Theor Chem Acc (2000) 103:205–208
DOI 10.1007/s002149900035

Theoretical
Chemistry Accounts

Perspective

Perspective on "Conduction in polar crystals. I. Electrolyte conduction in solid salts"

Mott NF, Littleton MJ (1938) Trans Faraday Soc 34: 485

C.R.A. Catlow

Davy Faraday Research Laboratory, The Royal Institution of Great Britain, 21, Albemarle Street, London W1X 4BS, UK

Received: 8 March 1999 / Accepted: 29 March 1999 / Published online: 28 June 1999

Abstract. We survey the consequences of the landmark paper in the development of the contemporary theories of defects in solids – a core area of modern solid-state science. We summarise the basic concepts behind the "Mott–Littleton" approach and the developments to which it has led.

Key words: Defects in solids – Iouic transport – Nonstoichiometry

---

1 Introduction

The structures, energies and mobilities of defects in crystalline solids play a central role in controlling the thermodynamic, transport, electrical and chemical properties of materials. The science of defects in solids began to develop in the 1920s and 1930s with the pioneering work of Frenkel, Schottky, Jost and Wagner which established the basic nature of point defects and defect reactions, and of their generation by thermal or chemical means.

An understanding of the behaviour and consequences of defects in solids requires knowledge of their formation and migration energies. The derivation of these crucial parameters from experimental data is frequently difficult, and in many cases impossible. Independent estimates from theory were therefore necessary for the development of the field. The pioneering work of Mott and Littleton [1] laid the foundation for the modern quantitative studies of defects in polar solids, which have had a major impact on contemporary solid-state chemistry and physics.

2 The Mott–Littleton method

The basic concept behind the technique advanced in this seminal paper is simple. In the region close to a defect, the forces exerted on the surrounding lattice are strong; this region is treated explicitly, i.e. atomic positions are adjusted to the equilibrium positions using knowledge of the interatomic forces. For more distant regions, the forces are weaker and in polar materials will essentially correspond to the polarisation of the crystal by the effective charge of the defect and can be estimated on the basis of the macroscopic dielectric constant. This approach, in its modern formulation, is summarised in Fi.g. 1, in which an interface region is used between the two regions. The defect formation energy depends on the position of the atoms (x) in the inner region and the displacements (y) in the outer region, and can be written as

$$E_D(x,y) = E_1(x) + E_{1,2}(x,y) + E_2(y) \ , \tag{1}$$

where the first and last terms on the right-hand side of the equation arise from the inner and outer regions, respectively, and the second term represents the interaction between the inner region and the displacements in the outer region. E_2 is generally considered to be quadratic in y and invocation of the equilibrium condition allows y to be written in terms of the

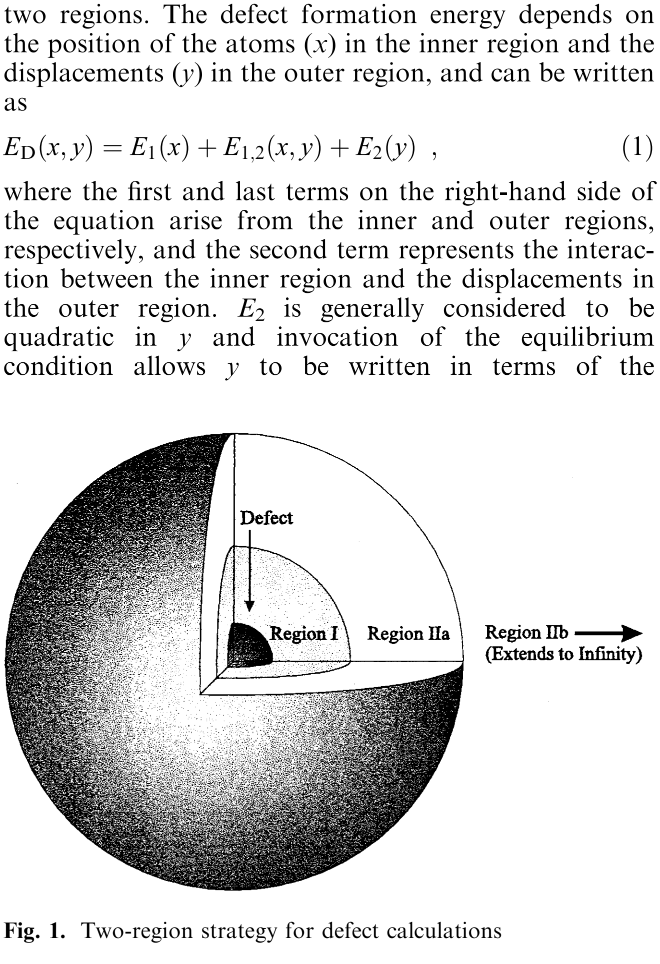

Fig. 1. Two-region strategy for defect calculations

derivative of $E_{1,2}$ and hence the explicit dependence of the total energy on E_2 is removed.

Details of the theory are given in Refs. [1–3]. Ref. [3] provides a good survey of the field up to the 1980s.

3 The development of the method

Since the application of the method to all but the simplest and most-restricted models requires intensive numerical calculations, its widespread use had to wait until the advent of modern computation. Useful progress was made by, for example, Barr and Lidiard [4] in the 1960s in applying the method to the classic problem of vacancy defects in ionic crystals. The major breakthrough was, however, the development by Norgett [5] of the first general-purpose computer code, HADES, for modelling defects in ionic crystals employing a methodology based on the Mott–Littleton approach. A crucially important feature of the implementation of the method in HADES was the use of the shell-model treatment of ionic polarisation [6], which is based on a simple mechanical model of polarisability in which a core is coupled to a shell (representing the polarisable valence shell electron) by a harmonic spring, which has proved very effective in modelling polarisation properties of these materials.

The field developed rapidly in the 1970s, with applications of the technique to both halide [7, 8] and oxide [9–11] crystals which demonstrated the qualitative reliability of the method for calculating both formation and migration energies of defects, given reliable interatomic potentials.

During the same period, it also became apparent that the method could be used to provide qualitative guidance as to the nature of complex defect structures in heavily doped and nonstoichiometric materials. One of the best examples was the study [12] of defect aggregation in nonstoichiometric wustite ($Fe_{1-x}O$) – a problem that still remains controversial. This study, however, established the stability of the defect aggregate shown in Fig. 2, in which four vacancies surround a central Fe^{3+} interstitial site moreover it suggested ways in which these "4:1" clusters could aggregate.

During the 1980s, there were four major developments. First, the method was extended to noncubic crystals in the HADES3 [13] and CASCADE [14] codes. Secondly, Gillan and Jacobs [15] and Harding [16] introduced methods for calculating defect entropies based on the perturbation of the vibrational density of states by the defect. Thirdly, the method was adapted by Tasker [17] and Mackrodt [18] to treat surface defects. Finally, work started on interfacing the Mott–Littleton approach with quantum cluster calculations. In such studies, the core of region I, comprising the defect and one or two surrounding shells of atoms, is treated quantum mechanically; care must be taken to ensure consistency between the relaxation of the quantum mechanically described component and the relaxed classically modelled lattice. Such an approach was implemented in the ICECAP code [19], and developments of the approach are still being actively pursued.

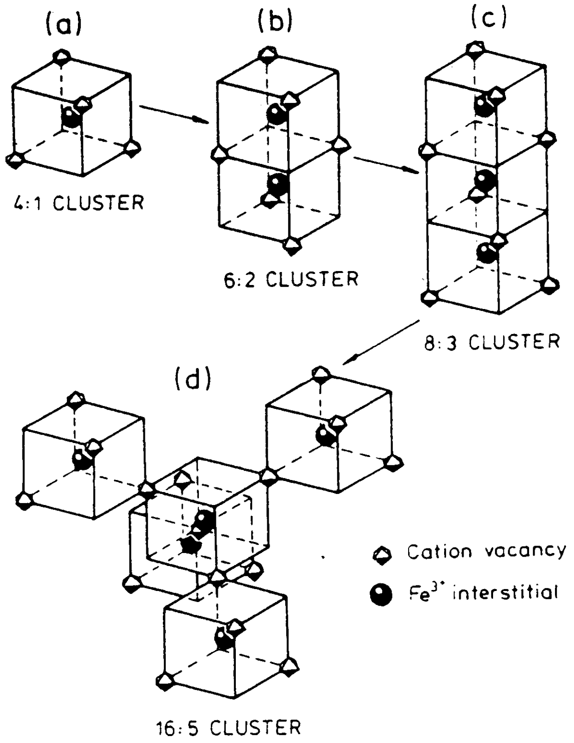

Fig. 2a–d. Vacancy–interstitial clusters in $Fe_{1-x}O$. **b, c** and **d** are different forms of linking the basic "4:1" cluster shown in **a**

During the same period, the range and sophistication of the applications developed. Representative new areas included the extensive range of simulation studies of defects in superionic conductors [20] in high-temperature superconductors (see, for example, Refs. [21, 22]) and the detailed studies of the complex defect chemistry arising from the creation of fission products in CUO_2 nuclear fuels [23].

4 Present status and future development

The Mott–Littleton method is now a routine tool in computational solid-state chemistry and physics, and is implemented, together with other static lattice modelling tools, in the GULP code [24], written by Gale. Two recent applications serve to illustrate the range and diversity of current applications.

The first relates to the crucial and controversial question of the nature of charge carriers in high-temperature superconductors. Early work [25] had established the usefulness of the Mott–Littleton approach in modelling localised electron states in ionic crystals. Recent work of Catlow, Islam and Zhang [26] (which built on earlier studies of the same authors) examined the stability of hole pairs or "bipolarons" in the La_2CuO_4 superconductor. It is generally accepted that electron holes in these materials are O(2*p*) in character, i.e. to a very simple approximation they correspond to localised O^- ions. Hole pairs would therefore correspond to O_2^{2-} i.e. peroxyanions, located at a pair of lattice sites. Mott–Littleton calculations indeed suggest that such species are weakly bound with respect to isolated hole species, in both configurations shown in Fig. 3. These results do not, of course, necessarily show that such species are the charge carriers in high-temperature superconductors. They do, however, suggest that peroxy bipolarons may play a significant role in the electronic behaviour of the material, either above or below the critical temperature.

The second example concerns the mobility of oxygen vacancies in doped perovskite-structured materials – a problem of substantial technological importance in view of the widespread use of these materials as oxygen-ion-conducting solid electrolytes. The materials are normally "acceptor doped", i.e. low-valence ions substitute for either the A or B metal ion of the ABO_3 perovskite–structured material. The work of Cherry et al. [27] established that the vacancies which are created as charge compensators for the dopant have a relatively low activation energy and migrate by the mechanism shown in Fig. 4a. More importantly, Cherry et al. [27] investigated the variation of the oxygen vacancy activation energy with the A/B cation radius ratio (expressed as the tolerance factor $t = (r_A + r_O)\sqrt{2}(r_B + r_O)$, where r_A, r_B and r_O are the A, B and oxygen ion radii, respectively). The results, illustrated diagrammatically in Fig. 4b, show the strong effect of t on the activation energy and indicate that a value for t of about 0.8 will give the lowest activation energy and the maximum conductivity. The result illustrates the increasingly predictive nature of these calculations and also their growing potential in materials design.

The future of the field will unquestionably be in this kind of predictive and design application. We can also anticipate rapid growth in the use of embedded-cluster techniques in which, as described earlier, the core region surrounding the defect is treated by a high-level quantum mechanical method. With these and other developments, methods building on the approach established in Mott and Littleton's remarkable paper are likely to continue to play a productive role in simulating the complex solid-state chemistry of defective compounds.

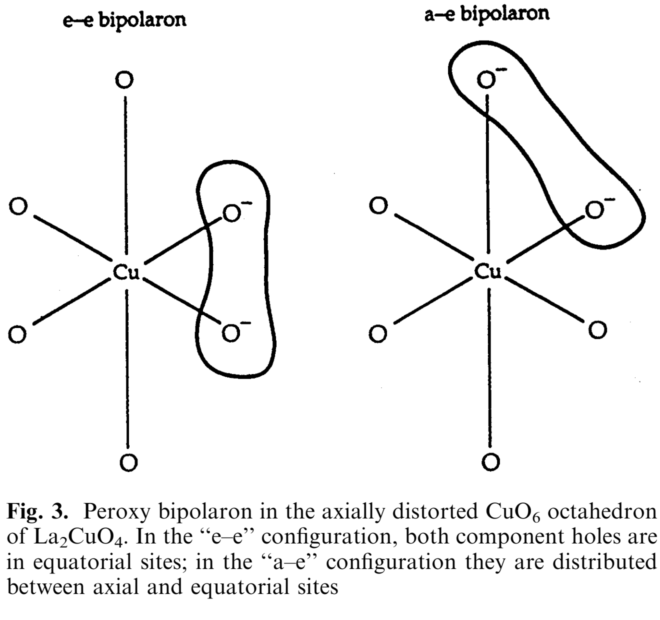

Fig. 3. Peroxy bipolaron in the axially distorted CuO_6 octahedron of La_2CuO_4. In the "e–e" configuration, both component holes are in equatorial sites; in the "a–e" configuration they are distributed between axial and equatorial sites

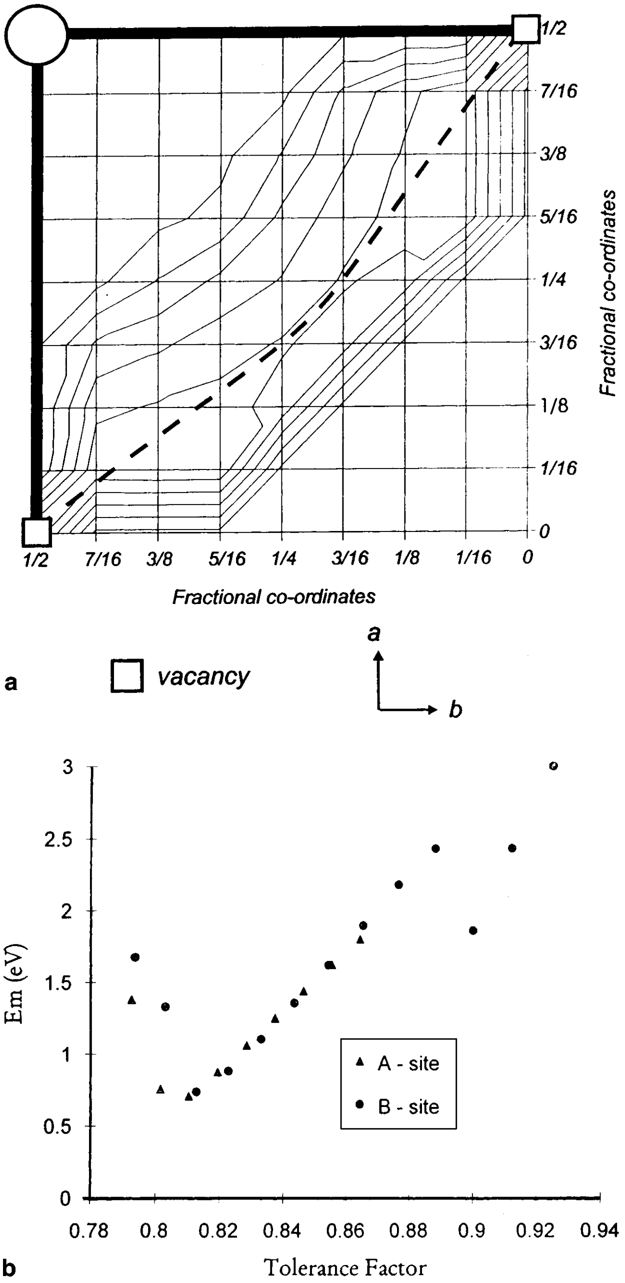

Fig. 4. Contour plot of the potential-energy surface for oxygen-vacancy migration, showing the curved path between adjacent anion sites of a BO_6 octahedron (in the *ab* plane). **b** Calculated migration energy as a function of the tolerance factor (from both the A and B site simulations)

Acknowledgements. I am grateful to many colleagues for collaboration and discussion relating to the Mott–Littleton method, but perhaps most notably to A.B. Lidiard, A.M. Stoneham, M.J. Norgett, J.H. Harding, R.W. Grimes, M.S. Islam, R.A. Jackson, P.W.M. Jacobs, J. Corish and A.V. Chadwick.

References

1. Mott NF, Littleton MJ (1938) Trans Farady Soc 34: 485
2. Catlow CRA, Mackrodt WC (1982) Lect Notes Phys 166: 3
3. (1989) J Chem Soc Faraday Trans 2: 85

4. Barr LW, Lidiard AE (1970) In: Eyring H, Henderson D, Joist W (eds) Physical chemistry – an advanced treatise, vol 10, chapter 3, Academic Press, New York
5. Norgett MJ (1974) UKAEA Report AERE–R7650
6. Dick BG, Overhauser AW (1958) Phys Rev 112: 90
7. Catlow CRA, Norgett MJ, Ross TA (1977) J phys C 10: 1627
8. Catlow CRA, Corsih I, Diller KM, Jacobs PWM, Norgett MJ (1979) J Phys C 12: 451
9. (a) Catlow CRA (1975) Proc R Soc Lond Ser A 353; (b) Catlow CRA (1977) Proc R Soc Lond Ser A 533
10. Catlow CRA, Mackrodt WC, Norgett MJ, Stoneham AM (1977) Philos Mag 35: 177
11. Mackrodt WC, Stewart RE (1979) J Phys C 12: L131
12. Catlow CRA, Fender BEF (1975) J Phys C 8: 3267
13. Catlow CRA, James R, Mackrodt WC, Stewart RE (1982) Phys Rev B Condens Matter 25: 1006
14. Leslle MJ (1984) Daresbury Laboratory Report DL/SCI/TM36T
15. Gillan MJ, Jacobs PWM (1983) Phys Rev B 28: 159
16. Harding JH (1989) J Chem Soc Faraday Trans 2 85: 351
17. Tasker PW (1979) Philos Mag 39: 119
18. Mackrodt WC (1989) J Chem Soc Faraday Trans 2 85: 541
19. Harding JH, Harker AH, Keegstra PB, Pandey P, Vail JM, Woodward C (1985) Physica B 131: 151
20. Catlow CRA (1983) Solid State Ionics 8: 89
21. Allan NL, Mackrodt WC (1988) Philos Mag A 58: 555
22. Allan NL, Mackrodt WC (1989) J Chem Soc Faraday Trans 2 85: 385
23. Grimes RW, Catalow CRA (1991) Philos Trans R Soc Lond, Ser A 335: 609
24. Gale JD (1997) J Chem Soc Faraday Trans 93: 629
25. Tasker PW, Stoneham AM (1977) J Phys Chem Solids 38: 1185
26. Catlow CRA, Islam MS, Zhang X (1998) J Phys Condensed Matter, 3: L49
27. Cherry M, Islam MS, Catlow CRA (1995) J Solid State Chem 118: 125