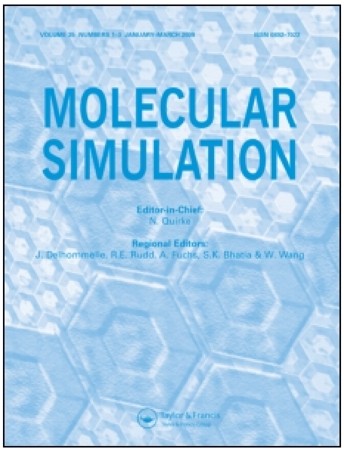

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WANNIER FUNCTION ANALYSIS FOR UNDERSTANDING DISORDERED STRUCTURES GENERATED USING CAR-PARRINELLO MOLECULAR DYNAMICS

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Maximally-localized Wannier functions are used to investigate the structure and bonding details in an amorphous boron nitride network generated using Car-Parrinello molecular dynamics. The location of Wannier function centers (WFCs) provides a means of reliably determining the existence of a bond and its type between atoms. In addition, defect states such as lone pairs of electrons can be directly observed. The use of Wannier Functions for the analysis of networks is considerably more reliable than the "coordination shell" approach, where bonding statistics strongly depend on the particular choice of radius.

Keywords: Car-Parrinello molecular dynamics; Wannier functions; Boron nitride; Bonding

INTRODUCTION

First principles or *ab-initio* molecular dynamics methods such as Car-Parrinello molecular dynamics (CPMD) [1] have proven able to provide insights into the structure of many types of systems at a level which is difficult to obtain from other methods. CPMD employs a classical description of the motion of ion cores

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with a quantum-mechanical description of the bonding electrons. The key component of this modeling approach is the use of Density Functional Theory (DFT) [2,3] to calculate interatomic forces by solving a set of Schrödinger-like equations at every time step. This method is based on a very general quantum mechanical description of the bonding electrons which gives it great predictive power with a minimum of adjustable parameters. When combined with experimental studies, this technique has proved extremely powerful in solving structural problems in chemistry, biology and physics.

We have employed CPMD to model the structure of a wide range of amorphous alloys including carbon [4,5], boron nitride and aluminium nitride [6], and the hydrogenated form of amorphous carbon [7]. The results from these simulations provided considerable information on the structure and several features compared well with experimental work. However, the analysis of the resulting bonding networks was complicated by the fact that it was often difficult to confidently determine bonding statistics. This is because bonding was usually determined using a coordination shell approach where atoms within a sphere are considered bonded to the central atom. Bonding statistics are particularly sensitive to the chosen radius value. In an amorphous system, where there can be a wide range of bond lengths for a particular bond type, this approach is unreliable. An alternative method for visualising bonding between atoms is to examine the electron density. However, it is often difficult to determine whether bonds exist, especially if the bonds are elongated and have a lower electron density. It is also difficult to distinguish between different bond types i.e. whether there are single, double or triple bonds.

Recently, maximally localized Wannier functions have been developed to aid in the interpretation of bonding in disordered systems [8,9]. This method was used to study the bonding properties of amorphous silicon and it was found that Wannier function centers (WFCs) provided an unambiguous picture of bonding configurations in a monoatomic amorphous system. In addition, lone pairs and defect configurations can be observed. In this work, we show how this Wannier function approach can provide a detailed description of the structure and bonding in the amorphous alloy boron nitride.

THEORETICAL CONSIDERATIONS

In this work, we have performed a Wannier function analysis of a 64 atom (32 of each species B and N), 3.0 g/cm^3 boron nitride simulation presented previously [6]. The simulation used gamma point sampling, a plane wave energy cutoff of 50 Ry with the BLYP [10,11] representation of the exchange and correlation energy. Periodic boundary conditions were applied in all three directions. Boron and nitrogen atom cores were described by pseudopotentials due to Goedecker [12]. Each pseudopotential was tested by optimising the geometry for several well-known molecules (e.g. N_2, BN) and it was found that for an energy cut off 50 Ry, bond lengths were within 1% of tabulated values. Further testing of the pseudopotentials was performed during the calculation of the bulk modulus for c-BN (see below) where calculated values where found to be within 5% of experiment.

In order to simulate the experimental formation of boron nitride, the "liquid-quench" molecular dynamics method was employed. This method simulates the rapid heating and cooling present in "thermal spikes" which occur during boron nitride formation using energetic condensation methods. Initially a "liquid" of the elements of interest at the desired density is generated within the simulation cell and allowed to equilibrate at between 4000 and 5000 K for between 380 and 500 fs. This period corresponds to the localized heating following ion impacts which occurs during film growth. Then the simulation is cooled to room temperature following an exponential curve over a period of 500 fs. This corresponds to the rapid draining of heat away from the impact site on a realistic timescale [13]. Finally, the system is allowed to equilibrate at room temperature in order to gather statistical data over a period of 500 fs.

Plane waves and Bloch functions are delocalized functions which describe electron states in a solid. When describing localized phenomena (such as bonding) these can be replaced with an optimally localized set of functions called "Wannier" functions. These functions are analogous to localized Molecular Orbitals and can be interpreted to give information about bonding in various materials. A practical method for generating maximally-localized Wannier functions starting from the occupied Bloch states has been developed and implemented in the CPMD code [14]. In Wannier analysis, a unitary transformation is applied to express the Bloch states as a sum of orthogonal, localized functions. However, even for the case of a single *k*-point (as used in this work), the unitary transformation is not uniquely defined since each Bloch state (Kohn Sham orbital in CPMD) can be multiplied by an arbitrary phase factor. Marzari and Vanderbilt [15] resolved this indeterminacy by requiring that the real-space spread of the Wannier functions be minimized. In a disordered material these maximally localized Wannier function have a complex spatial structure which is difficult to visualize, and so WFCs are computed which are more straightforward to interpret. The location of the *x*-coordinate x_n (with similar expressions for y_n and z_n) of the n^{th} WFC is given by

$$x_n = -\frac{L}{2\pi}\mathrm{Im}\ \ln\left\langle w_n \left| \mathrm{e}^{-i\frac{2\pi}{L}x} \right| w_n \right\rangle, \tag{1}$$

where L is the length of a cubic supercell and w_n is the nth maximally localized Wannier function, Details of the calculation of $w_n(r)$ can be found elsewhere [8,9]. The spread in real space of an individual Wannier function σ_n is given by

$$\sigma_n = \sqrt{\langle r^2 \rangle_n - \langle r \rangle_n^2}, \tag{2}$$

and provides a useful measure of localization in real space. Defect states are expected to be less localized than bonding states. Note that the quantity minimized during the determination of the w_n is the sum over all the σ_n.

RESULTS AND DISCUSSION

Figure 1 shows a snapshot of the boron nitride network complete with WFCs during the final 300 K anneal. The presence of WFCs between neighboring atoms indicates the presence of a bond. The number of WFCs located between a pair of atoms indicates whether a single, double or triple bond is present. Figure 2 shows the typical bonding arrangements found in the network. In crystalline c-BN, all atoms are 4-fold coordinated, with charge transfer between nitrogen and boron atoms to form $N(4)^+$ and $B(4)^-$ sites. Just under half of the boron and nitrogen

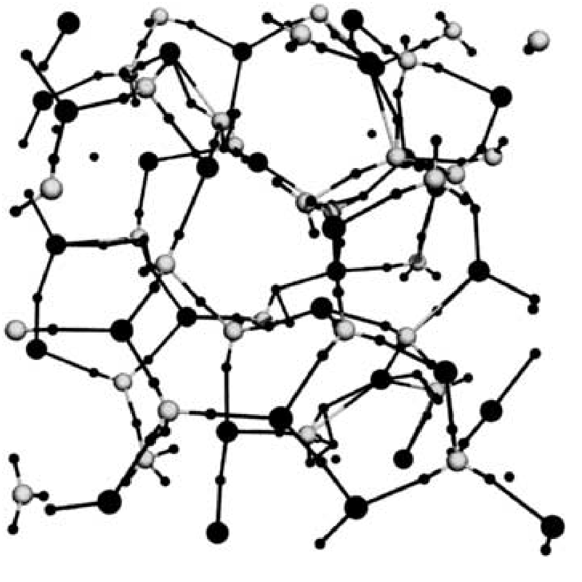

FIGURE 1 Snapshot of the 64 atoms BN simulation during the final 300 K equilibration. Wannier function centers (WFCs) are shown as small black atoms, while nitrogen atoms are large and light gray and boron atoms are large and dark.

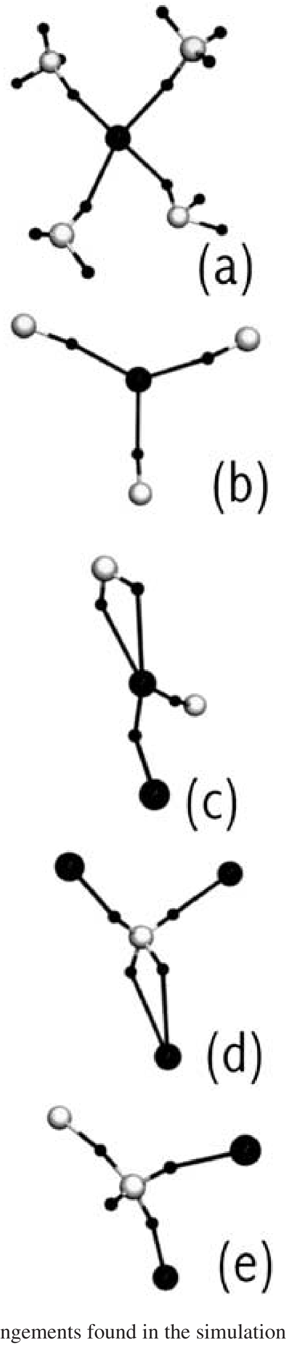

FIGURE 2 Typical bonding arrangements found in the simulation. WFCs are shown as small black atoms, while nitrogen atoms are large and light gray and boron atoms are large and dark.

TABLE I The number of each type of bonding configuration for both the boron and nitrogen atoms

	Bonding configuration					
Simulation	$B(4)^-$	$B(3)^0$	$B(3)^-$	$N(4)^+$	$N(3)^0$	$N(3)^+$
64 atom BN (3.0 g/cm^3)	14	14	4	14	14	4

TABLE II A comparison of the percentage of like bonds (i.e. N–N or B–B bonds) and coordination of the boron and nitrogen atoms determined using Wannier functions and the coordination shell approach (with a radius of 1.8 Å)

		B coordination			*N coordination*		
Analysis method	*% Like bonds*	2	3	4	2	3	4
Wannier functions	10	0	18	14	0	18	14
Coordination shell	11	2	17	13	0	19	13

atoms where found to be in these configurations (see Fig. 2(a) for an example). Other bonding arrangements found were 3-fold coordinated boron sites (B(3) e.g. Fig. 2(b)), 3-fold coordinated boron and nitrogen sites with two single and one double bond ($B(3)^-$ and $N(3)^+$ e.g. Fig. 2(c) and (d)), and 3-fold coordinated nitrogen atoms with a lone pair of electrons (N(3) e.g. 3(e)).

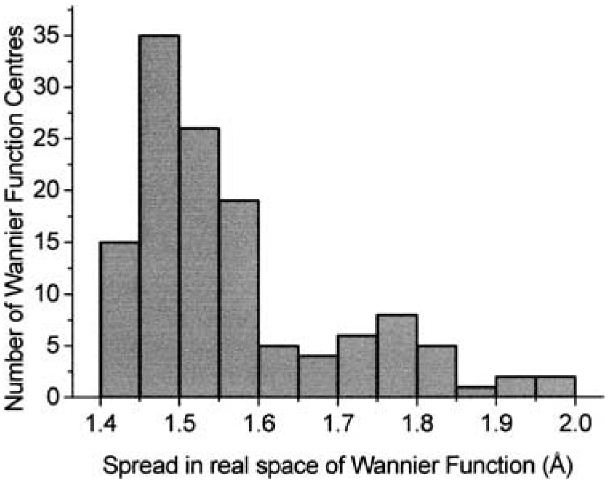

FIGURE 3 The spread in real space of the WFCs (σ_n) in Å. The values around 1.5 Å correspond to non-defective B–N single bonds. Spreads above this correspond to WFCs associated with unlike bonds (B–B or N–N), double bonds and lone pairs.

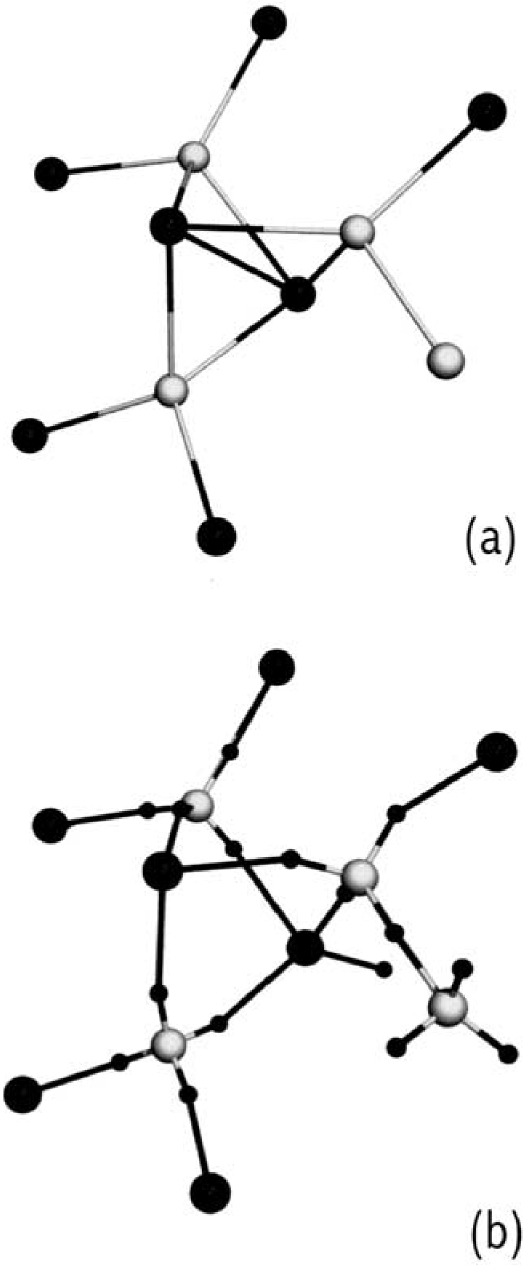

FIGURE 4 Snapshot of a section of the BN network showing an unusual arrangement of atoms where the interpretation of bonding is difficult (see text). WFCs are shown as small black atoms, while nitrogen atoms are large and light gray and boron atoms are large and dark.

Figure 2 also shows the effects of electronegativity on the position of the WFC, an effect not seen in the earlier monatomic silicon system where the WFC lay close to the midpoint of the bonded atoms. In this binary system, the WFC lie in a mixed bond lie close to the N atom due to the increased nuclear charge. In the case of like bonding (2(c)) the WFC between B atoms lies close to the midpoint.

Table I shows the number of each type of bond found in the network. In addition to the large number of four coordinated sites, the structure contained a considerable number of 3-fold coordinated boron and nitrogen atoms. Each nitrogen 3-fold coordinated site also contained a lone pair of electrons. Table II compares the coordination numbers which result from the Wannier Function analysis compared to the coordination shell approach with a radius of 1.8 Å. This radius corresponds to the minimum between first and second nearest neighbours in the pair correlation function [6]. There are some important differences including the absence of two coordinated boron atoms and changes in the numbers of three and four coordinated atoms.

Figure 3 shows the distribution in the spread of the WFCs within the BN network. The majority of values fall around 1.5 Å, and most of these correspond to WFCs associated with boron nitrogen single bonds. Values above this correspond to WFCs associated with like bonds (B–B or N–N), double bonds or lone pairs. Therefore the spread in real space of the WFCs can be used to distinguish between different bonding states in the network.

An example of how the coordination shell approach can be unreliable for determining bonding can be seen by comparing Fig. 4(a) with (b). Figure 4 shows a region of the BN network which has a unusual arrangement of atoms. Using the coordination shell approach (Fig. 4(a)), there appears to be a bond between the two boron atoms near the center of the figure which produces a structure with 3 three membered rings. However, since no WFC exists between the boron atoms, (Fig. 4(b)) we can confidently conclude that no bond is present between the two atoms.

CONCLUSION

In this paper, we showed that Wannier-functions analysis is a powerful tool for determining the location and the type of bond present in amorphous network produced using *ab-initio* modeling methods. This method also allows the identification of defect states such as lone pairs of electrons. We have found this method to be superior to the coordination shell approach for determining coordination or determining bonding by visualizing electron densities.

Acknowledgements

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