All-Electron Mixed-Basis Calculation of Structurally Optimized Titanium Nitride Clusters *

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1. Introduction

Ab initio total energy calculations based on the local density approximation (LDA) and the adiabatic approximation are important tool for understanding processes at the atomic level. It is capable to of describing dynamically the stability and reactivity of clusters, surfaces and bulk materials at finite temperatures without using any adjustable parameters. Consequently, Ohno et al. have developed the all-electron mixed-basis approach which is applicable to the molecular dynamics of objects in any atomic environment.

The mixed-basis methods are based on the local density approximation (LDA) and the adiabatic approximation are important tool for understanding processes at the atomic level. It is capable of describing dynamically the stability and reactivity of clusters, surfaces and bulk materials at finite temperatures without using any adjustable parameters. Consequently, Ohno et al. have developed the all-electron mixed-basis approach which is applicable to the molecular dynamics of objects in any atomic environment.

2. All-Electron Mixed-Basis Method

The all-electron mixed-basis method provides an accurate technique for the electronic states calculation. We solve self-consistently the Kohn-Sham equation

$$H \psi_i = \epsilon_i \psi_i,$$

where $H$ is the Hamiltonian, $\epsilon_i$ is the Kohn-Sham eigenvalue, and $\psi_i$ is the Kohn-Sham wave function. The all-electron mixed-basis method, not only valence AOs but also core AOs are incorporated and pseudopotentials are not used. Historically, the all-electron mixed basis method was first formulated by Bendt and Zunger, who incorporated just core AOs in the PW-expansion method. However, the method used in the present study is independent and different from Bendt and Zunger’s because our method incorporates valence AOs in the basis set also.

The present paper deals, for the first time, with the structural optimization of transition metal nitride clusters in the all-electron mixed-basis approach. Here, as an example we consider titanium clusters. Bulk titanium nitrides might someday be used for artificial bone and cutting tools because TiN has properties such as self-lubricity, good wear resistance, high melting point, and high hardness. However, the properties of titanium nitride clusters are not known. Therefore, as an initial investigation, we calculated the geometry and electronic structure of small TiN clusters.

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Fig. 3 Optimized structures of TiN and TiN2.

Fig. 4 Optimized structures of SiN and SiN2.

Table 1 Bondlengths in microclusters as computed with the all-electron mixed basis method and as found in bulk TiN with the NaCl type structure.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Ti/Si–N (nm)</th>
<th>N–N (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN</td>
<td>this work</td>
<td>0.157</td>
</tr>
<tr>
<td>TiN2</td>
<td>this work</td>
<td>0.174</td>
</tr>
<tr>
<td>SiN</td>
<td>this work</td>
<td>0.197</td>
</tr>
<tr>
<td>SiN2</td>
<td>this work</td>
<td>0.182</td>
</tr>
<tr>
<td>TiN (bulk)</td>
<td>exp.(16)</td>
<td>0.212</td>
</tr>
<tr>
<td>TiN (bulk)</td>
<td>LDA(17)</td>
<td>0.209</td>
</tr>
</tbody>
</table>

and those of SiN and SiN2 are shown in Fig. 4. The bond length in TiN is about 0.157 nm while the bond length between Ti–N in TiN2 is 0.174 nm, and between N–N is 0.140 nm. The optimized structures of TiN2 and SiN2 are isosceles triangles. The Ti–N bondlength in micro clusters is much shorter than that in the bulk, see Table 1.

4. Summary

We have applied the all-electron mixed basis approach to the titanium nitride micro clusters. Both TiN2 and SiN2 clusters form isosceles triangles. The Ti–N bondlengths in TiN and TiN2 are much shorter than in the bulk. We are now planning to calculate optimized structures of larger clusters.

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