# LOW TEMPERATURE YIELD STRESS INCREMENT DUE TO IMPURITY-VACANCY DIPOLES IN NaCl CRYSTALS*

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The yield stress increment of NaCl crystals caused by impurity-vacancy dipoles containing $Mg^{2+}$, $Sr^{2+}$ and $Ba^{2+}$ impurity ions is calculated on the assumption that it is essentially controlled by the interaction between the dipoles and screw or edge dislocations. For calculation of the elastic strength of the dipoles the ionic displacements around them are calculated using the semiclassical Born—Mayer theory of ionic solids. There is no fitting parameter applied throughout the calculations.

## Introduction

It is generally accepted that divalent cation impurities significantly influence the mechanical properties of NaCl type crystals [1, 2]. A theoretical calculation of the low temperature yield stress increment in NaCl crystals due to rigid $Ca^{2+}$ ion—cation vacancy dipoles was given in [3] recently. Following the method described there further calculations have been made to obtain the yield stress increment for the dopants Mg, Sr and Ba in NaCl crystals. Since the method of calculation has been detailed in [3], only a brief account of the main points is given here. The lattice distortion around the dipole, i.e. the displacements of the chlorine ions nearest to the dipole, are determined on the basis of the semiclassical Born—Mayer theory of ionic solids. From the displacements obtained in this way the mean strain tensors ascribed to dipoles of different impurity ions are calculated. The interaction energy and thus the force acting between the dipole and a dislocation are determined with the use of the continuum theory. Once a general formula is found for the force acting on the moving dislocation from the dipoles of different orientations with respect to and at different distances from the slip plane, the yield stress increment is straightforward to determine by Friedel's formula [4]. The calculation is carried out for screw and edge dislocations as well.

## Method of computation

In the lattice distortion calculation the crystal is divided into two regions. Region I includes the divalent impurity ion, the cation vacancy and their nearest neighbour chlorine ions (Fig. 1). Here all the variables (ionic displacements and ionic
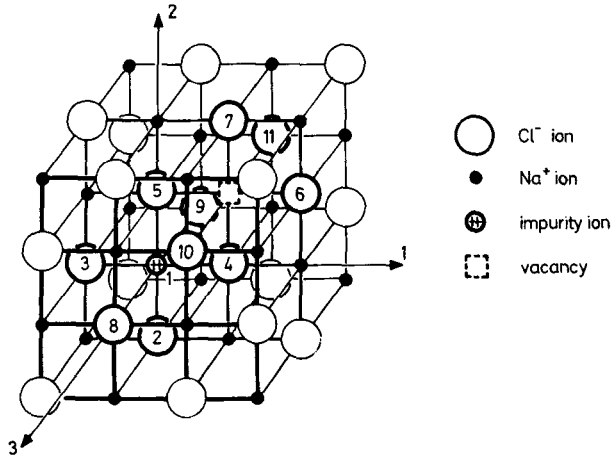
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*Fig. 1.* The frame of reference and region I used in lattice distortion calculation. The divalent impurity and all the ions numbered are in region I

polarizabilities) are calculated simultaneously. Region II contains the rest part of the crystal, where only the ionic polarizations are taken into account [5] using rigid boundary condition.

The equilibrium displacements and dipole moments (66 variables) of the ions in region I are determined by the solution of coupled nonlinear force balance and polarization equations. The number of independent variables and equations can be reduced to 22 through the symmetry relations of the n.n. dipole. The symmetry relations, the system of the remaining nonlinear equations and the two-body potentials together with the parameters used are given in paragraph 2 of [3].

Taking the dipole to be point-like, i.e. neglecting the variation of the stress field of the dislocation over the defect volume, the dipole—dislocation interaction energy

$$E_1^n = V_d \bar{\varepsilon}_{ij}^n \sigma_{ij}^D(\mathbf{x}_d), \tag{1}$$

where $V_d$ is the defect volume (in our case $8a_0^3$; $a_0$ is the cation—anion distance), $\sigma_{ij}^D(\mathbf{x}_d)$ is the stress of the dislocation at the centre $\mathbf{x}_d$ of the dipole and the mean strain tensor characteristic of the dipole $\bar{\varepsilon}_{ij}^n$ is the following

$$\bar{\varepsilon}_{ij}^n = \frac{1}{V_d} \int\limits_{V_d} \varepsilon_{ij}^n \, dV . \tag{2}$$

The suffix $n$ refers to the orientation of the dipole. When calculating the mean strain tensor from formula (2) the volume integral can be transformed into a surface integral of the displacement field over the defect surface, i.e. the surface covering the defect volume presented in Fig. 2. Furthermore, since the displacement field is given by the
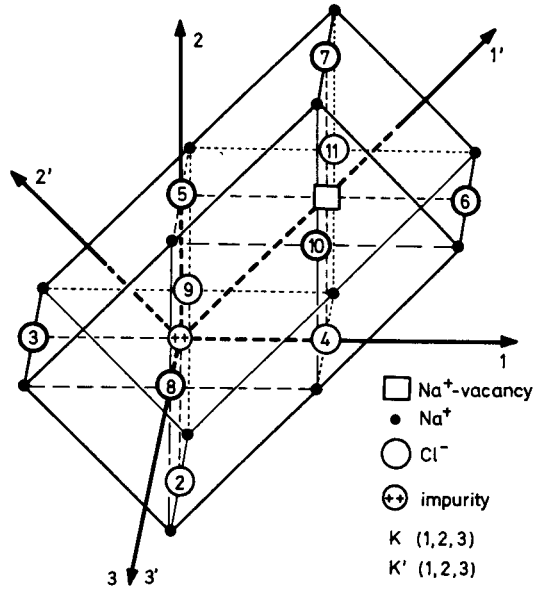
*Fig. 2.* The frames of reference, the defect volume and surface used in the calculation of the mean strain tensor of the impurity—vacancy dipole

discrete values of the ionic displacements the integral is approximated by a simple sum of the products of the displacements and the corresponding surface element vectors. As the mean strain tensor of the dipole obtained in this way is given in its principal axes system $K'$ (Fig. 2), it has to be transformed into the system of the dislocation, where the stress field $\sigma_{ij}^D$ is known [6]. The transformed mean strain tensor is denoted by $\bar{\varepsilon}_{ij}^n$. The suffix $n$ referring to the orientation of the dipole can take on integer values 1—12 according to the twelve possible orientations the dipole can have at a given location of the impurity ion. The explicit formulae for the appropriate dipole—dislocation interaction energies for edge and screw dislocations can also be found in [3].

The force $f_x^n$ acting on a moving dislocation can be deduced from the interaction energy $E_I^n(x, y)$:

$$f_x^n(x, y) = -\frac{\partial}{\partial x} E_I^n(x, y) \tag{3}$$

with the dislocation moving along axes $x$ in its slip plane at distance $y$ from the centre of the dipole of orientation $n$. The maxima $f_m^n(y)$ of the force can be computed from

$$\frac{\partial}{\partial x} f_x^n(x, y) = 0. \tag{4}$$

The yield stress increment caused by fixed, localized dipoles can be given by the generalized Friedel relationship [3, 4, 7]

$$\Delta \tau = \frac{1}{(2T)^{1/2}b}\left[\sum_{n,i}(f_m^n(y_i))^3 c_{pi}^n\right]^{1/2}.\qquad (5)$$

Here $c_{pi}^n$ is the planar concentration of dipoles of orientation $n$ in the $i$-th plane at distance $y_i$ from the slip plane, $f_m^n(y_i)$ is the maximum of the force the dislocation must overcome as it passes a corresponding obstacle, $T$ is the line tension of the dislocation and $b$ is the magnitude of its Burgers vector.

## Results and discussion

The ionic displacements around the dipoles of $Mg^{2+}$, $Sr^{2+}$ and $Ba^{2+}$ impurity ions are similar to those obtained in [3] for $Ca^{2+}$ impurity. The only difference appears in the magnitude of the displacements yielding different mean strain tensors for dipoles containing different impurity ions. The principal strains are given in Table I.

In the calculation of the yield stress caused by dipoles of given impurity the effects of those dipoles have been taken into account, which give a maximum force $f_m^n$ greater than one tenth of the greatest one. The problem of intersected dipoles is dealt with as before [3].

Rearranging Eq. (5) the yield stress increment can be expressed through the atomic concentration $c$ of the dipoles in the general form:

$$\Delta \tau = \beta \cdot c^{1/2}.\qquad (6)$$

The different values obtained for $\beta$ in the case of screw and edge dislocation for different impurity ions are given in Table II. It can be seen that similarly to the case of the $Ca^{2+}$ impurity [3] the $\beta$ values and thus the calculated yield stress values are much higher for edge dislocation than for screw dislocation.

In the following we discuss only the screw dislocations, firstly because the yield stress calculated for $Ca^{2+}$ ion—cation vacancy dipoles interacting with screw

**Table I**

The principal strains of the dipoles with different impurity ions

| Principal strain | Impurity ion | | | |
|---|---|---|---|---|
| | $Mg^{2+}$ | $Sr^{2+}$ | $Ba^{2+}$ | $Ca^{2+}$ |
| $\bar{\varepsilon}_{11}$ | 0.034 | 0.031 | 0.028 | 0.032 |
| $\bar{\varepsilon}_{22}$ | 0.041 | 0.229 | 0.192 | 0.066 |
| $\bar{\varepsilon}_{33}$ | −0.092 | −0.118 | −0.101 | −0.088 |

**Table II**

The $\beta$ values in formula (6) for edge and screw dislocations and for different impurity ions

| | | Impurity ion | | | |
|---|---|---|---|---|---|
| | | $Mg^{2+}$ | $Sr^{2+}$ | $Ba^{2+}$ | $Ca^{2+}$ |
| $\beta$ (MPa) | Screw | 1900 | 6 000 | 4 700 | 2 100 |
| | Edge | 5100 | 65 500 | 50 100 | 8 000 |

dislocations [3] are in agreement with the low temperature yield stress values measured in NaCl crystals doped with Ca [8], and secondly because the mechanism giving the lower yield stress is expected to control the process.

The calculated results are valid at 0 K, and can only be compared with those of low temperature measurements. Such experiments have been made in NaCl:Ca system [8], but no data of this kind are available for the other three impurities. However, some rough consideration can be made in order to compare our results with experimental data obtained at room temperature. We cannot compare of course the yield stress values themselves, because in these crystals the yield stress at room temperature is thought to be caused mainly by Snoek effect [9, 10] and not by the Fleischer-type [1] rigid obstacles used in our calculations. But one can use the tetragonality values ($\Delta\lambda$) characterizing the dipoles as obtained from room temperature yield stress measurements [11] on the basis of Frank's formula for the Snoek effect [12]. We can also evaluate the tetragonality values from our calculated yield stress data as if they were experimental ones using the expression for Fleischer-type interaction [1]. Since the tetragonality is in proportion to our $\beta$ value, we can use it for a rough comparison provided we compare only the relative quantities

$$\beta_r = \frac{\beta}{\beta_{Ca}}, \tag{7}$$

$$\lambda_r = \frac{\Delta\lambda}{\Delta\lambda_{Ca}} \tag{8}$$

for different impurities. Here $\beta_{Ca}$ and $\Delta\lambda_{Ca}$ means the appropriate quantities for Ca impurity. The $\beta_r$ and $\lambda_r$ values are given in Table III. As can be seen, the dependence of tetragonalities of both kinds on the type of the impurity ion has the same character.

**Table III**

Relative tetragonalities obtained from experimental ($\lambda_r$) and theoretical ($\beta_r$) yield stress data

| | Impurity ion | | | |
|---|---|---|---|---|
| | $Mg^{2+}$ | $Sr^{2+}$ | $Ba^{2+}$ | $Ca^{2+}$ |
| $\lambda_r$ | 0.8 | 2.1 | 1.5 | 1.0 |
| $\beta_r$ | 0.9 | 2.9 | 2.2 | 1.0 |

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