Ab initio mechanical response: internal friction and structure of divacancies in silicon.

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This letter introduces ab initio study of the full activation-volume tensor of crystalline defects as a means to make contact with mechanical response experiments. We present a theoretical framework for prediction of the internal friction associated with divacancy defects and give the first ab initio value for this quantity in silicon. Finally, making connection with defect alignment studies, we give the first unambiguous resolution of the debate surrounding ab initio verification of the ground-state structure of the defect.

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Among the most powerful applications of first principles ab initio approaches in condensed matter systems is the interpretation of experimental signatures from defects. The extremely efficient, albeit approximate, functionals available for density-functional theory have given this approach wide application in conjunction with experimental probes such as scanning tunneling microscopy, electron paramagnetic resonance, electron-nuclear double resonance, and nuclear magnetic resonance [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11]. Macroscopic mechanical response functions by providing a clear signature which terminates friction from a point defect, in this case defects to provide the first parameter-free tool in the study of defects in solid-state systems [12, 13, 14, 15, 16], providing key information on such issues as defect symmetries and concentrations. However, mechanical response studies remain largely ignored by the ab initio community to date.

Despite their successes, the aforementioned density-functional studies suffer a fundamental flaw: no underlying theorem ensures that density-functional theory provides the energy- or angular-momentum-resolved densities probed in the experiments involved in the application. Beyond this matter of principle, such quantities are not among those which available approximate functionals predict most reliably. This letter notes that the most reliable quantities which density-functional theory predicts (bond lengths, bond angles, and lattice parameters) relate directly to the key coupling parameter in macroscopic mechanical response experiments, the full activation-volume tensor. We thus propose ab initio study of mechanical response functions associated with this tensor as a powerful and particularly reliable new tool in the study of defects in condensed matter systems.

One such response function, internal friction, is a topic of current interest both experimentally and theoretically [17, 18, 19, 20, 21, 22]. Below we develop the theory of internal friction as applied to divacancy defects to provide the first parameter-free ab initio determination of friction from a point defect, in this case the singly negatively charged divacancy in silicon (Si$_2$$^-$). Although the structure of this defect has been inferred through a combination of experimental signatures and symmetry of electronic states [23], ab initio work to confirm the structure has resulted in an ongoing debate [24, 25, 26] which has arisen ultimately from a focus on delicate energy differences at or beyond the limits of accuracy of current density functionals. Here, we demonstrate the power of working with mechanical response functions by providing a clear signature which resolves the debate.

Mechanical response of defects — Within linear response, the stress-dependent part of the energy of a point defect $\Delta E$ has the form

$$\Delta E = -\Lambda_{ij}\sigma_{ij},$$

where we employ repeated index summation notation here and throughout this work and where $\sigma$ and $\Lambda$ are, respectively, the externally applied stress tensor and the defect activation-volume tensor.

The activation-volume tensor $\Lambda$ is accessible in terms of equilibrium supercell lattice constants, which are among the quantities most reliably determined within density-functional theory. This connection comes directly from the principle that the strain $u$ induced in a crystal containing a concentration $n$ of defects with activation volume tensor $\Lambda$ is $u_{ij} = n\Lambda_{ij}$, a result of minimizing the sum of the bulk and defect elastic energies. Accordingly, one may determine $\Lambda$ simply by creating a supercell containing a single defect and relaxing the defect structure along with the supercell lattice vectors.

Under applied stress, defects with lower symmetry than the host crystal tend to reorient so as to minimize the energy. Experimental stress-alignment studies, which observe the relative thermalized populations of different orientations of specific defect types as a function of applied stress, thus allow direct access to certain linear combinations of $\Lambda_{ij}$ for each type [23]. Such thermalization of defect populations under time-varying external stress $\sigma_{ij}(t)$ provide a mechanism for internal friction, dissipation of mechanical energy throughout the bulk of a material. We review this process here in some depth because, although our overall logic is the same, the final result for the divacancy differs from the oft-quoted result [27], which assumes that all defect orientations relax among each other at equal rates and hence does not apply to divacancies.
From Eq. (1), the total energy per unit volume stored at time $t$ among all defect orientations $m$ of a specific defect type is

$$\Delta E(t) = -n \sum_m P^m(t) \Lambda^m_{ij} \sigma_{ij}(t),$$

(2)

where $n$ is the total number density of defects of this type, and $P^m$ and $\Lambda^m_{ij}$ are the probability and activation volume tensor associated with each orientation. Dissipation results from energy lost irreversibly to the heat bath through transitions among defect orientations and thus occurs at the rate

$$\frac{dE}{dt} = n \sum_m \frac{dP^m}{dt} \Lambda^m_{ij} \sigma_{ij}(t).$$

(3)

Finally, stresses ultimately drive the transitions through the master equation

$$\frac{dP^m}{dt} = \sum_{m'} \nu_{mm'} \left(1 + \beta \Lambda^m_{ij} \sigma_{ij}(t)\right) P^{m'}(t) - \nu_{mm'} \left(1 + \beta \Lambda^m_{ij} \sigma_{ij}(t)\right) P^m(t),$$

(4)

where we take transitions from orientation $m'$ to $m$ to be thermally activated with rate $\nu_{mm'}$ in the absence of external stress and with stress dependencies which we have linearized. Solving (4) and substituting the result into (3) then gives the final dissipation rate.

Under the not uncommon special case underlying the result, in which the zero-stress transition rates among different orientations of a defect type are equal by symmetry, $\nu_{mm'} = \nu$, the master equation may be solved analytically, resulting in a defect contribution to the inverse quality factor $Q^{-1}$, the fraction of energy lost per radian of oscillation phase, of

$$Q^{-1} = n\beta \frac{\tilde{\omega}_g}{1 + (\tilde{\omega}_g)^2} \frac{\tilde{\sigma}_{ij} L_{ij;kl} \sigma_{kl}}{\tilde{\sigma}_{ij} S_{ij;kl} \sigma_{kl}}.$$  

(5)

$$L_{ij;kl} \equiv \frac{1}{g} \sum_{m} \Delta \Lambda^m_{ij} \Delta \Lambda^m_{kl}.$$  

Here, $\sigma_{ij}(t) \equiv \text{Re}(\tilde{\sigma}_{ij} \exp(i\omega t))$, $\Delta \Lambda^m_{ij} \equiv \Lambda^m_{ij} - \tilde{\Lambda}^m_{ij}$, $\tilde{\sigma}_{ij}$ is the standard elastic compliance four-tensor, and $L_{ij;kl}$ is an anelastic four-tensor sharing the symmetry of the full set of defect orientations.

In a system with more than one type of defect, the inverse quality factors for each type add. If the transition rate $\nu_s$ associated with each type $s$ has the same value $\nu$, then $Q^{-1}$ can be written as

$$Q^{-1} = \frac{\tilde{\omega}_g}{1 + (\tilde{\omega}_g)^2} \frac{\tilde{\sigma}_{ij} L_{ij;kl} \sigma_{kl}}{\tilde{\sigma}_{ij} S_{ij;kl} \sigma_{kl}}.$$  

(6)

Finally, we note here that there is a simple, exact relationship between the anelastic four-tensor and the results from experimental studies of the inverse quality factor of a mechanical oscillator as a function of temperature, which generally show a peak when the thermally activated, and thus temperature-dependent, transition rate $\nu(T)$ corresponds to the oscillator frequency $\frac{\omega}{g}$. In particular, from (5) we have that the experimentally accessible quantity $k_B T Q^{-1}$, where $k_B$ is Boltzmann's constant, has a maximum at precisely $\nu(T) = \omega/g$ with value

$$\max (k_B T Q^{-1}) = \frac{n \sigma_{ij} L_{ij;kl} \sigma_{kl}}{2 \tilde{\sigma}_{ij} S_{ij;kl} \sigma_{kl}}.$$  

(7)

Ab initio determination of $L_{ij;kl}$ thus gives a parameter-free relationship between the maximum temperature-internal friction product and the defect concentration, thereby allowing mechanical response experiments to provide a direct, parameter-free measure of absolute defect concentrations for the first time.

**Application to divacancy in silicon** — The importance of the divacancy in silicon has led to its extensive study, both theoretically and experimentally [6, 23, 24, 28, 29, 30, 31]. In contrast to single vacancies, which are quite mobile and thus anneal readily, divacancies have low mobility and are among the most common stable defects in silicon at room temperature. The defect has four charge states, singly positively charged, neutral, singly and doubly negatively charged, with the singly charged defect (Si-V) playing an important role in carrier recombination [32].

Since the publication of Watkins and Corbett’s pioneering study [23], the ab initio determination of the precise nature of the ground-state structure of Si-V has become the subject of debate [6, 24, 25, 26, 30, 31, 32]. The idealized defect has $D_{3d}$ symmetry along the $\langle 111 \rangle$ axis connecting the sites of the neighboring vacant atoms. The defect also introduces partially filled degenerate electronic states into the gap and thus undergoes a Jahn-Teller distortion which ultimately lowers the symmetry to $C_{2h}$. The debate arises because two stable structures, termed **pairing** and **resonant**, with very similar energies are consistent with the $C_{2h}$ symmetry of the defect.

Figure 1 shows the two competing ground-state structures as projected along the $\langle 111 \rangle$ defect **axis** connecting the sites of the two vacant atoms. The pairing configuration breaks symmetry by moving two pairs of atoms ($a'b'$ in the figure) toward each other along a (110) reconstruction axis to form stronger bonds at the expense of strain energy. In the resonant structure, the same pairs of atoms move away from each other to form a less favorable bonding configuration at a nearly correspondingly lower cost in strain. Whenever this work requires a specific coordinate system, it shall be such that the defect **axis** is $[111]$ and the **bonding axis** is $[110]$. 

...
The literature reports a number of density-functional values for the energy difference $\Delta E \equiv E_{\text{pair}} - E_{\text{exc}}$ between the two competing configurations: $0.0024 \text{ eV}$ [21], $0 \text{ eV}$ [22], $-0.12 \text{ eV}$ [23], $-0.18 \text{ eV}$ (present work). The fact that these differences are all quite small and of the order of the uncertainties due to the approximate density functionals which these works employ (all other computational uncertainties notwithstanding!) underscores the difficulty of using total energies to resolve the ground state structure of the Si-$V_2^-$ defect and indicates that previous studies are inconclusive. We propose instead to use the considerably different activation volume tensors of the competing reconstructions as a more appropriate signature to confirm the ground state.

Experimentally, Watkins and Corbett [22] explored the activation volume tensor of the Si-$V_2^-$ defect in depth using electron spin resonance to study thermal alignment of defect subpopulations under external $\langle 110 \rangle$ stresses. These experiments, as do also internal friction experiments, take place under conditions where $\langle 110 \rangle$ reconstruction axes have time to thermalize while $\langle 111 \rangle$ defect axes do not. Such $\langle 110 \rangle$ stresses split divacancies into two classes, $\alpha$ and $\beta$, according to the orientation of the defect axis, with $\alpha$ corresponding to the defect axis being perpendicular to the stress. Within each of these classes, there is a further splitting of the energy into two distinct values, for a total of four energetically different states [23].

As thermalization occurs only among choices of reconstruction axis, the quantities which stress-alignment experiments actually access are the energy splittings within each class, $\Delta E_\alpha$ and $\Delta E_\beta$, respectively, each of which relate directly to certain linear combinations of components of the defect activation-volume tensor,

$$\Delta E_\alpha = \frac{\sigma}{2} (\Lambda_{11} + 2\Lambda_{12} - 2\Lambda_{13} - \Lambda_{33}) \equiv -\sigma \Delta \Lambda_\alpha \quad (8)$$

$$\Delta E_\beta = \frac{\sigma}{2} (\Lambda_{11} - 2\Lambda_{12} + 2\Lambda_{13} - \Lambda_{33}) \equiv -\sigma \Delta \Lambda_\beta,$$

where $\sigma$ is the magnitude of the external $\langle 110 \rangle$ stress and $\Lambda_{ij}$ are the Cartesian components of the activation volume tensor in the cubic coordinate system defined above.

Calculations and results — The ab initio electronic structure calculations below employ the total-energy plane-wave density-functional pseudopotential approach [34] within the local spin-density approximation (LSDA) using a pseudopotential of the Kleinman-Bylander form [35] with $p$ and $d$ non-local corrections. The calculations expand the Kohn-Sham orbitals in a plane-wave basis set with a cutoff energy of 6 Hartrees within a cubic sixty-four atom supercell, sampling the Brillouin zone at eight k-points, reduced to four by time reversal symmetry. Finally, we employ the analytically continued functional approach [36] to minimize the Kohn-Sham energy with respect to the electronic degrees of freedom.

To determine $\Lambda$, we relax a supercell containing a single defect and compute the relaxed strain and thus $\Lambda$. In principle, this can be done in a single joint relaxation with the internal atomic coordinates. For the present study, however, we followed the nearly equivalent approach of minimizing the internal coordinates while minimizing separately along each of the six independent components of supercell strain while including the Poisson ratios of the supercell when appropriate. "Oğut and Chelikowsky [6] emphasize the need to tailor supercell shape to accommodate the relaxation pattern of $V_2^-$ to obtain accurate results for defect energy differences. To explore supercell-size effects on the extraction of the activation-volume tensor, we carried out a convergence study of $\Delta \Lambda_\alpha$ and $\Delta \Lambda_\beta$ from [5] employing the environment-dependent interatomic potential (EDIP) for silicon [37] for cubic supercells of lattice constant from $2a_0$ through $6a_0$, where $a_0$ is the lattice constant of the "primitive" eight-atom cubic cell. Over this range of cell sizes, we observe a total change of only 12.5% (6.3%) in $\Delta \Lambda_\alpha$ ($\Delta \Lambda_\beta$), with 70% (86%) of the change occurring between $2a_0$ and $3a_0$. We thus conclude that $\Lambda$ is not a particularly sensitive function of cell size and that a supercell of 64 atoms suffices to give ab initio values with an uncertainty on the order of 10%.

Table 1 summarizes our ab initio results for the activation volume tensors of the two candidate defect structures, and Figure 1 compares our predictions directly with the experimentally available linear combinations, $\Delta \Lambda_\alpha$ and $\Delta \Lambda_\beta$ [23]. Our predictions for the resonant configuration are clearly inconsistent with the measurements, whereas our results for the pairing configuration show good agreement with errors (+20% and -6% for $\Delta \Lambda_\alpha$ and $\Delta \Lambda_\beta$, respectively) consistent with supercell-convergence uncertainty we estimate above. The figure also compares our ab initio prediction of another linear combination of components of the activation volume tensor, $B_{33} = C_{33,ij} \Lambda_{ij}$ where $C_{ij,kl}$ is the elastic constant four-tensor, with an estimate of this quantity from [23].

Turning finally to the internal friction, because the de-
peting ground-state structures of singly negatively charged

| \( \Lambda_{\text{pair}} (\text{Å}^3) \) | \( \Lambda_{\text{res}} (\text{Å}^3) \) | \( L_{\text{tot}} (\text{Å}^6) \) |
|---|---|---|
| -11 18 1.5 | 0.6 -1.5 10 | \( L_{11} \) 100 38 |
| 18 -11 1.5 | -1.5 0.6 10 | \( L_{12} \) -50 -19 |
| 1.5 1.5 10 | 10 10 -13 | \( L_{44} \) 293 279 |

TABLE I: Activation-volume and anelastic tensors for competing ground-state structures of singly negatively charged divacancy in silicon

FIG. 2: DFT results and comparison to experiment of \( \Delta \Lambda_{\alpha} \), \( \Delta \Lambda_{\beta} \) and \( B_{33} \). For each data set the black bar corresponds to the experimental data, the white bar to our DFT results for the pairing configuration and the gray to those for the resonant configuration. \( B_{33} \) has been scaled by \( C_{11} \) for display purposes.

fect axes do not thermalize under typical experimental conditions, each choice of defect axis must be treated as a separate type of defect \( s \) in [6]. Under normal sample preparation, all four distinct choices of \( (111) \) defect axes will occur with equal probabilities, \( n_s = n/4 \), resulting in an \( L^{\text{tot}} \) with cubic symmetry. The thermalizing reconstruction axes then constitute the orientations \( m \) within each type and have sufficient symmetry to ensure the result [4]. Table II gives the three unique values of the resulting cubic anelastic four-tensor in contracted notation. This is the first \textit{ab initio} prediction for the components of the anelastic tensor for a defect, a quantity of current research interest, particularly in the optimization of micro- and nano-electromechanical devices. (See, for example [12, 20]) Our value of \( L^{\text{tot}} \) indicates that torsional (pure shear) oscillators will experience a maximum in divacancy-mediated loss in the range \( 5.5 \times 10^{-28} \text{cm}^3 K \leq \max(T\dot{Q}^{-1})/n < 8.5 \times 10^{-28} \text{cm}^3 K \), with the precise value depending on the crystallographic orientation of the device through [4].

In conclusion, this letter introduces \textit{ab initio} study of the full activation-volume tensor of crystalline defects as a quantity which current approximate density-functional give accurately and which is of direct use in making contact with mechanical response experiments, including both stress-alignment studies and measurements of macroscopic internal friction. Illustrating the power of the approach, this letter gives the first unambiguous \textit{ab initio} verification of the nature of the ground state of the singly negatively charged divacancy in silicon and the first parameter-free theoretical calculation of the peak internal friction associated with a point defect. This latter quantity then forms the basis for a straightforward method for determining defect concentrations via \textit{ab initio} interpretation of macroscopic mechanical response experiments.

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