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Space Charge in Ionic Crystals. II. The Electron Affinity and Impurity Accumulation*

K. L. Kliewer

Institute for Atomic Research and Department of Physics, Iowa State University, Ames, Iowa

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By relaxing the condition that all defect densities be small, the calculation of the defect distribution in ionic crystals containing divalent cationic impurities is extended to lower temperatures. The impurity accumulation near the surface and the electron affinity are discussed.

I. INTRODUCTION

In the preceding paper[1] a general method was presented for calculating the defect distribution in an ionic crystal of the form M^+X^- possessing the NaCl structure. It was shown that the presence of a space-charge region at the surface is an inherent aspect of thermal equilibrium. The discussion in I was limited to $\{100\}$ surfaces and to situations where all the defect concentrations were small.

We are now going to consider crystals of the same type discussed in I with emphasis on crystals containing divalent cationic impurities. We found in I that for such crystals, in the temperature range where the defect concentrations are essentially governed by the impurity content, the impurities tend to concentrate in the vicinity of the surface. An examination of this accumulation effect for moderate temperatures necessitates a relaxation of the condition that all impurity concentrations are small everywhere. The formal calculation is carried out in Sec. II. In Sec. III the extent of this accumulation is discussed for a model representing NaCl.

There have been several studies[2,3] in which the energy of the bottom of the conduction band with respect to the vacuum level was calculated for NaCl. These calculations did not yield results in agreement with experimental determinations of the electron affinity. The presence of the space-charge region at the surfaces will clearly contribute to the experimental electron affinity. In addition the crystal plane comprising the surface is of importance. These features are the subject of Sec. IV.

Inadequacies of the present treatment are discussed in Sec. V.

II. DEFECT DISTRIBUTION IN IMPURE CRYSTAL

Let us briefly review the model to be used in the calculation. We consider a crystal with free (100) surfaces at $x=0$ and $x=2L$ and of infinite extent in the y and z directions. The crystal is to have the NaCl structure with the intrinsic disorder being of the Schottky type. We assume that the smoothed charged-defect distribution gives rise to a potential satisfying Poisson's equation with the boundary conditions on the potential being $\Phi=0$ and $x=0$ and $x=2L$ and $d\Phi/dx=0$ at $x=L$ as discussed in I. The crystal, containing a mean divalent cation impurity content $\bar{C}$, is considered to be in thermal equilibrium.

The reason the solution presented in I becomes invalid for reduced temperatures is that the assumption $n_{if}/N \ll 1$ becomes invalid in the surface region, that is, a significant degree of impurity accumulation occurs near the surface. A measure of the breakdown of this assumption is that if we use the expression for n_{if} obtained in the low concentration approximation [Eq. (4.5) of I], then $n_{if}/N=1$ at the surface when the condition

$$\bar{C}=z_{nn}\exp\{-(F^+-B_+)/kT_1\} +\xi_+\exp\{-e\Phi_\infty/kT_1\} \quad (2.1)$$

is satisfied. The temperatures T_1 at which this occurs for the NaCl parameters introduced in I are given in Table I.

Table I. Values of T_1, the temperature which measures the breakdown of the assumption $n_{if}/N \ll 1$, in °K, for $L=1.0$ cm.

B_+(eV) \ $\bar{C}$	10^{-6}	10^{-5}	10^{-4}	10^{-3}
0.20	302	353	424	532
0.40	239	272	313	371
0.60	119	136	157	186

To obtain a solution to the problem when the assumption $n_{if}/N \ll 1$ is no longer valid, we must begin with the general expressions for the defect densities obtained from a minimization of the free energy [see Eqs. (4.3) of I]. We now assume that all defect concentrations except that of the free impurities are small everywhere. We then have

$$\begin{aligned} n_+/(N-n_{if})&=\exp\{-(F^+-e\Phi)/kT\}\,,\\ n_-/N&=\exp\{-(F^-+e\Phi)/kT\}\,,\\ n_{if}/(N-n_{if})&=\exp\{-(e\Phi+\alpha_L{}^+)/kT\}\,, \quad (2.2)\\ n_{ib}N/(N-n_{if})^2&=z_{nn}\exp\{-(F^+-B_++\alpha_L{}^+)/kT\}\,,\\ n_B/(N-n_{if})&=z_n\exp\{-(F^++F^--B)/kT\}\,, \end{aligned}$$

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[1] K. L. Kliewer and J. S. Koehler in preceding paper, Phys. Rev. 140, A1226 (1965), hereafter referred to as I. All notation in the present paper is the same as in I.

[2] S. Tibbs, Trans. Faraday Soc. 35, 1471 (1939).

[3] Z. Ya. Evseev, Fiz. Tverd. Tela. 5, 2345 (1963) [English transl: Soviet Phys.—Solid State 5, 1705 (1964)].

where α_L^+ is now the Lagrange multiplier which arises from the need for impurity conservation.[4] The charge density ρ given by

$$\rho = e(n_- + n_{if} - n_+) \tag{2.3}$$

becomes, using (2.2),

$$\rho = eN\left[\frac{1-\exp\{(-F^+ + 2e\Phi + \alpha_L^+)/kT\}}{1+\exp\{(e\Phi+\alpha_L^+)/kT\}}\right], \tag{2.4}$$

where we have ignored the anion vacancy contribution because of the temperatures we are considering.

We showed in I that there exists bulk neutrality within the crystal when $\kappa_+ L \gg 1$ where

$$\kappa_+^2 = (8\pi N e^2/\epsilon kT)\exp\{(e\Phi_\infty - F^+)/kT\}. \tag{2.5}$$

The potential in the region of bulk neutrality Φ_∞ is now given by

$$e\Phi_\infty = \tfrac{1}{2}(F^+ - \alpha_L^+), \tag{2.6}$$

as is clear from (2.4). Using (2.6) we can rewrite (2.4) as

$$\rho = \frac{-2eN}{\exp\{(F^+ + \alpha_L^+)/2kT\}} \times \left[\frac{\sinh z}{1+\exp\{-(F^+ + \alpha_L^+)/2kT\}\exp\{-z\}}\right], \tag{2.7}$$

where

$$z = \{(e\Phi(x) - e\Phi_\infty\}/kT. \tag{2.8}$$

Poisson's equation then becomes

$$\frac{d^2z}{ds_+^2} = \frac{\sinh z}{1+\exp\{-(F^+ + \alpha_L^+)/2kT\}\exp\{-z\}}, \tag{2.9}$$

with $s_+ = \kappa_+ x$.

At sufficiently low temperatures, the second term in the denominator of (2.9) will be much greater than one near the surface where $-z \gg 1$.[5] So, near the surface, Eq. (2.9) becomes

$$d^2z/ds_+^2 = -\tfrac{1}{2}\exp\{(F^+ + \alpha_L^+)/2kT\} \tag{2.10}$$

and

$$z = -\tfrac{1}{4}s_+^2 \exp\{(F^+ + \alpha_L^+)/2kT\} + K_1 s_+ + K_2, \tag{2.11}$$

where K_1 and K_2 are integration constants. At $s_+ = 0$, $z = -e\Phi_\infty/kT$, so

$$K_2 = -e\Phi_\infty/kT.$$

Equation (2.11) is the solution of (2.9) near the surface. Well within the crystal the second term in the denominator of (2.9) will be small compared to one and the potential distribution can be determined as shown in I. We are thus left with the problem of obtaining a solution of (2.9) in the region where the two terms in the denominator are comparable. This will be done in the following manner. The solution given in I, valid when all defect concentrations are small, will be used for all regions where n_{if}/N as given by the small concentration expression (Eq. (4.5) of I) is less than one. From the point x_0, where the low-concentration expression for n_{if}/N becomes one, to the surface, we will use Eq. (2.11) and the two solutions will be fitted at the point x_0. In approaching the surface from within the crystal, the concentration of free impurities is increasing very rapidly. Thus the solution we obtain will give only a small error in the potential distribution in the region where n_{if}/N becomes of the order of one.

Suppose now we have saturation, i.e., $n_{if}/N = 1$, for a distance x_0 into the crystal. Then at $x = x_0$ we must match (2.11) to the solution we have assumed valid for $x > x_0$ [see Eq. (3.19) of I],

$$z = 4\tanh^{-1}\{e^{-t}\tanh(z'/4)\}, \tag{2.12}$$

where

$$t = \kappa_+(x - x_0) \tag{2.13}$$

and

$$z' = z\,|_{t=0} = \{e\Phi(x_0) - e\Phi_\infty\}/kT. \tag{2.14}$$

The conditions which must be satisfied at $x = x_0$ are:

(1) Φ from interior $=$ Φ from saturated region; (2.15)

(2) $d\Phi/dx$ from interior $= d\Phi/dx$ from saturated region; (2.16)

(3) since we require $n_{if}/N = 1$ at x_0,

$$\exp\{-z'\}\exp\{-(F^+ + \alpha_L^+)/2kT\} = 1. \tag{2.17}$$

Condition (2.17) thus requires

$$z' = -(F^+ + \alpha_L^+)/2kT. \tag{2.18}$$

At $x = x_0$, from the interior,

$$z = z', \tag{2.19}$$

and

$$dz/d(\kappa_+ x) = -2\sinh(z'/2), \tag{2.20}$$

while from the saturated region

$$z = -\tfrac{1}{4}\kappa_+^2 x_0^2 \exp\{(F^+ + \alpha_L^+)/2kT\} + K_1\kappa_+ x_0 - e\Phi_\infty/kT \tag{2.21}$$

and

$$dz/d(\kappa_+ x) = -\tfrac{1}{2}\kappa_+ x_0 \exp\{(F^+ + \alpha_L^+)/2kT\} + K_1. \tag{2.22}$$

Using (2.15), (2.16), (2.18), (2.5), and (2.6), Eqs.

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[4] The change in the defect distribution when n_{if}/N can no longer be considered small everywhere produces an altered expression for the Lagrange multiplier as compared with the case when n_{if}/N is small everywhere. This means $\alpha_L^+ \neq \alpha_H^+$, where α_H^+ is the multiplier introduced in I.

[5] Since we are considering a crystal containing divalent cation impurities, the potential $e\Phi_\infty$ is positive in the temperature range now under discussion.

(2.19)–(2.22) can be solved for x_0 with the result

$$x_0=-4\left(\frac{\epsilon kT}{8\pi Ne^2}\right)^{1/2}\sinh\left\{\frac{F^{+}+\alpha_L{}^{+}}{4kT}\right\}\exp\left\{-\frac{(F^{+}+\alpha_L{}^{+})}{4kT}\right\}+\left(\frac{\epsilon kT}{8\pi Ne^2}\right)^{1/2}\left[16\sinh^2\left\{\frac{F^{+}+\alpha_L{}^{+}}{4kT}\right\}\times\exp\left\{-\frac{(F^{+}+\alpha_L{}^{+})}{2kT}\right\}-4\frac{\alpha_L{}^{+}}{kT}\right]^{1/2}. \quad (2.23)$$

At temperatures sufficiently low that $(F^{+}+\alpha_L{}^{+})\gg kT$, (2.23) can be simplified to

$$x_0=-\left(\frac{\epsilon kT}{2\pi Ne^2}\right)^{1/2}+\left(\frac{\epsilon kT}{2\pi Ne^2}\right)^{1/2}\left(1-\frac{\alpha_L{}^{+}}{kT}\right)^{1/2}. \quad (2.24)$$

The Lagrange multiplier $\alpha_L{}^{+}$ is evaluated in Appendix A. Using Eq. (A15) of Appendix A together with Eq. (2.6) we have

$$\exp\{e\Phi_\infty/kT\}=(2z_{nn})^{-1}\exp\{(F^{+}-B_{+})/kT\}\times[-1+(1+4z_{nn}C_L\exp\{B_{+}/kT\})^{1/2}], \quad (2.25)$$

where C_L, the impurity concentration beyond the transition region, is given by (A9). Equation (2.25) is the correct expression for Φ_∞ for temperatures such that $x_0\geq 0$. For $x_0<0$, the formalism presented in I is valid.

From (2.6) and (2.18) we see that

$$e\Phi(x_0)=-\alpha_L{}^{+}. \quad (2.26)$$

Thus the potential, zero at the surface, rises to $-\alpha_L{}^{+}/e$ at the edge of the saturation region, i.e., at $x=x_0$, and then goes from $-\alpha_L{}^{+}/e$ to Φ_∞ in a distance $\sim\kappa_{+}{}^{-1}$ beyond the saturation region as long as $\kappa_{+}L\gg 1$. So, for NaCl, Eq. (2.25) is a valid expression for the potential for temperatures between those of Table I and those for which $\kappa_{+}L\sim 1$. Since these latter temperatures for NaCl are of the order of 100°K for crystals with $L\sim 1$ mm, we shall not examine here the defect distribution in the range where $\kappa_{+}L\lesssim 1$. The validity of an equilibrium calculation in this temperature range is clearly questionable. It should be noted however that meaningful results for thin films require an examination of the case $\kappa_{+}L\lesssim 1$.

The calculation given above is based upon a continuum interpretation of the distributions. The translation of the results of the continuum theory into atomistic language is straightforward, but there is one point worthy of mention. Consider a {100} surface of a crystal. To determine the concentration of impurities in any atomic plane underlying the surface in an atomistic picture one must average the result from the continuum model over the volume covered by that plane. Thus, with the nearest-neighbor separation being a, the concentration of free impurities in the first atomic plane under the surface is

$$\frac{1}{a}\int_0^a \frac{n_{if}}{N}dx,$$

the concentration of free impurities in the second atomic plane under the surface is

$$\frac{1}{a}\int_a^{2a} \frac{n_{if}}{N}dx,$$

etc. Similar considerations apply, of course, to all the defect distributions. It is in this sense that the condition called saturation must be interpreted for the emergence of this condition is a consequence of the continuum model. Thus in the atomic sense we do not have $n_{if}=N$ near the surface.[6]

III. IMPURITY ACCUMULATION NEAR SURFACES

It has been shown above that for moderate temperatures the impurity ions tend to accumulate near the surface. The extent of this accumulation is illustrated in Tables II and III for a temperature of 300°K using the NaCl parameters.[7] L is the volume-to-surface ratio

TABLE II. For $L=0.10$ cm: (1) $\kappa_{+}{}^{-1}$ (cm); (2) number of impurities in the region $0\leq x\leq\kappa_{+}{}^{-1}$; (3) fraction of the crystal in the range $0\leq x\leq\kappa_{+}{}^{-1}$, $\kappa_{+}{}^{-1}/L$; (4) fraction of all impurities in the range $0\leq x\leq\kappa_{+}{}^{-1}$; (5) fraction of bulk impurities which remain free, $(1-p)$ [p is defined in Eq. (4.9) of I].

$\bar{C}$		10^{-6}			10^{-5}	
B_{+}(eV)	0.20	0.40	0.60	0.20	0.40	0.60
1	1.37×10^{-6}	3.87×10^{-6}	2.62×10^{-5}	4.68×10^{-7}	2.13×10^{-6}	1.46×10^{-5}
2	6.24×10^{13}	7.89×10^{12}	7.59×10^{11}	9.92×10^{13}	2.64×10^{13}	3.82×10^{12}
3	1.37×10^{-5}	3.87×10^{-5}	2.62×10^{-4}	4.68×10^{-6}	2.13×10^{-5}	1.46×10^{-4}
4	2.77×10^{-2}	3.51×10^{-3}	3.37×10^{-4}	4.41×10^{-3}	1.17×10^{-3}	1.70×10^{-4}
5	0.975	0.119	2.66×10^{-3}	0.818	3.92×10^{-2}	8.41×10^{-4}

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[6] It can be argued physically that we must have $x_0<a$. Details will be published elsewhere.

[7] $e\Phi_\infty$ is determined from (2.25) or (4.15) of I. $\kappa_{+}{}^{-1}$ is then obtained from (2.5). For situations where saturation exists, line 2 of the tables is calculated by integrating (A5) and (A7) to $\kappa_{+}{}^{-1}$ instead of L and then adding (A6). When saturation has not occurred, line 2 is obtained by integrating (D1) of Appendix D of I to $\kappa_{+}{}^{-1}$.

TABLE III. For $L=1.0\times10^{-3}$ cm; (1) κ_+^{-1} (cm); (2) number of impurities in the region $0\leq x\leq\kappa_+^{-1}$; (3) fraction of the crystal in the range $0\leq x\leq\kappa_+^{-1}$, κ_+^{-1}/L; (4) fraction of all impurities in the range $0\leq x\leq\kappa_+^{-1}$; (5) fraction of bulk impurities which remain free, $(1-p)$ [p is defined in Eq. (4.9) of I].

$\bar{C}$		10^{-6}			10^{-5}	
B_+(eV)	0.20	0.40	0.60	0.20	0.40	0.60
1	2.64×10^{-6}	4.24×10^{-6}	2.60×10^{-5}	6.55×10^{-7}	2.19×10^{-6}	1.46×10^{-5}
2	1.67×10^{13}	6.58×10^{12}	7.48×10^{11}	1.21×10^{14}	2.49×10^{13}	3.82×10^{12}
3	2.64×10^{-3}	4.24×10^{-3}	2.60×10^{-2}	6.55×10^{-4}	2.19×10^{-3}	1.46×10^{-2}
4	0.743	0.292	3.33×10^{-2}	0.536	0.111	1.70×10^{-2}
5	0.993	0.140	2.67×10^{-3}	0.898	4.16×10^{-2}	8.42×10^{-4}

for the crystal. We see from these tables that the extent of the surface accumulation is markedly dependent upon B_+ for a given L and $\bar{C}$. For $B_+=0.60$ eV, the fraction of impurity ions in the range $x\leq\kappa_+^{-1}$ is only slightly larger than the fraction of the crystal involved, κ_+^{-1}/L. However, for $B_+=0.40$ and 0.20 eV, the fraction of impurities within $x\leq\kappa_+^{-1}$ is several orders of magnitude larger than κ_+^{-1}/L. For $L=0.10$ cm, the combination $\bar{C}=10^{-6}$ and $B_+=0.20$ eV means that nearly 3% of the impurity ions are in the range $x\leq\kappa_+^{-1}$ while for $L=1.0\times10^{-3}$ cm, this figure becomes about 74%. Thus we must conclude that unless the binding energy is quite high (~0.6 eV), the impurity distribution will be markedly nonuniform and the impurity ions in the surface region, because of the high electric field in this region, should behave in a manner distinct from that of the bulk impurity ions.[8]

In determining the appropriate value of L for a given crystal, the existence of grain boundaries should be considered. Eshelby, Newey, Pratt, and Lidiard[9] have pointed out that grain boundaries arising from dislocations where the dislocation separation d is such that $d\ll\kappa_+^{-1}$ correspond essentially to surfaces back-to-back. Thus the presence of such gain boundaries would reduce the effective volume-to-surface ratio for a given crystal.

As was discussed in I, the presence of the excess of divalent-cation-impurity ions in the surface region is compensated by a negative surface charge, the result of an excess of anions in the surface layer. It is known that isotopic exchange between a NaCl crystal and a gaseous halogen atmosphere occurs with surprising ease.[10] While the controlling factor is the detailed energetics of the exchange we suggest that the anion excess in the surface layer might be of importance. Since the anion excess is a function of temperature and impurity content, an experimental test of this point should be possible.

IV. THE ELECTRON AFFINITY

We have seen in I and above that for temperatures where the defect concentrations are governed by the divalent-cationic-impurity content, the surface develops a negative charge and there exists a positively charged space-charge region within the surface. The negative surface charge consists of the deposited cation vacancies and the space charge essentially of impurity ions. Thus from an atomic point of view everything of interest is occurring on the cation fcc sublattice. To this point we have said nothing about the lattice plane comprising the surface other than to require it to be a {100} surface. However, the preceding remarks indicate clearly that there must exist cation sites in the surface plane and in the immediately adjacent planes. This will certainly be the case for an arbitrary surface and in particular for {100} and {110} surfaces. However for a {111} surface there exist cation cites only on alternate planes and the theory as presented will not be applicable to this case. The unique feature about a {111} surface is that it has a dipole moment in a perfect crystal whereas the {100} and {110} surfaces do not. With these ideas in mind we can then relax the condition that the surface must be a {100} plane to the condition that the surface must possess no innate dipole moment.

The electron affinity of a polar crystal is defined as that energy which must be supplied to take an electron from the bottom of the conduction band out of the crystal to a state of rest an infinite distance from the crystal. Clearly the existence of a dipole moment at a surface will contribute to the electron affinity for that surface. If the surface of a perfect crystal is a {100} or a {110} plane and the ions in the surface region are not displaced relative to their position in the ideal lattice, there will be no surface dipole moment and the electron affinity will be due solely to the position of the conduction band in the perfect crystal. However, as noted above, a {111} surface does possess a dipole moment which can be of either sign.

Consider now a perfect NaCl crystal bounded by {100} planes in which the ions retain the perfect lattice spacing. For such a crystal Tibbs[2] has calculated the wave function for the lowest state in the conduction band. Based on this wave function, Mott and Gurney[11]

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[8] Qualitative evidence for the existence of a significant degree of impurity accumulation near the surface for Ca-doped NaCl crystals has been obtained by E. Nadgornyi and A. Stepanov, Fiz. Tverd. Tela. **5**, 998 (1963) [English. transl.: Soviet Phys.—Solid State **5**, 726 (1963)].

[9] J. Eshelby, C. Newey, P. Pratt, and A. Lidiard, Phil. Mag. **3**, 75 (1958).

[10] G. Benson, P. Freeman, and E. Dempsey, in *Advances in Chemistry Series*, edited by R. Gould (American Chemical Society, Washington D. C., 1961), Vol. 33, p. 26.

[11] N. Mott and R. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, London, 1948), 2nd ed., p. 72.

concluded that the energy necessary to bring a single electron into this previously neutral NaCl crystal should be about zero although the calculation was not very accurate. Evseev[3] performed a somewhat more elaborate calculation and concluded that the bottom of the conduction band lay at an energy equal to -0.06 eV.

The assumption that there will be no relaxation in the vicinity of the surface is clearly an oversimplification. Benson *et al.*[10] have carried out an extensive calculation of the structure of a $\{100\}$ surface of NaCl at $T=0$. They permitted relaxation of the outer five atomic layers considering, in addition to Coulomb and nearest-neighbor repulsive interactions, van der Waal's forces, dipole-quadrupole forces, and quadrupole-quadrupole forces. The result of the calculation was that the dipole moment of this surface per unit area is 2.25×10^{-5} esu which would provide a contribution to the electron affinity of $+0.085$ eV.

On the basis of the calculations for a perfect crystal, we would then conclude that the electron affinity of a NaCl crystal bounded by $\{100\}$ planes is $\simeq0.1$ eV. However, we have shown in I that the presence of defects in the crystal gives rise to a surface dipole with a potential difference Φ_∞ as long as $\kappa_+L\gg1$. The contribution to the electron affinity due to the defect distribution would then be $+e\Phi_\infty$. Since crystals normally contain a divalent cation concentration of the order of 10^{-6}, the dominant contribution to the electron affinity might well be that due to the defect distribution. This would then imply a pronounced temperature dependence of the electron affinity. Note also that for thin films the defect contribution to the electron affinity would be less than $e\Phi_\infty$.[12]

Timusk and Martienssen,[13] using their measurements of the luminescence threshold together with the photoemission threshold determined by Taylor and Hartman,[14] concluded that the room-temperature electron affinity of NaCl was 0.8 ± 0.2 eV. These experiments were done on crystals of norminal but unknown purity. In addition, Taylor and Hartman[14] showed that the photoemission threshold for NaCl thin crystals was less than that for NaCl crystals by about 0.4 eV. These experimental results are in accord with the ideas presented above. It should be noted that the temperature dependence of the defect contribution to the electron affinity will occur in the photoemission threshold.

At low temperatures it is somewhat unlikely that thermal equilibrium will be obtained. This would tend to reduce the potential Φ_∞ from the equilibrium value as would impurity precipitation.

V. DISCUSSION

The principal objection to the present theory is the fact that it predicts defect densities near the surface which are sufficiently high that the satisfaction of the conditions under which an expression for the configurational entropy and thus the charge density was obtained becomes questionable in this region (see Appendices B and C of I). Within the bulk of the crystal, the defects are rather well represented by point charges since we can average over lengths Δx such that the distortion around a defect extends over a region much less than Δx. Near the surface the rapid change in the defect density as a function of position precludes such an average. Thus the expression for the charge density becomes invalid but only in a very narrow layer right at the surface. In addition, we have neglected all elastic interactions. These interactions will be of principal importance near the surface where the defect density is high and relaxation effects most pronounced. Thus we must conclude that the predicted defect distribution very near the surface is, in detail, suspect.

However, the fact remains that the state of thermal equilibrium with the attendent bulk neutrality requires a surface potential field such that the innate free formation energies can be appropriately modified. Since our treatment of the interior of the crystal is formally accurate within the context of the model, we suggest that, while the actual distributions in the surface region might differ from those we predict, the electrical moment of this region, and hence Φ_∞, should be essentially as calculated herein.

We have considered the interaction between defects of the opposite charge to be of the short range, near-neighbor type. However, the inclusion of the long-range effects of the Coulomb interaction has been discussed in I so we will not pursue the topic further here.

APPENDIX A: EVALUATION OF THE LAGRANGE MULTIPLIER AT TEMPERATURES FOR WHICH SATURATION EXISTS

The Lagrange multiplier is determined by the condition that the total number of impurity ions is conserved. For divalent cation impurities we have for $x\leq x_0$

$$n_{if}=N \tag{A1}$$

and

$$n_{ib}\simeq0, \tag{A2}$$

and for $x\geq x_0$

$$n_{if}=N\exp\{-(e\Phi_\infty+\alpha_L{}^+)/kT\}\exp\{-z\} \tag{A3}$$

and

$$n_{ib}=Nz_{nn}\exp\{-(F^+-B_++\alpha_L{}^+)/kT\}\,. \tag{A4}$$

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[12] For crystals such that $\kappa_+L\lesssim1$, the maximum potential difference between the surface and the interior is $<\Phi_\infty$.

[13] T. Timusk and W. Martienssen, Phys. Rev. **128**, 1656 (1962).

[14] J. W. Taylor and P. Hartman, Phys. Rev. **113**, 1421 (1959).

From the bound impurities, per unit area, we obtain

$$\int_0^L n_{ib}dx = (L-x_0)Nz_{nn} \times \exp\{-(F^+ - B_+ + \alpha_L^+)/kT\}. \quad \text{(A5)}$$

In the saturated region, the contribution from the free impurities is

$$\int_0^{x_0} Ndx = x_0 N. \quad \text{(A6)}$$

The contribution from the free impurities in the unsaturated region can be obtained from Appendix D of I by substituting $(L-x_0)$ for L, z' for z_0 and α_L^+ for α_H^+ since we are considering $\kappa_+ L \gg 1$. Thus

$$\int_{x_0}^L n_{if}dx = N\kappa_+^{-1} \exp\{-(\alpha_L^+ + e\Phi_\infty)kT\} \times [\kappa_+(L-x_0) + 2\exp\{-z'/2\} - 2\exp\{-2\tanh^{-1}(e^{-\kappa_+(L-x_0)}\tanh(z'/4))\}]. \quad \text{(A7)}$$

The total number of impurities per unit area is the sum of (A5), (A6), and (A7).

Assuming a mean impurity concentration $\bar{C}$ and $L \gg x_0$, we have

$$\bar{C} = z_{nn} \exp\{-(F^+ - B_+ + \alpha_L^+)/kT + (x_0/L) + \exp\{-(\alpha_L^+ + e\Phi_\infty)/kT\} + 2(\kappa_+ L)^{-1} \times \exp\{-(\alpha_L^+ + e\Phi_\infty)/kT\} \times [\exp\{-z'/2\} - \exp\{-2\tanh^{-1} \times (e^{-\kappa_+ L}\tanh(z'/4))\}]. \quad \text{(A8)}$$

Since $\kappa_+ L \gg 1$, the second term in the square brackets can be neglected. Using (2.5), (2.6), (2.18), and defining C_L by

$$C_L \equiv \bar{C} - \frac{1}{L}\left[x_0 + \left(\frac{\epsilon kT}{2\pi N e^2}\right)^{1/2}\right], \quad \text{(A9)}$$

Eq. (A8) becomes

$$C_L = z_{nn} \exp\{-(F^+ - B_+ + \alpha_L^+)/kT\} + \exp\{-(\alpha_L^+ + F^+)/2kT\} \quad \text{(A10)}$$

so that, in terms of C_L,

$$\exp\{-\alpha_L^+/2kT\} = (2z_{nn})^{-1} \exp\{(\tfrac{1}{2}F^+ - B_+)/kT\} \times [-1 + (1 + 4C_L z_{nn} \exp\{B_+/kT\})^{1/2}]. \quad \text{(A11)}$$

This expression has been derived under the assumption $\kappa_+ L \gg 1$.

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Optical Determination of the Symmetry of the Ground States of Group-V Donors in Silicon*

R. L. Aggarwal and A. K. Ramdas

Department of Physics, Purdue University, Lafayette, Indiana

Excitation lines from the doublet, $1s(E)$, and the triplet, $1s(T_1)$, states have been measured at temperatures ~80, 59, and 30°K for P, As, and Sb donors in silicon. On the basis of the relative intensities of the lines with the same final state it is deduced that the $1s(E)$ state lies above the $1s(T_1)$ state for all three impurities investigated. At ~30°K the $1s(T_1) \rightarrow 2p_0, 2p_\pm$ transitions for antimony impurity resolved into a doublet. Uniaxial stress measurements for P and Sb, with compression **F** parallel to [100] or [110] and with the electric vector **E** either parallel or perpendicular to **F**, indicate that the lines with $1s(T_1)$ as their initial state do not exhibit any splittings or shift in their energies. On the other hand, the lines with $1s(E)$ as their initial state exhibit splittings with dichroic features. Experimental observations of the number and the positions of the stress-induced components and their polarization characteristics are consistent with the ordering in which $1s(E)$ lies above $1s(T_1)$.

I. INTRODUCTION

Recently one of us reported[1] the observation of excitation spectra of Group-V donors P, As, and Sb in silicon originating from the higher-lying doublet and triplet ground states. The separations of these states from the lower-lying singlet state are of such magnitudes that they are significantly populated only at temperatures much higher than liquid-helium temperatures; thus the measurements reported in Ref. 1 were made at liquid-nitrogen temperatures. Similar measurements have also been reported by Ottensmeyer *et al.*[2] for As and Sb in silicon. Measurements of this kind were first made by Fisher[3] in the study of the ground states of Group-V donors in germanium. Following the same technique the ground states of isolated lithium and the lithium-oxygen complex in silicon have also been investigated by Aggarwal *et al.*[4] We have recently re-

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