PHYSICAL REVIEW B **84**, 224101 (2011)

Concise relation of substitution energy to macroscopic deformation in a deformed system

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(Received 12 July 2011; revised manuscript received 1 November 2011; published 9 December 2011)

An *ab initio* study of the effect of macroscopic deformation on energetics of twelve alloying elements in bcc Fe has been performed under three specially designed strain modes. A concise relation of the macroscopic deformation effect on the substitution energy of alloying elements with linear dependences on defect formation volume and relative volume change was found. Based on this concise relationship, the following behaviors can be predicted by comparing defect formation volumes: the strain-induced solubility change of alloying atoms and then the degree or possibility of redistribution and segregation of alloying atoms, the stability transition between monovacancy and divacancy, and self-interstitial atom reorientation under heavy loading.

DOI: 10.1103/PhysRevB.84.224101 PACS number(s): 81.05.Bx, 61.82.Bg, 62.20.F−, 71.15.Mb

I. INTRODUCTION

Fe-based alloys are among the most widely used materials, among which ferritic-martensitic (FM) steels represent a technologically important class with many applications in heavy loading and high-temperature conditions, such as in fission and fusion energy facilities. Since alloying solutes in Fe-based alloys are very important for modifying physical properties[1]—and particularly their contents strongly govern mechanical performances such as resistance to hardening and embrittlement induced by neutron and proton irradiation—their local structures, migrations, and interactions with other atoms or defects have been intensively studied in recent years.[2,3] It was found that an optimal Cr content of 2% to 6% reduces irradiation swelling compared with pure Fe, whereas 9% Cr reduces the ductile brittle transition temperature. Most previous investigations of alloying elements in FM steels have been performed in macroscopically undeformed crystals, free of any macroscopic strains except those induced by the solutes or defects themselves. Nonetheless, in fact most materials usually undergo macroscopic deformations due to externally applied loads or in special in-service conditions. So, recently, attention has been paid to the properties of point defects under macroscopic deformations based on electronic structure calculations. Gavini found that the volumetric strain associated with a deformation largely governs the formation energies of monovacancies and divacancies in Al, and concluded that the nucleation of these defects is increasingly favorable under volumetric expansion.[4] Chen *et al.* reported that the strain has remarkable influence on the stability, reorientation, and migration of self-interstitial atoms (SIAs) in bcc Fe: for instance, uniaxial expansion induces a SIA spontaneous reorientation from ⟨111⟩ to ⟨100⟩.[5] Zhu *et al.* found in zinc-blende GaP that the impurity formation energy changes monotonically in a linear fashion with the applied external strain, and thus they proposed that the strain-induced change in impurity formation energy can effectively enhance dopant solubility in a wide range of semiconductors.[6] Therefore it is reasonable that the substitution energy (E_{sub}) of the alloying elements in Fe-based materials may be also heavily influenced by macroscopic deformation, which would cause the redistribution and segregation of the alloying elements under heavy loading in long-term service, and would contribute a great deal to the phenomena of stress-induced erosion and abnormal fracture. Therefore, a comprehensive understanding of the macroscopic deformation effect on E_{sub} of alloying atoms in bcc Fe is significant for the design of new types of high-performance Fe-based alloys and for the optimization of steel process technology. Moreover, it is interesting to explore whether or not there exists a concisely universal description of the macroscopic deformation effect on the energetics of point defects in strained systems, as mentioned above.

In this paper, the effect of macroscopic deformation on E_{sub} by twelve alloying elements[7] (Al, Co, Cr, Cu, Mo, Nb, Ni, Si, Ta, Ti, V, and W) in bcc Fe in three different strain modes was investigated systematically using an *ab initio* method. Hydrostatic strain mode was used to explore the pure volume change effect, and a set of submodes in both normal strain and shear strain modes were used to explore the system shape distortion (or nonhydrostatic strain) effect. It was found that for all studied alloying elements the macroscopic deformation effect on E_{sub} can be described concisely and universally by a linear function of volume change with a slope completely determined by the defect formation volume for a single solute and by the system shape factor.

II. COMPUTATIONAL METHOD

The present calculations were performed within spin-polarized density-functional theory as implemented in the Vienna *ab initio* simulation package.[8] The interaction between ions and electrons was described by the projector augmented wave method.[9] Exchange and correlation functions were taken in a form proposed by Perdew and Wang[10] within the generalized gradient approximation. The supercell approach with periodic boundary conditions was used, where the supercell contains 127 Fe atoms and one alloying atom. The energy cutoff for the plane-wave expansion of wave functions was 350 eV and a $3 \times 3 \times 3$ k-point mesh was adopted for Brillouin-zone sampling according to the Monkhorst-Pack scheme. All atomic relaxation calculations were performed at constant volume and shape using the conjugate gradient algorithm. For simplicity the side length of the aforementioned bcc cubic supercell in equilibrium was set to be four times the

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TABLE I. Strain components (%) in NS and SS modes.

	e_{11}, e_{22}, e_{33} (NS1–4)/e_{11}, e_{33}, e_{12} (SS89–85)		
	Vol. contracted by 3.0%	Vol. unchanged	Vol. expanded by 3.0%
NS1	−1.98, −1.0, −0.01	−0.99,0,1.0	0,1.0,2.01
NS2	−2.94, −1.0, 0.98	−1.96,0,2.0	−0.98,1.0,3.02
NS3	−3.88, −1.0, 1.97	−2.91,0,3.0	−1.94,1.0,4.03
NS4	−4.81, −1.0, 2.96	−3.85,0,4.0	−2.88,1.0,5.04
SS89	−0.996, −1.0, 0.864	0.004,0,0.873	1.004,1.0,0.881
SS88	−0.985, −1.0, 1.73	0.015,0,1.75	1.02,1.0,1.76
SS87	−0.966, −1.0, 2.59	0.034,0,2.62	1.03,1.0,2.65
SS85	−0.906, −1.0, 4.33	0.096,0,4.37	1.10,1.0,4.41

optimized lattice constant of bcc Fe (2.833 Å). E_{sub} can be calculated using the following formula:

$$E_{\mathrm{sub}} = E_{n\mathrm{Fe}+1M} - \frac{n}{n+1} E_{(n+1)\mathrm{Fe}} - E_M, \qquad (1)$$

where $E_{n\mathrm{Fe}+1M}$ is the total energy of a bcc cubic supercell containing n Fe atoms and one alloying atom M, $E_{(n+1)\mathrm{Fe}}$ is the total energy of the same bcc cubic supercell filled with only Fe atoms under the same deformation, and E_M is the energy per atom of pure crystal M with most stable phase.

In this work, the macroscopic deformation is described by the macroscopic strain tensor with the coordinate axes 1, 2, and 3 being chosen along the [100], [010], and [001] directions, respectively, of a perfect bcc crystal. Because the strain tensor belongs to a six-dimensional space, a complete characterization of the deformation effect on the energetics of alloying atoms is beyond reach. Here only three different modes of strain are considered: hydrostatic strain (HS), normal strain (NS), and shear strain (SS) within a relative volume variation from −3.0% to 3.0%. This variation is used for exploring the relation between the E_{sub} of the solute alloying elements and the volume change, although such a large volume variation rarely occurs in service conditions. Both the NS and SS modes include four submodes: NS1–NS4 and SS89–SS85, as listed in Table I, where the nonzero strain components are presented. For all submodes of SS the following equations exist: $e_{11} = e_{22}$, $e_{23} = e_{31} = 0$. Here, for example, SS89 denotes that the included angle between two adjoining surfaces changes from 90° to 89°. Note that when any two strains in each submode of NS or SS are applied on the perfect cubic system and its isometric replica, respectively, their volumes will be different but the shapes will be similar. For example, in any strain of NS1 the system maintains a rectangular parallelepiped shape with the ratio of the three different edges fixed at 0.99 : 1.0 : 1.01. From NS4 to NS1 or from SS85 to SS89 the shape distortion from a perfect cube reduces gradually. For each NS and SS submode the degree of strain-induced system shape distortion can be scaled by the strain components e_{33} and e_{12}, respectively, in strained systems with equilibrium volume.

III. RESULTS AND DISCUSSION

Figure 1 displays E_{sub} as a function of volume ranging from $0.97V_0$ to $1.03V_0$ in the HS mode, where V_0 is the equilibrium volume of the system. It can be seen that E_{sub} of all alloying elements except Si depends linearly on the volume, with a negative slope. The E_{sub} of Si is almost insensitive to hydrostatic deformation (with a very small positive slope). The absolute slope for elements Al, Co, Cr, Cu, Ni, and V is smaller than that for elements Mo, Nb, Ta, Ti, and W. These results suggest that E_{sub} of the alloying atoms studied except Si can be considerably influenced by hydrostatic deformation, which may in turn change the solubility of these alloying atoms in bcc Fe and cause segregation of these elements if the strain in the system is not homogenous. The observed linear volume dependence of E_{sub} in bcc Fe is similar to the reported linear behavior of doping energy in GaP in the HS mode by Zhu *et al.*[6] Interestingly, a similar linear volume dependence of E_{sub} was also found in submodes of NS and SS with volumes of $0.97V_0$, V_0, and $1.03V_0$. The linearity has been further checked via the added calculations for Al, Cr, and W in NS1, NS4, SS89, and SS85 modes with volumes of $0.982V_0$, $0.994V_0$ and $1.018V_0$. Here the results of W in NS4 and SS85 modes are displayed in Fig. 2 as examples. In the studied volumetric range the change range of E_{sub} in any submode of NS or SS is smaller than that in the HS mode. For example, in the HS mode the volumetric increase from $0.97V_0$ to $1.03V_0$ leads to an E_{sub} decrease of 0.234 eV for Cr and

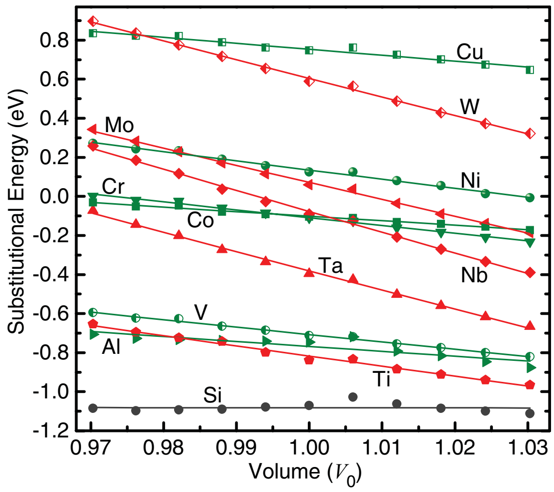

FIG. 1. (Color online) Substitution energy versus volume for twelve different alloying elements in the HS mode. Symbols represent the calculated results and solid lines are the corresponding linear fits.

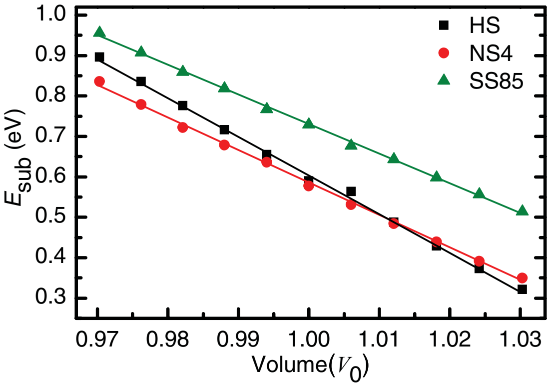

FIG. 2. (Color online) Substitution energy (E_{sub}) of W versus volume for HS, NS4, and SS85. Lines are linear fits to the data.

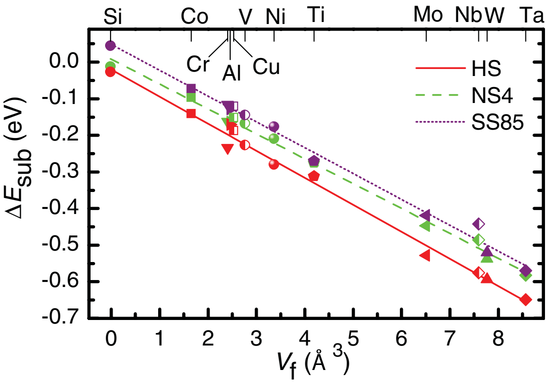

FIG. 3. (Color online) Substitution energy change (ΔE_{sub}) versus defect formation volume (V_f) for HS, NS4, and SS85 with volume change from $0.97V_0$ to $1.03V_0$ for twelve alloying elements. Lines are linear fits to the data.

0.575 eV for W, while in NS4 and SS85 modes the decrease of E_{sub} is about 0.162 and 0.116 eV for Cr and 0.486 and 0.442 eV for W. Since ΔE_{sub} ($=E_{sub}|_{V=1.03V_0} - E_{sub}|_{V=0.97V_0}$) divided by $0.06V_0$ is identical to the slope of the linear function, the aforementioned larger decrease of E_{sub} means a larger absolute slope. It was also reported that the doping energy change range of Be in GaP under biaxial strain is smaller than that under hydrostatic strain.[6] Thus, nonhydrostatic strains can modulate to some extent the volume dependence of E_{sub} compared to pure isotropic volumetric change in the HS mode.

The above results reveal for every studied alloying atom the existence of a linear volume dependence of E_{sub} as the system is under macroscopic deformation in any strain mode. Such linear volume dependence of E_{sub} in the HS mode can be explained by the simple strain model proposed by Zhu *et al.*[6] According to the strain model, the slope of the linear relation of E_{sub} versus V in the HS mode should be proportional to the defect formation volume (V_f) (in Ref. 6 it is called as the effective size difference). V_f, originating from the intrinsic size difference and the change in the electronic environment, can be calculated by subtracting the equilibrium system volume of pure Fe from the equilibrium volume of the system with one solute.[11] In addition, the solute size factor Ω_{sf}^M is also usually used in metallurgy to describe the resulting size difference of solutes from the host.[3] There is a simple relationship between V_f and Ω_{sf}^M: $\Omega_{sf}^M = V_f/\Omega_{Fe}$ (here Ω_{Fe} is the atomic volume of bcc Fe). So the slope of the linear relation of E_{sub} versus V in the HS mode should also be proportional to Ω_{sf}^M. If the V_f (or Ω_{sf}^M) of the alloying atom correctly describe the intrinsic size difference and the change in atomic interaction due to the substitution of Fe by alloying atom, then there may be a universal law of the macroscopic deformation effect on E_{sub}. So the substitution energy changes ΔE_{sub} of twelve alloying elements were plotted as a function of V_f, and the results for HS, NS4, and SS85 are displayed in Fig. 3. As expected, in each mode or submode whose system maintains a similar shape, ΔE_{sub} exhibits a universal linear dependence on V_f: for all studied alloying elements, ΔE_{sub} (i.e., the slope of linear volume dependence of E_{sub} if divided by $0.06V_0$) is proportional to V_f with a negative slope that is dependent on the strain mode or submode. According to the relation between V_f and Ω_{sf}^M, no doubt ΔE_{sub} also exhibits a universal linear dependence on Ω_{sf}^M. Further analysis unveils that this universal linear dependence on V_f for all solutes can be expressed by the following relation:

$$E_{sub}|_V = -f_{ss}B(V/V_0 - 1)V_f + E_{sub}|_V = V_0. \qquad (2)$$

Here, B is the bulk modulus of the system and f_{ss} is the system shape factor, a unitless parameter that describes the system shape change under strained conditions ($f_{ss} = 1$ in the HS mode). Does this relation well describe the above observed dependence of E_{sub} on the volume and on V_f? And how can f_{ss} be measured or estimated?

To answer these two questions, we first use our present data, and the published data about the doping energy difference resulting from strain changes between −2% and 2% in the HS mode in GaP (from Ref. 6), to test Eq. (2) as shown in Fig. 4. Here $f_{ss} = 1$ due to the system shape being unchanged. Figure 4 clearly shows that the two sets of data are located on a single line, indicating that Eq. (2) well characterizes the volume and V_f dependence of E_{sub}. Using Eq. (2) to fit the calculated data for the NS1–NS4 and SS85–SS89 submodes, one can obtain the values of f_{ss} in the different submodes

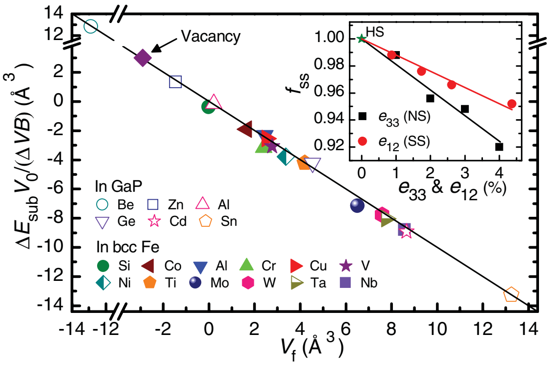

FIG. 4. (Color online) Comparison of substitution energy change (ΔE_{sub}), under HS with volume change from $0.97V_0$ to $1.03V_0$ in bcc Fe and with the strain changes from −2% to 2% in zinc-blende GaP (from Ref. 6), between Eq. (2) (line) and the calculated results (symbols). Inset: System shape factor (f_{ss}) as a function of strain component e_{33} in the NS mode and e_{12} in the SS mode with the equilibrium volume (the straight lines are guides for the eye).

TABLE II. The system shape factor ($f_{\rm ss}$) of each NS and SS submode. The system shape factor in HS mode is 1.

	NS4	NS3	NS2	NS1	SS85	SS87	SS88	SS89
$f_{\rm SS}$	0.920	0.948	0.956	0.988	0.952	0.966	0.976	0.988

listed in Table II. As expected, from NS4 to NS1 and from SS85 to SS89, when the system shape distortion is weakened $f_{\rm ss}$ increases monotonically and approaches the value for the HS modes, suggesting that $f_{\rm ss}$ correctly describes the degree of system shape distortion. The inset of Fig. 4 shows $f_{\rm ss}$ in NS (SS) modes as a function of e_{33} (e_{12}) of the strained system with the equilibrium volume. $f_{\rm ss}$ decreases monotonically with the increase of e_{33} or e_{12}, suggesting that in presently studied NS and SS modes $f_{\rm ss}$ can be measured with e_{33} or e_{12} of the strained system at equilibrium volume.

Now the question arises: What is the significance of the obtained concise relation of $E_{\rm sub}$? First, this relationship could be naturally extended to the deformation effect on the formation energy of the vacancy and the interstitial. The result of a single vacancy in bcc Fe under HS is presented in Fig. 4, indicating that this relation is indeed suitable for the vacancy. However, it should be stressed that the defect formation volume is the volume change due to the relaxation of introducing a vacancy rather than that generally used as in Ref. 12, where it is defined as the volume change plus the equilibrium atomic volume of the host. Second, using this relation and the defect formation volume, which can be obtained from first-principles calculations, one can explicitly predict the strain-induced solubility change of alloying atoms on the basis of the concentration equation as a function of temperature: $c = c_0 \exp[-(E_{\rm sub} - TS_{\rm f})/(k_{\rm B}T)]$; herein c_0, $S_{\rm f}$, and $k_{\rm B}$ are the coefficient, defect formation entropy, and Boltzmann's constant respectively. For example, the increase (decrease) of $E_{\rm sub}$ by 96 meV for 1% compressive (expansive) hydrostatic strain in bcc Fe leads to reduction (enhancement) of W solubility by 6.4 times at 600 K (the change of formation entropy is not considered here). This plays a key role in evaluating the degree or possibility of redistribution and segregation of alloying atoms under heavy loading. Third, using this relation along with the change in entropy one could predict the thermodynamically favorable stability transition between monovacancy and divacancy under deformation (e.g., as reported in Ref. 4) and similarly predict the strain-induced reorientation of self-interstitial atoms via comparison with V_f. These predictions could greatly help us to understand defect nucleating and clustering and the defect-induced degradation of mechanical properties under heavy loading in long-term service, and could help us to design new types of high performance alloys.

IV. CONCLUSIONS

In summary, we find a concise and universal relation of the substitution energy of alloying elements in a strained system: $E_{\rm sub}|_V = -f_{\rm ss}B(V/V_0 - 1)V_f + E_{\rm sub}|_{V=V_0}$. $f_{\rm ss}$ is in fact a simplified description of the nonhydrostatic strain effect on $E_{\rm sub}$ and can be estimated from e_{33} or e_{12} of the strained system with the equilibrium volume in our cases. Although this universal relation is a simple formation enthalpy expression, it concisely expresses the deformation effect on the formation energy using the bulk modulus and the defect formation volume along with the system shape factor. Thus it may have broad applications, such as in predicting strain-induced solubility change and strain-induced stability transitions of vacancies and interstitials via comparison with defect formation volume.

ACKNOWLEDGMENTS

We thank Professor B. C. Pan at the University of Science and Technology of China for his suggestions. This work was supported by the Strategic Priority Research Program of the Chinese Academy of Sciences (Grants No. KJCX2-YW-N35 and No. XDA03010303), the National Natural Science Foundation of China (Grant No. 91026002), the National Magnetic Confinement Fusion Program (Grants No. 2009GB106005 and No. 2011GB108004), and by the Center for Computation Science, Hefei Institutes of Physical Sciences.

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