

LETTER TO THE EDITOR

Volume changes and dipole tensors for point defects in crystals

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Abstract. Results for the volume change and dipole tensor for point defects are derived using a generalisation of the Betti reciprocity theorem. These results incorporate the correction terms derived by Flynn, by Lidiard and by Gillan in a simpler way, and allow some more general results to be obtained straightforwardly.

Calculations of volume changes caused by defects in solids often use an expression involving the virial of the defect forces (Hardy 1968, Temkin 1970):

$$\Delta V = \sum_{\substack{i,j \\ \text{axes}}} \sum_k \sum_{\substack{l \\ \text{sites}}} s_{ijkk} R_{il} F_{lj} \quad (1)$$

with \mathbf{s} the elastic compliance, and \mathbf{F}_l the defect force on the neighbouring ion at site \mathbf{R}_l . The expression has, however, been consistently unsuccessful in its predictions. Whilst some of the weaknesses can be shown to result from inadequacies in working approximations commonly made in evaluating the virial (Schober and Ingle 1980, Gillan 1983), the main problem is, in fact, an inconsistency in the expression itself. Whilst this point is comprehensively discussed by Gillan, it proves both useful and revealing to give a re-analysis parallel to the elegant discussion of Temkin.

Temkin exploited the so-called Betti reciprocity theorem (for fuller references see Stoneham 1975). We cannot use the same theorem, for it relies on an assumption of a harmonic host, and so it specifically excludes some of the critical corrections noted by Flynn (1971), Schober and Ingle (1980), Lidiard (1981) and Gillan (1983). Fortunately, we can exploit the central idea used in the proof of the Betti theorem, and hence we can produce a generalised theorem as a by-product. The central thesis is this: the final state reached by applying two sets of forces \mathbf{F}_1 and \mathbf{F}_2 to a solid is independent of their order of application.

In our case, the forces \mathbf{F}_1 will be the defect forces, and the forces \mathbf{F}_2 will correspond to an external pressure p . The two sequences of application of these forces are shown schematically in figure 1, together with the displacements (represented in the diagram as a scalar, essentially a projection of the displacements corresponding to the volume change) to which they give rise. We are free to choose the pressure p (i.e. \mathbf{F}_2) such that $x_{II} \gg x_I, x_{III}$. Quantitatively, this requires a pressure p producing a volume change for the whole crystal which greatly exceeds the volume change due to a single defect, i.e. a fractional volume change in excess of 10^{-22} typically. Our final result will be independent

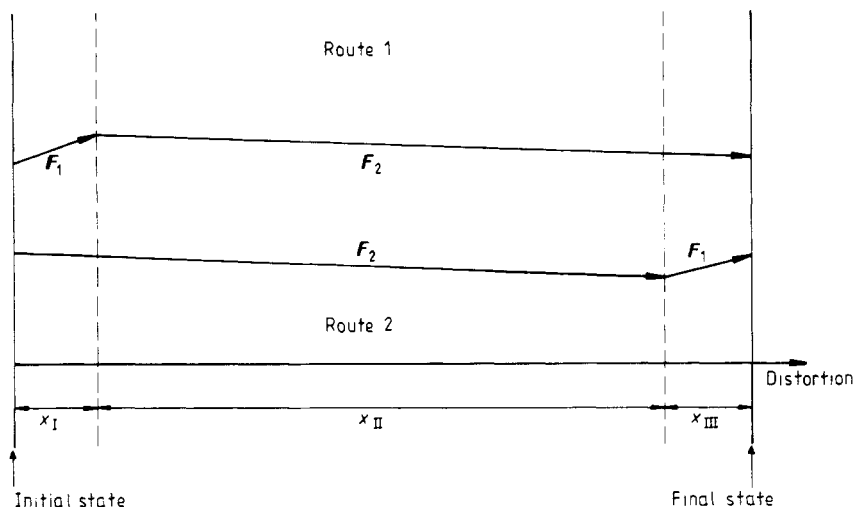


Figure 1. This shows schematically the two sequences by which the forces F_1 and F_2 are applied. The distortion is represented for this figure alone by a scalar x , and the changes in x in the three regimes of distortion referred to in the text are labelled. For practical purposes x may be thought of as a measure of volume.

of p . With this choice the interatomic force constants and elastic constants may be assumed constant within regime I and constant (though different) with regime III. Any averages over the distortion-dependent force constants in the combined regimes (I + II) will be essentially the same as in the combined regimes (II + III). These assumptions about force constant changes are sufficiently general to include all the extra terms identified by Gillan, yet allow one to minimise algebraic complexity.

When F_1 is applied first, the work done between the initial and final states contains three terms:

- E_1^I relaxation energy under forces F_1 with force constants appropriate to regime I.
- $E_2^{II,III}$ relaxation energy under forces F_2 with force constants appropriately averaged over regimes (II + III).
- $F_1 \cdot \Delta_2$ work done against F_1 by the displacements due to F_2 ; $\Delta_2 \equiv x_{II} + x_{III}$ here.

When F_2 is applied first, there are again three terms:

- $E_2^{I,II}$ relaxation energy under forces F_2 . With the assumption $x_{II} \gg x_I, x_{III}$ this term is identical to $E_2^{II,III}$ to order $(\Delta V)^2$.
- E_1^{III} relaxation energy under forces F_1 with force constants appropriate to regime III.
- $F_2 \cdot \Delta_1$ work done against forces F_2 by the displacements due to F_1 (strictly with force constants appropriate to regime III, though this distinction is not needed for present purposes).

Collecting terms, and cancelling $E_2^{II,III}$ and $E_2^{I,II}$ consistent with our assumptions, we find a generalised form of the reciprocity theorem:

$$F_2 \cdot \Delta_1 = F_1 \cdot \Delta_2 + (E_1^I - E_1^{III}). \quad (2)$$

It is Δ_1 which will prove proportional to the defect-induced volume change. The first term on the right leads to the standard expression of Hardy and Temkin, and the second term on the right leads to the correction of central interest here.

We can now derive the key result for the volume change ΔV . If F_2 corresponds to an external pressure, then (cf Temkin 1970 or Stoneham 1975) the left-hand side is merely $-p\Delta V$, and the first term on the right-hand side reduces by previous methods to $-p\Delta V_{\text{virial}}$. Thus we have now

$$\Delta V = \Delta V_{\text{virial}} + (E_1^{\text{III}} - E_1^{\text{I}})/p. \quad (3)$$

But E_1^{III} and E_1^{I} differ merely by the change in relaxation energy under forces F_1 as the force constants are changed by the applied pressure p . Simply rewritten:

$$\begin{aligned} \Delta V &= \Delta V_{\text{virial}} + \partial E_{\text{rel}}/\partial p \\ &= \Delta V_{\text{virial}} - V\partial E_{\text{rel}}/B\partial V \end{aligned} \quad (4)$$

where E_{rel} is the *relaxation* energy and B the bulk modulus. Since it is well known from other work that ΔV is $(\partial E_{\text{formation}}/\partial p)$, it is clear that ΔV_{virial} corresponds to the pressure dependence of an 'unrelaxed' defect formation energy calculated with forces appropriate to the relaxed geometry. This division is slightly different from the usual convention, which refers to forces for the unrelaxed geometry. The present choice stems from two features. First, our arguments leading to equation (2) assume F_1 is constant, unaffected by F_2 . Secondly, these arguments require equilibrium at each stage. Both these points can be satisfied (subject to restrictions discussed later) if one replaces the real (configuration-dependent) forces by effective (constant) defect forces which give the same equilibrium distortions, i.e. forces appropriate to the relaxed geometry.

We may now exploit our result (4). First, consider a neutral defect in a solid for which the Gruneisen constant is $\gamma \equiv -\partial \ln \omega/\partial \ln V$. The relaxation energy is proportional to ω^{-2} in simple models, so that we have

$$\Delta V = \Delta V_{\text{virial}} - 2\gamma E_{\text{rel}}/B. \quad (5)$$

Secondly, consider a charged defect in a non-metal with dielectric constant ϵ . The relaxation energy is dominated by the polarisation term $(e^2/2R)(1 - \epsilon^{-1})$, where the cavity radius R is not normally the nearest-neighbour distance (Mott and Gurney 1948). We find immediately a result corresponding to that given by Lidiard:

$$\Delta V - \Delta V_{\text{virial}} = (E_{\text{rel}}/B) \left(\frac{1}{\epsilon - 1} \frac{d \ln \epsilon}{d \ln V} - \frac{1}{3} \right). \quad (6)$$

Instead we may regain Flynn's result at once by concentrating only on terms in $\partial \epsilon/\partial p$ and using equation (4):

$$\Delta V - \Delta V_{\text{virial}} = [(e^2/2R\epsilon)] \frac{d \ln(\epsilon)}{dp}. \quad (7)$$

Since previously we had decided against Flynn's suggestion as an explanation of discrepancies between theory and experiment (Mainwood and Stoneham 1975), it is useful to note how that erroneous conclusion arose. In the earlier work, we (correctly) used forces F_1 obtained from a model which (correctly) included electrostriction. The error lay not in the codes used, nor in the models of interatomic forces, but in the omission of the $\partial E_{\text{rel}}/\partial p$ term; at that time the virial term alone appeared (incorrectly) to be adequate.

We note that the relaxation energy is *quadratic* in the defect forces, i.e. dependent on their magnitude only. In particular, defects with opposite net charges $+e$ and $-e$ will still have the same sign of $(\Delta V - \Delta V_{\text{virial}})$ in a given host. Defects both large and small in an elastic medium will also contain a term with the same sign of $(\Delta V - \Delta V_{\text{virial}})$. It is terms such as these which can contribute to deviations from Vegard's law for alloy lattice parameters.

Thirdly, we may ask what effect occurs on the anisotropic components of the defect's elastic dipole tensor. This is especially important for ionic systems, since anomalies were noted here (Mainwood and Stoneham 1975). There are exactly parallel terms, which generalise Stoneham's (1973) results in terms of the virial. The relative importance depends on the relative magnitudes of the stress derivatives of the dielectric constant. If one writes

$$\varepsilon \rightarrow \varepsilon + \sum_{i,j} \gamma_{ij} \sigma_{ij}$$

then, for cubic crystals, the volume change will depend on $(\gamma_{11} + 2\gamma_{12})$, the cube-axis dipole strength on $(\gamma_{11} - \gamma_{12})$ and the trigonal axis dipole strength on γ_{44} . For non-polar crystals we can relate the γ_{ij} to the photoelastic constants:

$$\delta \varepsilon_{ij} = -\varepsilon^2 p_{ijkl} e_{kl}.$$

The expressions of Stoneham (1973) for the asymmetric length change gain an extra term, i.e. $(x_{\parallel} - x_{\perp})$ is given by its virial component, plus a correction. If the relaxation energy is taken as $E_{\text{rel}} \equiv (e^2/2R)(1 - \varepsilon^{-1})$, and if we ignore any variation of R , the corrections to $(x_{\parallel} - x_{\perp})$ are of the form $(-e^2/2R)(p_{11} - p_{12})/(c_{11} - c_{12})$ for (100) defects and $(-e^2/2R)3p_{44}/2c_{44}$ for (111) defects.

One final point of caution is needed. If the defect forces F_1 change between regimes I and III, a further generalisation is needed. Such problems can be anticipated, for example, when the defect forces result from a major change in electronic state. When an F centre is excited, one expects a volume change between the relaxed excited state (F_c^*) and the relaxed ground state (F_g), and one would expect the difference in defect forces to be pressure-dependent. That this is so is easily demonstrated by a very general argument. If the cycle $F_g \rightarrow F_c^* \rightarrow F_g$ is completed, there must be no net volume change, for the system has returned to its original state. This is automatically satisfied when ΔV_{virial} appears alone. But the sum of the relaxation energies in the two stages is given by the observable Stokes shift, the difference between optical absorption and emission energies. If the Stokes shift shows any pressure dependence, expression (4) is not adequate, and one should return again to a more general form.

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