LATTICE DYNAMICS AND HOMOLOGY OF ALKALI METALS

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TO MY BELOVED PARENTS

PREFACE

Among all the solids, the lattice dynamical study of alkali metals has attracted the maximum theoretical and experimental attention in the past mainly, because of their nearly free conduction electrons and spherically symmetric ion cores. The phonon frequencies of all alkali metals except cesium have been measured along the principal symmetry directions using the inelastic scattering of neutrons. A large number of force constant models, differing in their assumptions regarding the nature and range of the atomic interactions as well as a variety of pseudopotential models have been developed for this purpose. Their experimental dispersion curves including the anomalous crossover of [ζ00] branches in lithium could not be fitted as well as predicted rather well by many theoretical models. Nevertheless, the exact nature and range of the atomic interactions or the actual form of potential energy function, in any of the alkali metals is not known. Further, none of these force constant models has, so far, succeeded in reproducing the phonon dispersion curves of all alkali metals especially, the observed crossover in lithium. It is, therefore, necessary to ascertain whether the nature and range of the atomic interactions vary from one metal to another, in order to understand the origin of the anomalous crossover in lithium and to varify the claims regarding the homology of the phonon frequencies of alkali metals. The apparent contradiction between these two has not been resolved so far.

The presence of conduction electrons in metals, invariably, complicates their lattice dynamical study. Most of the previous force constant models failed to satisfy the translationa symmetry of the lattice mainly, because they treated the electron gas as a continuum in evaluating the volume forces. It is these deficient models which have obstructed our understanding of the interatomic forces in alkali metals. To overcome these difficulties four lattice dynamical models viz. DAF, CGW, AS and GTF models differing in range of ion-ion interactions have been formulated. Besides, a new electron gas model which represents the electrons by Bloch wave functions has been developed, in order to incorporate the electron-ion interactions into these models without destroying their translational symmetry. The author has made use of these models to investigate the dependence of the phonon frequencies of alkali metals on the nature and range of interatomic forces. Comparison of these theoretical frequencies with the corresponding experimental frequencies should reveal whether the interatomic potentials of alkali metals have any similarities and their phonon frequencies are homologous The dispersion relations of these models along [ξ00] direction have been analysed to isolate the factors responsible for the anomalous crossover of these branches in lithium. In addition the dependence of experimental phonon frequencies of lithium, sodium, potassium and rubidium on a variety of lattice dynamical parameters have been investigated to determine the degree of homology that exists among the lattice vibrations of alkali metals as well as to ascertain the factors responsible for their homology.

The present investigations seem to suggest that the phonon frequencies of alkali metals are insensitive to the nature and range of ion-ion interactions and consequently any of these four models could reproduce the experimental dispersion curves of all alkali metals including the anomalous crossover in lithium. On the contrary, the strength of the electron-ion interactions varies significantly from one model to another. Besides, the present analysis reveals that the stronger electron-ion interactions are responsible for the observed crossover in lithium, whereas the weaker electron-ion interactions in other alkali metals apparently make it anomalous. Inspite of these differences phonon frequencies of alkali metals are homologous to a very high degree. The present study has shown that the atomic masses of alkali metals are related to their interatomic distances and therefore, their lattice vibrations are homologous. The homologous frequencies of cesium, which are equivalent to their experimental values have been determined for the first time. The phonon frequency spectra, specific heat as well as the temperature variation of Debye Θ of the alkali metals have also been deduced using the force constant models and compared with the relevant experimental data.

The entire work on the lattice dynamics of alkali metals has been devided into seven Chapters. In the first Chapter of this thesis previous work on the lattice dynamical study of alkali metals with special reference to the phenomenological approach as well as on the homology of these metals is reviewed and the scope of the present work is discussed. The second Chapter deals with the development of a variety of force constant models for ion-ion interactions, while the third Chapter describes the evaluation of volume forces due to electron-ion interactions, using a new electron gas model. Phonon frequencies of alkali metals calculated using these four lattice dynamical models along the principal symmetry directions are compared with the experimental and other theoretical results and discussed in Chapter IV whereas these models and their dispersion relations along $[\xi 00]$ direction are analysed in Chapter V to understand the origin of the observe crossover in lithium. All aspects of homology are dealt with and the homologous phonon frequencies of cesium are compared with their theoretical values in Chapter VI. The last Chapter describes the calculation of the specific heats of alkali metals and their comparison with the corresponding experimental data.

Part of this work has been published in the following four papers whereas the remaining part has been submitted or is being prepared for publication in the near future.

1. Analysis of phonon frequencies of alkali metals, Phys. Stat. Sol.(b)90, 117 (1978).

2. On the homology of lattice vibrations of alkali metals, Czech. J. Phys. B30, 167 (1980).

3. Phonon dispersion curves of alkali metals, Physica, 104B, 343 (1981).

4. Phonon frequencies of cesium, Physica 111 B, 297 (1981).

5. Analysis of the crossover of dispersion curves of alkali metals in $[\xi 00]$ direction, Phys. Stat. Sol. (Submitted).

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Satish Kumar

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