A Polarizable Point Ion Model for Partially Covalent Semiconductors

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Abstract. A valence-bond model is used to describe the crystal quantum-mechanically. The resultant energy expectation value is transformed into a classical one by means of a simplified dipolar model. For the numerical calculation, the zone centre optic frequencies are used as input parameters and the ionic charge, the force constant and the covalency parameter are evaluated for 30 compounds with zincblende and rocksalt structure respectively. In addition an ionicity scale based on the valence-bond model is presented which agrees fairly well with other ionicity scales.

1. Introduction

Calculations concerning deep impurity centres in semiconductors are complicated by the breakdown of the effective mass approximation. In addition, the electronic polarization and the deformation of the lattice, both caused by the impurity, cannot be neglected.

To overcome these difficulties, Stumpf [1] developed a polarizable point ion (PPI) model for impurities in ionic crystals, i.e. the ions of the perturbed host crystal are represented by point charges, electronic and displacement dipoles. The theory was successfully applied to F- and F'-centres in alkali halides [2].

We have improved and generalized Stumpf’s ideas developing a PPI model for semiconductors with both ionic and covalent binding. This will be used to study deep centres in these materials. Calculations on this problem are currently in progress.

In the present paper, our model is established investigating an ideal partially covalent crystal disturbed by lattice vibrations only. There is a vast amount of literature about this subject. The main approaches will be briefly discussed but for details, we refer to the most recent reviews given in [3].

A very general microscopic theory is the dielectric function method [4] which is able to deal with both metallic and insulating materials. For the numerical calculation, however, one has to know the dielectric function of the crystal. This information is rarely available for the semiconductors we are interested in. Besides, one has to use some approximations about the formfactor and the localization of the dipole distribution representing the response of the valence electrons. The niceties of the general theory are lost thereby.

The phonon spectra are commonly interpreted in terms of the so-called dipolar models. These are the dipole model developed by Tolpygo and coworkers [5], Hardy’s deformation dipole model [6] and the familiar shell model [7, 8] with its various extensions [9]. All of them contain a large number of adjustable parameters which have to be chosen to fit the experimental dispersion curves. The familiar dipolar models are very flexible but their parameters cannot be uniquely determined as discussed in [10] theoretically. In [11], it was explicitly shown that using the shell model with many adjustable parameters gives ion charges and force constants which depend on the fitting procedure. These quantities, however, are essential for impurity centre calculations and have to be known unambiguously.

To achieve this, we propose a simplified dipolar model which has been stripped down to its essentials. The number of adjustable parameters and the computational effort are kept as small as possible similar
to the point ion model of [12] and the linear chain model of [13]. The electronic polarization, however, in contrast to these models, is treated properly. This and the connection between our approach and the dipolar models mentioned above will be discussed after having established our model which will be done as follows.

In Sect. 2, the quantum-mechanical problem is treated by means of the valence-bond (VB) model presented by Coulson et al. [14]. Using phenomenological approximations for the intrinsic energy of the ions and the exchange interactions together with a multipole expansion for the Coulomb interactions, the quantum-mechanical energy expression is transformed into a classical one in Sect. 3. After the calculation of the phonon frequencies in the limit of long wave length (Sect. 4), the numerical results are given and discussed in Sect. 5.

The electron mass, the elementary charge and \( h \) have been chosen as units.

2. The Quantum-Mechanical Model

The core electrons are strongly localized around the nuclei and form closed shells. Their charge density is assumed to be spherical symmetric and not disturbed by the lattice vibrations. Hence, the ion-core, i.e. the nucleus together with the core electrons of an ion, is approximately represented by a point charge. The system of ion-cores and valence electrons is treated in the adiabatic approximation as usual. This gives the Schrödinger equations for the valence electrons and the ion-cores respectively.

\[
H \chi (\xi, R) = U(R) \chi(\xi, R), \\
[\sum_{i} (2m)_{i}^{-1} A_{i \mu} + U(R)] \phi(R) = E \phi(R).
\]  

(2.1 a)

(2.1 b)

The set of the electronic coordinates and the set of the position vectors of the ion-cores are represented by \( \xi \) and \( R \). \( R_{i \mu} \) is the position vector of the \( \mu \)-th ion-core in the \( \ell \)-th unit cell and \( m_{\mu} \) is its mass. \( U(R) \) and \( E \) are the adiabatic and the total energy of the crystal respectively whereas the wave functions of the electrons and the ion-cores are given by \( \chi \) and \( \phi \) accordingly.

Neglecting relativistic effects, the Hamiltonian in (2.1a) is given by

\[
H = \frac{1}{2} \left[ -\sum_{\ell} A_{\ell} + \sum_{\mu, \rho} |r_{\mu} - r_{\rho}|^{-1} + 2 \sum_{i, \rho} v(r_{\ell} - R_{i \mu}) + \sum_{i \mu, k \rho} z_{i \mu} z_{k \rho} |R_{i \mu} - R_{k \rho}|^{-1} \right].
\]  

(2.2)

The electrons are labeled by the indices \( i, j \). The charge of the \( \mu \)-th ion-core is \( z_{\mu} \). \( v(r_{\ell} - R_{i \mu}) \) is the electron-ion pseudopotential which is assumed to be Coulombic if \( |r_{\ell} - R_{i \mu}| \) is greater than the core radius \( r_{\mu} \) of the \( \mu \)-th ion, i.e.

\[
v(r_{\ell} - R_{i \mu}) = -z_{\mu} |r_{\ell} - R_{i \mu}|^{-1} \quad \text{for} \quad |r_{\ell} - R_{i \mu}| > r_{\mu}.
\]  

(2.3)

According to [14], the wave function of the valence electrons is constructed as follows. Let \( N \) be the number of unit cells in the crystal, \( i_{\ell} \) the index of the four bonds in the \( \ell \)-th unit cell and \( \mathcal{A} \) a suitable antisymmetrizer. \( \chi \) is then given by

\[
\chi(\xi, R) = \mathcal{A} \prod_{\ell=1}^{N} \prod_{i_{\ell}=1}^{4} \chi_{i_{\ell}}(\xi_{i_{\ell}}, \xi', R).
\]  

(2.4)

The wave function of the \( i \)-th bond in the \( \ell \)-th unit cell is

\[
\chi_{i_{\ell}}(\xi_{i_{\ell}}, \xi', R) = \Phi_{i_{\ell}}(r, R)\Phi_{i_{\ell}}(r', R) \frac{1}{\sqrt{2}} [\alpha(s) \beta(s') - \alpha(s') \beta(s)],
\]  

(2.5)

where \( \alpha(s) \), \( \beta(s) \) are the spin functions and \( r \), \( r' \) the position vectors of the two electrons in the bond. The one electron wave function is of the bonding type, i.e.

\[
\Phi_{i_{\ell}}(r, R) = (1 + 2\lambda S + \lambda^{2})^{-1} [\Phi_{i_{\ell}}(r, R) + \lambda \Phi_{i_{\ell}}(r, R)].
\]  

(2.6)

where \( \lambda \) is the covalency parameter and \( S \) the overlap between \( \Phi_{i_{\ell}A} \) and \( \Phi_{i_{\ell}B} \) which are wave functions localized at ion \( A \) (anion) and ion \( B \) (cation) respectively and directed towards each other. In the static case, when the ions are at their equilibrium positions \( R_{i_{\ell}A} \), \( \Phi_{i_{\ell}A}(r, R^{0}) \) are the well known sp\(^{3}\)-hybrids. But in the dynamic case, these wave functions are disturbed by the lattice vibrations and contain, therefore, an admixture of exited states \( \Phi_{i_{\ell}A}(r) \). The wave function at the anion site is then given by

\[
\Phi_{i_{\ell}A}(r, R) = \Phi_{i_{\ell}A}(r, R^{0}) + \sum_{v} c_{v} \Phi_{i_{\ell}A}(r).
\]  

(2.7)

\( \Phi_{i_{\ell}B} \) can be represented in a similar form and orthogonalized to \( \Phi_{i_{\ell}A} \) without loss of generality as shown in [5]. Hence, one has

\[
S = \int \Phi_{i_{\ell}A}^{*}(r, R) \Phi_{i_{\ell}B}(r, R) dr = 0,
\]  

(2.8)

i.e. the overlap vanishes exactly, as it is always assumed in the ordinary VB model [14, 15]. We have to emphasize, however, that this orthogonalization is reasonable for partially covalent crystals only as discussed below.

Taking the expectation value of (2.2) with respect to (2.4) gives the adiabatic energy of the crystal. After some tedious but straightforward calculations, one