

About the Mott and Littleton method for calculating the formation energy of point defects

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Abstract. Mott and Littleton developed a method to calculate the formation energy of point defects. This method was successfully used from 1938 to 1952, and it is the foundation of most of the subsequently developed efforts concerning the calculation of defect energies. Therefore, it is important to show an inconsistency in that fundamental work. In order to solve the problem which arises due to the inconsistency, we suppose that the ions (and the vacancies they leave), which surround the point defect, have a certain volume instead of considering them as points (as Mott and Littleton did). In this way, and following the rest of the Mott and Littleton formalism, we conclude that the displacements of the nearest neighbors to the point defects are very small, and sometimes even zero. When the displacements are considered to be zero, the theoretical value of the formation energy of Schottky pairs gets closer to the experimental values reported by other authors.

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1. Introduction

The Mott and Littleton [1] method was developed to calculate the formation energy of point defects in ionic crystals. Later on, this method was extended by Reitz and Gammel [2], Bassani and Fummi [3] and Ruíz-Mejía *et al.* [4], in order to calculate the formation energy of M^{2+} -cation complexes in different alkali halides. This method was also used by Tosi and Fumi [5], Tharmalingam and Lidiard [6], and Dienes [7], to calculate the formation energy of vacancies. An excellent review of the lattice defect studies carried prior to 1957 has been given by Lidiard [8].

The calculations of defect formation energies have been subsequently repeated by a number of authors, and nearly all of them have used the Mott and Littleton [1] description of the displacement field or some simple modification of it; for example: relaxation mechanisms such as the elastic relaxation first introduced by Brauer [9], and the deformation dipole relaxation considered by Kurosawa [10]. Tosi and Doyama [11] have made a consistent treatment of point defects in ionic crystals, using the Mott and Littleton [1] description and using the improved short-range potential constants of Fumi and Tosi [12,13]. Hardy [14,15] introduced a new

approach to the problem of neutral point defects in ionic crystals by making use of a technique due to Kanzaki [16] which has come to be called the method of "lattice statics".

Boswarva and Lidiard [17] and Boswarva [18] have performed several calculations within the Mott and Littleton [1] formalism. They determine the dependence of the Schottky formation energies on the electrostatic, elastic, and deformation dipole effects. They also study the dependence of the Schottky energies on the constants used in the Born-Mayer [19] short-range potential, and the applicability of the Born-Mayer-Verwey [20] potential.

The first attempt to replace the region, which Mott and Littleton [1] considered as a continuum, by a lattice model appeared in the work of Hatcher and Dienes [21,22]. In these papers, the aim of the extension of the Mott and Littleton [1] method was primarily the determination of the activation energies for the formation of neutral defects in ionic crystals. Quigley and Das [23,24] performed calculations in KCl, KBr and CsCl with Li^+ impurities. They allowed the defect to move along the $\langle 111 \rangle$, $\langle 100 \rangle$ and $\langle 100 \rangle$ directions in the lattice and they found a $\langle 111 \rangle$ off center place to have the minimum energy. In all of these papers, the primary technique used was the Mott and Littleton [1] method modified in some aspects: elastic relaxation [9], deformation dipoles [10], lattice statics [14,15], and rigid-ion model [21,22,23,24].

Scholz [25,26], the only one that does not use the Mott and Littleton [1] approach, calculated Schottky pair formation using a computer simulation of the lattice.

A very good review of the lattice defect energy calculations carried before 1970 was given by Hardy and Flochen [27].

The theory of point defects in ionic crystals is largely concerned with the treatment of lattice relaxation and the evaluation of the interionic potentials. The majority of defect calculations currently made are based on two-body potentials in which the non-coulombic forces are represented by Born-Mayer repulsive interactions. In many more recent papers [28,29,30], electronic polarization is accounted for by the use of a shell model suggested by Dick and Overhauser [31]. The contributions in this field of the theoretical group at Harwell are given by Catlow and Mackrodt [32].

The interionic potentials in alkali halides derived by Tosi and Fumi [13] have been used in many calculations of physical properties of liquids and solids [33,34,35].

There have been numerous attempts to present other potentials in ionic crystals [32,36]. These potentials have been critically studied by Eggenhoffner *et al.* [37,38], who have demonstrated that none of them is capable of yielding better agreement with experimental results than those obtained with the Fumi and Tosi parameters. Recently, Boswarva [39,40] and Gupta *et al.* [41] have reevaluated the Tosi and Fumi [13] potential parameters and they found good agreement with experimental results.

In the present paper, we review the Mott and Littleton [1] method and we claim that there is a missing term in their expression for the electric force. As the introduction of this term leads to an unsolvable system of equations, we suggest an alternative procedure to obtain the Schottky energies.

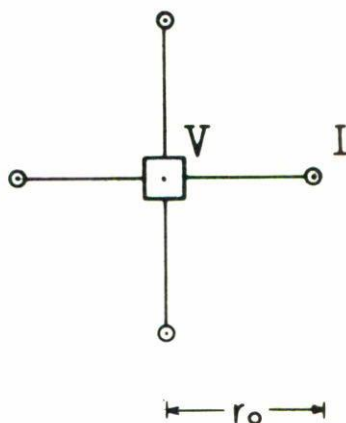


FIGURE 1. Region I: Vacancy (V) and its first nearest neighbors (I). r_0 = anion-cation distance.

2. Theory

In the Mott and Littleton [1] method, the crystal is divided into an inner region, region I, whose equilibrium is explicitly evaluated, and an outer region, region II, where the dipole moments and the displacements of the ions are obtained from the macroscopic polarization caused by the effective charge on the point defect.

In the first order approximation, the vacancy and its six nearest neighbors are chosen as region I. The outward displacement of the neighbors is called ξr_0 , and mer_0 is the outward induced dipole moment, where r_0 is the anion-cation distance, e is the electrostatic charge, and ξ and m are adjustable parameters. The configuration of region I is shown in Fig. 1.

As a rule [1,2,3,4], the electric force along (100) direction on any of the six nearest neighbors is presented as:

$$F_{\mp}^e = \frac{e^2}{r_0^2} \left[\frac{1 + \sqrt{2} + 0.25}{(1 + \xi)^2} - \frac{4(1 + \xi)}{(2 + 2\xi + \xi^2)^{3/2}} - \frac{1}{(2 + \xi)^2} \right. \\ \left. \mp \frac{(0.25 + 3/\sqrt{2})m}{(1 + \xi)^3} - (1.965M'_{\pm} + 0.388M'_{\mp}) \right] \quad (1)$$

where the negative sign corresponds to a positive ion vacancy and the positive sign to a negative ion vacancy. M'_+ and M'_- are related to the dipoles induced at distant positive and negative lattice sites (region II). Those dipoles are respectively

$$\frac{M'_+ r_0^3 e}{r^2} \quad \text{and} \quad \frac{M'_- r_0^3 e}{r^2}$$

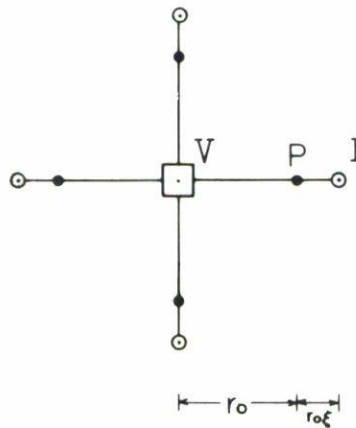


FIGURE 2. Vacancy (*V*), displaced nearest neighbors (*I*) and oppositely charged points (*P*) left by the ions. r_0 = anion-cation distance. ξr_0 = outward displacement.

at the position r in the lattice.

In order to notice that there is a missing term in equation (1), we will obtain it in some detail. The non displaced ions, which are the vacancy nearest neighbors, are in the positions $(\pm 1, 0, 0)r_0$, $(0, \pm 1, 0)r_0$ and $(0, 0, \pm 1)r_0$. When the displacement takes place, the new positions of the ions are $(\pm(1 + \xi), 0, 0)r_0$, $(0, \pm(1 + \xi), 0)r_0$ and $(0, 0, \pm(1 + \xi))$, and they leave points oppositely charged at their old positions (Fig. 2).

The electrical force F_{\mp}^e is calculated on the displaced ion $(1 + \xi, 0, 0)r_0$ and it is due to the vacancy, the rest of the displaced ions, the oppositely charged points and the dipoles formed in the displaced ions and in region II.

The electrical force in $(1 + \xi, 0, 0)r_0$ due to the vacancy is

$$\overline{F}_{\mp}^e(\text{vacancy}) = \frac{e^2}{r_0^2} \frac{1}{(1 + \xi)^2} \hat{i}. \tag{2}$$

The electrical force due to the charged point at $(-1, 0, 0)r_0$ is

$$\overline{F}_{\mp}^e((-1, 0, 0)r_0) = -\frac{e^2}{r_0^2} \frac{1}{(2 + \xi)^2} \hat{i}. \tag{3}$$

And that due to the ion at $(-1 - \xi, 0, 0)r_0$ is

$$\overline{F}_{\mp}^e((-1 - \xi, 0, 0)r_0) = \frac{e^2}{r_0^2} \frac{1}{[2(1 + \xi)]^2} \hat{i}. \tag{4}$$

We also have

$$\overline{F}_{\mp}^e((0, 1, 0)r_0) = -\frac{e^2}{r_0^2} \frac{(1 + \xi)\hat{i} + \hat{j}}{[1 + (1 + \xi)^2]^{3/2}} \tag{5}$$

$$\overline{F}_{\mp}^e((0, 1 + \xi, 0)r_0) = \frac{e^2}{r_0^2} \frac{(1 + \xi)\hat{i} - (1 + \xi)\hat{j}}{[2 + (1 + \xi)^2]^{3/2}}. \tag{6}$$

The charged points at $(0, -1, 0)r_0$, $(0, 0, 1)r_0$ and $(0, 0, -1)r_0$ give equations analogous to equation (5). There is an equivalent result (equation (6)) for the displaced ions associated with those charges points.

The \hat{i} component of \overline{F}_{\mp}^e in equations (2), (4) and 4 times (6) gives the term

$$\frac{e^2}{r_0^2} \frac{(1 + 0.25 + \sqrt{2})}{(1 + \xi)^2}. \tag{7a}$$

Four charged points give the same contribution (component \hat{i} of equation (5)), so we obtain the second term of equation (1)

$$-\frac{e^2}{r_0^2} \frac{4(1 + \xi)}{(2 + 2\xi + \xi^2)^{3/2}}. \tag{7b}$$

From equation (3), we get the third term of equation (1),

$$-\frac{e^2}{r_0^2} \frac{1}{(2 + \xi)^2}. \tag{7c}$$

The fourth term in equation (1) comes from the electronic moments on the first nearest neighbors to the vacancy calculated at the point $(1 + \xi, 0, 0)r_0$. The last term comes from the moments in region II, and the numerical coefficients were calculated by Mott and Littleton [1]. As the fourth and fifth terms are not important for our purposes, we will not discuss them.

Aparently, all the contributions to the electrical force have been taken into account in equation (1). However, and to point out this fact is the main purpose of this paper, there is one term that has not been considered in equation (1): the corresponding to the charged point at $(1, 0, 0)r_0$. The electrical force due to it is

$$\overline{F}_{\mp}^e((1, 0, 0)r_0) = \frac{e^2}{r_0^2 \xi^2} \hat{i}, \tag{8}$$

so equation (1) must actually be

$$F_{\mp}^e = \frac{e^2}{r_0^2} \left[\frac{1 + \sqrt{2} + 0.25}{(1 + \xi)^2} - \frac{4(1 + \xi)}{(2 + 2\xi + \xi^2)^{3/2}} - \frac{1}{(2 + \xi)^2} - \frac{1}{\xi^2} \right. \\ \left. \mp \frac{(0.25 + 3/\sqrt{2})m}{(1 + \xi)^3} - (1.965M_{\pm}' + 0.388M_{\mp}') \right] \quad (1')$$

In this way, we do not arbitrarily omit the contribution of the charged point at $(1, 0, 0)r_0$.

In order to obtain the displacement ξ and the moment m through the force balance method, it is necessary the repulsive force

$$F_{\mp}^r = -A \exp \left[- \left(1 - \xi - \frac{M'}{4} \right) \frac{r_0}{\rho} \right] + \frac{4A}{d} \left[\xi + \frac{M'}{2\sqrt{2}} \right] \exp - \left[\frac{dr_0}{\rho} \right] \\ + 2\sqrt{2}C_{\mp} \left[-\sqrt{2}(1 + \xi) \frac{r_0}{\rho} \right] + \frac{4C_{\mp}}{\lambda} \left[\xi - \frac{M'}{3\sqrt{3}} \right] \exp - \left[\frac{\lambda r_0}{\rho} \right] \quad , \quad (9) \\ - \frac{4C_{\mp}}{\eta} \left[1 - \xi + \frac{2M'}{5\sqrt{5}} \right] \exp - \left[\frac{\eta r_0}{\rho} \right]$$

where

$$A = C_{+-} b \rho^{-1} \exp \left(\frac{r_+ + r_-}{\rho} \right), \quad C_{\mp} = C_{\mp\mp} b \rho^{-1} \exp \left(\frac{2r_{\mp}}{\rho} \right),$$

$$d = \sqrt{\left(\xi + \frac{M'}{2\sqrt{2}} \right)^2 + \left(1 - \frac{M'}{2\sqrt{2}} \right)^2},$$

$$\lambda = \sqrt{\left(\xi - \frac{M'}{3\sqrt{3}} \right)^2 + 2 \left(1 + \frac{M'}{3\sqrt{3}} \right)^2},$$

and

$$\eta = \sqrt{\left(1 - \xi + \frac{2M'}{5\sqrt{5}} \right)^2 + \left(1 + \frac{M'}{5\sqrt{5}} \right)^2}$$

with $C_{+-} = 1$, $C_{--} = 0.75$, $C_{++} = 1.25$, $\rho = 0.345 \times 10^{-8}$ cm, $b = 0.299 \times 10^{-12}$ ergs and $e = 4.8025 \times 10^{-10}$ esu.

The other necessary equations are

$$\frac{\alpha_{\mp} F_{\mp}^e}{e} = \pm mer_0 \quad (10)$$

$$F_{\mp}^e + F_{\mp}^r = 0. \quad (11)$$

Then, ξ and m are obtained through equations (1), (9), (10) and (11). However, if we use the correct equation (equation(1')) instead of equation (1), there is no solution to the system of equations. As a matter of fact, the term given by equation (8) is numerically much bigger than any of the terms in equation (1), and cannot be neglected in equation (1').

In order to be able to use (1'), we have considered that the holes left behind by the ions (vacancy nearest neighbors) when they move to their displaced positions, are not merely charged points, but they have spherical volume and a uniformly distributed charge. We make the same assumption for the ions. Then equation (1') changes to

$$F_{\mp}^e = \frac{e^2}{r_0^2} \left[\frac{1 + Q(\sqrt{2} + 0.25)}{(1 + \xi + x)^2} - \frac{4Q(1 + \xi + x)}{[(1 + \xi + x)^2 + (1 - x)^2]^{3/2}} - \frac{Q}{(2 + \xi)^2} - \frac{Q}{(\xi + 2x)^2} \mp \frac{(0.25 + 3/\sqrt{2})m}{(1 + \xi)^3} - (1.965M'_{\pm} + 0.388M'_{\mp}) \right] \quad (12)$$

where

$$Q = \frac{3\xi}{4y} - \frac{\xi^2}{16y^3}, \quad x = \frac{2}{3}y - \frac{\pi}{2}\xi \quad \text{and} \quad y = \frac{r_{\mp}}{r_0};$$

r_{\mp} is the radius of the negative and positive ions.

According to this model, the overlapping parts of the charge of the spherical ion and the spherical hole left behind do not contribute to the electrical force.

3. Results and discussion

Table I shows the displacements of the first nearest neighbors of a positive ion and a negative ion vacancies using equations (9), (10), (11), and (12). For a negative ion vacancy there is solution for all the alkali halides. In the case of a positive ion vacancy there is no solution for some of the alkali halides. When there are no solutions we see that $|F_{\mp}^e|$ and $|F_{\mp}^r|$ are closer to each other in value when ξ tends to zero.

For the calculations of the displacements we have taken into account the Brauer [9] term ξ (1.965 - 0.388) in the electrical force in order to include the elastic effect.

	ξ_-	E_-^v	ξ_+	E_+^v
LiCl	0.0166	5.3997	0.0133	5.7856
NaCl	0.0216	4.7677	0.0195	5.1663
KCl	0.0000		0.0155	5.0924
RbCl	0.0000		0.0032	5.7776
LiBr	0.0118	4.4398	0.0112	4.8122
NaBr	0.0128	4.2406	0.0169	4.5846
KBr	0.0000		0.0122	7.8800
RbBr	0.0000		0.0035	6.9862
LiI	0.0071	5.3322	0.0090	6.1785
NaI	0.0060	5.4033	0.0136	5.7535
KI	0.0000		0.0090	6.5442
RbI	0.0000		0.0029	9.1364
LiF	0.0598	5.8011	0.0255	6.2388
NaF	0.0551	5.6707	0.0355	5.9174
KF	0.0331	5.2366	0.0291	5.6400
RbF	0.0259	4.9644	0.0167	5.6161

TABLE I. Displacements (ξ_- , ξ_+) of the vacancy first nearest neighbors, and formation energies (E_+^v , E_-^v ; in eV) of positive and negative ion vacancy.

When the Van der Waals term was included for the cases in which $\xi = 0$, we obtained non-physical solutions ($\xi \approx 0.5$). Then, in Table I we take into account the elastic effect only. Table I also shows the formation energy of the vacancies corresponding to each ξ and m .

The formation energy of a Schottky pair [8] is $E^s = E_+^v + E_-^v - E_L$, where E_+^v and E_-^v are the formation energies of a positive and a negative ion vacancy respectively, and E_L is the lattice energy per pair of ions. In order to compare our results with the experimental ones, we have done the calculation of E_+^{v0} and E_-^{v0} when $\xi = 0$. Also in the cases when ξ is different from zero but very small, we have put $\xi = 0$ and we used the expression for E_+^{v0} and E_-^{v0} . Table II shows the energies E_+^{v0} , E_-^{v0} (order zero) [1] and E_L for all the alkali halides.

Table III shows the theoretical and experimental values of the Schottky energies and they are compared with the values obtained by Boswarva and Lidiard [17].

4. Conclusions

We have used the balance force method in order to find ξ and m . The expression for F_{\mp}^e had to be change from equation (1) to equation (12), But even when a minimization energy method [17] is used, and expression for F_{\mp}^e is necessary to find the value of m .

From Table III we can see that for the alkali halides with $\xi = 0$ (marked with an asterisk) the value of E^s is in good agreement with experimental results [17].

	$E_-^{v_0}$	$E_+^{v_0}$	E_L
LiCl	5.0513	5.5785	8.6881
NaCl	5.0140	5.4639	8.0000
KCl	4.8054	4.9706	7.2561
RbCl	4.4574	4.5473	6.8160
LiBr	4.7545	5.2729	8.1740
NaBr	4.7556	5.1571	7.5980
KBr	4.5617	4.7962	6.9491
RbBr	4.4033	4.5628	6.6900
LiI	4.4457	4.9293	7.5541
NaI	4.3674	4.7989	7.0662
KI	4.2340	4.5388	6.5251
RbI	4.1817	4.4277	6.3700
LiF	6.4041	6.7815	10.7930
NaF	6.1024	6.1887	9.5560
KF	5.5412	5.3997	8.4260
RbF	5.3879	5.1852	6.8162

TABLE II. Order zero formation energies ($E_+^{v_0}, E_-^{v_0}$; in eV), and lattice energy (E_L in eV) per pair of ions.

	E^* (B-L)	E^* (this work)	E^* (experimental [17])
LiCl	1.0830	3.7817	2.1200
NaCl	1.7940	3.8236	2.1200
KCl	1.9780	2.5201*	2.2200
RbCl	1.9840	2.1887*	
LiBr	0.9170	3.9752	1.8000
NaBr	1.6220	3.7184	1.6800
KBr	1.8690	2.3147*	2.5300
RbBr	1.8720	2.2761*	
LiI	0.6400	1.8210*	1.3400
NaI	1.3500	2.1004*	
KI	1.7000	2.2478*	
RbI		2.2395*	
LiF	1.6430	4.9438	2.6800
NaF	2.2900	4.4649	
KF	2.0402	4.2127	
RbF	1.8490	4.2989	

TABLE III. Theoretical (B-L = Boswarva and Lidiard; and this work) and experimental values [17] of formation energy (E^* in eV) of a Schottky pair. Asterisk corresponds to $\xi = 0$.

The main conclusion is that the picture of point charges must be changed if we one conserve the Mott and Littleton [1] formulation.

References

1. N.F. Mott and M.J. Littleton, *Trans. Faraday Soc.* **34** (1938) 485.
2. J.R. Reitz and J.L. Gammel, *J. Chem. Phys.* **19** (1951) 894.
3. F. Bassani and F.G. Fumi, *Nuovo Cimento* **11** (1954) 274.
4. C. Ruíz-Mejía, U. Oseguera, H. Murrieta and J. Rubio, *J. Chem. Phys.* **73** (1980) 60; U. Oseguera, H. Murrieta, C. Medrano, J. Rubio and C. Ruíz-Mejía, *J. Chem. Phys.* **73** (1980) 1132.
5. M.P. Tosi and F.G. Fumi, *Nuovo Cimento* **7** (1958) 95.
6. K. Tharmalingam and A.B. Lidiard, *Philp. Mag.* **6** (1961) 1157.
7. G.J. Dienes, *J. Chem. Phys.* **16** (1948) 620.
8. A.B. Lidiard, *Handbuch der Physik* **20** 246, Springer, Berlin (1957).
9. P. Brauer, *Z. Naturforsch.* **7a** (1952) 327.
10. T. Kurosawa, *J. Phys. Soc. Jap.* **13** (1958) 153.
11. M.P. Tosi and M. Doyama, *Phys. Rev.* **151** (1966) 642.
12. J.G. Fumi and M.P. Tosi, *J. Phys. Chem. Solids* **25** (1964) 31.
13. J.G. Fumi and M.P. Tosi, *J. Phys. Chem. Solids* **25** (1964) 45.
14. J.R. Hardy, *J. Phys. Chem. Solids* **15** (1960) 39.
15. J.R. Hardy, *J. Phys. Chem. Solids* **23** (1962) 113.
16. H. Kanski, *J. Phys. Chem. Solids* **2** (1957) 24.
17. S.M. Boswarva and A.B. Lidiard, *Phil. Mag.* **17** (1967) 805.
18. S.M. Boswarva, *Phil. Mag.* **17** (1967) 827.
19. M. Born and J.E. Mayer, *Z. Phys.* **75** (1932) 1.
20. E.J.W. Verwey, *Rec. Trav. Chim.* **65** (1946) 521.
21. R.D. Hatcher and G.J. Dienes, *Phys. Rev.* **124** (1961) 726.
22. R.D. Hatcher and G.J. Dienes, *Phys. Rev. A* **134** (1964) 214.
23. R.J. Quigley and T.P. Das, *Phys. Rev.* **164** (1967) 1185.
24. R.J. Quigley and T.P. Das, *Phys. Rev.* **177** (1969) 1340.
25. A. Scholz, *Phys. Stat. Sol.* **7** (1964) 973.
26. A. Scholz, *Phys. Stat. Sol.* **25** (1968) 285.
27. J.P. Hardy and J.W. Flocken, *Crit. Rev. Sol. State Sci.* 605 (1970).
28. I.D. Faux and A.B. Lidiard, *Z. Naturforsch.* **26a** (1971) 62.
29. C.R.A. Catlow and M.J. Norgett, *J. Phys. C: Solid St. Phys.* **6** (1973) 1325.
30. C.R.A. Catlow, I.D. Faux and M.J. Norgett, *J. Phys. C: Solid St. Phys.* **9** (1976) 419.
31. B.G. Dick and A.W. Overhauser, *Phys. Rev.* **112** (1958) 90.
32. C.R.A. Catlow and W.C. Mackrodt, *Computer Simulation of Solids*, Springer-Verlag, Heidelberg, New York (1982).
33. F.M. Ree and A.C. Holf, *Phys. Rev. B* **8** (1973) 826.
34. M.J.L. Sangster and M. Dixon, *Adv. Phys.* **25** (1976) 247.
35. J.W.E. Lewis, K. Singer and L.V. Woodcock, *J. Chem. Soc. Faraday Trans.* **112** (1975) 301.
36. M.J.L. Sangster and R.M. Atwood, *J. Phys. C* **11** (1978) 1523.
37. R. Eggenhoffner, F.G. Fumi and C.S.N. Murthy, *J. Phys. Chem. Solids* **43** (1982) 583.
38. R. Eggenhoffner, C.S.N. Murthy and F.G. Fumi, *J. Phys. Chem. Solids* **39** (1978) 1295.
39. I.M. Boswarva, *J. Phys. Chem. Solids* **42** (1981) 487.

40. I.M. Boswarva and C.S.N. Murthy, *J. Phys. Chem. Solids* **42** (1981) 409.
41. R.K. Gupta, A. Shiromany, P.S. Bakhshi and J. Shanker, *J. Phys. Stat. Sol. (b)* **127** (1985) 473.

Resumen. Mott y Littleton desarrollaron un método para calcular la energía de formación de defectos puntuales. Este método se usó con éxito de 1938 a 1952 y es la base de la mayoría de los desarrollos subsecuentes relacionados con el cálculo de energías de defectos. Por lo tanto es importante mostrar una inconsistencia en ese trabajo fundamental. Con el fin de resolver el problema que surgió de la inconsistencia, nosotros suponemos que los iones (y las vacancias correspondientes), los cuales rodean al defecto puntual, tienen un cierto volumen, en vez de considerarlos como defectos puntuales (tal como lo hicieron Mott y Littleton). De esta manera y siguiendo, en lo demás, el método de Mott y Littleton concluimos que los desplazamientos de los iones vecinos al defecto son pequeños y en algunos casos son iguales a cero. Cuando los desplazamientos son iguales a cero la energía de formación de pares de Shottky calculada resulta muy cercana al valor experimental.