

## CHAPTER 1

### GENERAL INTRODUCTION

#### 1.1 An Outline of the Growth of Lattice Dynamics

The static (non-vibrating) lattice model of crystalline solids is not in consonance with Heisenberg's uncertainty principle according to which  $\Delta p \Delta x \gtrsim h$ , where  $\Delta p$  and  $\Delta x$  represent the uncertainties in the momentum and position of a quantum particle of mass  $m$  and  $h$  is Planck's constant. Since  $\Delta p \sim \frac{h}{\Delta x}$ , the uncertainty in the particle energy  $\sim \frac{h^2}{2m(\Delta x)^2}$ , and if the particle is localised ( $\Delta x \rightarrow 0$ ) it will require an infinite energy. Hence the atoms (or ions) constituting a crystalline solid cannot just sit on the lattice sites. They have to vibrate even at 0°K temperature which gives rise to the zero-point energy. As the temperature increases the amplitude of the atomic vibrations increases.

It is the object of Lattice Dynamics to study the vibrations of the atoms (or ions) about their mean positions in the crystal lattice as well as the effects of these lattice vibrations on various physical properties of solids.

It is well known now that lattice vibrations play an important (even crucial) role in deciding the equilibrium

and transport properties of solids as well as in their interaction with electromagnetic radiation (X-rays, laser light, infrared) and thermal neutrons.<sup>1-4</sup>

Einstein<sup>5</sup> was the first to apply Planck's quantum theory to atomic vibrations in solids and thus to provide an explanation for the temperature variation of the specific heat. Considering the collective motions of atoms as equivalent to the propagation of elastic waves in a continuum with frequencies ranging from zero to a maximum, Debye<sup>6</sup> succeeded in getting better agreement with experiment. Indeed, because of its simplicity and ability to match experimental specific heat data available at the time, Debye's theory eclipsed the more elaborate atomistic theory of Born and von Karman<sup>7</sup> for over 20 years.

It was after the careful and elaborate work of Blackman<sup>8-10</sup> that the deficiencies of the Debye theory were realized and the superiority of the Born-Von Karman approach was established. Careful comparisons with accurate experimental data have shown that the Debye theory gives incorrect values of the specific heat if a single Debye temperature is used for the calculation of specific heat at different temperatures. If the limiting value of the Debye temperature at low temperature ( $\theta_0$ ) is used for the evaluation of the specific heat, the disagreement with experiment becomes evident at temperatures even a few degrees above

absolute zero. However, because of its simplicity, the Debye theory continues and is likely to continue to be used for approximate evaluations of thermodynamic properties of solids.

The progress of the Born-von Karman approach to lattice dynamics in explaining the thermodynamic properties of crystals has been well summarized in the classic work of Born and Huang<sup>11</sup>, and the review articles of Leibfried<sup>12</sup>, Blackman<sup>13</sup>, de Launay<sup>14</sup> and Cochran<sup>15</sup>.

The advent of neutron spectroscopy and high speed electronic computers in the 50's started a new spurt of activity in the study of the dynamical properties of solids.

Coherent inelastic scattering of thermal neutrons from crystals has provided accurate data on phonon dispersion relations. These results have shown the inadequacy of the rigid-ion model for ionic crystals and the simple force constant models of metals which take into consideration only the nearest or nearest and next-nearest neighbour interactions into account.

This situation has resulted in the development of microscopic theories of lattice dynamics for metallic<sup>16-18</sup>, covalent<sup>19-21</sup> and ionic<sup>19,22</sup> crystals. At the same time efforts to develop more realistic phenomenological models are continuing.<sup>23-25</sup>

The study of the localized vibrations of atoms in perfect and imperfect crystals has achieved much attention in the past two decades. These have been admirably presented by Maradudin et al<sup>26</sup>.

The study of anharmonic effects in crystals has been a very active field in the recent past. The articles of Cowley<sup>27</sup>, Barron and Klein<sup>28</sup>, Horner<sup>29</sup> and the book by Wallace<sup>30</sup> are valuable sources for the study of this topic.

Lattice dynamics has also found application in the study of phase transitions<sup>31</sup>. The fields of application of lattice dynamics are growing with time<sup>32-35</sup> and hence the importance of the study of lattice dynamics.

## 1.2 The Secular Equation for a Vibrating Metallic Crystal

In a macroscopic metallic crystal many-body interactions are essentially present because of the presence of a large number of ions and free electrons and the exact solution of the dynamical problem is a formidable task. Hence some essential approximations have to be introduced to tackle the problem.

In the Born-von Karman approach, three essential approximations are made to solve the lattice dynamical problem:

### (1) The rigid ion approximation

It is assumed that the electrons forming the core

about the nuclei move rigidly with the nuclei and are not excited to higher energy states.

(2) The adiabatic approximation

This approximation plays a cardinal role in lattice dynamics. It was proved by Born and Oppenheimer<sup>36</sup> that because of their comparatively smaller mass the conduction electrons follow the thermal motion of the nuclei instantaneously or adiabatically so that there is no change in the electronic ground state energy. The net effect of the adiabatic approximation is that the effective potential energy for the vibration of the nuclei (or ions) can be written as

$$\phi(\vec{r}) = \phi^i(\vec{r}) + \phi^e(\vec{r}) \quad (1.1)$$

where  $\phi^i(\vec{r})$  is the potential energy due to the ionic lattice and  $\phi^e(\vec{r})$  is the ground state energy of the electronic system, obtained as a function of the ionic positions.

Thus the effect of the conduction electrons on the motion of the nuclei (ions) is incorporated by adding an extra term in the potential energy expression written as a function of the nuclear (ionic) coordinates. The validity of the adiabatic approximation in the case of metals has been discussed by Chester<sup>37</sup> and Brovman and Kagan<sup>38</sup>.