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First-principles Calculation on Screw Dislocation Core Properties in BCC Molybdenum

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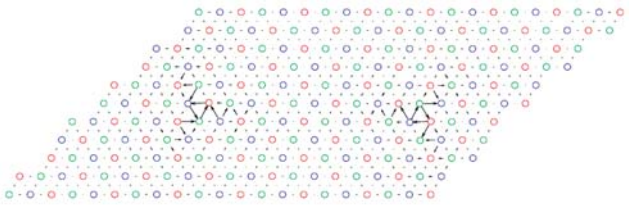
Abstract Predicting atomistic properties of a dislocation is a first step toward an understanding of plastic behavior of materials, in particular BCC metals. The core structure and Peierls stress of a screw dislocation in BCC metals have been studied over the years using the first-principles and empirical methods, however, their conclusions vary due to the inefficiency of the methods. We have executed first-principles calculations based on the density functional method, employing the most accurate 1 × 1 × 20 k-point samplings, to determine the core structure and Peierls stress of the $a_0/2$[111] screw dislocation of molybdenum. We have concluded that the core has a 6-fold structure, and determined the Peierls stress of 1.8 GPa for the simple shear strain along the $(\bar{1}10)$<111> direction.

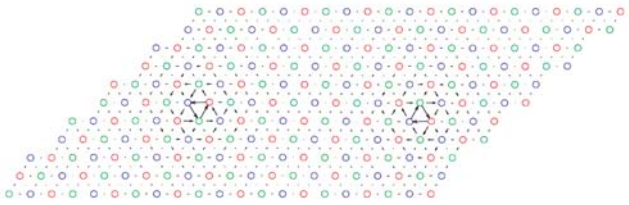
Keywords: first-principles calculation, screw dislocation, Peierls stress, BCC, molybdenum

1. Introduction

Hydrogen embrittlement in BCC metals is one of the most important and fundamental phenomena associated with the environmental assisted cracking observed in structural materials. Before studying the interaction of hydrogen atoms and a dislocation, it is first necessary to understand a behavior of a screw dislocation in BCC metals, in particular, the dislocation core structure and Peierls stress. Numerous studies using first-principles and empirical atomistic methods have been carried out to determine the accurate core properties, however, the results of the core structure and Peierls stress differ depending on the simulation methods. Two core structures have been proposed for a screw dislocation in BCC molybdenum by different computational approaches [1][2][3]; the 3-fold structure (Fig. 1(a)) is obtained using the Finnis-Sinclair potential and the modified generalized pseudopotential theory (MGPT) potential, while the 6-fold structure (Fig. 1(b)) is obtained by the tight-binding and the density functional theory (DFT) methods. The estimated value of the Peierls potential depends on simulation methods, ranging from 2 GPa to 4 GPa.



(a) 3-fold structure



(b) 6-fold structure

Fig. 1 Differential displacement map of two proposed screw dislocation core structures in BCC molybdenum.

There are essentially two factors to be paid attention in determining the core structure of a screw dislocation using the atomistic method. One is the boundary condition, and the other is the interatomic potential. Since a screw dislo-

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cation has a long-range strain field around the core, the simulation region should be taken as large as possible to reduce the effects of the boundaries. In order to take a large simulation region, an empirical potential, such as, the embedded atom method (EAM), is introduced to reduce the computational burden of calculating the interatomic forces. However, the empirical potentials are basically constructed by fitting the parameters to the equilibrium states, and there is no guarantee for the empirical potential to describe the disordered core region accurately. On the other hand, although the first-principles calculation based on the density functional theory gives the most accurate results even for the core structure, the computational region is limited to a very small area. Woodward and Rao [2] proposed a boundary condition for the supercell containing one screw dislocation, in which atomic displacements due to a screw dislocation in the cell are allotted by the Green function method. Recently, Li *et al*. [3] introduced a pair of screw dislocations in a skew supercell in such a way as to cancel the strains among dislocations effectively. In this paper, we perform the DFT calculations using the latter supercell setup and report the result of the most accurate determination of Peierls stress for the screw dislocation in BCC molybdenum.

2. Method

The detailed structure of electronic and atomic bonding states is required to understand fundamental mechanical properties of materials [4][5]. For the electronic simulations, the DFT is the most dependable method to determine the core structure of dislocations. We use the Vienna *ab initio* Simulation Package [6] (VASP), based on the DFT with the ultrasoft pseudopotential and the generalized gradient approximation (GGA), and implement this on the Earth Simulator (ES), which is a highly parallel vector supercomputer system of the distributed-memory type, and consists of 640 processor nodes connected by 640 × 640 single-stage crossbar switches. The re-parallelized VASP code in combination with the high performance both of the processors and the interconnection network of the ES enables the DFT calculation of the unprecedented scale, such as 231 atoms and 2 × 2 × 40 k-points, as described below.

2.1 Reliability test using the large supercell

There are two conditions to be considered for the accurate calculation of the DFT method. One is the energy cutoff convergence for the plane wave expansion of the wavefunction, and the other is the k-point sampling in using the supercell. For the energy cutoff convergence, we have adopted the value of 233 eV since this value is confirmed to be highly accurate for the calculation of elastic constants [5] and the energy cutoff convergence depends mostly on the atom species. As a preliminary examination to check the accuracy of calculation for the system of Mo, we performed the relaxation of the BCC Mo perfect lattice structure with 250 atoms by increasing the k-points. The results are shown in Table 1. Increasing the k-point samplings to the highly accurate 6 × 6 × 6 k-points, we have achieved the convergence accuracy of the total energy in nearly 0.1 eV in the relaxation process. With the 6 × 6 × 6 k-points, we have derived the phonon dispersion curve of BCC Mo, where we have successfully obtained the detailed structure near the H point which agrees well with experiment [7] as shown in Fig. 1.

Table 1 The total energy for the BCC Mo perfect lattice structure with 250 atoms.

k-points	Total energy [eV]	Energy difference [eV]
1 × 1 × 1	–2695.249	
		–7.182
2 × 2 × 2	–2702.430	
		–1.810
3 × 3 × 3	–2704.241	
		0.078
4 × 4 × 4	–2704.163	
		0.150
5 × 5 × 5	–2704.012	
		–0.042
6 × 6 × 6	–2704.055	

2.2 Re-parallelization of the VASP code

The “hot spot” of the DFT calculation contains a triple loop for traversing spin states, k-points, and energy bands. Although the parallelization over k-points is the simplest and the most effective, the original VASP code offers only a parallelization program over the energy bands and the plane wave coefficients, where energy bands are distributed among a group of processors. This parallelization strategy is predicted to be employed because the VASP code assumes a small number of k-point samplings in usual calculations. To achieve a high efficiency by reducing communication overhead, the residual minimization method and the direct inversion in the iterative subspace (RMM-DIIS) matrix diagonalizer algorithm [8], which reduces the number of orthonormalization steps considerably, should be used since it is the only algorithm which works for the distributions simultaneously over energy bands and plane wave coefficients. However, in the case of the present BCC molybdenum system consisting of approximately 200 atoms with a pair of screw dislocations, it was found that the RMM-DIIS algorithm has a poor convergence and the procedure requires exceedingly vast amounts of calculation time. Since the present simulation

Table 2 Parallel performance of the original and k-point parallelized VASP code.

Number of Nodes (NPROC)	1 (8)	2 (16)	5 (40)	8 (64)	10 (80)
Original code (KPAR=1)					
Elapsed Time (sec)	38828.3	20746.0	11309.2	9533.2	10165.1
Average Vector Length	229.3	224.0	212.2	197.7	185.9
Vector Operation Ratio (%)	99.3	99.2	99.0	98.8	98.7
GFLOPS (%peak)	42.5(66.4)	81.2(63.4)	169.1(52.8)	240.4(47.0)	285.9(44.7)
k-point parallelized: KPAR		2	5		10
Elapsed Time (sec)		19751.7	8138.1		4210.1
Average Vector Length		229.0	229.2		229.1
Vector Operation Ratio (%)		99.3	99.2		99.1
GFLOPS (%peak)		83.6(65.3)	203.0(63.4)		392.9(61.4)

requires more k-points, we employed the Davidson block iteration algorithm by re-parallelizing the program in terms of k-point samplings. The range for the outermost loop of the total number of k-points, NKPTS, is divided and distributed among a group of processes in a block distribution scheme; each process group is responsible for the part of calculation for NKPTS/KPAR k-points, where KPAR is the number of process groups. The innermost loop, meanwhile, is still performed in parallel by the original scheme. Furthermore, the initialization code is modified to allocate only the part of the array variables for wavefunctions to accomplish the efficient use of distributed memory. In order to exploit the vector processors on the ES system effectively, we have tuned the program by using the one-dimensional FFT routine in the numerical library ASL/ES.

Table 2 shows the performance evaluation results of the original program and k-point parallelized program on the ES. Here, the DFT calculations are done for the supercell containing 231 Mo atoms with a pair of screw dislocation using 1 × 1 × 20 k-points. It is confirmed that high vector operation ratio of 99.3% using a single node results in an excellent performance of 66.4% of the peak performance of the ES. We also found that the k-point parallelization has almost no influence on the average vector length; the average vector length is 229.3 using a single node and 229.1 using 10 nodes, where the maximum length of the ES is 256. The total performance using 10 nodes is 392.9 GFLOPS. The advantage of the k-point parallelized program over the original program is obvious; the former achieves almost a linear speedup while the original program has reached its plateau using 64 processes as shown in Fig. 3.

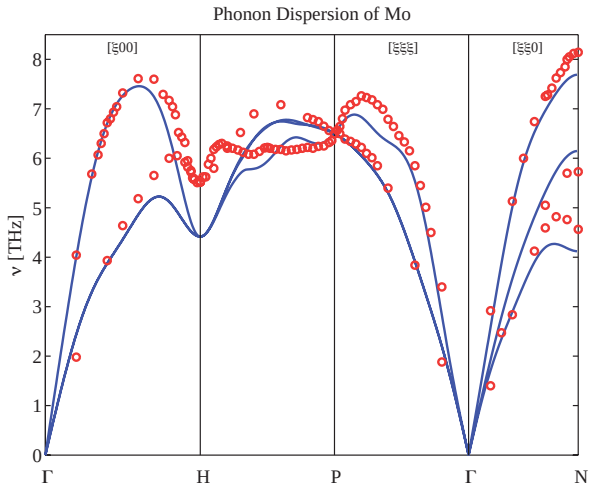

Fig. 2 Phonon dispersion curve of BCC Mo 250 atoms with 6 × 6 × 6 k-points (lines) compared with the experimental data [7] (open circles). The detailed structure near the H point has been reproduced.

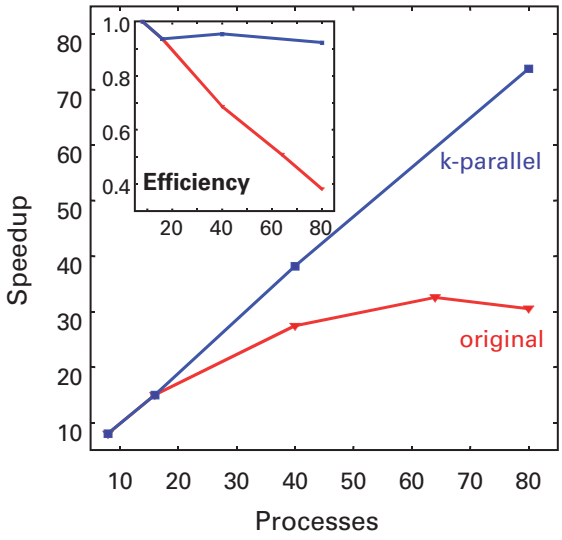

Fig. 3 Performance of k-point parallelized VASP code. The speedup of (red curve) the original program and (blue curve)the k-point parallelized program with KPAR = 1, 2, 5, and 10 at NPROC = 8, 16, 40, and 80, respectively. The calculations are done for the supercell containing 231 molybdenum atoms with a pair of screw dislocation using 1 × 1 × 20 k-points. The data are normalized as 8 at NPROC (number of processors) = 8. (inset) the parallel efficiency normalized as 1 at NPROC = 8.

3. Results

We have examined the effects of k-point samplings using the supercell containing 231 atoms with a pair of the 3-fold structured screw dislocations. The initial setup is shown in Fig. 4. This system is scrutinized in calculating the accuracy of the core energy by changing the size of the supercell, and it is concluded that the size of 231 atoms is good enough [3]. In Table 3, the results of the relation between the total energy and the number of k-points are shown. We find that the results with 2 × 2 × 40 k-points have already converged to the energy difference of 4.7 meV corresponding to 0.02 meV per one atom. Then the detailed studies on the core structure and the determination of the Peierls stress using the k-points of 1 × 1 × 20 have been performed.

3.1 Core structure

Starting from the initial supercell with a pair of the 3-fold core structured screw dislocations, the system is relaxed under the condition of fixed supercell shape. It is found that the initial configuration turns into a stable 6-fold core structure, and there exists no energy barrier between the two structures. This indicates that the 6-fold core structure is stable, and the 3-fold core structure is not even meta-stable. The energy difference between the 3-fold and the 6-fold core structures for the whole system is estimated to be 0.798 eV, which is 0.399 eV for each dislocation. Then, using the k-points of 2 × 2 × 40, we have evaluated the forces on each atom and the total energy for the systems containing the initial 3-fold and the 6-fold core structures, respectively, keeping the positions of the atoms fixed. As a result, in the case of the 3-fold core structure, the forces on each atom using the 2 × 2 × 40 k-points correspond to those using 1 × 1 × 20 k-points with the energy order of 0.01 eV per each atom. The accuracy of the results for the case of the 6-fold core structure between the two cases of k-points is also within the energy of 0.01 eV per each atom. On the basis of these results, we conclude that the 6-fold core structure should be obtained by the relaxation process using the k-points of 2 × 2 × 40 and that the core of a screw dislocation in the BCC molybdenum has a 6-fold structure.

Table 3 The total energy for the model system with a pair of screw dislocations having 3-fold core structure.

k-points	Total energy [eV]	Energy difference [eV]
1 × 1 × 20	–2493.898	
		–0.158
2 × 2 × 40	–2494.056	
		0.005
3 × 3 × 60	–2494.051	

3.2 Peierls stress

Using the initial configuration of the 6-fold core structure obtained in the relaxation simulation, we applied the additional shear strain along the $\mathbf{e}_3$ direction in Fig. 4 to study the stress-driven instability of the dislocation core. The parameter x in Fig. 4 corresponds to the shear strain γ_{23}. With each value of x being increased, atoms are relaxed to a minimum energy state by the conjugate gradient or the quasi Newton's algorithm. Figure 5 shows the result of calculation for stress-driven instability of the dislocation core in the $(\bar{1}10)\langle 111\rangle$ slip system of BCC molybdenum. At a critical value of $x_c \approx 0.146$, which corresponds to the shear strain of $\gamma_c \approx 1.6\%$, it is found that the core structures can no longer be stabilized and the Peierls stress is estimated to be $\tau_p \approx 1.8$ GPa. At the value of $x = 0.16$, the two cores in the supercell have moved toward each other by $a_0/3[11\bar{2}]$, and the shear stress as well as the energy of the system decreases significantly (Fig. 5 (c)).

4. Discussion

There have been two proposed core structures of a screw dislocation as a result of the calculations using the empirical potentials, tight binding method, and the density functional theory. The density functional theory is the

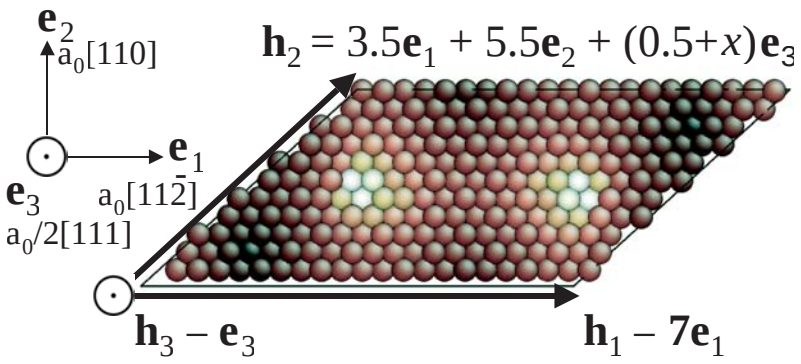

Fig. 4 The BCC Mo supercell consisting of 231 atoms.

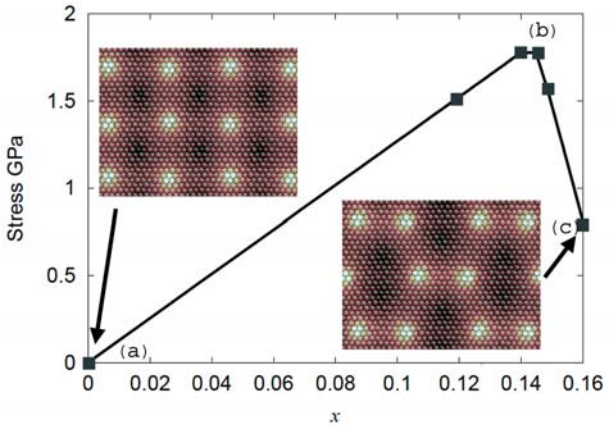

Fig. 5 Stress-driven instability of dislocation cores: (a) an initial position, (b) a critical position, and (c) a displaced position of the cores. The parameter x corresponds to the shear strain γ_{23}. Positions of dislocation cores are seen as highlighted atoms in the inset images.

most dependable method, but its k-point convergence was still unclear. In order to find a definitive solution to this problem, the following three points must be considered. First, we need to have a well-defined boundary condition for this problem. This has been already checked and the system consisting of 231 atom supercell, as shown in Fig. 4, is found to be accurate for this purpose[3]. Secondly, we need to evaluate the accurate total energy for this system. The VASP code, which implements the density functional theory with the ultrasoft pseudopotential, suits this purpose. Thirdly, computational conditions have to be clarified by the careful error estimation, including the plane wave and k-point convergence checks.

Under the same supercell setup, Li *et al.* [3] gave the Peierls stress of $\tau_p \approx 2.4$ GPa and ≈ 3.8 GPa using the Finis-Sinclair potential and the tight-binding model, respectively. Using the different first-principles Greens function boundary condition where the supercell contains one dislocation, Xu and Moriarty [1] used the MGPT and obtained the value of $\tau_p \approx 3.4$ GPa, while Woodward and Rao [2] derived $\tau_p \approx 2.1$ GPa by the DFT calculation with four special k-points. We do not find any correlation between core structures and Peierls stresses predicted by various methods, that is, higher and lower τ_p values are estimated with the core structure of both the 3-fold and 6-fold.

In this work, we have performed the most accurate DFT calculations with twenty k-points using the periodic boundary condition where the supercell contains two screw dislocations, and obtained the 6-fold core structure and the lowest τ_p value of 1.8 GPa in BCC molybdenum. Although we use the different boundary condition and k-points sampling, our result generally comes close to the DFT result of Woodward and Rao [2].

5. Conclusion

We have implemented the VASP (Vienna *ab-initio* simulation package) code on the Earth Simulator by parallelization in terms of k-point samplings and achieved a good parallel performance. Using this code and the largest $1 \times 1 \times 20$ k-point samplings, we have performed DFT calculations and obtained Peierls stress of 1.8 GPa for the $a_0/2$[111] screw dislocation in BCC molybdenum under the simple shear stress condition in the $(\bar{1}10)$<111> slip system.

(This article is reviewed by Dr. Tetsuya Sato.)

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