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A Bond-Order Potential Incorporating Analytic Screening Functions for the Molybdenum Silicides

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Abstract

The intermetallic compound $MoSi_2$, which adopts the $C11_b$ crystal structure, and related alloys exhibit an excellent corrosion resistance at high temperatures but tend to be brittle at room and even relatively high temperatures. The limited ductility of $MoSi_2$ in ambient conditions along with the anomalous temperature dependence of the critical resolved shear stress (CRSS) of the {110}<111], {011}<100] and {010}<100] slip systems and departure from Schmid law behavior of the {013}<331] slip system can all be attributed to complex dislocation core structures. We have therefore developed a Bond-Order Potential (BOP) for $MoSi_2$ for use in the atomistic simulation of dislocations and other extended defects. BOPs are a real-space, $O(N)$, two-center orthogonal tight-binding formalism that are naturally able to describe systems with mixed metallic and covalent bonding. In this development novel analytic screening functions have been adopted to properly describe the environmental dependence of bond integrals in the open, bcc-based $C11_b$ crystal structure. A many-body repulsive term is included in the model that allows us to fit the elastic constants and negative Cauchy pressures of $MoSi_2$. Due to the internal degree of freedom in the position of the Si atoms in the $C11b$ structure which is a function of volume, it was necessary to adopt a self-consistent procedure in the fitting of the BOP. The constructed BOP is found to be an excellent description of cohesion in $C11_bMoSi_2$ and we have carefully assessed its transferability to other crystal structures and stoichiometries, notably $C40$, $C49$ and $C54$ $MoSi_2$, $A15$ and $D0_3$ Mo_3Si and $D8_m$ Mo_5Si_3 by comparing with *ab initio* structural optimizations.

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ABSTRACT

The intermetallic compound $MoSi_2$, which adopts the $C11_b$ crystal structure, and related alloys exhibit an excellent corrosion resistance at high temperatures but tend to be brittle at room and even relatively high temperatures. The limited ductility of $MoSi_2$ in ambient conditions along with the anomalous temperature dependence of the critical resolved shear stress (CRSS) of the {110)<111], {011)<100] and {010)<100] slip systems and departure from Schmid law behavior of the {013)<331] slip system can all be attributed to complex dislocation core structures. We have therefore developed a Bond-Order Potential (BOP) for $MoSi_2$ for use in the atomistic simulation of dislocations and other extended defects. BOPs are a real-space, $O(N)$, two-center orthogonal tight-binding formalism that are naturally able to describe systems with mixed metallic and covalent bonding. In this development novel analytic screening functions have been adopted to properly describe the environmental dependence of bond integrals in the open, bcc-based $C11_b$ crystal structure. A many-body repulsive term is included in the model that allows us to fit the elastic constants and negative Cauchy pressures of $MoSi_2$. Due to the internal degree of freedom in the position of the Si atoms in the $C11_b$ structure which is a function of volume, it was necessary to adopt a self-consistent procedure in the fitting of the BOP. The constructed BOP is found to be an excellent description of cohesion in $C11_b$ $MoSi_2$ and we have carefully assessed its transferability to other crystal structures and stoichiometries, notably $C40$, $C49$ and $C54$ $MoSi_2$, $A15$ and $D0_3$ Mo_3Si and $D8_m$ Mo_5Si_3 by comparing with *ab initio* structural optimizations.

INTRODUCTION

The intermetallic compound $MoSi_2$ and related alloys are promising materials for use at high temperatures. $MoSi_2$ has very good resistance to oxidation and corrosion, high thermal conductivity and a relatively low density [1]. $MoSi_2$ adopts the body-centered tetragonal $C11_b$ crystal structure and this complex crystal structure leads to five active slip systems, the activity of which depends on load orientation with respect to the crystallographic axes [2]. Single crystals of $MoSi_2$ can be plastically deformed in compression along [001] only at temperatures above 1300 °C but plastic deformation can occur even at room temperature for other load orientations.

The {110)<111], {011)<100] and {010)<100] slip systems are observed to exhibit at intermediate temperatures an anomalous increase of their critical resolved shear stresses with increasing temperature which suggests that thermal activation is responsible for transformations of dislocation core structures to some sessile configurations. The critical resolved shear stress for the {013)<331] slip system, which is controlling plastic flow, does not obey the Schmid law. This suggests that <331] dislocations possess a non-planar core structure. The complicated deformation modes found in $MoSi_2$, along with their temperature dependencies, indicate complex dislocation core structures and to perform dependable atomistic simulations, the mixed metallic and covalent bonding must be accurately captured.

In order to generate a reliable and transferable model of interatomic bonding in the molybdenum silicides, in particular $MoSi_2$, that are appropriate for the atomistic simulation of extended defects, it is essential to capture the non-central bonding character arising from the unsaturated $4d$ and $2p$ bands. Therefore, many-body central force schemes such as the Embedded Atom Method [3] or Finnis-Sinclair potentials [4] are not adequate for this purpose. Instead, we have adopted the Bond-Order Potential (BOP) formalism advanced by Pettifor and coworkers, see for example [5, 6]. BOPs are a real-space, $O(N)$ scaling tight-binding based framework that naturally describe materials that exhibit mixed metallic and covalent bonding. BOPs have been successfully developed for both transition metals and intermetallics such as Mo and Ir [7, 8] and TiAl [9]. Recent advances in the implementation of BOPs to the study of materials that exhibit negative Cauchy pressures [6, 9, 10] allow us to fit the negative Cauchy pressures of $C11_b$ $MoSi_2$ through a physically transparent, environmentally dependent many-body repulsive term in the total energy.

Intersite bond integrals in open structures, such as bcc or the bcc-based $C11_b$, show strong environmental dependencies owing to the effects of screening by the local environment. These environmental effects are properly captured in non-orthogonal tight-binding models however such schemes are not an appropriate basis for a semi-empirical interatomic potential due to the large number of adjustable parameters required. The effects of the non-orthogonality of electron orbitals have been captured in the orthogonal BOP scheme through the introduction of analytic screening functions that were derived from non-orthogonal tight-binding theory [7, 11]. These screening functions are described in more detail in the next Section.

There is a degree of freedom in the $C11_b$ structure that permits the Si atoms to move from their ideal lattice sites and the magnitude and direction of the displacement of the Si atoms, Δ, is found to depend on applied strain. Consequently, when fitting elastic constants, lattice parameters and cohesive energy during the construction of the BOP for $MoSi_2$, we have to allow for internal relaxations which requires a self-consistent procedure. The efficacy of the BOP as a description of cohesion in $C11_b$ $MoSi_2$ along with its transferability to other crystal structures and stoichiometries was assessed by comparing the predictions of the BOP to mixed-basis augmented plane-wave plus local orbitals (APW+lo) *ab initio* structural optimizations performed using the WIEN2k package of codes [12].

THEORY

In the BOP formalism, the total energy is written as a sum of three terms, $E_{tot} = E_{bond} + E_{env} + E_{pair}$, where E_{bond} is the bonding contribution arising from the overlap of atomic-like electron orbitals, E_{env} is a many-body repulsive term that describes the overlap

repulsion caused by *sp*-electrons that are being squeezed into the interstitial volumes by strong interatomic bonding and E_{pair} is a pairwise term used to describe any remaining interactions that are not explicitly included in the first two terms [7, 9, 13]. The bond term is constructed using interatomic bond integrals calculated *ab initio*, along with band occupancies and energy differences between different orbitals. The BOP formalism provides for calculation of the bond order, $\Theta_{j\beta,i\alpha}$, between lattice sites *i* and *j* and orbitals α and β in real space for a given Hamiltonian, $H_{i\alpha,j\beta}$, using the concept of reconstructing the densities of states through the moments theorem of Ducastelle and Cyrot-Lackman [14] and the Lanczos recursion method of continuous fractions [15].

In order to describe the strong environmental dependence of interatomic bond integrals in the open $C11_b$ structure, we introduce a screened Hamiltonian matrix (see [11] for details). In short, the screened Hamiltonian matrix, $\tilde{\mathbf{H}}$, is written in terms of the unscreened Hamiltonian, $\mathbf{H}$, and the nonorthogonality matrix, $\mathbf{S}$, *i.e.*,

$$\tilde{\mathbf{H}} = \frac{1}{2}\left(\mathbf{S}^{-1}\mathbf{H} + \mathbf{H}\mathbf{S}^{-1}\right) \tag{1}$$

The nonorthogonality matrix can be written as $\mathbf{S} = \mathbf{I} + \mathbf{O}$ where $\mathbf{I}$ is the identity operator and $\mathbf{O}$ is the overlap matrix. The elements of the inverse matrices $(\mathbf{I}+\mathbf{O})^{-1}$ can then be determined using the BOP theory and can be expressed in terms of the unscreened elements of the Hamiltonian and overlap matrices. The screened bond integrals, $\tilde{\beta}$, can then be written as,

$$\tilde{\beta}_{ll'\tau}^{ij} = \beta_{ll'\tau}^{ij}\left(1 - S_{ll'\tau}^{ij}\right) \tag{2}$$

where $l = s, p$ or d and $\tau = \sigma, \pi$ or δ. See references [11] and [7] for the functional form used for the screening function, *S*.

The BOP for the molybdenum silicides is constructed using a minimal basis of electronic states, *i.e.*, *d*-orbitals and *p*-orbitals centered on Mo and Si, respectively. We assume that valence *s*-orbitals on both the Mo and Si atoms are responsible for the screening of the bond integrals and that the elements of the unscreened Hamiltonian and overlap matrices decay in the same manner and only differ in magnitude. Figure 1 illustrates that our screening formalism accounts very successfully for the environmental dependence of bond integrals in $C11_b$ $MoSi_2$. Not only are the magnitudes of the screened bond integrals in excellent agreement with bond integrals calculated using first principles LMTO, but also their gradients on the isotropic expansion or contraction of the lattice.

The bond term in the BOP correctly predicts the order of structural stability in the $MoSi_2$ system as determined by *ab initio* APW+lo density functional theory calculations: $C11_b \rightarrow C40 \rightarrow C54$ at band fillings of $N_d = 6.0$ and $N_p = 2.6$ electrons with $E_d - E_p = -1.106$ eV. Good convergence to *k*-space results is found when the bond term is evaluated at five levels of Lanczos recursion, *i.e.*, the first nine moments of the DOS are included in the calculation.
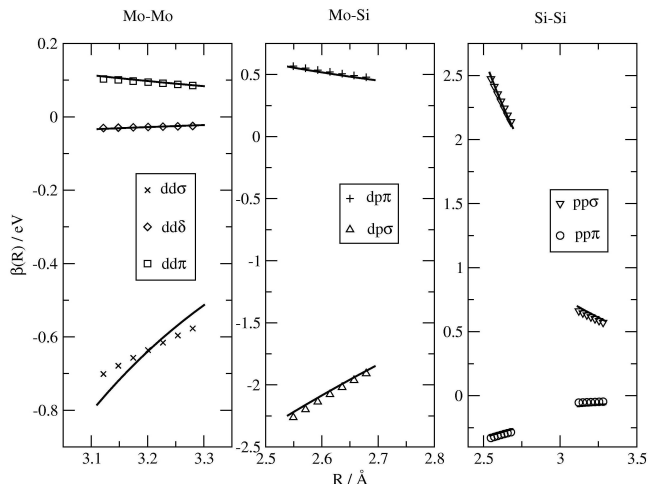
Figure 1. Radial dependencies of bond integrals in $C11_b$ MoSi$_2$. Points represent first principles LMTO calculations and solid lines screened bond integrals in BOP.

The many-body repulsive term, E_{env}, takes the form of a screened Yukawa potential [9, 10] and is fitted to the experimental values of the two Cauchy pressures in $C11_b$ MoSi$_2$, $C_{13} - C_{44}$ and $C_{12} - C_{66}$. The last term in the BOP is the pairwise interaction, E_{pair}, takes the same form as in [9] and is fitted to reproduce as closely as possible the cohesive energy, lattice parameters and remaining elastic constants.

As mentioned above, great care must be taken when fitting the BOP since it is essential to account for the internal degrees of freedom in the $C11_b$ unit cell. Since the effects of the relaxation of the Si atoms can only be evaluated once all three terms in the BOP have been parameterized, the potential must be constructed in a self-consistent manner. This means that in any given step of the potential construction, the effect of the relaxation of silicon atoms on the elastic constants and internal stresses has to be evaluated and the pairwise and many-body repulsive terms then reparameterized in order to improve the fit of experimental elastic constants and lattice parameters.

RESULTS

The BOP developed for the molybdenum silicides is found to be not only a good description of cohesion in $C11_b$ MoSi$_2$ but it also exhibits good transferability to other crystal structures. Table I shows the lattice parameters, internal relaxation parameter, Δ, and cohesive energy per formula unit given by the BOP, compared with experimental or *ab initio* calculated values. It is evident that the BOP provides a good description of the crystal structure of $C11_b$ MoSi$_2$ and predicts the displacement of the Si atoms in the correct direction although the magnitude of this displacement is by a factor of 6 larger than experimental and *ab initio* calculated values. However, it has to be recognized that Δ is very small compared to the lattice parameter and precision less than 1% can not be expected.

In Table II we present the elastic constants for $C11_b$ MoSi$_2$ from both BOP and experiment in units of eV Å^{-1}. Although some elastic constants, in particular C_{11}, C_{12} and C_{33}, are in relatively poor agreement with experiment it is important to note that all elastic constants and shear moduli are positive meaning that the $C11_b$ crystal structure is stable and thus the BOP is suitable for the atomistic simulation of defect structures in MoSi$_2$. The BOP is also able to reproduce the two negative Cauchy pressures in $C11_b$ MoSi$_2$, $C_{13} - C_{44}$ and $C_{12} - C_{66}$, even though their magnitudes are not reproduced accurately.

	BOP	Experiment / *Ab initio*
a / Å	3.0650	3.2056 [16] / 3.21817
c / Å	8.0885	7.8450 [16] / 7.87695
Δ / c	0.0117	0.00195 [16] / 0.00181
E_{coh} / eV f.u.$^{-1}$	-19.307	-17.1406

Table I. Crystallographic parameters for the $C11_b$ structure from BOP compared with experiment or values calculated *ab initio*.

	BOP	Experiment [17]
C_{11}	3.852	2.559
C_{12}	1.234	0.717
C_{13}	0.718	0.546
C_{33}	1.689	3.203
C_{44}	1.023	1.289
C_{66}	1.658	1.246
$C_{13} - C_{44}$	-0.306	-0.743
$C_{12} - C_{66}$	-0.809	-0.529

Table II. Elastic constants and Cauchy pressures calculated using BOP compared with experimental values in units of eV Å^{-1}.

The transferability of the BOP for $MoSi_2$ to crystal structures other than $C11_b$ and also to different stoichiometries versus predictions from *ab initio* calculations was generally found to be very good. A notable success of the BOP for $MoSi_2$ is its transferability to the hexagonal $C40$ and orthorhombic $C54$ structures and also its excellent predictions of the basic structural properties of tetragonal $D8_m$ Mo_5Si_3. These results are presented in Table III. Structural energy differences predicted by the BOP for $MoSi_2$ are also in good agreement with *ab initio* calculation where $E(C40) - E(C11_b) = 307.4$ meV f.u.$^{-1}$ and $E(C54) - E(C11_b) = 239.0$ meV f.u.$^{-1}$ compared with *ab initio* values of 81.1 and 236.3 meV f.u.$^{-1}$ respectively. It is evident that the BOP overestimates the $C11_b \rightarrow C40$ energy difference although the $C11_b \rightarrow C54$ energy difference is in very good agreement with *ab initio* results. However, the transferability of the BOP to Mo_3Si in the $A15$ and $D0_3$ structures is very limited due to the very small interatomic separations in these structures compared with $C11_b$ $MoSi_2$ and the short-range repulsion provided by the pairwise term in the BOP formalism.

	C40 MoSi$_2$	**C54 MoSi$_2$**	**D8$_m$ Mo$_5$Si$_3$**
c / a	1.491 (1.432)	1.119 (1.089)	0.563 (0.506)
b / a	N/A	0.565 (0.572)	N/A
Volume / Å^3 f.u.$^{-1}$	37.218 (40.723)	37.691 (40.760)	117.330 (115.525)
Δ / a	0.00326 (0.00268)	-0.010 (0.00318)	Δ_{Mo}: -0.00193 (0.00176) Δ_{Si}: -0.00663 (0.000658)
E_{coh} / eV f.u.$^{-1}$	-19.000 (-17.059)	-19.068 (-16.904)	-58.732 (-49.224)

Table III. Predictions of the BOP for the crystallographic parameters and cohesive energies of $C40$ and $C54$ $MoSi_2$ and $D8_m$ Mo_5Si_3. Values calculated *ab initio* are given in parentheses.

CONCLUSIONS

A Bond-Order potential incorporating analytic screening functions to describe the environmental dependence of bond integrals in the open $C11_b$ structure has been successfully developed for the molybdenum silicides. The BOP provides an excellent description of interatomic bonding in $C11_b$ MoSi$_2$ and is suitable for the atomistic simulation of extended defects in this material. The BOP also exhibits good transferability to the $C40$ and $C54$ structures that were not explicitly fitted, as well as to $D8_m$ Mo$_5$Si$_3$ that is a promising engineering material in its own right.

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