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## The Charge on Dislocations in Alkali Halides for the Case of a Saturated Region<sup>3)</sup>

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The case of a charged dislocation with a saturated region is considered, allowing for the discrete nature of charges and defects on the core of the dislocation. The potential due to the charged dislocation is obtained by combining the results of Kliever and Koehler with those of Whitworth. The method used in this case to determine the charge on the dislocation, is the same as that of Whitworth.

On considère le cas d'une dislocation chargée, ayant une région saturée, en prenant compte de la nature discrete des charges et des défauts au voisinage de la ligne de dislocation. Le potentiel produit par cette dislocation est obtenu par considération des résultats de Kliever et Koehler et ceux de Whitworth. La méthode utilisée pour déterminer la charge dans la dislocation est celle de Withworth.

### 1. Introduction

Atomistic models to determine the core structure of dislocations in ionic crystals have been published recently [1]. Using these models it is possible to formulate the problem of the charge on a dislocation in a more precise manner. Nevertheless, it is still necessary and worthwhile to work with the general ideas concerning the more common models of the charge on a dislocation.

Eshelby et al. [2] were the first to extend the ideas connected with charged surfaces to the case of a dislocation. Brown [3] and Phariseau [4] took these ideas further solving the problem of the charge on a dislocation, but only in the limit of high temperatures. Koehler et al. [5] presented a series of calculations attempting [6] to determine the charge on a dislocation for any temperature. Later on, Kliever and Koehler [7] and Kliever [8] came up with a new and more complete theory of charged surfaces which could be easily extended to charged dislocations.

Whitworth [9], on the other hand, presented a model very similar to those already referred to, but taking into account that dislocations are not infinite sources or sinks of vacancies. In a somewhat more recent review paper, Whitworth [10] has discussed the present situation regarding the problem of the charge on a dislocation.

### 2. Theory

In this work we have considered a charged dislocation in which there is a saturated region. This problem has not been adequately treated using the more recent results of Whitworth [11]. Furthermore, the ideas of Kliever and Koehler [7] have been extended to the case of charge dislocations and combined with the results of Whitworth

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[11] in such a way that the formulation of the theory for charged dislocations comes out in a more satisfactory manner, as will be discussed in our concluding remarks.

Initially, it was intended to extend the work by Koehler et al. [5] in such a way that the results of Kliewer and Koehler [7] and Kliewer [8] could be incorporated; however, it was not possible to accurately match the solution of the equation for the charged dislocation, namely

$$\nabla^2 p = w \sinh(p - p_0) \quad (1)$$

in three regions of space. The first of these three regions used by Koehler et al. [5] is the saturated region in which  $\nabla^2 p = 4\pi N e^2 / \epsilon k T$ , where  $p = e\Phi/kT$ . Here  $\Phi$  is the electrical potential,  $e$  the electron charge,  $k$  the Boltzmann constant, and  $T$  the temperature. The second region is one in which  $\sinh(p - p_0) \approx -\exp(p - p_0)/2$ , with  $p_0 = e\Phi_0/kT$  (in the paper of Koehler et al. [5],  $\Phi_0 = \Phi_R$ , the electrical potential at midpoint between neighboring dislocations). In our present work, however,  $\Phi_0 = -\Phi_c$  (the potential at the core of the dislocation). The third region is that for which  $\sinh(p - p_0) \approx 1.192(p - p_0)$ , calculated at the point where  $p - p_0 = -1.5$ . The mathematical reasons why these solutions cannot be accurately matched, have been discussed in a previous work by Ruíz Mejía et al. [6], and thus, following the method outlined in [5], it is not possible to determine the charge on the dislocation. Thus, we have solved equation (1) numerically as outlined in the present work, with  $w = (8\pi^2 N e^2 / \epsilon k T) C$ , where  $N$  is the density of anion or cation sites,  $\epsilon$  the dielectric constant, and  $C$  the fractional divalent positive ion concentration as in the work of Koehler et al. [5], but in our case  $C = \exp[(-e\Phi_c - F^+)/kT]$ , where  $F^+$  is the free energy of formation for cation vacancies [7]. In the case discussed in [5], equation (1) is valid for cases in which  $\frac{1}{2}C \gg \exp[-(F^+ + F^-)/2kT]$ , where  $F^-$  is the free energy of formation for anion vacancies. In our case, in which  $w = 8\pi N e^2 / \epsilon k T \times \exp(-e\Phi_c - F^+)/kT$ , equation (1) is always valid. The work of Koehler et al. [5] has been criticized by Whitworth [9] and others authors like Hirth [12] basically because they did not take into account the fact that dislocations are not infinite sources or sinks of vacancies. Such an objection could in fact be raised against the papers of Kliewer and Koehler [7] and Kliewer [8]. A more complete discussion on the formulation of the problem has already been given by Hirth and Lothe [13] allowing for different types of jogs on the dislocation. Finally, a solution to the problem of determining the charge on a dislocation has been given by Whitworth [11], taking into account the discrete nature of the charges on a dislocation, which can also be applied to semiconductors, but in the case of alkali halides reduces to our equation (1).

We have followed Whitworth's [11] idea of dividing the free energy,  $G$ , into the sum of three contributions, i.e., the electrostatic energy for a uniform distribution of charge on the core of the dislocation, the free energy associated with the defects on the dislocation core, and the corresponding free energy of the defects in the rest of the crystal.

The main difference between the present work and Whitworth's [11] is our consideration of a saturated region and that we have solved equation (1) following a different method. The procedure for determining the charge is the same in both cases.

### 3. Solution of Poisson's Equation for the Case of a Saturated Region

In reference [11], solutions of (1) have been given for a set of values of  $q_1/T$ , where  $q_1$  is the charge on a dislocation and  $T$  the temperature (in K). Following Kliewer [8], we have considered a set of values of  $q_1$  and a set of values for the number of free impurities on the core per  $\text{cm}^3$ , which varies from  $2.25 \times 10^{22}$  to  $(2.25 \times 10^{22})/180$ . In fact, Kliewer [8] considered that in the saturated region the number of divalent impurities was equal to the number of cation sites ( $N = 2.25 \times 10^{22}$  in NaCl). Physically, however, lower concentrations are possible.

According to Kliever [8] we have learned that in the saturated region the Lagrange parameter is given by

$$\alpha_L^- = kT \ln \left( \frac{N - n_{if}}{n_{if}} \right). \quad (2)$$

For a given fixed temperature, several  $\alpha_L^\pm$  were calculated for different values of  $n_{if}$ . It can easily be shown [8] that the potential on the dislocation core,  $\Phi_c$ , satisfies

$$-p_c = -\frac{e\Phi_c}{kT} = \frac{1}{2} \frac{F^+ - \alpha_L^\pm}{kT}. \quad (3)$$

In fact, in references [5, 7, 8] the boundary condition is that the potential on the dislocation or on the surface of the crystal is zero. We have followed Hirth and Lothe [13] in assuming that the potential on the core of the dislocation has the value  $\Phi_c$  different from zero. This assumption slightly modifies Kliever's [8] and Kliever and Koehler's [7] equations.

In the saturated region, equation (1) has an analytical solution of the form

$$p = b \ln Kr - Br^2, \quad (4)$$

where  $b$  and  $K$  are integration constants. For  $B$  we have

$$B = \frac{\pi n_{if} e^2}{\epsilon kT}. \quad (5)$$

Then, using (4) and (5) and if  $a$  is the core radius, one can write

$$K = \frac{1}{a} \exp \frac{\alpha_L^\pm - F^+}{2kTb} + \frac{Ba^2}{b}. \quad (6)$$

Now, if  $r_0$  denotes the width of the saturated region, then

$$b \ln (Kr_0) - Br_0^2 = -\frac{\alpha_L^\pm}{kT} \quad (7)$$

must hold [8]. Equations (6) and (7) form a set of two equations with three unknowns, i.e.  $b$ ,  $K$ , and  $r_0$ . On the other hand, one of the boundary conditions at the core of the dislocation will be given by

$$\left( \frac{\partial p}{\partial r} \right)_c = -\frac{2eq_1}{\epsilon kTa} \quad (8)$$

which would allow us to fix  $b$  according to

$$b = 2Ba - \frac{2q_1 e}{\epsilon kT}. \quad (9)$$

Thus, it becomes possible to solve equation (6) and the transcendental equation (7).

In Table 1 we show a list of solutions to (7) for a set of values of  $n_{if}$  and  $q_1$ .

Knowing  $b$  and  $K$ ,  $p_c$  can be determined from (4). Using this value and that of  $(\partial p / \partial r)_c$ , we can then integrate equation (1) numerically. In Table 2 we give some values of the potential determined in this way, as a function of  $r$ .

There are certain values of  $n_{if}$  and the charge for which there are no solutions of (7). In general, however, one cannot find solutions to (7) if the values for  $n_{if}$  are kept below  $N/180$  and the charge  $q_1$  is smaller than 0.01 e.s.u./cm, which is the maximum possible charge on the dislocation. Numerical solutions to (1) were found for all the values of  $p_c$  and  $(\partial p / \partial r)_c$  which were used.

Table 1

Solutions of equation (7) for different values of the charge  $q$  (e.s.u.) and the density of impurities,  $n_{if}$  ( $\text{cm}^{-3}$ ), in the saturated region.  $r_0$  is given in  $\text{cm}$

$n_{if}$ ( $10^{21} \text{ cm}^{-3}$ )	$q$ (e.s.u.)	$r_0$ ( $10^{-7} \text{ cm}$ )
0.35	-0.01	0.857
0.27	-0.01	0.843
0.21	-0.009	0.8298
0.35	-0.009	0.864
0.27	-0.009	0.848
0.21	-0.009	0.833
0.35	-0.008	0.873
0.27	-0.008	0.854
0.21	-0.008	0.837
0.35	-0.007	0.886
0.27	-0.007	0.864
0.21	-0.007	0.843
0.35	-0.006	0.903
0.27	-0.006	0.875
0.31	-0.006	0.851
0.33	-0.004	0.927
0.27	-0.004	0.924
0.21	-0.004	0.895
0.17	-0.002	0.914
0.15	-0.002	0.871

The potentials obtained are all negative and cross the  $r$  axis for certain large values of  $r$ . This is due to the fact that the solution of (1), for large values of  $r$ , is the sum of two Bessel functions:

$$p = A K_0\left(\frac{r}{\lambda}\right) + B' I_0\left(\frac{r}{\lambda}\right), \quad (10)$$

where  $I_0$  is a function which diverges with distance. The second boundary condition on the potential is applied setting  $B' = 0$ . That is, in the numerical solution, for large values of  $r$ , but such that the potential is negative and  $I_0(r/\lambda)$  is small, we set the numerical value of  $p$  equal to  $A K_0(r_1/\lambda)$  and determine  $A$ . For values of  $r > r_1$ , we substitute the numerical solution with the analytical solution  $A K_0(r/\lambda)$ . This is in fact equivalent to the procedure followed by Whitworth [11] of considering  $A K_0(r/\lambda)$  as the solution at great distances and integrating numerically a more general equation than (1), taking as the starting point one in which  $A K_0(r/\lambda)$  is the valid solution for the potential. Thus, one would expect a set of solutions to (1) for different values of the charge and  $n_{if}$ , at a given temperature. But not all those potentials, however, obey the condition

$$n_d \left[ \int_a^R n_{ib} 2\pi r \, dr + \int_a^R n_{if} 2\pi r \, dr \right] = c, \quad (11)$$

where  $n_d$  is the number of dislocations per  $\text{cm}^3$ ,  $R$  is half the distance between neighboring dislocations, and  $c$  is the number of impurities per  $\text{cm}^3$ .

Each integral in (11) splits into the sum of two more:

$$n_d \left[ \left( \int_a^{r_0} n_{ib} + \int_{r_0}^R n_{ib} \right) 2\pi r \, dr + \left( \int_a^{r_0} n_{if} + \int_{r_0}^R n_{if} \right) 2\pi r \, dr \right] = c, \quad (12)$$

Table 2

Left-hand side of equation (11) as a function of the charge  $q$  (e.s.u.) and the impurity density,  $n_{if}$  ( $\text{cm}^{-3}$ ), at the core. Also given are the values of  $p$  and  $w$  of (1) for temperature  $T = 500\text{K}$  and  $F^\tau = 1.09 \times 10^{-12}$  erg, the free energy of formation for a cation

$q$ (e.s.u.)	$n_{if}$ ( $10^{21} \text{ cm}^{-3}$ )	$p$	$w$ ( $10^{11} \text{ cm}^{-2}$ )	l.h.s. equation (11) $\times 10^{-17}$
0.01	0.17	-5.50	0.2538	2.688
0.01	0.15	-5.44	0.2239	2.369
0.01	0.13	-5.37	0.1941	2.050
0.009	0.17	-5.50	0.2538	3.012
0.009	0.15	-5.44	0.2239	2.653
0.009	0.13	-5.37	0.1941	2.296
0.008	0.17	-5.50	0.2538	3.423
0.008	0.15	-5.44	0.2239	3.015
0.008	0.13	-5.37	0.1941	2.610
0.007	0.17	-5.50	0.2538	3.963
0.007	0.15	-5.44	0.2239	3.492
0.007	0.13	-5.37	0.1941	3.022
0.006	0.17	-5.50	0.2538	4.707
0.006	0.15	-5.44	0.2239	4.146
0.006	0.13	-5.37	0.1914	3.588
0.005	0.17	-5.50	0.2538	5.793
0.005	0.15	-5.44	0.2239	5.102
0.005	0.13	-5.37	0.1941	4.416
0.004	0.17	-5.50	0.2538	7.529
0.004	0.15	-5.44	0.2239	6.632
0.004	0.13	-5.37	0.1941	5.739

where  $n_{ib}$  is the density of bound impurities, and we have two expressions for them, one inside the saturated region and the other outside of it. Equations (11) and (12) are equivalent to those given by Kliewer [8] for the surface case, but in our expression  $c$  has a meaning different from that of  $c$  and the dislocation density takes part. The expressions for  $n_{ib}$  and  $n_{if}$  in the saturated region have been given by Kliewer [8] for the surface case and are also valid for the dislocation case, except that we substitute  $\Phi - \Phi_c$  for  $\Phi$ . The corresponding expressions outside of the saturated region have been given by Kliewer and Koehler [7], where we have also substituted  $\Phi - \Phi_c$  for  $\Phi$ . In fact, in the saturated region  $n_{if}$  is constant and can take any value between  $N$  and  $N/180$ . Outside of the saturated region,

$$n_{if} = N \exp \left( p_c + \frac{\alpha_L^+}{kT} \right) \exp(-p). \quad (13)$$

For the case of the surface, one can obtain an analytical solution for the potential  $p$  [7], and it is then possible to obtain a closed expression starting from the equation equivalent to our equation (12), which relates  $\alpha_L^+$  with  $p_c$  and other crystal parameters. In our case, there is no analytical solution for  $p$  [6] and thus, we have used a numerical solution of (1) in order to find the potential  $p$  for a given charge, temperature, and impurity concentration  $c$ , that satisfies equation (12). An example of that calculation is shown in Fig. 1, for  $T = 400 \text{ K}$ ,  $q = 0.01$  e.s.u.,  $n_{if} = 0.14 \times 10^{21} \text{ cm}^{-3}$ , and  $c = 2.25 \times 10^{17} \text{ cm}^{-3}$ .

We have considered several temperatures and two  $c$ -values. It was found that for each charge on the dislocation,  $q_1$ , there is at the most one solution to (12) that corresponds to a certain  $n_{if}$ . In each case, the dislocation density was determined in an

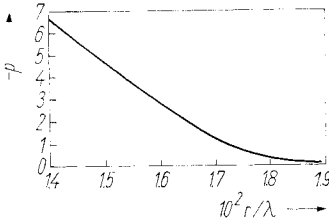


Fig. 1. Graph of the potential  $p$ , obtained by solving numerically (1), for a charge  $q = 0.01$  e.s.u.,  $T = 400$  K,  $n_{if} = 0.14 \times 10^{21}$  cm $^{-3}$ , and  $c = 2.25 \times 10^{17}$  cm $^{-3}$

approximate way, assuming that the distance between dislocations is about  $1/\lambda$ , and using the relation [7]

$$n_d = \frac{1}{\pi R^2 l}. \quad (14)$$

For charges between 0.01 and 0.008 e.s.u./cm one always finds a value  $n_{if}$  between  $N$  and  $N/180$ , which satisfies equation (12). For smaller charges, one can get an optimum  $n_{if}$ , but it will not satisfy (12) exactly. If the charge is lowered, the error becomes larger. The results are shown in Table 3. When a set of potentials associated with a given charge, temperature, and  $c$  is obtained, Whitworth's [11] method can then be followed in order to determine the charge in the case of the saturated region.

Table 3

Left-hand side of equation (11) as a function of temperature ( $kT$  in erg), impurity concentration in the crystal,  $c$  (cm $^{-3}$ ), and  $F_M$  (eV) related to the cation free energy of formation,  $F^+$ , in the form:  $F_M = F^+ + 3.1kT$ . The impurity concentration at the core,  $n_{if} = 0.13 \times 10^{21}$  cm $^{-3}$ , and the charge on the dislocation,  $q = 0.007$  e.s.u., are the same in all cases

$kT$ ( $10^{-13}$ erg)	$c$ ( $10^{17}$ cm $^{-3}$ )	$F_M$ (eV)	l.h.s. equation (11) $\times 10^{-17}$
0.69	2.25	0.7	2.964
0.75	2.25	0.8	2.989
0.69	0.225	0.8	3.016
0.85	2.25	0.8	2.905
0.4	2.25	0.8	3.088
0.69	2.25	0.6	2.812
0.69	2.25	0.8	3.022

#### 4. Conclusions

We have extended Kliever and Koehler's [7] and Kliever's [8] works in order to consider the case of a charged dislocation. The results obtained in this way are then combined with those of Whitworth [11] to take into account the electrostatic energy and the discrete nature of the defects on the line of the dislocation. Both Whitworth [11] and the authors solve (1) before considering the electrostatic energy and the free energy of the defects on the dislocation core. In a general sense, we claim that our method of solving that equation is better, since in [11] the starting point is the solution valid for large distances, namely  $A K_0(r/\lambda)$ , where  $A$  is determined from the condition given by (8) at the core of the dislocation. Once  $A$  has been determined, they then obtain the potential  $p$  and its derivative at a distant point, and with that information integrate

(1) immediately for all  $r$ . It must be observed, however, that in applying (11) to the function  $A K_0(r/\lambda)$ , it is implicitly assumed that such a function is valid at the core of the dislocation, and that this assumption is not necessarily correct in all cases. The determination of a point  $r$ , where the potential due to a distribution of discrete charges and the solution to (1) have the same slope (equation (19) in [11]), presents problems in our case as those already discussed in [11].

On the other hand, the potentials we have obtained from (1) and the solutions reported by Whitworth [11] are very similar, except that the value of the potential that we obtain at the core, is apparently slightly larger than that reported by Whitworth [11]. (In fact, in that reference curves are shown for  $r/\lambda > 0.1$ , but  $r = 0.1\lambda$  does not necessarily correspond to the dislocation core.)

Finally, it may be noted that equation (12) holds only for large values of the charge, which itself implies large values of  $n_{if}$ . This may be due to several reasons: First, we note that the equations from Kliewer [8], that we have used, are only valid for large values of  $n_{if}$ . We must also point out that the way we have determined  $n_d$  is only approximate, and if larger values of that quantity are possible, equations (12) will hold in an exact manner for a greater number of cases.

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