

A three-body force shell model calculation of Schottky defect formation energies of ionic crystals with CsCl structure

V MISHRA, S P SANYAL* and R K SINGH†

Department of Physics, Bhopal University, Bhopal 462 026, India

*Present address: Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, D-7000, Stuttgart-80, Federal Republic of Germany.

†Centre for Science and Technology Development Studies, MAPCOST, Bhopal 462 016, India

MS received 19 May 1986; revised 4 November 1986

Abstract. A three-body force shell model (TSM) for the calculation of Schottky defect formation energies in solids with cesium chloride structure has been developed by incorporating the effects of long-range three-body interactions (TBI) in the shell model. These TBI in the defect lattice arise from the deformation of electron shells when the nearest neighbour ions get relaxed from their equilibrium position. This model has been used to calculate the cation and anion extraction and Schottky defect formation energies of CsCl, CsBr, CsI, TlCl, TlBr and NH_4Cl crystals. The calculated values of these defect properties agree reasonably well with their measured values.

Keywords. Schottky defect energy; rigid shell model; polarizable point ion model; three-body force shell model.

PACS No. 61.70

1. Introduction

In an earlier paper (Mishra *et al* 1986) (referred to as I), we have reported a modified polarizable point ion (PPI) model which includes the effects of long-range three-body interactions (TBI) for the calculation of point defect formation energies of solids with CsCl structure. As pointed out in I, the PPI model neglects the dependence of the short-range forces on the electronic polarization of ions and predicts substantially higher values of static and dielectric constants. In the presence of an electric field, the electrons get displaced and consequently, the short-range forces between the ions also change. Since the PPI model considers the ions to be point charges, it fails to account for the electronic polarization and hence fails to predict the Cauchy violation in the elastic constants, phonon dispersion curves, dielectric and optical properties of ionic solids.

A satisfactory prediction of the polarization effects in ionic solids has been achieved from the rigid shell model (RSM) developed by Woods *et al* (1960). The ionic charges (Ze) in RSM consists of core (Xe) and shell (Ye) charges such that $Ze = Xe + Ye$. Its shell can move bodily with respect to its core and this mechanism gives rise to electronic polarization. The corresponding cation (α_+) and anion (α_-) polarizabilities have been defined in terms of the core-shell force constant (K_{\pm}) as (Woods *et al* 1960):

$$\alpha_{\pm} = (Ye)^2 / (K_{\pm} + R_0), \quad (1)$$

†To whom all correspondence should be addressed.