The Elastic Interaction Between Dislocations and Defects Associated with Calcium Impurities in Sodium Chloride*

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The elastic interaction between edge and screw dislocations and defects associated with calcium impurities in NaCl is studied. The treatment covers all the possible calcium-impurity–cation-vacancy pairs where the cation vacancy occupies the nearest, second-nearest and third-nearest neighboring positions of the calcium impurity. The study is extended to include defect clusters containing two or more calcium-impurity–cation-vacancy pairs. The strong interaction between a screw dislocation and the various impurity–vacancy defects in sodium chloride containing calcium and its effects on the strengthening of the NaCl structure are discussed.

Introduction

In recent years there have been a number of investigations of the effects of divalent impurities on the properties of polar crystals, in particular upon the ionic conductivity, dielectric loss, optical absorption, electron spin resonance, *etc.* These studies have shown that the impurity cations enter the structure by direct substitution. The enhanced conductivity is, for example, a consequence of the requirement that an equal number of cation vacancies must be simultaneously created in order to achieve charge balance. These divalent impurities and cation vacancies can be distributed in various ways. They could be present as individual defects independent of one another, or they could be present as impurity–vacancy pairs or in larger aggregates. For the paired defects, the cation vacancies can assume the nearest, second-nearest, third-nearest neighboring positions with respect to that of the divalent impurity. For those cation vacancies occupying higher-order neighboring positions than the third, one is approaching the region of separation beyond which it is no longer necessary to speak of the defects as associated into pairs (Lidiard, 1955).

There also has been a growing realization of the different mechanical effects that defects have on crystalline solids. Defects have been categorized as causing 'gradual hardening' and 'rapid hardening' due to their effect on the resistance to the motion and multiplication of dislocations in a crystalline solid (Fleischer, 1962; Chang & Wiedersich, 1962). For the 'gradual hardening' defects the increase in resolved critical shear stress per unit concentration of defect is in the range of $G/100$ to $G/10$, while for the 'rapid hardening' types the increase is around G to $10G$, where G is the shear modulus of the solid. It has been suggested that the former type of defect produces a symmetric

distortion of the lattice and does not interact with screw dislocations (according to isotropic elasticity theory) while the latter produces non-symmetric distortions which interact strongly with screw dislocations. The nature of the elastic interaction between dislocations and defects producing non-symmetric distortions in a crystalline lattice is therefore of considerable scientific interest.

The present article discusses specifically the nature of the elastic interaction between edge and screw dislocations and defects associated with calcium impurities in sodium chloride. The treatment can easily be extended to the more general case of polyvalent cation impurities in solids of the NaCl structure.

General considerations of the elastic interaction energy

The calculation of the interaction energies between the different types of defect pairs and dislocations will be carried out in the manner of Cochardt, Schoek & Wiedersich (1955) and of Fleischer (1962). The same assumptions will be made, namely that the stress due to the dislocation is constant over the volume of the defect, the strain due to the defect is constant over a small volume near the defect and negligible elsewhere, and that the concentration of defects is small so that defect–defect interactions can be neglected. Also, the theory of elasticity as developed for an isotropic continuum will be used. With these simplifying assumptions, the interaction energy is merely the product of the tensor components of the dislocation stress and the defect strain. The problem is then reduced to specifying these tensors in the same coordinate system and performing the indicated operations.

A calculation will then be made to find the lattice strain of a defect cluster containing more than one calcium-vacancy pair in sodium chloride and its interaction energy with a dislocation. The model for

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the cluster will be that of a coherent calcium chloride inclusion in sodium chloride, and the lattice strains calculated will be used to give an idea of the strains produced by a single defect pair.

Stress tensor of a dislocation at a Ca impurity-vacancy site

(a) Screw dislocation

Consider a screw dislocation line segment which lies along the [101] direction in the NaCl lattice. Consider also a defect in the lattice located a perpendicular distance r from the dislocation line. Its crystallographic position around the dislocation is defined with respect to the NaCl unit cell and the dislocation by the vector $\mathbf{r}$ and the angle θ as illustrated in Fig. 1. This is possible because of the symmetry of the stress field of the screw dislocation. The stress tensor in the x-, y-, z-coordinate system defined by the edges of the NaCl unit cell is (Fleischer, 1962):

$$\sigma_{ij} = +\frac{Gb}{2\pi_r} \begin{pmatrix} -\cos\theta & -\dfrac{\sin\theta}{\sqrt{2}} & 0 \\ -\dfrac{\sin\theta}{\sqrt{2}} & 0 & -\dfrac{\sin\theta}{\sqrt{2}} \\ 0 & -\dfrac{\sin\theta}{\sqrt{2}} & +\cos\theta \end{pmatrix} \quad i,j = x,y,z \quad (1)$$

where G is the shear modulus and $\mathbf{b}$ is the Burgers vector.

(b) Edge dislocation

Edge dislocation in NaCl lie in the {110} planes and have their Burgers vector in the ⟨110⟩ directions. Consider the (110) [1$\bar{1}$0] edge dislocation and the defect located a distance r from the dislocation line as illustrated in Fig. 2. The position around the dislocation at which the defect lies is defined by the angle θ between the Burgers vector, $\mathbf{b}$, and the radius vector, $\mathbf{r}$. The stress tensor of the dislocation at a point r, θ around the dislocation referred to the x-, y-, z-coordinate system is (Cochardt et al., 1955):
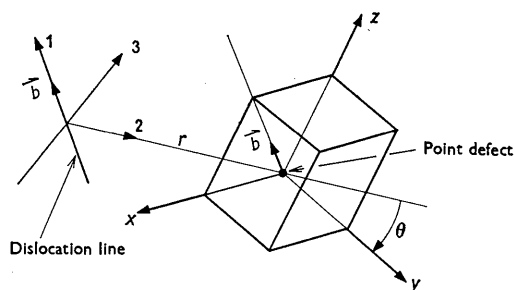

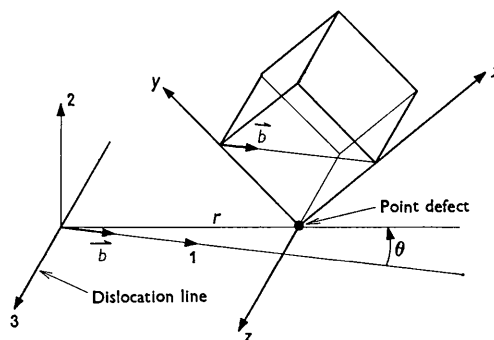Fig. 1. Crystallographic position of a point defect around a screw dislocation.

Fig. 2. Crystallographic position of a point defect around an edge dislocation.

not have the symmetry that is present around the carbon interstitial in iron considered by Cochardt et al. (1955), where there is a large expansion of the lattice in one direction and a slight, uniform, contraction in directions normal to this. In the present case, there is a large contraction in the lattice along the axis of the defect pair, but in the directions normal to this one would expect different values of strain in the regions surrounding the calcium ion and the sodium ion vacancy.

To sidestep this complexity one makes the simplification of assuming an average uniform expansion in the

$$\sigma_{ij} = \frac{Gb}{2\pi(1-\nu)_r}$$

$$\times \begin{pmatrix} +[\cos\theta\,\cos2\theta - \frac{1}{2}(\sin^3\theta + \sin\theta)] & +[\frac{3}{2}\sin\theta\,\cos^2\theta] & 0 \\ +[\frac{3}{2}\sin\theta\,\cos^2\theta] & [-\cos\theta\,\cos2\theta - \frac{1}{2}(\sin^3\theta + \sin\theta)] & 0 \\ 0 & 0 & -[2\nu\sin\theta] \end{pmatrix} ; \quad i,j = x,y,z, \quad (2)$$

where ν is the Poisson's ratio.

Strain tensor of a Ca impurity-vacancy pair

The lattice strain around a Ca impurity–vacancy pair is difficult to determine exactly. Because of the two different species making up the pair, this defect does

lattice normal to the axis of the defect pair. The strain tensor of the defect is then

$$\varepsilon_{k,l} = \begin{pmatrix} \varepsilon_{\mathrm{I}} & 0 & 0 \\ 0 & \varepsilon_{\mathrm{II}} & 0 \\ 0 & 0 & \varepsilon_{\mathrm{III}} \end{pmatrix} ; \quad k,l = x',y',z' \quad (3)$$

where $\varepsilon_{\mathrm{III}} < 0$ is the contraction along the axis of the

defect (z' axis) and $\varepsilon_I \cong \varepsilon_{II} > 0^*$ is the expansion normal to this axis. This tensor represents merely a tetragonal distortion about the defect.

After rotating this tensor into the coordinate system of the sodium chloride unit cell, the interaction energy between this type defect and a screw dislocation is

$$E = -\frac{Gbv}{2\pi r}[\sigma_{xx}(\varepsilon_{xx}-\varepsilon_{zz})+2\sigma_{xy}(\varepsilon_{xy}+\varepsilon_{yz})] \quad (4)$$

since $\sigma_{yy}=0$, $\sigma_{xz}=0$, $\sigma_{xx}=-\sigma_{zz}$, and $\sigma_{xy}=\sigma_{yz}$ in the x-, y-, z-coordinate system. v is the volume of the defect. The interaction energy with an edge dislocation is

$$E = -\frac{Gbv}{2\pi(1-\nu)r}[\sigma_{xx}\varepsilon_{xx}+\sigma_{yy}\varepsilon_{yy}+\sigma_{zz}\varepsilon_{zz}+2\sigma_{xy}\varepsilon_{xy}] \quad (5)$$

since $\sigma_{xz}=0$ and $\sigma_{yz}=0$.

Interaction energies between defect pairs and dislocations

(a) Nearest neighbor defect pairs

There are 12 nearest neighbor Na$^+$ sites around a Ca^{2+} site that a sodium ion vacancy could occupy, but only half of these are non-equivalent according to the present model. The interaction energies between these defects and a screw dislocation are (Fleischer, 1962):

$$E_{1,2,5,6} = \frac{Gbv}{2\pi r}\left[\pm\cos\theta\left(\frac{\varepsilon_I-\varepsilon_{III}}{2}\right)\pm\sqrt{2}\sin\theta\left(\frac{\varepsilon_I-\varepsilon_{III}}{2}\right)\right]^\dagger$$

$$E_{3,4} = 0. \quad (6)$$

The interaction energies with an edge dislocation are

$$E_{1,2} = \frac{Gbv}{2\pi(1-\nu)r}\left[(\sin^3\theta+\sin\theta)\left(\frac{\varepsilon_I+\varepsilon_{III}}{2}\right)\right.$$
$$\left. + (2\nu\sin\theta)\varepsilon_I\pm 3(\sin\theta\cos^2\theta)\left(\frac{\varepsilon_I-\varepsilon_{III}}{2}\right)\right]$$

$$E_{3,5} = E_{4,6} = \frac{Gbv}{2\pi(1-\nu)r}\left[\{\tfrac{1}{2}(\sin^3\theta+\sin\theta)\right.$$
$$\mp(\cos\theta\cos 2\theta)\}\left(\frac{\varepsilon_I+\varepsilon_{III}}{2}\right)$$
$$+\{\tfrac{1}{2}(\sin^3\theta+\sin\theta)\pm(\cos\theta\cos 2\theta)\}\varepsilon_I$$
$$\left.+ (2\nu\sin\theta)\left(\frac{\varepsilon_I+\varepsilon_{III}}{2}\right)\right]^\ddagger. \quad (7)$$

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* This holds true only for the next nearest neighbor defect pairs. For the other defect pairs, $\varepsilon_I \neq \varepsilon_{II}$. The approximation $\varepsilon_I \cong \varepsilon_{II}$, however, is not too serious in the present case where the host lattice is NaCl.

† This is the same as Fleischer's equation (9) if the latter is corrected by changing the $\cos\theta$ coefficient from $\sqrt{2}$ to $1/\sqrt{2}$.

‡ When there are 4 energies involved differing by $\pm$ factors in the expressions $E_{i,j,k,l}=\pm A\pm B$, E_i corresponds to $+A+B$, E_j corresponds to $+A-B$, E_k corresponds to $-A+B$, and E_l corresponds to $-A-B$. Equation (7) is the exception where the two energies correspond to $+A-B$ and $-A+B$ only.

In equations (6) and (7), the E_i are for defects whose axes are [110], [$\bar{1}$10],[101], [$\bar{1}$01], [011], and [0$\bar{1}$1] respectively.

(b) Second-nearest neighbor defect pairs

The second nearest neighbor defect pairs have axes along the $\langle 100\rangle$ directions so there are only three nonequivalent orientations to consider here. The interaction energies with a screw dislocation can be found as before to be

$$E_{1,2} = \frac{Gbv}{2\pi r}[\pm\cos\theta(\varepsilon_I-\varepsilon_{III})]$$

$$E_3 \doteq 0. \quad (8)$$

This is the same as Fleischer's equation (7), except for a difference in the defect volume used.

The interaction energies with an edge dislocation are

$$E_1 = \frac{Gbv}{2\pi(1-\nu)r}[(\sin^3\theta+\sin\theta)\varepsilon_I+(2\nu\sin\theta)\varepsilon_{III}]$$

$$E_{2,3} = \frac{Gbv}{2\pi(1-\nu)r}[\pm(\cos\theta\cos 2\theta)(\varepsilon_I-\varepsilon_{III})$$
$$+(\sin^3\theta\sin\theta)(\varepsilon_I+\varepsilon_{III})+(2\nu\sin\theta)\varepsilon_I]. \quad (9)$$

In equations (8) and (9) the E_i are for defects whose axes are [001], [100], and [010], respectively.

(c) Third-nearest neighbor defect pairs

There are 24 third-nearest neighbor Na$^+$ sites around a Ca^{2+} impurity, but again only one-half of these are non-equivalent. The interaction energies with a screw dislocation are

$$E_{1,7,3,9} = \frac{Gbv}{2\pi r}\left[\pm\cos\theta\left(\frac{\varepsilon_I-\varepsilon_{III}}{2}\right)\mp\sqrt{2}\sin\theta\left(\frac{\varepsilon_I-\varepsilon_{III}}{2}\right)\right]$$

$$E_{4,10,12,6} = \frac{Gbv}{2\pi r}\left[\pm\cos\theta\left(\frac{\varepsilon_I-\varepsilon_{III}}{2}\right)\mp\sqrt{2}\sin\theta\left(\frac{\varepsilon_I-\varepsilon_{III}}{6}\right)\right]$$

$$E_{2,8} = \frac{Gbv}{2\pi r}\left[\mp 2\sqrt{2}\sin\theta\left(\frac{\varepsilon_I-\varepsilon_{III}}{3}\right)\right]$$

$$E_{5,11} = 0. \quad (10)$$

The interaction energies with an edge dislocation are

$$E_{1,4} = E_{10,7} = \frac{Gbv}{2\pi(1-\nu)r}\left[(\sin^3\theta+\sin\theta)\left(\frac{5\varepsilon_I+\varepsilon_{III}}{6}\right)\right.$$
$$\left.+(2\nu\sin\theta)\left(\frac{\varepsilon_I+2\varepsilon_{III}}{3}\right)\mp(\sin\theta\cos^2\theta)\left(\frac{\varepsilon_I-\varepsilon_{III}}{2}\right)\right]$$

$$E_{2,3,5,6} = E_{11,12,8,9}$$
$$= \frac{Gbv}{2\pi(1-\nu)r}\left[\mp(\cos\theta\cos 2\theta)\left(\frac{\varepsilon_I-\varepsilon_{III}}{2}\right)\right.$$
$$+(\sin^3\theta+\sin\theta)\left(\frac{7\varepsilon_I+5\varepsilon_{III}}{12}\right)$$
$$\left.+(2\nu\sin\theta)\left(\frac{5\varepsilon_I+\varepsilon_{III}}{6}\right)\mp(\sin\theta\cos^2\theta)(\varepsilon_I-\varepsilon_{III})\right]. \quad (11)$$

Interaction energy between defect clusters and dislocations

In order to get an idea of the magnitudes of the tetragonal strain components at a Ca impurity-vacancy pair, the strain at a coherent precipitate particle of calcium chloride in a sodium chloride lattice will now be calculated.

In Fig. 3 the relative lattice orientation of calcium chloride precipitate in sodium chloride is shown as determined by X-ray analyses (Suzuki, 1955). Here $a_0 = 6.24$, $b_0 = 6.43$, and $c_0 = 4.20$ Å are the calcium chloride and $a_N = 5.63$ Å the sodium chloride unit-cell dimensions. It should be kept in mind that Fig. 3 shows only one of 24 possible orientations of the x-, y-, z-coordinate system. This will be important later when the interaction energy between a precipitate particle and a dislocation is considered.
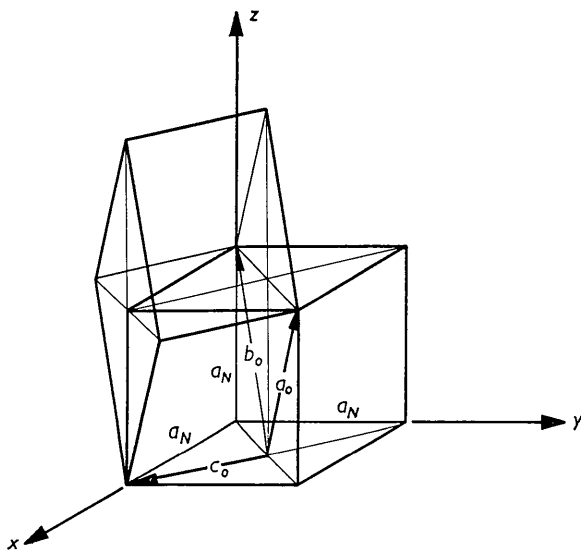

Fig. 3. Lattice orientation of calcium chloride precipitate in sodium chloride.

The lattice strain between the matrix and the precipitate particle can be found by imposing the dimensions and angular relationships of the calcium chloride unit cell upon the sodium chloride unit cell of Fig. 3, calculating the distorted sodium chloride unit-cell shape, and comparing it with the shape of the undistorted unit cell to arrive at the strain components. When this is done the strain tensor is found to be

$$\varepsilon_{ij} = \begin{pmatrix} 0.091 & 0.032 & -0.011 \\ 0.032 & 0.091 & -0.011 \\ -0.011 & -0.011 & -0.204 \end{pmatrix} i, j = x, y, x. \quad (12)$$

The principal strains associated with this strain tensor form a tetragonal strain tensor of the type of equation (3) with the III axis about $2.5°$ from the z axis of the sodium chloride lattice. This corresponds very closely to the state of strain assumed for the second-nearest neighbor or [100] type defect pairs considered previously. The strains caused by the precipitate particle can be considered to be entirely within the particle for the calculation of its interaction energy with a dislocation. This is consistent with the choice of the interaction volume being just the volume of the particle.

Taking into consideration the 24 possible orientations of the x-, y-, z-coordinate axes with respect to the calcium chloride unit cell it can be shown that there are twelve different values for the interaction energy of a particle with a screw dislocation and six with an edge dislocation. These are, for a screw dislocation,

$$E_{1-8} = \frac{Gbv}{2\pi r}[\pm 0.295 \cos\theta + \sqrt{2}(\pm 0.0322 \pm 0.0109) \sin\theta]$$

$$E_{9-12} = \frac{Gbv}{2\pi r}[\sqrt{2}(\pm 0.0109 \pm 0.0109) \sin\theta]. \quad (13)$$

In this case E_{11} and E_{12} are zero.
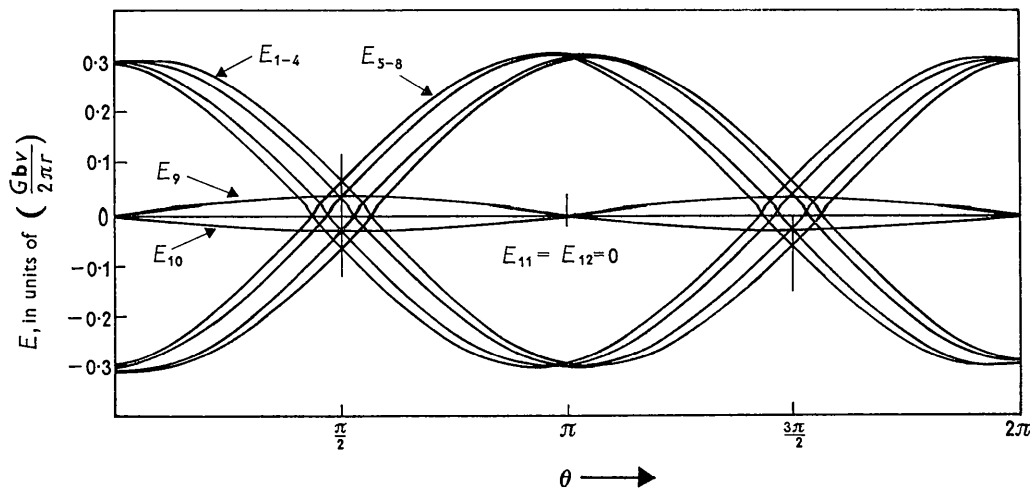For an edge dislocation they are

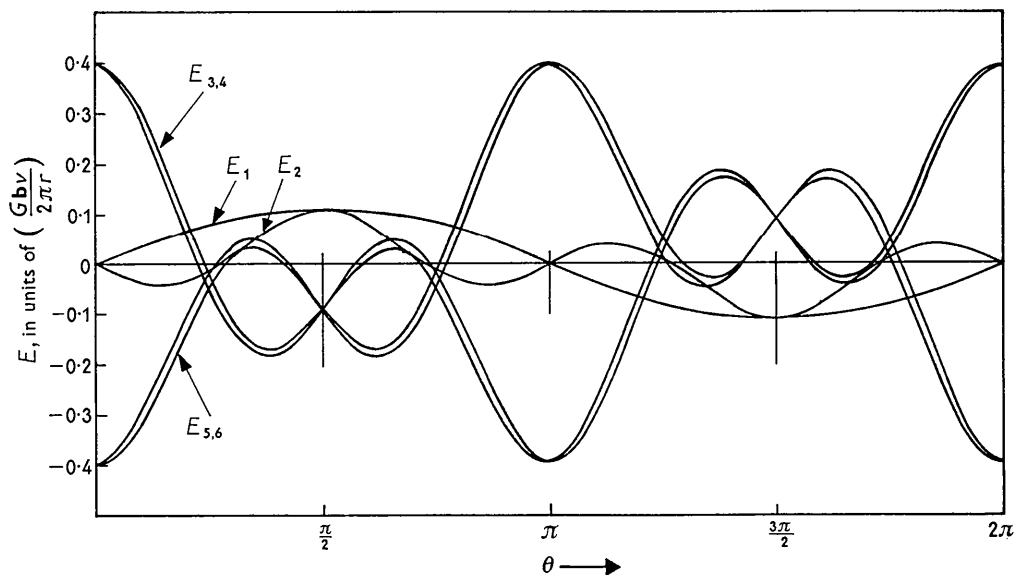Fig. 4. Interaction energy of a screw dislocation with a Ca defect cluster.

Fig. 5. Interaction energy of an edge dislocation with a Ca defect cluster (Poisson's ratio, $\nu = 0.25$).

$$E_{1,2} = \frac{Gbv}{2\pi(1-\nu)r}[0.0908(\sin^3\theta + \sin\theta) - 0.408\nu\sin\theta$$

$$\pm 0.0966\sin\theta\cos^2\theta]$$

$$E_{3-6} = \frac{Gbv}{2\pi(1-\nu)r}[\pm 0.2948\cos\theta\cos 2\theta - 0.0566$$

$$\times(\sin^3\theta + \sin\theta) + 0.1816\nu\sin\theta$$

$$\pm 0.0327\sin\theta\cos^2\theta]. \qquad (14)$$

The interaction energies, in the units of $Gbv/2\pi r$, are plotted versus θ in Fig. 4 for a screw dislocation and Fig. 5 for an edge dislocation. It can be seen that if the terms in equations (13) and (14) due to the shear strains of equation (12) are omitted, the interaction energies shown in these Figures are of the same form as those for the single [100] Ca impurity–vacancy pairs, equations (8) and (9).

Discussion

The strong interaction between a screw dislocation and the various impurity–vacancy defects in sodium chloride containing calcium is noteworthy. An exact evaluation of the tetragonal strain associated with the calcium impurity–vacancy pairs in sodium chloride is difficult. Some idea of the distortion, however, may be gained from a comparison with that given by equation (12) for the defect clusters. Since the distortion for a defect cluster is essentially tetragonal in the $\langle 100 \rangle$ direction, the tetragonal strain for a $\langle 100 \rangle$ Ca impurity–vacancy defect will be of the order of, or more probably slightly greater than, that given by equation (12). If one uses the approximate relationship that the tetragonal strain associated with the defect pairs varies inversely as the square of the distance between the Ca impurity and the sodium ion vacancy, the following estimates of the tetragonal strain parameter $(\varepsilon_I - \varepsilon_{III})$ are obtained: ~ 0.6 to 0.8 for a $\langle 110 \rangle$ defect, ~ 0.3 to 0.4 for a $\langle 100 \rangle$ defect, and ~ 0.2 to 0.25

for a $\langle 112 \rangle$ defect. It is hoped that mechanical relaxation experiments using sodium chloride containing the various defect pairs will lead to an experimental evaluation of the magnitude of the shear distortions. Such studies are now being undertaken by the authors.

Since the mobility of screw dislocations is particularly important in the plastic deformation of crystalline solids, the strong interaction is expected to lead to significant strengthening of the NaCl structure. For single impurity–vacancy pairs where reorientation of the pairs with respect to the stress fields of a moving dislocation takes place by one or two nearest neighbor jumps of the sodium ion vacancy around the calcium impurity, strengthening is most probably due to a cloud-dragging mechanism similar to the Snoek effect proposed for the case of carbon in α iron (Schoeck & Seeger, 1959). For the case of defect clusters where reorientation will depend on coordinated movements of both the impurity ions and the cation vacancies, strengthening takes place most likely by a slightly different mechanism such as the one proposed by Fleischer (1962). A detailed discussion of the subject is being published separately (Pratt, Chang & Newey, 1963).

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