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Doping of PbTe with Group-III elements: An ionic lattice approach

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It is shown that donor or acceptor behavior for a Group-III element in PbTe depends on the balance between the energy needed to promote the s-level electrons of the element above the top of the valence band of the host crystal (donor action) and the lattice energy gained as a result of the increased charge and smaller radius of the impurity. The lattice energy for the element in its donor and acceptor state is calculated on the basis of an ionic host-lattice model which enables one to take into account lattice distortions. The calculations predict that Tl and Ga should act as acceptors and In and Al as donors. They also predict that, with the exception of Al, the major fraction of these elements will remain electrically inactive.

I. INTRODUCTION

Studies of the doping behavior of Group-III elements in lead telluride (PbTe) have revealed a rather puzzling behavior. Tl, the heaviest element studied, behaves as an acceptor but In, Ga, and Al behave as donors.[1] Such unsystematic behavior for elements of a given column of the periodic table is very unusual if one assumes that the element always substitutes for the same atom of the host crystal. We shall assume without proof in this paper that in the case of PbTe, Group-III elements always substitute for Pb as has been proven for In by studying changes in the lattice parameter as In is added to PbTe.[2] A few remarks about two other possibilities seem, however, appropriate. Substitution on a Te site seems highly improbable since the valence band would be strongly electron deficient if an element with three valence electrons were to substitute for a chalcogenide atom with six valence electrons. As for the second possibility, namely, that of entering the lattice interstitially, it should be borne in mind that the interstitial cavity in PbTe is irregularly shaped because of the difference in ionic radii of Pb and Te. Using ionic radii of 1.14 and 2.11 Å for the two ions, respectively (see Table I and attendant text), we obtain a width of 0.7 Å for the diameter of the largest interstitial cavity available for the impurity ion. As seen in Table I none of the ions considered has a small enough diameter to "fit" into this cavity even in the triply ionized state. In all cases incorporation as an interstitial impurity would therefore involve considerable repulsive energy between it and the surrounding host atoms and make incorporation in this form unlikely.[3] We shall therefore restrict ourselves to an examination of whether donor or acceptor action

TABLE I. Parameters used in calculating the energy of incorporation of impurities.

Symbol	Definition	Values	Source or comments
$V_{\mathrm{IP\,II}}$	2nd ionization energy (eV)	18.8 (Al), 20.5 (Ga), 18.9 (In), 20.4 (Tl)	Reference 7
$V_{\mathrm{IP\,III}}$	3rd ionization energy (eV)	28.4 (Al), 30.7 (Ga), 28.0 (In), 29.8 (Tl)	Reference 7
r_+, r_-	cation and anion (Te) radii in Å	0.5 (Al^{3+}), 0.91 (Al^{+}),[a] 0.62 (Ga^{3+}) 1.13 (Ga^{+}), 0.81 (In^{3+}), 1.32 (In^{+}) 0.95 (Tl^{3+}), 1.40 (Tl^{+}), 1.14 (Pb^{2+})[b] 2.09 (Te^{2-})[b]	Reference 21
α_+	cation polarizability (cm^3)	0.24×10^{-24}	See discussion after Eq. (7)
α_-	anion polarizability (cm^3)	7.1×10^{-24}	See discussion after Eq. (7)
A	Repulsion-energy pre-exponential constant	0.23 eV	See discussion after Eq. (8)
ρ	Repulsion-energy stiffness constant	0.38×10^{-8} Å	See discussion after Eq. (8)
E_W	work function of PbTe	4.1 eV	Reference 8
E_G	band gap of PbTe	0.2 eV	Reference 9
a	interionic distance of PbTe	3.23 Å	Reference 15

[a] We have not been able to locate an experimental value for this radius and have therefore assumed that the ratio of the trivalent to the nonavalent radii for Al is similar to that for Ga, namely, 0.55. With this assumption and using the experimental value of 0.5 Å for the trivalent ion we arrive at the value listed in the table.

[b] See discussion following Eq. (6).

occurs for the case of the element substituting for Pb and shall start by considering the energy levels of Group-III elements and those of the host crystal.

In Fig. 1 we show the density of states for PbTe as calculated by Martinez, Schlueter, and Cohen[4] and in the main confirmed by photoemission experiments[5]; we also show the energy levels of p and s electrons of Group III elements. Consider now a *Gedankenexperiment* in which the first step is the creation of a lead vacancy. This step produces two holes in the valence band, a fact well known experimentally and understood theoretically.[6] When the Group-III element is now introduced its p electron will readily fill the empty valence-band state produced by the lead vacancy since the p levels of all these elements lie close to the top of the valence band. If the s level of the element remains unchanged or merges with the valence band the two s electrons will be electrically inactive since the level is doubly occupied. Since only one electron has entered the valence band to neutralize one of the two holes the impurity will have acted as an acceptor. If, on the other hand, the s level is pushed above the top of the valence band by more than the band-gap energy it will merge with the conduction band. One of its two s electrons will then drop into the valence band to neutralize the second hole and the second electron will remain in the conduction band. The impurity will then have acted as a donor. Which of these alternatives occurs can, in principle, be predicted by a calculation of energy levels starting with the band structure of PbTe and introducing a perturbation by the Group-III impurity. This technique was used successfully by Parada and Pratt[6(a)] to predict donor behavior for a Te vacancy and acceptor behavior for a Pb vacancy though their calculations ignored lattice distortions.

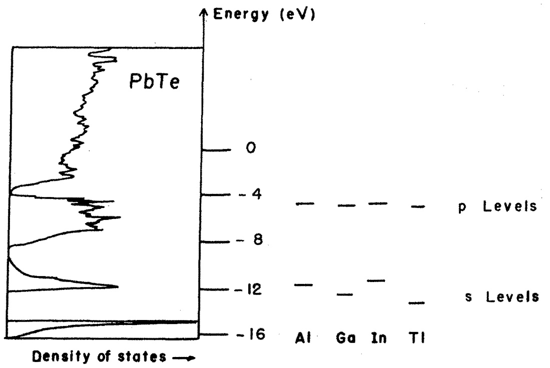

FIG. 1. Density of states of valence band of PbTe according to Ref. 4 and energy levels of s and p electrons of Group-III elements [from F. Herman and S. Skillman, Atomic Structure Calculations (Prentice-Hall, Englewood Cliffs, 1963)].

In this paper we attempt to predict donor or acceptor behavior by means of a completely different approach. We ask whether, starting with a lead vacancy and the element in the vapor phase, it takes more energy to incorporate the element as a donor or as an acceptor. As already mentioned, for acceptor action to occur only the p electron is stripped from the element and transfered to the valence band of the host crystal. For donor action to occur all three electrons are stripped from it, with two electrons entering the valence band and one electron entering the conduction band. Thus, as far as the electrons are concerned the difference in energy between incorporation as a donor and an acceptor is the sum of the second and third ionization energy[7] of the impurity minus the energy gained when the two electrons enter the host crystal. The latter energy is simply twice the work function of 4.1 eV,[8] or about 8.2 eV, if we ignore the bandgap energy of about 0.2 eV at 0 K (Ref. 9). The sum of the second and third ionization energy of the four Group-III elements considered here ranges from 47 to 50 eV, with an average of 48.7 eV. Typically, it would therefore require an excess electron energy of 40.5 eV, the difference between 48.7 and 8.2 eV, to incorporate the element as a donor rather than as an acceptor. In order for donor action to be possible one must therefore gain more than 40.5 eV when the remaining ion is incorporated in its triply charged state (donor case) rather than in its singly charged state (acceptor case). The heart of the problem is thus to estimate the energy of incorporation of the ion in its two charge states. We shall see that using a rather crude model, which, however, allows us to estimate lattice distortions, we are able to predict that for some Group-III element the overall energy balance favors incorporation as a donor and for others it favors incorporation as an acceptor.

In order to estimate the energy of incorporation of the ions in the two charge states we shall treat the host lattice as an ionic lattice. In such a model the two p electrons of the Pb atoms are transferred to the Te atoms to complete its p shell, producing an ionic lattice of Pb^{2+} and Te^{2-} ions. The total energy of the lattice is then the sum of an attractive Madelung energy and a repulsive energy due to closed ion shell interaction as treated in elementary texts.[10] We justify our use of such a simple model on the basis of two calculations. In the first place, Tanaka and Morita[11] carried out a quantum-mechanical calculation based on this ionic model which yields the cohesive energy of the crystal to within 10% of the experimental value. In the second place, extensive pseudopotential calculations of the band structure by Schlueter, Martinez, and Cohen[12] produced results which generally confirm the ionic model. Although these authors found that the various valence bands shown in Fig. 1 are not simply based on atomic wave functions centered on the individual atoms as in the Tanaka and Morita model it was nevertheless concluded that the lattice is considerably ionic. In particular, these authors conclude that of the ten outer-shell electrons which fill the valence band 75% reside on the Te atoms and 25% on the Pb, compared to 80% and 20% for a purely ionic model in which two electrons are on the Pb and eight electrons are on the Te.

In calculating the energy of the impurity-host lattice system with this ionic model we make one more assumption, namely, that the hole is not localized near the impurity when the impurity is present as an acceptor and that the electron is not localized near it when it is present as a donor. This assumption is certainly justified since no freeze-out of carriers has been observed in PbTe.[13] The impurity thus sits in an environment in which the nearest neighbors are assumed to be Te ions with a charge of -2, the next-nearest neighbors are Pb ions with a charge of $+2$, and so forth. If lattice "reaction" is not taken into account the potential at the impurity site would then simply be the Madelung potential and would be the same for the impurity ion in its donor and acceptor state. The energy of the donor ion will, however, be much lower since it carries a charge of $+3$ compared to a charge of $+1$ for the acceptor ion. The Madelung potential for an ionic crystal with the NaCl structure and an ionic charge Z of two is $2\times 1.75e/a$, where e is the electronic charge and a is the interionic distance.[14] With $a = 3.23$ Å (Ref. 15) the energy of incorporation of the ion in its triply charged state is thus -46.5 eV compared to -15.5 eV in the singly charged state. Previously, we pointed out that in order for the Group-III element to enter the lattice as a donor rather than as an acceptor an energy of 40.5 eV would have to be expended in order to place its s electrons into higher-energy states. Owing to a difference of -31 eV in the energy of the donor ion and the acceptor ion the total energy difference in favor of incorporation as an acceptor is now reduced to 9.5 eV. It will be shown, however, that this difference is further reduced due to the fact that the potential at the impurity site is not simply the Madelung potential but actually differs considerably for the donor and acceptor case. The reason that the potential is not simply of the Madelung type is first of all due to the fact that the impurity ion carries an effective charge relative to the rest of the lattice. In the donor case the charge is $+1$ since a triply charged ion has replaced a doubly charged Pb ion; by analogy the effective charge is -1 for the acceptor case. It will be shown that the difference in charge produces a different host reaction in the donor and in the acceptor case. Additional effects occur due to the difference in ionic sizes between the impurity ion and the Pb ion. In Sec. II we calculate how the lattice "reacts" to the foreign charge and to the difference in ionic radii. In Sec. III we use the results of Sec. II in order to estimate the potential at the impurity site, which turns out to be considerably larger than the Madelung potential for the donor case and considerably smaller for the acceptor case. We also calculate the change in lattice energy due to the distortion of the lattice. We shall see that when the polarization of the lattice and its distortions are taken into account the difference in the energy of incorporation of the impurity as a donor and as an acceptor is much reduced and can be either positive or negative, depending on the impurity. In Sec. IV we consider the role of the neutral, electrically inactive species. Finally, in Sec. V we discuss the merits and shortcomings of our approach and make some remarks about its relevance to other systems.

II. POLARIZATION AND DISTORTION OF HOST LATTICE BY THE IMPURITY

As mentioned above, the effective charge on the impurity will induce dipoles on the host ions. Furthermore, these ions will move from their normal positions under the influence of electrical forces and as a result of the difference between the radius of the impurity ion and the lead ion which it replaces. Any displacement of two ions toward each other will give rise to a restoring force because of the repulsive interaction which exists between ions with closed shells.[16] Since all the host ions move, the motion is a collective phenomenon which must be calculated in a self-consistent way. The equilibrium configuration of the lattice after the incorporation of the impurity will be determined by the condition that all electrical forces and all closed-shell repulsive forces cancel each other for all ions in the crystal. In Brauer's method[17] for calculating this equilibrium configuration, the displacement of a first shell ion, say, at (1, 0, 0) next to the impurity at (0, 0, 0), is determined in a self-consistent fashion. In estimating this displacement Brauer takes into account the forces on such an ion which are due to displacement of all the other ions of type (100) as well as the forces which originate from the dipoles induced on those ions which are also calculated in a self-consistent manner. The force due to the impurity is also taken into account as are the forces exerted by the displacements and polarization of outer-shell ions. The displacement and polarization of outer-shell ions, however, is estimated in a somewhat more approximate fashion. These displacements are assumed to be uniquely determined by those of the first-shell ions and the force exerted by the effective impurity charge. Similarly, the dipoles induced on outer-shell ions are calculated from the electric field produced by the impurity without explicitly taking into account dipole-dipole interactions. The reader is referred to Brauer's original article[17] and the review article by Lidiard[18] for further discussion of the method. With the approximations just described the electrical force in the radial direction on a first-shell ion becomes[17,18]

$$\begin{aligned} F_e = e^2/a^2\{ & -qZ/(1+\xi)^2 + (\sqrt{2}+0.25)Z^2/(1+\xi)^2 - 4(1+\xi)Z^2/[1+(1+\xi)^2]^{3/2} \\ & - Z^2/(2+\xi)^2 + 2.3713Z\nu/(1+\xi)^3 ea \\ & + qZ(0.388M'_+ + 1.965M'_+ + \xi(1.965Z^2 - 0.388Z^2)\} \; . \end{aligned} \qquad (1)$$

The first term in Eq. (1) is the force due to the impurity of charge ±q. (As discussed in Sec. I the positive value must be chosen if the impurity is present as a donor and the negative value if it is present as an acceptor.) The next three terms result from radial displacements of the other first-shell ions. These displacements are equivalent to producing dipoles of moment $e\xi a$ at each lattice point where a is the interionic distance and ξ is the relative displacement x/a. Note that the sum of these three terms goes to zero as ξ goes to zero. The fifth term is the force due to the dipoles ν induced on the first-shell ions. The sixth and seventh terms of Eq. (1) represent the sum of the forces on a first-shell ion produced by the induced dipoles and the displacement dipoles of outer-shell ions. In considering the dipoles produced by the displacement of outer-shell ions, Brauer[17] assumes that these displacements are brought about independently by two factors, namely, the Coulomb forces due to the perturbing charge ±q of the perturbing ion and the "mechanical" or "elastic" forces due to the displacement of the first-shell ions. In order to grasp the significance of separating the Coulombic and the elastic forces it is instructive to visualize a situation in which $\xi = 0$ as illustrated in Fig. 2. Such a situation may arise, for example, if the impurity enters as an acceptor with effective charge $-q$, which tends to force the nearest (anion) neighbors outwards. If, however, the impurity is small, the opposing tendency to move inward will also exist and it is then possible that the displacement of a first-shell ion becomes zero for fortuitous values of the impurity radius and repulsive-force constants. In this unlikely case the impurity ion will still exert a force on outer-shell ions which will be displaced. The sixth term of Eq. (1) represents the lattice sum of these dipole forces. The constants M_+ and M_- reflect both the lattice polarization due to ion displacements and the polarization of the individual ions as a result of the distortion of the electron distribution, M'_+ and M'_- are given by the expressions[17,18]

$$M'_\pm = (1/4\pi)(1-1/\epsilon)(\alpha+\alpha_\pm)/[\tfrac{1}{2}(\alpha_+ + \alpha_-)+\alpha] \; . \qquad (2)$$

Here ϵ is the dielectric constant, α_+ and α_- are the electron polarizabilities of cations and anions, respectively, and α is lattice polarizability, which is obtained from the relation

$$\alpha = Z^2q^2[4A(1/\rho^2 - 2/\rho a)]^{-1} \qquad (3)$$

as derived by Lidiard.[18] Equation (3) is obtained by

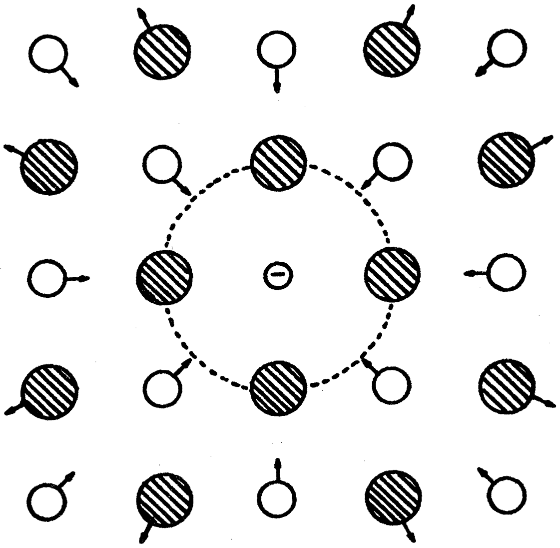

FIG. 2. Lattice distortion around acceptor ion with radius smaller than lead ion. As explained in text, a fortuitous cancellation of forces can result in no displacement of nearest neighbors, shown here with circle drawn through them. Outer-shell ions, however, will still be displaced as indicated by arrows. Shaded circles are anions, blank circles are cations, central circle with minus sign is the acceptor ion.

combining Eqs. (12.9) and (12.10) of Ref. 18 and letting $r_+ + r_-$ equal a. For the sake of consistency with other equations used in this paper we use the symbol A instead of b as used by Lidiard. The symbols A and ρ are discussed below in conjunction with Eq. (4). Essentially, α is a measure of the ability of ions to move under the influence of the electric field against the restoring force due to closed-shell repulsion. Finally, the seventh term of Eq. (1) represents those dipole forces produced by outer-shell ion displacements which are solely due to the displacement of first-shell ions. In carrying out this lattice sum it is assumed that ξ_{lmn} is given by $\xi/(l^2+m^2+n^2)$.

Since the fifth term of Eq. (1) can be expressed in terms of the electrical force through the relation $\nu = -F_e \alpha_-/e$ the equation can be rewritten in a manner which shows explicitly the dependence of the electrostatic force on the displacement of first-shell ions. Using the values for the various parameters as listed in Table I we have evaluated F_e for $q = \pm 1$ as a function of ξ with results shown in Figs. 3(a) and 3(b). It is interesting to note that F_e is a rather weak function of ξ, varying more or less linearly and changing by only a few percent over the range of interest. The choice of parameters is discussed at the end of this section.

The electrical forces which tend to push the ions inwards or outwards are opposed by closed-shell repulsive forces which depend much more drastically on lattice distortions. These forces are very asymmetric since the increase in repulsion between two ions upon decreasing their separation is much stronger than the decrease upon increasing their separation. Brauer uses the Born-Mayer repulsion law[18] for the repulsive interaction between closed-shell ions of radii r_i and r_j, at a distance a apart:

$$U_{\mathrm{rep}} = A_{ij} e^{-(r_i + r_j - a)/\rho_{ij}} \,. \tag{4}$$

To obtain the repulsive force on a first-shell ion it is first of all necessary to write down the displacement of the ion and its neighbors in a radial direction, bearing in mind that the displacement of outer-shell ions is composed of a term due to the displacement ξ of first-shell ions and a term independent of it which is due to the charge.[17] Instead of a in Eq. (4) we must now write $a(1+\xi_i + \xi_j)$, where ξ_i and ξ_j are the displacements of ions i and j, and a is taken to be their separation in the unperturbed crystal (the displacement of the impurity ion is, of course, zero). The repulsive force between the two ions is then obtained by taking the derivative of the Born-Mayer expression. In this manner the following expression for the repulsive force on a first-shell ion is obtained[17,18]:

$$\begin{aligned} F_r = {} & (A'/\rho')\exp[r_I + r_- - (1+\xi)a]/\rho' + (A_1/\rho)\exp(r_+ + r_-)/\rho \\ & \times\{-\exp(-\beta a/\rho) + (4/\gamma)\exp(-\gamma a/\rho)(\xi - 2[+]/2\sqrt{2})\} + (4A_2/\rho)\exp(2r_-/\rho) \\ & \times \boldsymbol{(}(1/\sqrt{2})\{\exp[-\sqrt{2}(1+\xi)a/\rho]\} - (1/\eta)[\exp(-\eta a/\rho)]\,(1 - \xi + 2[-]/5\sqrt{5}) + (1/\zeta)[\exp(-\zeta a/\rho)]\,(\xi - [-]/3\sqrt{3})\boldsymbol{)}\,, \end{aligned} \tag{5}$$

in which

$$[+] = \xi + q/zM', \quad [-] = \xi - q/zM', \quad \beta = 1 - \xi + \frac{1}{4}[+]\,,$$

$$\gamma = \{(1 + [+]/2\sqrt{2})^2 + (\xi - [+]/2\sqrt{2})^2\}^{1/2}\,,$$

$$\eta = \{(1 + [-]/5\sqrt{5})^2 + (1 - \xi + 2[-]/5\sqrt{5})^2\}^{1/2}\,,$$

$$\zeta = \left\{\left(\sqrt{2} + \frac{\sqrt{2}\,[-]}{3\sqrt{3}}\right)^2 + (\xi - [-]/3\sqrt{3})^2\right\}^{1/2}.$$

The new symbol M' is identical with the symbol $M'_\pm$ of Eq. (2) except that $\alpha_\pm$ is removed from the numerator. In Eq. (5) the first term represents the force between a first-shell ion and the impurity, the second term the forces due to its displacement relative to its other cation neighbors, and the third term the forces due to its displacement relative to its anion neighbors. It should be noted that the interaction constant A is different for the impurity-anion pair, the host cation-anion pairs, and the host anion-anion pairs. As for the constant ρ only two values need to be considered if only nearest-neighbor interaction is taken into account, namely, that for the impurity-anion pair and the cation-anion pairs. In Figs. 3(a) and 3(b) we plot the repulsive forces as a function of the displacement of first-shell ions for the parameter set of Table I. Where F_e and F_r are numerically equal, i.e., at the intersection of the two forces when they are plotted in the same direction first-shell ions are in equilibrium. We see that equilibrium occurs when the displacement ξ is a few percent. Not surprisingly, the displacement is largest for larger ions when the impurity is present as an acceptor so that the electrical force is outward and is smallest for the larger ions when the impurity is present as a donor so that the electrical force is inward. In obtaining the results of

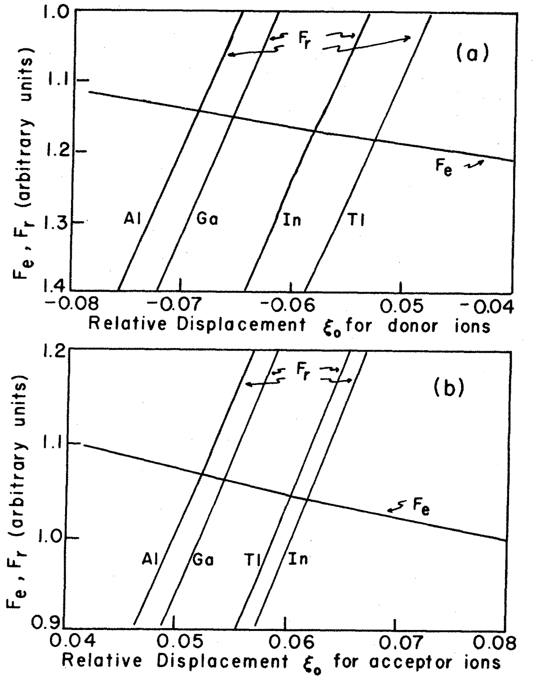

FIG. 3. Electrostatic and repulsive forces on nearest-neighbor ions as function of their relative displacement ξ. F_e and F_r are in opposite directions but are drawn in the same direction in order to facilitate finding the value of ξ at which they are numerically equal. (a) Triply charged donor ions. Note that ξ_0's are negative, i.e., nearest neighbors move inward. (b) Singly charged acceptor ions. Note that ξ's are positive.

Figs. 3(a) and 3(b) the same value of ρ was used for the impurity-anion pair as for the host cation-anion pair as for the host cation-anion pairs. The effect of varying ρ for the impurity-anion pair is discussed in Sec. III.

We now discuss how values were assigned to the various constants listed in Table I. Since we employ an ionic model we must choose values of the ionic radii which add up to the experimental ionic distance and ionic polarizabilities which satisfy the Clausius-Masotti relation.[19] Furthermore, in estimating the values for the constants A and ρ which appear in Eqs. (4) and (5) we must use an ionic model for the cohesive energy of the crystal per ion pair, namely,[20]

$$U = zAe^{-(r_+ + r_{-a} - a)/\rho} - \alpha_M Z^2 q^2/a\,, \tag{6}$$

where α_M is the Madelung constant, Z the ionic charge, and q the electronic charge; Z is the number of nearest neighbors or six for PbTe. [Equation (6) corresponds to Eq. (20) of Ref. 20 by making the substitution $Ae^{-(r_+ + r_-)}$ for λ.]

The values for the impurity radii in the two charge states were taken from Pauling's tabulation[21] without attempting to make corrections for the fact that no cubic compound exists of the form XTe, where X is the impurity element. The host-crystal radii were, however, adjusted slightly from the values given by Pauling since the two radii ($\mathrm{Pb}^{2+} = 1.20$ Å and $\mathrm{Te}^{2-} = 2.21$ Å) do not add up to the experimental interionic distance of 3.23 Å.[15] We assume that the ratio of the two radii is the same as that given by Pauling and thus arrived at the values given in Table I, which add up to 3.23 Å. To obtain the ionic polarizabilities we have employed the Clausius-Mossoti equation[19]:

$$(n^2 - 1)/(n^2 + 2) = 4\pi/3(N_+ \alpha_+ + N_- \alpha_-)$$
$$= \alpha_+/r_+^3 + \alpha_-/r_-^3\,, \tag{7}$$

where N_+ and N_- are the number of positive and negative ions per unit volume, respectively, and n is the high-frequency dielectric constant which we took as 5.8.[22] Using the ionic radii of Pb^{2+} and Te^{2-} of Table I we obtain the values $\alpha_+ = 0.24\ \mathrm{cm}^3$ and $\alpha_- = 7.1 \times 10^{-24}\ \mathrm{cm}^3$ based on the following procedure: We assume that the ratio of polarizabilities of Te, Se, and S is the same as that obtained by Tessman, Kahn, and Shockley[23] for other ionic cubic compounds, namely, 1:0.72:0.56. We also assume that the ratio of the radii of the anions is the same as that given by Pauling,[21] namely, 1:0.79:0.83. Equation (7) could then be solved for α (Pb) and α (Te) using the refractive indices for PbTe and one of the other two compounds.

Finally, using the ionic model one obtains the constant ρ from a knowledge of bulk modulus B[24] and the interatomic distance a via the relation[25]

$$B = \alpha_M Z^2 q^2/18a^4(a/\rho - 2)\,, \tag{8}$$

where the symbols α_M, Z, q, and a have been defined previously. By differentiating Eq. (6) with respect to a, setting the derivative equal to zero, and substituting ρ from Eq. (8), one can obtain the value for A for the host crystal.

III. ELECTROSTATIC POTENTIAL AND REPULSIVE ENERGY FOR DONORS AND ACCEPTORS

Having estimated the displacement of the ions and the dipoles induced on them, it is a simple matter to write down the expression for the electrostatic potential at the impurity site. Knowing the displacements one can also estimate the change in the Born-Mayer repulsive interaction energy in the crystal. The electrostatic potential at the impurity site will be given by the Madelung potential plus corrections due to the "reaction" of the lattice to the impurity[17,18]

$$\phi_{(000)} = -\alpha_M Ze/a + 6Ze\xi/a(1+\xi) - 6\nu/a^2(1+\xi)^2$$
$$-qe/a(6.3346M'_+ + 4.1977M'_-)$$
$$-e\xi/a(6.3346Z - 4.1977Z). \qquad (9)$$

The first term is the Madelung potential, the second and third terms are the contributions to the potential from the displacement and the polarization of first-shell ions, and the fourth and fifth terms are similar contributions from outer-shell ions. The fourth term contains both those contributions which arise from the polarizabilities of the ions and those which arise from that part of their displacement which is due to the effective charge on the impurity, as discussed in the previous section. The contribution from the part of the displacement of outer-shell ions which arises from the displacement of first-shell ions is contained in the fifth term. While the displacement of anions and cations due to the effective charge on the impurity is in opposite directions, the displacements which result from ξ not being zero are in the same direction and therefore the lattice sums due to positive and negative ions in the fifth term have opposite signs. In evaluating the electrostatic potential from Eq. (9) q must be taken with a positive sign when the impurity is present as a donor and with a negative sign when present as an acceptor. Similarly, the dipoles ν on first-shell ions are taken with different signs in the two cases. Clearly, since the ξ's as well as the dipoles ν are numerically slightly different for the donor and acceptor cases (see Fig. 1) the positive and negative deviations from the Madelung deviation of the potential are not numerically equal. In Table II we list the electrostatic energy at the impurity site for the four impurities considered here, as well as the difference between the donor and acceptor case. The ionic energies differ from those calculated simply on the basis of the Madelung potential by 15% to 20%, which can amount to close to 10 eV for donors. In order to avoid unnecessary details of presentation we do not list a breakdown of contributions from the various terms of Eq. (9). Suffice it to say that the contributions of all these terms are comparable in magnitude. Further discussions of the electrostatic energies will be given below.

Owing to the displacement of the ions the repulsive energy U_{rep} stored in the crystal will change from its initial value $U_{\text{rep}} = \Sigma A_{ij} \exp(r_i + r_j - a)/\rho_{ij}$, where the summation is over all ion pairs of the lattice. If we restrict ourselves to nearest-neighbor interactions, only the initial value is simply ΣA since we have defined r_i and r_j so that their sum equals a. Owing to the displacement of the ions in the crystal, U_{rep} will change. The change in U_{rep} will be given by

$$\Delta U_{\text{rep}} = 6A' e^{-r_1 + r - a(1+\xi_0)/\rho'}$$
$$+ \sum_{1j} A_{ij} \left(e^{-r_i + r_j - a(1+\xi_i+\xi_j)/\rho_{ij}} - 1\right), \qquad (10)$$

where the first term represents the interaction between the impurity of radius r_1 and the nearest anions and the second term the change in repulsive energy for all other ions in the crystal. In principle, each pair of ions has its characteristic value of A and stiffness constant ρ. In this paper we have used the same value of A and ρ for the cation-anion, cation-cation, and anion-anion pairs of the host lattice but we have considered variations in ρ' for the different impurity–nearest-neighbor pairs. We have extended the summation of the second term of Eq. (10) to include third-shell ions, which involved 96 ion pairs grouped into eight sets. In Table II we list the values of ΔU_{rep} for the donor and acceptor case of the four impurities considered. In these calculations we have used the same value of A for the impurity–nearest-neighbor pairs as for the host-crystal pairs and have also let $\rho' = \rho$. For the sake of simplicity of presentation we omit a breakdown of the contributions to ΔU_{rep} of the various displacements.

TABLE II. Energies of incorporation (eV) of Group-III elements as donors and acceptors with $\rho' = \rho = 0.38 \times 10^{-8}$ cm. The relative displacements ξ for nearest-neighbor ions for this set of parameters are as follows: −0.058 $(\text{Tl})^{3+}$, −0.066 (In^{3+}), −0.073 (Ga^{3+}), −0.076 (Al^{3+}), +0.060 (Tl^{+}), +0.054 (In^{+}), +0.040 (Ga^{+}), +0.036 (Al^{+}).

Element	Electron energy	Ionic energy donors (a) Electrost.	Ionic energy donors (b) Repuls.	Ionic energy acceptors (a) Electrost.	Ionic energy acceptors (b) Repuls.	Difference in ionic energy (a) Electrost.	Difference in ionic energy (b) Repuls.	Net difference in energy
Tl	42.2	−53.9	+0.29	−12.3	+0.75	−41.6	−0.46	+0.1
In	38.9	−54.9	+0.12	−12.3	+0.53	−42.6	−0.41	−4.1
Ga	43.2	−55.8	+0.05	−13.1	+0.16	−42.7	−0.11	+0.4
Al	39.2	−56.2	−0.01	−13.3	+0.03	−42.9	−0.04	−3.7

Having estimated the change in electrostatic and repulsive energy for donor and acceptor ions we can calculate the final result, namely, the difference between the energy required to incorporate the element as a donor and as an acceptor. The values for this difference ΔU are listed in column 6 of Table II and are obtained as follows: We first take the algebraic sum of columns 5(a) and 5(b) to obtain the difference in energy between incorporating the ion as a donor and as an acceptor. This energy difference ΔU_{ion} is always negative since more energy is gained when the ion is incorporated as a donor because of its triple charge and because its radius is smaller than that of the acceptor ion. [The reason why the smaller radius of the donor ion enhances the probability of incorporation as a donor is that it increases the electrostatic energy by allowing the lattice to move close to the impurity ion. Furthermore, a comparison of columns 3(b) and 4(b) shows that the repulsive energy is lower for the donors than for acceptors.] ΔU_{ion} is then added algebraically to column 2 to obtain the values listed in column 6. Note that column 2 is always positive since it represents the energy needed to promote the two *s* electrons to the top of the valence band and the bottom of the conduction band, respectively. Column 2 is given by the sum of the second and third ionization energies minus twice the work function plus the band-gap energy. Essentially, the ΔU's of column 6 are the differences between the cost involved in incorporating the element as a donor rather than as an acceptor (column 2) and the gain as given by the algebraic sum of columns 5(a) and 5(b). We see that column 6 predicts that Tl and Ga prefer to be incorporated as an acceptor ($\Delta U > 0$), while donor action is preferred for In and Al. It is gratifying to see that even with our first approximation ($\rho' = \rho$) the calculations predict the observed behavior for Tl and In though in the former case the preference for incorporation as an acceptor is quite small.

The most questionable approximation in the calculations presented thus far is to use the same values of ρ for the impurity-anion pairs as for the host cation-anion pairs. Generally, closed-shell ions become "stiffer" as they become smaller, a trend which becomes evident when the ρ's for ion pairs from different rows of the Periodic Table are examined.[26] This observation suggests that ρ' should be smaller when the ion is in the donor state than when it is in the acceptor state and that ρ' should be smaller than the host-crystal value when the impurity comes from a lower row of the Periodic Table. We have therefore investigated our results with a variable set of values for ρ' with results shown in Table III. We see that this reasonable variation of parameters has the effect of favoring acceptor action since the effect of the smaller radius which favors incorporation as a donor is reduced as the triply charged ion becomes stiffer. In particular, allowing ρ' for Tl^{3+} to be 0.36 Å and for Tl^{+} to be 0.38 Å pushes Tl more strongly into the acceptor category. Note, however, that the relative preference for acceptor versus donor action among the elements remains unchanged.

It is instructive to compare columns 5 and 2 of Table III. Taking Tl and In as examples we see that ΔU_{ion}, the sum of columns 5(a) and 5(b), is numerically greater for In than for Tl by 0.6 eV. The difference between Tl and In in column 2, on the other hand, is 3.3 eV. Most of the preference for donor incorporation for In and acceptor incorporation for Tl, therefore, comes from the lower ionization energies of the former rather than from vastly different energies of incorporation of the ions. It is also interesting to compare the differences in the electrostatic and repulsive energies between impurities. Again taking Tl and In as examples we find that for the donor ions of the two impurities the difference in electrostatic energies is 0.6 eV and in repulsive energies it is 0.11 eV; in the acceptor case the differences are negligible.

TABLE III. Energies of incorporation (eV) of Group-III elements as donors and acceptors with the following values for ρ' (in Å): 0.36 (Tl^{3+}), 0.34 (In^{3+}), 0.32 (Ga^{3+}), 0.30 (Al^{3+}), 0.38 (Tl^{+}), 0.36 (In^{+}), 0.34 (Ga^{+}), 0.32 (Al^{+}). The relative displacements ξ of nearest-neighbor ions for this set of parameters are as follows: −0.053 (Tl^{3+}), −0.059 (In^{3+}), −0.066 (Ga^{3+}), −0.069 (Al^{3+}), +0.060 (Tl^{+}), +0.062 (In^{+}), +0.054 (Ga^{+}), +0.052 (Al^{+}).

		Ionic energy donors		Ionic energy acceptors		Difference in ionic energy		
Element	Electron energy	(a) Electrost.	(b) Repuls.	(a) Electrost.	(b) Repuls.	(a) Electrost.	(b) Repuls.	Net difference in energy
Tl	42.2	−53.3	0.29	−12.3	0.75	−41.0	−0.46	0.7
In	38.9	−53.9	0.18	−12.3	0.70	−41.6	−0.52	−3.2
Ga	43.2	−54.9	0.01	−12.5	0.34	−42.4	−0.33	0.5
Al	39.2	−55.3	−0.08	−12.6	0.29	−42.7	−0.37	−3.9

Clearly then, the main differences between the energies comes from the differences in electrostatic energies of the donor ions. It should be stressed, however, that this effect is brought about by the difference in the impurity size factor $e^{-r_I/\rho'}$, which produces differences in the lattice distortion which have a larger effect on the electrostatic energies than on the repulsive energies.

Clearly it is also important to consider the effect of changing the values of the host parameters, such as α_+, α_-, or ρ. Such changes would affect both U_{ion} and U_{rep} explicitly through Eqs. (9) and (10). U_{ion} and U_{rep} also depend on the host parameters implicitly since the displacement ξ in turn depends on them. While we have carried out a few calculations in which we have changed some of these parameters we do not believe that a systematic investigation of this sort is worthwhile since there is no criterion by which an "optimum" set of values can be chosen. This would be possible if, for example, the energies of incorporation of the impurities starting from the vapor phase were known. It would even be possible if the ratio of donor and acceptor concentrations as a function of temperature were known since this ratio should be given by a Boltzmann factor $e^{-\Delta U/kT}$. It would then be possible to find a set of parameters which yields a ΔU which is in best agreement with the experimental value. Since, however, none of this information is available an optimization procedure for the choice of host parameters is not possible. We have therefore presented our results only for the "best" set of host-crystal parameters chosen in the manner explained at the end of Sec. II, and have varied only the impurity-anion stiffness parameter ρ'. [The two impurity-anion parameters A' and ρ' always appear together as the product $A' e^{r_I/\rho'}$ in Eqs. (5) and (10). Hence, by changing ρ' we have essentially investigated changes in the total impurity "size factor."]

IV. ROLE OF NEUTRAL SPECIES

In our treatment we have thus far ignored the possibility that the element remains neutral respect to the lattice. In this case the impurity carries the same charge as the doubly charged Pb ion which it replaces and does not introduce carriers into the system. The difference between the energies of incorporation as a donor and as a neutral atom will be given by

$$\Delta U^{DN} = V_{\text{IP }111} - E_W + E_G - (U^D_{\text{ion}} - U^A_{\text{ion}}) . \qquad (11)$$

The superscript DN denotes the neutral to donor transition; U^D_{ion} is the energy of incorporation of the triply charged donor ion as given by the sum of columns 3(a) and 3(b) of Table II or III; the energy of incorporation as the neutral atom is denoted as U^N_{ion}. As a crude estimate for U^N_{ion} we shall take it as twice the Madelung energy $2 \times 1.75e/a$, where the 2 comes from the charge on the ion and 1.75 is the Madelung potential. This estimate is valid if we assume that the electron which remains in the s level does not interact with the valence-band electrons. We have also neglected repulsive-energy effects which are small even for the donor and acceptor ions (see Tables II and III) and should be even smaller for an ion which carries no effective charge relative to the lattice. By analogy, the difference in energy between the neutral and the acceptor atoms becomes

$$\Delta U^{NA} = V_{\text{IP }11} - E_W - (U^N_{\text{ion}} - U^A_{\text{ion}}) . \qquad (12)$$

In Table IV we show ΔU^{DN} and ΔU^{NA} for Group-III elements. (We chose the values of U^D_{ion} and U^A_{ion} from Table III rather than from Table II since we believe these values to be more realistic for reasons discussed in the preceding section.) In all cases but Al the signs of ΔU^{DN} and ΔU^{NA} display an interesting effect: The energy of the electrically active state is higher than that of the neutral state. Taking Tl and Ga as examples we see that it takes more energy to incorporate these elements as acceptors than as neutral atoms; of course, it would take even more energy to incorporate them as donors. Similarly, according to the results of Table IV, it would take more energy to incorporate In as a donor than as a neutral atom. Only in the case of Al does the model predict that the energy of incorporation as an electrically active species is less than that of the neutral species. The theory therefore predicts that for all elements except Al only a fraction of the soluble atoms will be electrically active. As discussed in the following section we believe that the energy differences listed in Table IV are too large. The predictions of the model are, however, borne out by experiments on In[27] and therefore are probably qualitatively correct. Whether similar effects exist for Tl and Ga and whether all Al is indeed electrically active does not seem to have been reported in the literature.

TABLE IV. Difference between the energy of incorporation (eV) as donors or acceptors. The symbols ΔU^{DN} and ΔU^{NA} are defined in Eqs. (11) and (12).

	Tl	In	Ga	Al
ΔU^{DN}	3.6	1.1	2.6	−0.1
ΔU^{NA}	−3.0	−4.6	−2.3	−3.9

V. DISCUSSION

The method used here to calculate the energy of incorporation of an impurity in an ionic crystal was developed mainly in an attempt to understand the solubility of impurities in such crystals and was quite successful in this aim.[28] We do not believe that it has been used for the purpose employed here, namely, to understand the charge state of an impurity in a conventional semiconductor. Before turning to some remarks about its limitations for such a purpose we briefly summarize the results obtained in this paper: (1) The model predicts that some Group-III elements will be donors and some acceptors. (2) The model predicts that, with the exception of Al, the concentration of electrically inactive species will exceed that of the active species. The first prediction correctly predicts the behavior of Tl, In, and Al but not that of Ga. Not all experimental data should be given equal weight. In the first place it is well known that nonstoichiometric effects are very important in the lead chalcogenides and it is therefore necessary to know whether the doping action of a given element is that in stoichiometric material. Furthermore, data on polycrystalline or powdered material may be suspect. We believe, however, that the role of Tl and In as an acceptor and donor, respectively, is well established. For these elements Strauss[1(a)] has studied doping behavior in single-crystal material with attention being paid to nonstoichiometry effects. The data for Ga are very sparse[1(f),1(g)] but at least one of the investigations[1(g)] reports that Ga doping of PbTe produces high-resistivity material. If this behavior is corroborated by further work it would suggest that the energies of incorporation as a donor and as an acceptor are very close for Ga. If that is the case, the model could be refined by choosing slightly different stiffness parameters for Ga so as to reduce the net difference in energy to zero. Alternatively, the same effect would be achieved by slight changes in one or more of the host-crystal parameters. As an example, if the work function were taken as 4.35 eV instead of 4.1 eV, column 6 of Table III would yield zero for the net energy differences for Ga but would leave In and Al in the donor camp and Tl in the acceptor camp. Clearly, such small changes in either the impurity or the host parameters cannot be ruled out. At least the model can be considered successful in predicting the correct relative tendency for donor versus acceptor action of the various elements as seen in column 6 of Table III. As for the second prediction of the model, it has only been tested quantitatively for In. In this case, Rosenberg and Wald[27] report that In doping of PbTe leads to *n*-type material but that the donor concentration is only about one-hundredth that of the amount of In in the lattice. Assuming a Boltzmann distribution, this ratio of 10^{-2} would yield a difference between the energy of incorporation as the neutral and as the donor species of about 0.36 eV at the melting point. This value should be compared to a value of about 1 eV shown in Table IV. We consider the agreement adequate since slight changes in the various parameters could easily change the results by several tenths of an eV.

Probably one of the shortcomings of the purely ionic model employed here is the assumption that the electrons which remain in the *s* level of the impurity (two for the acceptor state of a Group-III element and one for the neutral state) do not interact with the electrons in the valence band of the host lattice. Probably such interaction will, however, occur, i.e., there will be some covalent bonding between the *s* electrons and valence-band electrons. The result will be that the energy of the electrons in the *s* level will be pulled down and this will stabilize the energy of the acceptor state. In the case where the theory predicts a strong preference for donor action, e.g., for In, we therefore expect that tendency to be reduced since the energy of the acceptor state will not be as much above that of the donor state as predicted by the simple theory.

Inclusion of the interaction of *s* electrons with the valence-band electrons may also shed light on the behavior of In in PbTe-SnTe alloys. As the SnTe content of these alloys is increased, In changes from a shallow donor with no freeze-out behavior in PbTe to a deeper impurity with a tendency to self-compensation.[29-31] The theory developed here, when corrected for interaction of the *s* electrons with the valence-band electrons, would account for this behavior. As SnTe is added to the PbTe one would expect that the second valence band, which is mainly composed of metal *s* levels,[4,12] would broaden toward higher energies since the *s* level of Sn is above that of Pb. Interaction with Group-III element *s* levels, which lie even above those of Sn, would thus become easier. The result will be that with increasing SnTe content the difference between the donor and acceptor states will narrow and may even disappear at some critical concentration. When this happens In will enter as a self-compensating impurity, i.e., in equal amounts as a donor and an acceptor.

In conclusion we believe that the ionic model presented here produces qualitatively correct insights into the doping behavior of Group-III elements in PbTe and, by extension, similar compounds. The charge state and hence the doping behavior of the impurity was seen to be determined by a subtle balancing of electron and ion-core energies. In particular, we believe that our calculations can provide good starting points for the perturbation potential produced by the impurity due to charge and lattice distortions. These potentials can then be used in a quantum-mechanical treatment of the problem.

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