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ATOMISTIC MODELS OF POINT-DEFECT/DISLOCATION INTERACTIONS IN OXIDES

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1. Introduction.- At temperatures above about half the melting temperature, plastic flow processes can influence the mechanical properties of oxide crystals. The discussions of the first Workshop on point-defect/dislocation interactions at Bellevue, France /1/ showed that for a theoretical understanding of observed dislocation behaviour, we need to be able to develop models which allow us to rationalize 1) the observed slip planes in some materials for which simple arguments appear to fail, 2) the amount of dislocation dissociation, particularly climb dissociation that is observed in some materials and, 3) the role of point defects in inhibiting dislocation motion. It is evident that all of these are problems involving the interaction of the dislocation
either with the lattice (Peierls-Nabarro stress and dislocation dissociation) or with point defects (solution hardening, jog formation and dislocation climb). In either case, an accurate representation of the dislocation's core is required. This necessitates the development of atomistic models, as these are the only models capable of dealing adequately with the two most important features determining dislocation core properties: the crystal structure and non-linear interatomic interactions.

In this paper we give a brief review of the methods and models which have been developed to accomplish objectives 1) to 3) above and summarize some of the results. It is convenient to concentrate on the point-defect/dislocation interaction problem, since the dislocation/lattice interaction has already been discussed extensively in a recent review /2/.

2. Background.- Over the last twenty years, the vast majority of atomistic models of point-defect/dislocation interactions have been developed for metals. This emphasis on metals is a result of the technological importance of these materials. Nonetheless, the earliest calculations of association energies were carried out by Bassani and Thomson /3/ for cation vacancies and impurities situated in the core of a 1/2 [110] (110) edge dislocation in the ionic crystal NaCl. These computations were performed before the development of large, high-speed computers. Consequently, it was impossible to consider explicitly more than a few atoms surrounding the point defect in the core of the dislocation. In addition to this limitation, it was necessary to employ a number of simplifying assumptions in order to make the equations giving the equilibrium positions of the atoms tractable. Attempts to improve upon these pioneering calculations were not made until some twenty years later by Woo et al. /4/ and by Granzer et al. /5,6/. The contributions of Granzer et al. were in the form of conference abstracts giving few details as to either methods or results. Puls et al. /7/, subsequently gave a more detailed account of the formulation of their own method, given earlier in reference /4/. They also presented results for the association energies of simple cation and anion vacancies with 1/2 [110] (110) edge dislocation in MgO. These calculations were later extended by Puls, firstly to include a greater number of positions surrounding the dislocation's core /8/ and, secondly, to examine the association energies of the \( \text{Fe}^{+}_{\text{Mg}} - \text{V}^{+}_{\text{Mg}} - \text{Fe}^{+}_{\text{Mg}} \) trimer (1) with the same dislocation /9/.

(1) In this and the following, we use the Kröger-Vink /10/ notation in describing point defects and their complexes.
The programs developed by Puls et al. /7/ employ an ionic interaction model for the solid. They are suitable for studying defect interactions in the alkali halides. They can also be used to determine association energies in a variety of oxides as long as it is established that these oxides have a predominantly ionic interaction. In considering the applicability of these programs to a wide variety of oxides, it is, however, important to understand the limitations and strengths of the ionic model and the technique used to determine defect energies. With this in mind, we will outline below the models and methods used to determine association energies and we will examine possible sources of errors and uncertainties inherent in the present approach.

3. Potential model.- The basic assumption of ionic interactions implies that the ions have integral (or close to integral) charge with a spherically symmetric non-overlapping electron distribution. This means that the total energy of the crystal can be approximated as the sum of central-force pair potentials, $\phi(r)$, for which we assume a suitable analytic form. The most commonly used pair potentials have what are generally referred to as the Buckingham form consisting of the long-ranged electrostatic (Coulomb) interactions of the usual $r^{-1}$ form and shorter ranged repulsive and attractive terms$^{(2)}$. These latter terms are usually made up of a repulsive (exponential) Born-Mayer term representing overlap and exchange contributions and some attractive $r^{-6}$ and $r^{-8}$ van der Waals dispersion terms. An extensive compilation of some of the more recently used potentials (i.e., used in defect calculations) is given in a handbook by Stoneham /11/. The unknown constants in the short-ranged part of $\phi(r)$ are derived by fitting to a number of experimentally measured constants such as the lattice parameter, the elastic constants and the cohesive energy. For some materials, particularly oxides and fluorides, supplementary quantum mechanical calculations are used to deduce the second neighbour anion-anion repulsive interaction. Two further refinements to the simple point ion model (PIM) are often introduced. These are the shell and breathing shell models (SM and BSM, respectively) which attempt to include ionic polarization (SM) and many-body effects (BSM). The SM is now standard in point defect calculations, whereas the BSM has, so far, been used only rarely. In the SM each ion is divided into a separately charged core and shell to simulate the ionic polarization. There is no Coulomb interaction between core and shell of the same ion, only an harmonic spring coupling. Because the interatomic forces act through the shells,

$^{(2)}$ In the following, we will refer to these as the short-ranged interactions.
the short-ranged forces are modified by ionic polarization. This simple shell model is capable of describing both the elastic and dielectric properties of an ionic solid. The SM parameters are obtained by fitting to the high and low frequency dielectric constants plus the transverse optic frequency. Often, to obtain a better fit to the known dispersion curves, the total ionic charge is also varied. However, this can result in too low a cohesive energy /12/. Since the SM is a central-force, pair interaction model, its applicability is strictly limited to solids for which the Cauchy condition $C_{12} = C_{44}$ on the second-order elastic constants is obeyed. Deviation from this condition can be accounted for by the BSM /13, 14/ in which the effective ion separation is modified by the symmetric breathing deformation of the shells; the shell radius responds harmonically to the total effective overlap pressure of all surrounding ions. In this way, many-body forces may be simulated and the model need not satisfy the Cauchy condition.

The above approach to potential interactions is highly empirical. Although the form of the potential roughly derives its justification from quantum mechanical models, the parameters governing the strength of the interaction are determined from experimental data. Potential parameters derived by means of such a procedure cannot be unique and in order to check the validity of a potential so derived, it is necessary to establish different versions by varying the fitting procedure. The sensitivity of calculated defect properties must then be tested against these variations in the potential. A further criterion for the reliability of the potential is assumed to be its ability to reproduce a defect property, such as a vacancy migration energy, for which reliable experimental results are deemed to exist /15/. Because of the highly empirical nature of these models, it is difficult to make rigorous estimates of the magnitudes of the probable errors due to the approximations made and hence to gauge the reliability of the models. Fundamental questions such as the degree and nature of ionicity, for instance, and its effect on the nature of the bonding can only be tackled in an ad hoc manner within the above framework. This last question seems to be of lesser importance in the alkali halides but could play an important factor in many of the oxides and remains to be explored in more detail.

4. Method of computation.- 4.1 Energy formulation.- The approach to calculating the formation energy of point defects in either a dislocated or a perfect lattice has been previously described in some detail by Puls et al. /7/. It suffices here to expand upon this earlier derivation. In addition, we give a brief outline of the computer program PDINT
which has been designed to implement this method.

The objective of the PDINT program is to calculate the formation energy, $E_F^D$ or $E_F^P$, of a point defect in a dislocated or a perfect lattice, respectively. The interaction (or association) energy $E_{\text{int}}$ then follows as the difference in formation energy of the point defect in the dislocated and in the perfect lattice; that is

$$E_{\text{int}} = E_F^D - E_F^P$$

(1)

This is negative for attractive interactions following the same sign convention as is employed in the usual elastic interaction model /16/ but opposite to that used by Bassani and Thomson /3/. The calculation of $E_F^D$ or $E_F^P$ follows a generalized Mott-Littleton scheme /17/ whereby the (effectively infinite) crystal is divided into a region 1, which includes the defect and in which region interactions between the ions are considered explicitly. This region is surrounded by an harmonically relaxed region 2 of which only a small finite boundary layer needs to be explicitly considered.

Formally, the total formation energy is made up of the sum of three terms: the energy of region 1, $E_1 (\vec{r})$, the interaction energy between regions 1 and 2, $E_2 (\vec{r}, \vec{R})$, and the harmonic relaxation energy of region 2, $E_3 (\vec{R})$; that is,

$$E_F = E_1 (\vec{r}) + E_2 (\vec{r}, \vec{R}) + E_3 (\vec{R})$$

(2)

where $\vec{r}$ are the ion coordinates in region 1 and $\vec{R}$ the (harmonic) displacements in region 2. For the PIM:

$$E_1 (\vec{r}) = \sum_{i \in \text{reg.1}} \psi_i^M (\vec{r}_i) - \sum_{i \in \text{reg.1}} \psi_i^M (\vec{R}_i) + \sum_{i \in \text{reg.1}} \sum_{j > i \in \text{reg.1}} \left\{ \frac{q_i q_j}{|\vec{r}_i - \vec{r}_j|} - \frac{q_i q_j}{|\vec{R}_i - \vec{R}_j|} - \frac{q_i q_j}{|\vec{r}_i - \vec{R}_j|} - \frac{q_i q_j}{|\vec{R}_i - \vec{r}_j|} \right\}$$

$$+ \phi_{ij}^{SR} (|\vec{r}_i - \vec{r}_j|) - \phi_{ij}^{SR} (|\vec{R}_i - \vec{R}_j|)$$

(3)
\[
E_2(\xi_i, \xi_j) = \sum_{i \in \text{reg.1}} \sum_{j \in \text{reg.2A}} \left\{ \frac{q_i q_j}{|\xi_i - \xi_j|} - \frac{q_i q_j}{|\xi_i - R_j|} - \frac{q_i q_j}{|R_i - \xi_j|} \right\} + \\
\phi_{i,j}^{SR} (|\xi_i - \xi_j|) - \phi_{i,j}^{SR} (|R_i - \xi_j|)
\]

\[
E_3(\xi_i) = -\frac{1}{2} \sum_{i \in \text{reg.1}} \sum_{j \in \text{reg.2A}} \left\{ q_i q_j \frac{(\xi_i - \xi_j)}{|\xi_i - \xi_j|^3} - q_i q_j \frac{(R_i - \xi_j)}{|R_i - \xi_j|^3} \right\} + \\
\frac{\partial \phi_{i,j}^{SR}}{\partial x_j} (|\xi_i - \xi_j|) - \frac{\partial \phi_{i,j}^{SR}}{\partial x_j} (|R_i - \xi_j|)
\]

\[
- \frac{Q^2}{2} \sum_{k \text{ sublattices}} q_k K_k \frac{1}{V_c} \int_{R_{2B}} \frac{4\pi r^2}{4} dr
\]

where

\[
\psi_i^M(\xi_i) = q_i \sum_{j \neq i} \frac{q_j}{|\xi_i - R_j|} = \text{the Madelung (electrostatic) potential of an ion at any point } \xi_i \text{ in the R-lattice}
\]

all ions

\[
\psi_i^M(R_i) = q_i \sum_{j \neq i} \frac{q_j}{|R_i - R_j|} = \text{the Madelung potential of an ion at any point } R_i \text{ in the R-lattice}
\]

all ions
\( \chi_i \) = defect lattice sites,
\( R_i \) = reference lattice sites,
\( \vec{x}_j - R_j = \vec{\xi}_j \) = harmonic displacements in region 2,
\( R_{2B} \) = outer radius of region 2A,
\( q_\perp \) = ionic charges,
\( Q \) = net charge of the defect,
\( K_k \) = Mott-Littleton displacement factor,
\( V_c \) = unit-cell volume,

Note that the contributions due to the electrostatic interactions of the ions in \( E_1(\chi) \) and \( E_2(\chi, \xi) \) have been divided into two components: a Madelung term, representing the electrostatic energy of interaction of an ion with all the other ions in the crystal, plus four other terms which, combined, are equivalent to a dipole-dipole interaction. This latter contribution also ranges over all ions in region 2 (i.e., the rest of the crystal) but at a reasonable distance away from the centre of region 1, the displacement pattern resembles a continuous spherical dipole distribution which does not interact with displacement dipoles in region 1. The only remaining long-range interaction with region 2 is due to the net defect charge \( Q \). This interaction, listed under \( E_3(\xi) \), really consists of the sum of two terms, one of which belongs to \( E_3(\xi) \), the other coming from \( E_2(\chi, \xi) \). Note that the summations in the above expressions are over two lattices, the reference (\( R_i \)) and the defect (\( \chi_i \)) lattice. When calculating \( E_D^P \), the reference lattice is the dislocated lattice, whilst when calculating \( E_F^P \), the reference lattice is the perfect lattice. The dislocated reference lattice coordinates are the equilibrium (relaxed) coordinates from an atomistic model\(^3\) of the single dislocation containing no point defects. A special difficulty is presented by the Madelung sums, \( \Psi^M_1(\chi_i) \) and \( \Psi^M_1(R_i) \), since unlike the other sums in \( E_F^P \), these extend over all ions of the (infinite) crystal. It is thus necessary to find rapidly convergent expressions which can reduce the summations to a finite and manageable number of terms. This is accomplished in our case by exploiting the periodicity along the dislocation line direction using the infinite ion string method \( /18,19/ \). This method works for both the perfect and the

\(^3\) such as, say, generated by our DIPOS program \( /18-21/ \).
dislocated lattice. However, the method only converges well for alternate-
nately charged strings, presently restricting the application of the 
program to dislocation lines oriented along these favourable direc-
tions (for instance the 1/2 [110] (110) dislocation in the NaCl 
structure).

The present method allows free variation only of the coordinates 
of ions in region 1 whilst the region 2 coordinates are held rigidly 
in place. The ion displacements in region 2 are estimated, following 
the method of Mott and Littleton/22/, by assuming the material responds 
as a dielectric continuum. Specification of the displacements is 
straightforward because we can determine the strength of the displace-
ment field simply from the net charge, Q, of the defect (or defects) 
in region 1. Appropriate expressions are given by Norgett /17/. Strict-
ly speaking, there should also be displacements due to the elastic 
response of the medium to the defect. Introducing this latter field 
however, is less straightforward, as the strength of the interaction 
is not known beforehand /23/. Additionally, even in cubic crystals, the 
displacements can be strongly anisotropic. So far, we have assumed 
that for a charged defect, the most significant contribution to the 
displacements field comes from the induced polarization and this has 
also been the practice in the majority of defect calculations done for 
otherwise perfect ionic crystals /23/. Additionally, this approximation 
has been used for point defect complexes which carry no net charge /24, 
25/ but, in this case, the errors in neglecting the elastic field may 
be significant. A flexible elastic treatment which can take full account 
of the elastic anisotropy of the boundary region will be necessary to 
fully explore the consequences of this approximation.

The expressions for $E_p$, given by equations (2) to (5) are for the 
PIM. To extend these to the SM, the Coulomb interactions are simply sub-
divided into separate interactions due to the core and shell charges, 
whilst short-range interactions are restricted to interactions between 
shell centres only. The only term formally not included in equations 
(2) to (5) in the SM version, then, is the spring-constant energy due 
to the separation of the shell and core of the same ion. This added 
energy is the SM contributes to $E_1(\tau)$ and $E_3(\tau)$ as follows:

$$E_{\text{sp.-cst.}} = \sum_{i \in \text{reg.1}} \left\{ \frac{1}{2} k_i (\vec{r}^C_i - \vec{r}^S_i)^2 - \frac{1}{2} k_i (\vec{r}^C_i - \vec{r}^{\text{core}})^2 \right\}$$

(6)
where $k_i = \text{shell-core spring-constant}$ and $c$ and $s$ refer to core and shell coordinates, respectively. The sum in equation (7) should, strictly speaking, range over all ions in region 2 but, at a reasonable distance from the defect centre, the ionic polarizations have generally become negligible and can thus be safely neglected. In the SM, in addition to the above energy, there is also a small ambiguity in assigning separate harmonic displacements to the shell and the core in region 2. This ambiguity can be circumvented as discussed in more detail by Norgett /17/.

4.2 Minimization. - Given the relations (2) to (7), the problem is to find the coordinates, $r_{ik}$, which minimize the total formation energy, $E_F$. That is, we need to find the minimum of a function of many variables. Two particularly efficient methods for accomplishing this are the variable metric and the conjugate gradient methods /26,27/. The variable metric method is by far the more efficient of the two, but requires storage of the matrix of second derivatives of the energy. This is manageable for point defects in perfect crystals, since the high degree of lattice symmetry can be exploited to reduce the total number of matrix elements that actually need to be stored. It has been implemented in Norgett's HADES program /17/, contributing significantly to the efficiency of this program. For dislocated lattices, on the other hand, the conjugate gradient method is more appropriate, since only first derivatives of the energy need to be stored. We have used a version of the conjugate gradient method developed by Sinclair (as cited by Puls /19/) which requires no calculation of the energy during the minimization procedure. We have mainly used this version in the PDINT calculations because the usual version, utilizing both forces and total energy generally terminates too early due to rounding error difficulties. In those cases (*) where both versions were able to reduce the forces to the specified level (usually about 0.003 eV/Å), the $E_F$-values obtained with either method were within 0.01 eV.

4.3 Structure of the Program. - A feature of the present formulation which contributes to the complexity of PDINT, is the need to provide a correspondence between three lattices. It is evident that at least (*)All perfect lattice minimizations and a few dislocated lattice cases.
two lattices are needed because of the presence, in equations (2) to (7), of terms depending on both $R_i$, the current lattice and $R_0$, the reference lattice. This latter lattice, however, must also, as required, take on a non-cyclic or a cyclic form. The cyclic form is necessary when evaluating the Madelung energies and forces. In our method of evaluating these terms, each ion in $R_i$ or $R_0$ interacts with an infinitely long row of ions in $R_0$. (It is implicit in this approach that the ions in the row have maintained their lattice periodicity). Thus for the dislocated lattice, the row direction must coincide with that of the dislocation line. If the ion charges do not alternate in sign along that row, there will be convergence difficulties for force variations perpendicular to the row and this particular method of estimating Madelung sums breaks down.

The program is organized as follows. The first step is to set up cyclic and non-cyclic lattices including a mapping scheme which makes it possible to go from a location in the non-cyclic lattice to a corresponding location in the cyclic lattice. The reference lattice is stored in these two configurations. The non-cyclic lattice is subsequently rearranged into a spherical configuration consisting of a sphere of region 1- atoms surrounded by a sphere of boundary atoms (region 2A). This is the desired configuration for which the calculation of the defect formation energies will be carried out as outlined in section 4.1. The initial coordinate positions in this final arrangement are given by the reference lattice locations polarized (displaced) according to the electric displacement field due to the net charge of the defect located at the centre of spherical region 1. In conjunction with setting up the spherical regions, another mapping scheme is given which makes it possible to find, given an atom in the spherical lattice, its corresponding reference lattice location as stored in the cyclic and non-cyclic lattices. Note that when the reference lattice is dislocated, the atom positions for the single dislocation containing no point defects must also be supplied. In our case these coordinates are generated using the flexible boundary package DIPOS /18 - 20/. Given this fairly complex scheme for locating atoms in their various lattices, the remaining part of the program consists of straightforward energy and force calculations and their respective minimization. Note, though, that in the present generalized Mott-Littleton scheme, only coordinates in region 1 of the spherical regions need to be varied.

5. Results.- Actual applications of the PDINT program have, so far, been fairly limited. Using mostly the shell model version, the program has been applied to determine the formation energy of anion and cation
vacancies surrounding the core of $1/2 \ [110]$ (110) edge dislocation in MgO /7,8/. $E_{\text{int}}$ values for vacancy positions up to 4b from the core (where b is the Burgers vector) have been calculated and the results compared with the predictions of the usual isotropic elastic model assuming that the point defect acts as a misfitting inhomogeneity (the latter referring to the difference in elastic properties of the defect and the matrix).

As expected, near the dislocation's edge, there was neither qualitative nor quantitative agreement between the predictions of the two models. The lack of agreement at distances as great as 4b from the dislocation's centre was, however, surprising. This disagreement may reflect as much the uncertainties evident in some of the parameters of the elastic model (i.e., the relaxation volume and the effective elastic constants of the defect) as in the elastic model itself. In the absence of reliable experimental determinations, these parameters are not accessible within the elastic model but must be derived using atomistic methods. Recent discussions illustrate some of the difficulties and uncertainties inherent in estimates of relaxation volumes based on atomistic calculations /28 - 30/.

Following a suggestion that neutral point defect complexes may be the more important dislocation pinners /31,32/, we also looked at the interaction of the $(\text{Fe}^{\text{3+}}_{\text{Mg}} - \text{V}^{\text{\textprime}}_{\text{Mg}} - \text{Fe}^{\text{\textprime\textprime}}_{\text{Mg}})^{\text{Xtrimer}}$ with the above edge dislocation and reported some preliminary results /9/. The work in hand includes extension of these types of studies to NaCl /34/ and a more detailed analysis of the Fe$^{3+}$-trimer study in MgO /35/.

The results to date on MgO for both the simple vacancies and the trimer give a maximum binding energy which is in the range -1 to -2 eV (see below for a discussion of some corrections to the published results), but the results for the trimer are quite sensitive to the impurity potentials used. We have not found any particularly steep variations of $E_{\text{int}}$ versus distance between defect and dislocation centres as anticipated by Whitworth /36/ or inferred by Ritchie and Sprungmann /37/. In fact, for the simple vacancies, the x-variation (6) is similar to what one might expect from the elastic model. We have also sought, but have not found, any indication, as suggested by Whitworth /38/, that a vacancy located at the edge of the extra plane of atoms (i.e., at the

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(5) At the present workshop it was pointed out (Brian Henderson, private communication) that this trimer had actually not been experimentally observed. However, recent results suggest that this defect may now have been identified /33/.

(6) $x$ is the distance between defect centres.
maximum binding position, the 'D' position shown in figure 1 of reference /8/ may be able to move along with the core in an athermal manner as the dislocation glides along the slip plane. From the $E_{\text{int}}$ versus radial distance profiles, it is possible to obtain a rough estimate of the interaction force between defect and dislocation. This is of the order of $10^{-10}$ N for both the vacancies and the trimer and is about an order of magnitude smaller than inferred from solution hardening experiments /32/. The results to date suggest that, in terms of pinning strength, it is not possible to distinguish between the two types of defects.

Recently we have also found an error in the shell model version of the program involving the spring-constant energy. We found that the reference energy term in equation (6) had been inadvertently omitted. This omission was not noticed when comparing our results of vacancy formation energies in the perfect lattice with those of Catlow et al./23/, because in that case this term is zero. However, when the dislocated lattice is the reference lattice, this situation no longer applies. Moreover, the spring-constant energy varies with position; that is, it depends on where the centre of region 1 is located with respect to the dislocation's centre. This reference-lattice spring-constant energy contributes an additional energy of about $-0.35$ eV to $-0.11$ eV to $E_{\text{int}}$. Since it is a constant term in $E_F$, omission of it, fortunately, had no effect on the previously determined relaxed coordinates. Details of the corrected results will be reported elsewhere /39/ including a reanalysis of the comparison between the results of the atomistic and elastic models. This reanalysis was further prompted by the recent improved theoretical estimates of the volume of formation in ionic crystals /28-30/.

In references /7/ and /8/, attempts were made to estimate the accuracy of the calculation by looking at the effects of varying a) the sizes of the regions, b) the desired reduction in the forces, and c) the potential. It will be instructive to amplify on this here by looking at the various components which combine to give $E_F$. As can be seen from equations (3) to (5) for the PIM, the total energy consists of two types of interactions, electrostatic and short-range. For the SM there is also the spring-constant energy given by equations (6) and (7), which may be viewed as simply another contribution to the short-range interaction energy. In the examples shown in table I, we have thus separated the energy into Coulomb terms from $E_1$ and $E_2$ (these are further subdivided into Madelung and dipole-dipole contributions), short-range terms from $E_1$ and $E_2$ plus the two main terms making up $E_3$. 


Table I.-
Energies of formation* of a cation vacancy in MgO

<table>
<thead>
<tr>
<th>Position</th>
<th>Energies (eV)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total: $E_F$</td>
<td>Madelung</td>
<td>Dipole-dipole</td>
<td>Short-range</td>
<td>Spring-constant</td>
<td>$E_{23A}$ $E_{23B}$</td>
</tr>
<tr>
<td>P.L.†</td>
<td>23.92</td>
<td>47.82</td>
<td>-23.12</td>
<td>-0.03</td>
<td>0.26</td>
<td>1.38 - 2.39</td>
</tr>
<tr>
<td>A ‡‡</td>
<td>24.49</td>
<td>49.91</td>
<td>-23.60</td>
<td>-1.14</td>
<td>0.33</td>
<td>1.38 - 2.39</td>
</tr>
</tbody>
</table>

* All calculations employ a region 1 radius of 3.1$r_o$ region 2 radius of 5.1$r_o$ where $r_o$ is the interionic distance = 0.2106 nm.
† Perfect lattice
‡‡ Central atom above jog edge for a type I symmetry 1/2 [110] (110) edge dislocation (illustrated in references /7/ and /8/).

Table II.-
Interaction energy*, $E_{int}$, for a cation vacancy in MgO

<table>
<thead>
<tr>
<th>Position†</th>
<th>Energies (eV)</th>
<th></th>
<th></th>
<th></th>
<th>Total: $E_{int}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.61</td>
<td>-1.11</td>
<td>0.07</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>A2</td>
<td>2.16</td>
<td>-1.75</td>
<td>0.07</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>A3</td>
<td>2.32</td>
<td>-2.60</td>
<td>0.07</td>
<td>-0.21</td>
<td></td>
</tr>
<tr>
<td>A4</td>
<td>0.82</td>
<td>-0.89</td>
<td>0.07</td>
<td>0.00</td>
<td></td>
</tr>
</tbody>
</table>

* The same conditions were used as those to generate the data of table I.
†-row for a type-I symmetry 1/2 [110] (110) edge dislocation (illustrated in reference /8/).
(the one involving the braces, the other the integral; we have called these E23A and E23B, respectively). In addition, for the SM, we keep track of the spring constant energies in region 1 (the corresponding energy in region 2 is negligible). In table II we show the same energies which add up to give the interaction energy of a cation vacancy at various positions parallel to the slip plane along the A-row (illustrated in /8/) of a 1/2 [110] (110) edge dislocation of type-I symmetry in MgO. Table I shows that, as expected, the largest contribution to the formation energy comes from the Coulomb interaction, the short-range and spring-constant energies constituting only about 1 to 3% of the total energy(7). This picture is, however, significantly changed when looking at the interaction energy, given in table II. Now both the Coulomb and the short-range contributions are of comparable magnitude. Since they are of opposite sign, the interaction energy is much smaller than either of these quantities. This latter result, with some exceptions, has been found to be the rule for most of the other positions studied. The large contribution that the short-range potential makes to the interaction energy means that we cannot be anywhere nearly as confident of the accuracy of E_{int} as we can of the formation energy. This was also evident in our earlier study /8/ where we compared E_{int} values calculated using two different potentials and found differences of as much as 0.4 eV between the two models, the largest differences being for some atom positions located close to the dislocation's edge. It is at these positions that some of the interionic distances are most severely altered from their perfect lattice separations and the validity of the model potential, based on properties pertinent to perfect lattice separations, is most suspect.

It is difficult, with the present models and methods, to arrive at a very precise estimate of the accuracy of the E_{int} values. The only practical method seems to be to repeat the calculations using different potentials and to compare the results. In the present case, this is an expensive and time-consuming process which, as a result, is unlikely to be exhaustive. Based on this approach, the previous study by Puls /8/ indicates that the maximum interaction energy for simple vacancies at the edge of the extra plane can be estimated to no better than $\sim 40\%$. Although this is much less than the accuracy we can achieve in the formation energy, it is still a great improvement compared to the only other practical alternative, the elastic continuum interaction

(7)This is less than the usual 10% obtained in the alkali halides, because the ionic charge in the alkaline earth oxides is twice that of the halides.
model. Moreover, although absolute values of the interaction energy have a large uncertainty associated with them, variations of $E_{\text{int}}$ with point-defect/dislocation separation seem to be much less sensitive to uncertainties in the potential.

6. Conclusions.— We have described the methods and models developed to evaluate point-defect formation energies in perfect and dislocated ionic solids. The methods are implemented by means of the computer program PDINT. The theoretical basis for the evaluation of formation energies is a generalized Mott-Littleton method. This method has found wide application in the study of point defects in perfect ionic crystals through Norgett's program HADES. The computer program PDINT represents a natural extension of the basic formalism of HADES to a more general type of lattice such as a dislocated lattice. It is evidenced from the limited studies published to date that, compared to point defect calculations in perfect crystals, corresponding efforts in dislocated crystals are still in their infancy. Aside from those results generated with PDINT /7-9/ and the earliest evaluations of Bassani and Thomson /3/, there appear to be no other published accounts of atomistic calculations of point-defect/dislocation interactions in ionic solids. The calculations reported are shown to be complex, requiring two different computer programs. They are also time consuming, both in terms of preparation and computer time (8).

There is thus an onus to choose the topics to be studied judiciously. In particular, for the more complex defects, it seems unproductive to cover all the possible orientations and defect-dislocation separations. The object, in these cases, would appear to be to use the results of the atomistic model primarily as a guide to improve upon the more approximate models.

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(8) For the published results, typical CPU time per $E_{\text{int}}$-value is from 0.5 h - 1 h on a CDC CYBER 170/175 computer.
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