Role of Macroscopic Deformations in Energetics of Vacancies in Aluminum

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Electronic structure calculations on million-atom samples are employed to investigate the effect of macroscopic deformations on energetics of vacancies in aluminum. We find that volumetric strain associated with a deformation largely governs the formation energies of monovacancies and divacancies. The calculations suggest that nucleation of these defects is increasingly favorable under volumetric expansion, so much to the point that they become thermodynamically favorable under large positive volumetric strains. On the contrary, on an average, existing vacancies are found to bind preferentially under compressive volumetric strains. Shear deformations did not affect the formation energies of vacancies, but strongly influenced the $\langle 110 \rangle$ divacancy binding energies, causing them to orient under energetically preferential directions.

A wide range of materials properties are influenced significantly by various defects present in materials. Of these, vacancies play a crucial role in the nucleation, evolution, and kinetics of larger defects, which eventually govern the macroscopic deformation and failure mechanisms observed in a variety of metals. For example, recent theoretical studies predict that vacancies lubricate dislocation motion [1], which explain the observed softening in cold-worked high-purity aluminum at very low temperatures. Also, vacancies seem to play a crucial role in hydrogen embrittlement in metals [2]. Studies suggest that in the presence of hydrogen atoms vacancies clusters to nucleate voids, which further grow and result in ductile rupture. Moreover, recent electronic structure simulations indicate that vacancies can nucleate prismatic dislocation loops [3], which are responsible for the hardening phenomenon observed in metals subjected to irradiation.

Given this crucial role of vacancies, many efforts in the past decade have focused on determining the properties of vacancies from electronic structure theories [4–9], especially density-functional theory (DFT). However, most electronic structure calculations performed thus far are restrictive in two important aspects. First, owing to the computational complexity of electronic structure calculations, simulations were performed on small cell sizes (~ 100 atoms) using periodic boundary conditions. The assumption of periodicity, in conjunction with cell-size limitations, limits the scope of these calculations to very high concentrations of vacancies that rarely—if ever—are realized in nature. Second, previous investigations, barring a recent study [9], have focussed on properties of vacancies in macroscopically undeformed crystals—free of any macroscopic strain and stress, except those introduced by the vacancies themselves. But, an undeformed crystal state is a hypothetical situation—all materials undergo macroscopic deformations due to externally applied loads, and in the presence of extended defects like cracks, surfaces, and dislocations. Strains of the order of 10% or more are not

uncommon in regions exposed to a shock wave, or close to defect cores in materials. The influence of macroscopic deformations on energetics of vacancies can be very significant as discussed in this Letter.

The first of the aforementioned limitations on previous electronic structure calculations has been resolved by the recent development of quasicontinuum orbital-free density-functional theory (QCOFDFT) [10]. This method has enabled for the first time a calculation of the electronic structure using orbital-free density-functional theory (OFDFT) [11] of samples with millions of atoms subjected to arbitrary boundary conditions. This is achieved through a real-space formulation of OFDFT [12], and construction of an adaptive basis set using a finite-element discretization [10]. Importantly, the method is completely seamless, uses OFDFT as its only input, and enables convergence studies of its accuracy. In a recent work, QCOFDFT was used to study the energetics of vacancies and divacancies in an undeformed aluminum crystal [10]. Computed vacancy formation energies as well as divacancies binding energies were in agreement with experimental observations. Importantly, these calculations indicate a very strong cell-size (concentration) dependence owing to the long-ranged elastic and electrostatic effects. Specifically, it was found that $\langle 110 \rangle$ divacancies were repulsive for small cell sizes (<100 atoms), in agreement with previous DFT calculations [7,8]. The same divacancies were attractive for larger cell sizes (>1000 atoms) corresponding to realistic vacancy concentrations [13], with binding energies in agreement with experimental measurements [14,15]. This suggests that previous discrepancies between computations and experiments may be the result of small cell sizes used in computations.

In this Letter, we address the second limitation of previous electronic structure studies, and investigate the effect of macroscopic deformation on energetics of vacancies in aluminum. In the light of strong cell-size effects on the properties of vacancies demonstrated in recent studies [3,10], QCOFDFT method is used in the present study

which is free of any cell-size restrictions. Though the limitations of the kinetic energy functionals in OFDFT are well understood, OFDFT has been shown to be a good electronic structure theory to compute materials properties in aluminum [6]. Further, the combination of Thomas-Fermi-Weizsacker kinetic energy functional, local density approximation for the exchange-correlation effects [16] and a modified form of Heine-Abarenkov pseudo-potential [17] for aluminum has been demonstrated to correctly predict the bulk and vacancy properties in aluminum [10,12], and is employed in the present study.

The effect of macroscopic deformation on vacancy properties is measured in terms of the influence of a homogeneous macroscopic strain tensor on the energetics of vacancies. Strain tensor is defined as the symmetric gradient of a displacement field, $\epsilon_{ij} = \frac{1}{2}(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i})$, where u_i is the displacement of the deformed configuration with respect to the undeformed reference configuration. Without loss of generality, the coordinate axes 1,2, and 3 are chosen along [100], [010], and [001] crystallographic directions, respectively. To compute the energetics of vacancies at a prescribed macroscopic strain, we begin by homogeneously deforming a perfect, undeformed crystal (computational cell) into a state corresponding to the imposed macroscopic strain. We then introduce vacancies into this deformed crystal and compute the formation energies of a monovacancy, $\langle 110 \rangle$ divacancies, and $\langle 100 \rangle$ divacancies. The formation energy of a monovacancy at a prescribed macroscopic strain is given by

$$E_v^f(\epsilon_{ij}) = E(N-1, 1; \epsilon_{ij}) - \frac{N-1}{N} E(N, 0; \epsilon_{ij}),$$

where $E(N-1, 1; \epsilon_{ij})$ is the energy of a system with $N-1$ atoms and one vacancy under a macroscopic strain ϵ_{ij}, and $E(N, 0; \epsilon_{ij})$ is the energy of a system with N atoms and no vacancy under the same strain. The formation energies of divacancies are similarly defined. All simulations are performed on large computational domains consisting of 10^6 atoms, which are free of any cell-size effects and also correspond to a realistic vacancy concentration in materials of a few parts per million [13]. Numerical parameters are chosen to keep the error in formation energies due to discretization and coarse graining to be less than 0.01 eV.

As the strain tensor belongs to a six-dimensional space, a complete characterization of its influence on the energetics of vacancies is beyond reach. Hence, we focus on three commonly encountered modes of deformation—volumetric, uniaxial, and shear. We begin by investigating the effect of isotropic volumetric deformation. Figure 1(a) shows a very strong dependence of the formation energies of vacancies on volumetric strain (ϵ_{vv}). First, we analyze the two sets of results pertaining to a monovacancy: one, where atomic relaxations are suppressed (unrelaxed) and all effects are solely due to the electronic structure, and another, where the atoms are allowed to relax. It is evident from these results that, even without atomic relaxations,
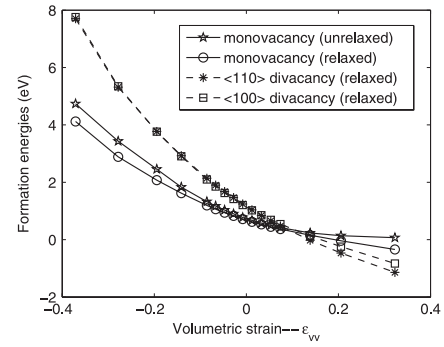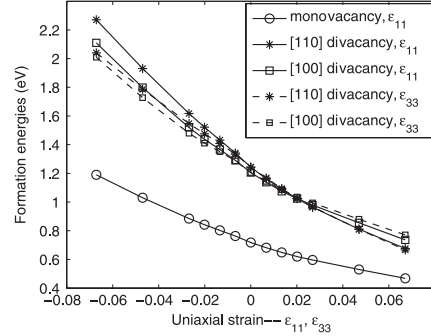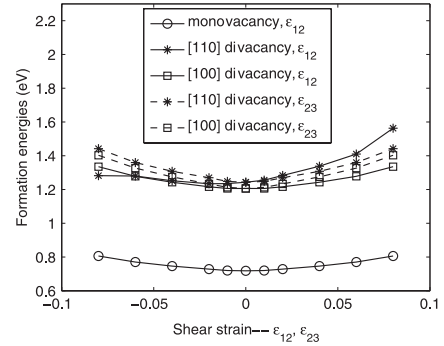
FIG. 1. Influence of various macroscopic deformations (strains) on the formation energies of a monovacancy, [110] divacancy, and [100] divacancy: (a) Volumetric strain; (b) uniaxial strains; (c) shear strains.

there is a very significant influence of volumetric deformation on the monovacancy formation energy—4.73 eV at −0.36 volumetric strain (95 GPa pressure) to 0.07 eV at 0.33 strain (−21 GPa pressure). This allows us to unambiguously conclude that the electronic structure of the defect core is strongly affected by volumetric deformations. This point is further highlighted, visually, by Fig. 2, which depicts the contours of electron-density perturbation in the presence of a monovacancy for two cases: (a) no volumetric strain, and (b) 0.33 volumetric strain. As expected, in both cases, electron density is depleted around the vacancy (blue contours) and augmented around the first and second ring of atoms (red contours). However, the nature of these perturbations are quite different. In com-
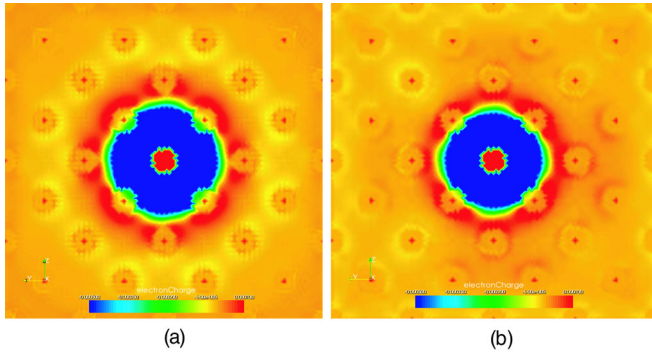
FIG. 2 (color online).   Contours of electron-density perturbation around a monovacancy: (a) no volumetric strain; (b) 0.33 volumetric strain. These contours are plotted with a reduced range from -0.0005 (blue) to 0.0001 (red) to highlight the changing features in the electronic structure with volumetric strain. The little red dots denote the positions of atoms. The slight increase in the electron-density at the center of the vacancy is the effect of using a pseudopotential.

parison with Fig. 2(a), the contours of electron-density perturbations move towards the vacancy in Fig. 2(b). This suggests that the relative size of the defect-core is shrinking with volumetric expansion. Further, the core in (b) is visually anisotropic in comparison to (a). Also, these perturbations are oscillatory in (a), but appear more diffuse in (b).

The unrelaxed formation energy of a monovacancy is positive for the range of volumetric deformations considered. However, upon relaxing the positions of atoms, which is the scenario realized in nature, the formation energy changes sign at about 0.2 volumetric strain and is computed to be -0.34 eV at 0.33 volumetric strain. These results suggest that forming a vacancy becomes thermodynamically favorable under large volumetric expansions as the energy spent in creating a vacancy is more than compensated by atomic relaxations around it. Thus, we conclude that vacancies can spontaneously cavitate under such deformations. We also note that the nature and extent of atomic relaxations changed under varying volumetric deformations, which is another evidence of changing electronic structure. Under -0.36 volumetric strain, the displacement field is predominantly radially inwards, towards the vacancy, with a maximum displacement of 0.17 a.u. The nature of relaxations are similar in an undeformed crystal, but with a maximum displacement of 0.03 a.u. However, in the case of 0.33 volumetric strain, the nature of atomic relaxations changed—atoms moved away from the vacancy, and the maximum displacement is computed to be 0.19 a.u. Further, the reduction in the formation energy due to atomic relaxations is significant under large volumetric deformations—0.62 eV in the case of -0.36 volumetric strain, and 0.41 eV in the case of 0.33 strain.

The divacancy formation energies are found to exhibit similar trends as a monovacancy under volumetric deformations [Fig. 1(a)]. It is interesting to observe that around

0.15 volumetric strain, which corresponds to a hydrostatic pressure of about -11 GPa, formation energies of both divacancies are lower than the monovacancy formation energy. This indicates that under large volumetric expansions nucleation of divacancies is energetically favorable compared to nucleating a single vacancy. Further, just over 0.15 volumetric strain the divacancy formation energies, too, are found to be negative, making these defects thermodynamically stable. Figure 3(a) shows the influence of volumetric deformation on divacancy binding energies, which is the energy released during the coalescence of two monovacancies. The divacancy binding energies are positive over the range of volumetric strains considered, suggesting that vacancies attract. However, both divacancy binding energies are found to vary significantly with volumetric deformations, and exhibit different characteristics. The results indicate, on an average, vacancies bind more preferentially under volumetric compression than under volumetric expansion. Hence, although nucleating divacancies is energetically preferable under volumetric expansion, forming divacancies from existing vacancies appears more favorable in compression.

Next, we investigate the influence of various uniaxial strains (up to symmetry) on the energetics of vacancies. Figure 1(b) shows that all formation energies monotonically decrease under uniaxial strains, similar to the influence of volumetric deformation. Comparing results from uniaxial and volumetric deformations [Figs. 1(a) and 1(b)], we note a very important consequence. The formation energies of these defects (monovacancy as well as divacancies) at any prescribed uniaxial strain are very close to their corresponding formation energies at the same volumetric strain. In most cases, the deviation is under 10%. Further, we note that, for small uniaxial deformations the volumetric strain associated with the deformation is equal to the uniaxial strain. Thus, it appears that the volumetric strain associated with a deformation is the dominant parameter governing the formation energies of vacancies. This key observation is further corroborated by results from biaxial deformations (not presented here), and shear deformations discussed below. Figure 3(b) shows that divacancy binding energies are also considerably influenced by uniaxial strains. However, no clear trends have emerged. It appears, on average, binding is preferred under uniaxial compression as opposed to tension.

Last, we investigate the influence of shear strains. Figure 1(c) shows that the monovacancy formation energy has almost no dependence on shear strains, and divacancy formation energies are not significantly influenced either. This is in sharp contrast to our findings on the influence of volumetric and uniaxial deformations. Noting that shear deformations do not result in volume changes, these results further support the dominant role of volumetric strain on the formation energies of vacancies. Considering the binding energies of divacancies, Fig. 3(c) shows that the influence of out-of plane shear (ϵ_{23}) is almost negligible on binding energies of both divacancies. But, the binding
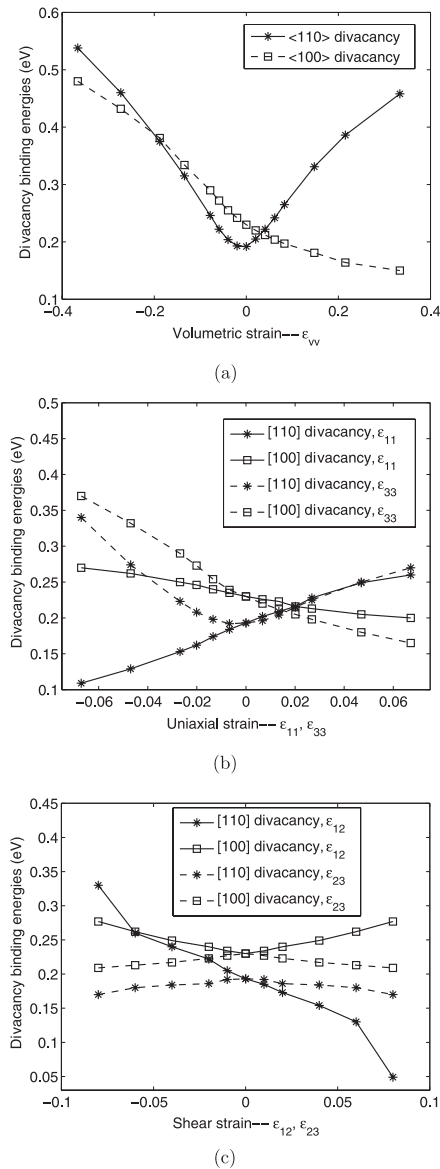
FIG. 3. Influence of various macroscopic deformations (strains) on the binding energies of [110] divacancy, and [100] divacancy: (a) Volumetric strain; (b) uniaxial strains; (c) shear strains.

deformation plays a dominant role in governing the formation energies of vacancies, so much to the point that these defects become thermodynamically favorable under large volumetric deformations. This effect is closely tied with changes in the electronic structure of the cores of these defects under volumetric deformations, which is demonstrated through numerical results, visual features of the electronic structure of a monovacancy, and atomic relaxation patterns. We find that formation energies of vacancies monotonically decrease with increasing volumetric strain, suggesting that nucleation of these defects is favorable under expansion as opposed to compression. However, the divacancy binding energies, on an average, are higher in compression, suggesting that vacancy clustering may preferentially happen under compressive deformations. Shear deformations did not have a considerable influence on the formation energies, but affected $\langle 110 \rangle$ divacancy binding energies strongly in a way that will preferentially orient them in energetically favorable directions.

[1] G. Lu and E. Kaxiras, Phys. Rev. Lett. **89**, 105501 (2002).
[2] G. Lu and E. Kaxiras, Phys. Rev. Lett. **94**, 155501 (2005).
[3] V. Gavini, K. Bhattacharya, and M. Ortiz, Phys. Rev. B **76**, 180101 (2007).
[4] N. Chetty, M. Weinert, T. S. Rahman, and J. W. Davenport, Phys. Rev. B **52**, 6313 (1995).
[5] D. E. Turner, Z. Z. Zu, C. T. Chan, and K. M. Ho, Phys. Rev. B **55**, 13 842 (1997).
[6] Y. A. Wang, N. Govind, and E. A. Carter, Phys. Rev. B **60**, 16 350 (1999).
[7] K. Carling, G. Wahnström, T. R. Mattsson, A. E. Mattsson, N. Sandberg, and G. Grimvall, Phys. Rev. Lett. **85**, 3862 (2000).
[8] T. Uesugi, M. Kohyama, and K. Higashi, Phys. Rev. B **68**, 184103 (2003).
[9] G. Ho, M. T. Ong, K. J. Caspersen, and E. A. Carter, Phys. Chem. Chem. Phys. **9**, 4951 (2007).
[10] V. Gavini, K. Bhattacharya, and M. Ortiz, J. Mech. Phys. Solids **55**, 697 (2007).
[11] R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).
[12] V. Gavini, J. Knap, K. Bhattacharya, and M. Ortiz, J. Mech. Phys. Solids **55**, 669 (2007).
[13] M. J. Fluss, S. Berko, B. Chakraborty, K. R. Homann, P. Lippel, and R. W. Siegel, J. Phys. F **14**, 2831 (1984).
[14] P. Ehrhart, P. Jung, H. Schultz, and H. Ullmaier, *Atomic Defects in Metal*, Landolt-Börnstein, New Series, Group 3 Vol. 25 (Springer-Verlag, Berlin, 1991).
[15] T. Hehenkamp, J. Phys. Chem. Solids **55**, 907 (1994).
[16] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[17] L. Goodwin, R. J. Needs, and V. Heine, J. Phys. Condens. Matter **2**, 351 (1990).

energy of [110] divacancy is significantly influenced by shear strain ϵ_{12}, and unlike other shear strains this dependence is not symmetric about the origin. This, we believe, is a consequence of the broken fourfold (C_4) symmetry in the 1–2 plane because of electronic perturbations and atomic relaxations. These results suggest that shear does not sharply influence the nucleation of vacancies, in comparison to deformations which produce changes in the volume. However, it has a significant effect on the binding energies of $\langle 110 \rangle$ divacancies, and cause these defects to preferentially orient in energetically favorable directions.

To conclude, we find a strong influence of macroscopic deformations on the energetics of vacancies in aluminum. Our results indicate that volumetric strain associated with a