problems than the coherent potential approxima-

tion [21]. However, since this approach has been formulated very recently [18] only a small body of evidence supporting the applicability of this technique to solid solutions is available [22–24]. In particular, it has not yet been established whether this method is capable of modelling Al/Si order/disorder. As this would be central to its widespread use in silicate chemistry we now demonstrate that the VCA gives useful results for two structures with long-range Al/Si disorder.

The first structure is  $\text{K}(\text{AlSi}_3)\text{O}_8$ -hollandite. This is one of the few phases in which Si is in sixfold coordination. The coordinating octahedron is slightly distorted, and the reproduction of this structural feature is a subtle test for the validity of the approach explored here. The second structure is gehlenite,  $\text{Ca}_2\text{Al}(\text{AlSi})\text{O}_7$ . Gehlenite is of interest as one of the two tetrahedral sites, the  $T_1$ -site, is exclusively occupied by Al, while there is (Al,Si)-disorder on the second tetrahedral, the  $T_2$ -site. An analysis of the results of geometry optimizations of these two phases will therefore provide evidence for the general applicability of the VCA approach to study Al/Si disorder.

## 2. Computational details

The quantum mechanical calculations described here are based on density functional theory and the PBE-version of the GGA. Ultrasoft pseudopotentials were used with a maximum cutoff energy of the plane waves of 380 eV. In addition to the cutoff energy, one further parameter determines the quality of the calculations, namely the density of points with which the Brillouin zone is sampled. The wave vectors for the sampling points were chosen according to the scheme proposed by Monkhorst and Pack [25]. Here, we use a sampling of reciprocal space such that distances between grid points are about  $0.05 \text{ \AA}^{-1}$ . Full geometry optimization calculations were performed in which all structural parameters not constrained by the space group symmetry were relaxed. For the ordered models, the space group was  $P1$ . After the final self-consistency cycle, the remaining forces on the atoms were less than  $0.02 \text{ eV/\AA}$ , and the remaining stress was less than 0.1 GPa. The present

calculations are restricted to the athermal limit, in which temperature effects and zero-point motions are neglected. For all calculations we used academic and commercial versions of the CASTEP program, which has been described elsewhere [26–28]. The implementation of the VCA follows the description of Bellaiche and Vanderbilt [18].

### 3. Results and discussion

The results of the full geometry optimization of  $\text{K}(\text{AlSi}_3)\text{O}_8$  in the hollandite structure type are given in Table 1 and those for  $\text{CaAl}(\text{AlSi})\text{O}_7$  gehlenite are given in Table 2. It is obvious that in both cases the computed structural parameters agree with the corresponding experimental values to within the accuracy usually obtained in DFT-based calculations [29,28]. For example, the relative magnitudes of the small bond-length distortions around the  $(\text{Al},\text{Si}_3)$ -site in  $\text{K}(\text{AlSi}_3)\text{O}_8$ -hollandite are reproduced very well.

In gehlenite, there are two tetrahedral sites, the  $\text{T}_1$  and the  $\text{T}_2$ -sites. The ordering of Al and Si over these sites has been determined experimentally [30,31]. It follows from these investigations that the  $\text{T}_1$ -site is occupied solely by Al while the  $\text{T}_2$ -sites are occupied in equal parts by Al and Si. This is also the result of the calculations presented here as a fully disordered structure, i.e., with an occu-

pation of  $\frac{2}{3}$  Al and  $\frac{1}{3}$  Si for the  $\text{T}_1$  and  $\text{T}_2$ -sites, is less stable by more than 110 kJ/mol as compared to a structure in which the  $\text{T}_1$ -site is occupied exclusively by Al, while the  $\text{T}_2$ -sites are modelled as being fully disordered with 0.5 Al and 0.5 Si. A comparison of the structure with disorder in only the  $\text{T}_2$ -site is given in Table 2 and again very good agreement with the experimental results is observed.

In contrast to the configurational approach, the VCA model does not take into account the relaxation around a site on substitution. However, the results obtained in the VCA model can be used as a reference for models with a specific atomic configuration. For example, natural gehlenite can exhibit stripe domains and cross-hatched texture [32]. This may be due to short-range ordering into a lower-symmetry structure [2]. From empirical potential model calculations, a possible ordering scheme causing the appearance of a spontaneous strain has been suggested [2], with short-range ordering, so that each  $\text{T}_2$ -pair is occupied by one Al and one Si. The structural parameters of this ordered structure have been computed here, and they are given in Table 2.

The computations show that the  $c$ -lattice parameter is essentially unaffected by the ordering in the  $\text{T}_2$ -sites. Hence the elastic interaction between the  $\text{T}_2$ -sites along  $[001]$  is very small, which is consistent with the absence of long-range order

Table 1  
Comparison of experimentally determined [33] and theoretical predicted structure of  $\text{KAlSi}_3\text{O}_8$

		Experimental	Theoretical	Difference
$a$	(Å)	9.315	9.294	-0.2%
$c$	(Å)	2.723	2.699	-0.9%
(Al, Si <sub>3</sub> )	$x$	0.3501	0.35009	
	$y$	0.1661	0.16573	
O(1)	$x$	0.1526	0.15459	
	$y$	0.2036	0.20476	
O(2)	$x$	0.5406	0.54112	
	$y$	0.1648	0.16418	
K–O(1)	(Å)	2.733	2.740	+0.3%
(Al, Si <sub>3</sub> )–O(1a)	(Å)	1.873	1.852	-1.1%
(Al, Si <sub>3</sub> )–O(1b)	(Å)	1.825	1.809	-0.9%
(Al, Si <sub>3</sub> )–O(2a)	(Å)	1.774	1.775	+0.1%
(Al, Si <sub>3</sub> )–O(2b)	(Å)	1.800	1.807	+0.4%

The K-atom occupies the position  $0, 0, \frac{1}{2}$ , the  $z$ -coordinates of all other atoms are fixed by symmetry to 0. The Al and Si positions, which are relaxed independently, agreed to within 0.0002 fractional coordinates. Labeling of O-atoms is according to Zhang et al. [33].

Table 2

Comparison of the experimentally determined [30] and predicted structure of gehlenite. In the VCA model, the  $T_1$ -site, occupied by Al, has Wyckoff position 2a with coordinates 0, 0, 0, the space group symmetry is  $P4_2m$  with  $a = b$

			Experimental	Theoretical VCA	Theoretical ordered
$ab$ (Å)			7.6580	7.6407	7.6433/7.6777
$c$ (Å)			5.0636	5.0455	5.0644
Ca	4e	$x$	0.33873(4)	0.3383	0.3428
		$y$	0.16127(4)	0.1617	0.1818
		$z$	0.5116(1)	0.5143	0.5165
Al/Si	4e	$x$	0.14310(6)	0.1425	0.1414/0.3567
		$y$	0.3569(6)	0.3575	0.3570/0.8569
		$z$	0.95630(13)	0.9557	0.9623/0.0479
O	2c	$z$	0.17670(54)	0.1734	0.1729
O	4e	$x$	0.14299(18)	0.1426	0.1420
		$y$	0.35701(18)	0.3574	0.3613
		$z$	0.28352(37)	0.2796	0.2960
O	8f	$x$	0.08768(20)	0.0876	0.0892
		$y$	0.16731(16)	0.1681	0.1620
		$z$	0.80722(27)	0.8120	0.8123
$T_1$ -O (Å)			1.747(1)	1.731	1.718–1.751
$T_2$ -O (Å)			1.655–1.693(1)	1.629–1.675	1.583–1.634 (Si) 1.690–1.745 (Al)

The ordered model has been derived by empirical model calculations [2]. In this model, each  $T_2$ -pair is occupied by one Al and one Si atom. This leads to a symmetry lowering to  $P1$  so that all lattice parameters and atomic positions become symmetrically independent. After the relaxation  $\alpha = 89.5^\circ$ , while  $\beta$  and  $\gamma$  do not deviate significantly from  $90^\circ$ . As in the ordered model the Al/Si-sites are distinct, two values are given. The other structural parameters in the ordered model show the shifts with respect to the atomic positions in the VCA model, but due to the space group symmetry  $P1$  they represent the positions of the formerly symmetrically equivalent atoms only approximately.

along  $[001]$ . The  $a$ - and  $b$ -lattice parameters differ, with a strain of about 0.2%, which is noticeably smaller than the result of about 1% obtained from model calculations based on empirical potentials [2]. The local relaxations are noticeable. Instead of  $T_2$ -O bond-lengths of 1.629–1.675 Å obtained with a VCA model with complete disorder over the  $T_2$ -sites, in a fully short-ranged model the bond lengths are 1.583–1.634 Å for Si-O and 1.690–1.745 Å for Al-O. According to the present calculations, the fully short-range ordered configuration (which, of course, is invariably also long-range ordered in our approach) is more than 310 kJ/mol more stable than the model with the short-range disorder. For comparison, one further ordering scheme was used in which the unit-cell dimensions were also maintained, but where one  $T_2$ -pair was occupied by two Si atoms, while the other one was occupied by Al. The enthalpy difference between the two structures with different ordering schemes is 0.479 eV/unit cell, thereby confirming the magnitude of the interaction parameter  $J$  for the reaction  $(Al-O-Al) +$

$(Si-O-Si) = 2(Al-O-Si) - J$ , which had previously been determined to be  $J = 0.52$  eV by empirical model calculations [2].

In summary, the VCA approach presented here is useful for the modelling of Al/Si order/disorder in both tetrahedrally and octahedrally coordinated sites, as in both cases a good agreement of the calculated to the experimentally observed distances has been observed. As the underlying approach allows the investigation of large, low-symmetry structures and their properties, further applications, e.g., to zeolites, and for the investigation of other properties, such as elastic stiffness coefficients as a function of Al/Si order or the high-pressure behaviour, are possible.

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