STUDY OF SOME OF THE THERMAL PROPERTIES OF CAESIUM HALIDES IN HARMONIC AND QUASI-HARMONIC APPROXIMATIONS WITH A SUPPLEMENT ON THE LOW TEMPERATURE STUDY OF THE SPECIFIC HEAT OF ALPHA-IRON

BY

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PREFACE

The present investigation is an ambitious attempt to explore a hitherto relatively uninvestigated field i.e. the thermal properties of caesium chloride type of structures. The caesium halides form a favourite subject of study for their following peculiarities:

(i) of all the alkali halides only three namely, CsCl, CsBr and CsI crystalise in the body-centred cubic structure.

(ii) Heaviness of the particles, strong ionic binding and simplicity of the structure, make caesium halides particularly suitable for treating their vibrational properties under harmonic approximation.

(iii) The maximum thermal strain i.e. the ratio of the lattice constant near the melting point and at absolute zero and the cohesive energies of caesium halides are much greater as compared with the other alkali halides.

(iv) The theoretical elastic constants C_{12} and C_{44} obtained by Krishnan and Roy are the same for all the caesium halides is stimulating for a fresh theoretical investigation.

(v) There is no satisfactory study on the thermal expansion of these halides.

In order to explain some of these properties the present author has focussed his attention mainly on the study of the three important properties i.e. specific heats, elastic constants and thermal expansion of these solids. The specific heats and the elastic constants have been studied under the harmonic approximation whereas thermal expansion has been studied under the quasi-harmonic approximation.

Since, of all the caesium halides it is only caesium chloride which undergoes a phase transformation to the sodium chloride type of structure at 640°K which is much lower than its melting point, therefore, it has been studied in greater detail, for it all the three properties specific heats, elastic constants and the thermal expansion for both the structures have been calculated.

In writing the thesis, a considerable attention has been paid, in presenting the ideas in a simple, clear and unambiguous fashion. A considerable effort has been made in providing the necessary historical background, for developing the subject in a logical, systematic manner and to avoid sweeping statements as far as possible. An attempt has also been made to make thesis self contained (complete in itself). This has been done to save time which is spent very often by the reader in making references to literature and especially to that which is normally inaccessible. This has, however, increased the bulk of the thesis but the author feels it is worth it, for the aim kept in view.

The Chapter I of the present thesis gives a historical development and a general survey of the lattice dynamics of crystal with particular reference to the ionic crystals.

The Chapter II gives a brief description about the recent shell models proposed by Cowley and Cochran etc. and points out the inadequacy of these models in the case of caesium halides.

The Chapter III deals with the equation of motion. In this chapter, the lattice dynamics of caesium halide type of structures has been developed in the harmonic approximation by assuming the crystal to be perfect, made up of spherical and non-deformable ions and having only two-body interactions. The total interaction has been divided into two parts coulombian and non-coulombian. The net effect of the non-coulombian term is repulsive and it includes the effect of all the attractive forces other than the coulombian. Following the method outlined by Kellermann for sodium chloride, coulombian part of the coupling coefficients (elements of the secular matrix) have been evaluated. It may be remarked that the evaluation of the coupling coefficients involves lattice sums, for long range coulomb force they involve tedious summations. However, the series has been made rapidly convergent by using Gauss's error function and Ewald's Θ function transformation. There occurs a

parameter ϵ in the expressions for the coupling coefficients, the values of the coupling coefficients are independent of the value of ϵ, so two arbitrary values of ϵ were chosen to cross-check the results of numerical calculations. Table 3.1 presents the new values of the coupling coefficients for the caesium halides type of structures. For purposes of calculation the phase space has been divided into 10x10x10 equal parts; which gives rise to 56 nonequivalent points. The present method is superior to Kellermann as it assigns correct statistical weights and gives a total of 6,000 coupling coefficients.

The Chapter IV deals with the determination of the repulsive coupling coefficients. It gives a brief description about the various forms of repulsive potentials available in literature and the methods of disposing off the adjustable constants in these potentials. It has been shown that for constant volume, the values of the coupling coefficients are independent of the form of the potential function. The present method also differs from the traditional method used by Kellermann of using the conditions of equilibrium and the compressibility for determining the constants of the repulsive term. Instead of compressibility, whose experimental values may be in error by 10%, more reliable <u>reststrahlen</u> frequency has been used for determining the constants of the repulsive term. The relation between the <u>reststrahlen</u> frequency and the repulsive constants can be

obtained by solving the secular determinant in the long wave-length limit. Unlike the coulombian coupling coefficients, the repulsive coupling coefficients are substance dependent. New results for the total (sum of coulombian repulsive terms) coupling coefficients for 56 nonequivalent wave vectors are given in Tables 4.3 and 4.5 for caesium chloride and caesium iodide respectively.

The Chapter V deals with the elastic constants of caesium halides. The theory of the elastic constants has been discussed from a very general stand point. The inapplicability to the present case of Laval's ideas of 45 elastic constants for a very general ionic crystal has been clearly brought out. There is a general discussion about the relative merits of various methods namely method of comparison, method of identification, method of homogeneous deformation and the method of long waves for the determination of the elastic constants of crystals. The superiority of the method of long waves has been clearly shown. This is followed by a general discussion of the Cauchy relations and the attempts to remove the discrepancies. The difference between the isothermal and the adiabatic elastic constants has always been kept in view.

The expressions for the elastic constants have been deduced by the present author and have been given in the chapter. The present expressions are an improvement

over Kellermann in two important respects

(i) they are consistent with the symmetry requirements of the lattice and

(ii) explicit statement of the conditions under which they hold.

New results of the present calculations on the elastic constants of caesium halides are given in Table 5.1. To complete the discussion values of the Poisson ratio σ and compressibility β_0 have also been given in Table 5.2.

A new fact which has been brought to the light is that the expressions for β_0 and σ have been deduced by assuming the conditions of isotropy in literature. According to the present author an alternative definition is also possible e.g.

Traditional definition	$\sigma = \frac{C_{12}}{C_{11}+C_{12}}$	$\frac{1}{\beta_0} = \frac{C_{11}+2C_{12}}{3}$
New definition	$\sigma' = \frac{C_{12}}{2(C_{12}+C_{44})}$	$\frac{1}{\beta_0'} = \frac{3C_{12}+2C_{44}}{3}$

The two definitions are equal only if the condition of isotropy namely $C_{11} - C_{12} = 2C_{44}$ is satisfied. In other words, for crystals which are not isotropic, the values of the compressibilities deduced from the measurements of elastic constants from the usual definition are misleading.

The present analysis of the experimental and theoretical elastic constants has given a new and a very important information about the nature of the interatomic

forces i.e. the magnitude of the repulsive term should be smaller than what is normally obtained by adjusting the parameters.

The Chapter VI deals with the relative merits of computational methods of solving the secular determinant and reports new results on the specific heats of caesium chloride and caesium iodide. The secular determinants for CsCl have been solved by using Aitken's method and for CsI by using a computer IBM 1620. The specific heats from these frequencies have been found by adopting Blackman's sampling technique. The new results of the present calculations for the vibration frequencies and specific heats of caesium chloride have been given in Tables 6.1 and 6.2 and the corresponding results of the present calculations on caesium iodide in Tables 6.3 and 6.4.

The departures of the present theory in the calculation of the specific heats at low temperatures have been associated with the differences in the present and the experimental values of the elastic constants.

The Chapter VII deals with the equation of state of caesium chloride type of structures. The present author following the method chalked out before by Verma and Dayal for the sodium chloride has developed new expressions for the equation of the state of caesium chloride type of structures. In a preliminary investigation the effects of zero point energy have been ignored. However, it has been

made explicitly clear that the inclusion of the zero point energy would alter the values of the adjustable constants in the repulsive term and so also the elastic constants in which the Cauchy relation will no longer be satisfied. The new results on total pressure for various values of the volume ratio $\eta = \frac{V}{V_0}$ have been given in Table 7.4. These have used to plot isotherms. New results of the investigation on the variation of isobaric coefficient of thermal expansion and isothermal compressibility with temperature, melting point and cohesive energy, have been reported in Tables 7.5 and 7.6.

The most important conclusion drawn from the present analysis is that for a consistent explanation of the differences between the experimental and the theoretical elastic constants, cohesive energy and thermal expansion the total interaction potential adopted for the present investigation must be augmented by a term such that it will increase the theoretical cohesive energy of caesium chloride.

The present author has also done some supplementary work on the vibrational properties and the specific heats of alpha-iron which is being reported in Chapter VIII. The inclusion of the work should be considered in place, in a general discussion on the lattice dynamics of solids. The chapter discusses the Cauchy discrepancy invariably encounted in the case of metals and the limitation of the models based on central forces which always yield the Cauchy relation $C_{12}=C_{44}$.

de Launay has given a phenomenological model to meet the problem. New results based on this model for the vibrational frequencies, dispersion relations and the specific heats of alpha-iron have been presented in Tables 8.2 and 8.3. Here, also for the purposes of calculation the phase space of the first Brillouin zone has been divided into 10x10x10 equal parts which gives 47 nonequivalent points. It has been pointed out that this division becomes coarse at low temperatures. To overcome this difficulty, the present author has adopted a new method i.e. of dividing the first Brillouin zone into two parts the central part consisting of 4x4x4 points which are replaced by an equivalent Debye sphere and the outer part in between the Debye sphere and the boundaries of the first Brillouin zone. The calculations based on this model give a better agreement with the experiments.

Some of the results of the present investigation have been published or accepted for publication, the details of which are given below:

1. The Coupling Coefficients and Elastic Constants of Caesium Halides, Phys. Stat. Sol. 7, 39 (1964).
2. Phonon Spectrum and Specific Heat of Caesium Chloride, Phys. Stat. Sol. 8, 265 (1965).
3. Phonon Frequency Distribution of Alpha-iron, Phys. Stat. Sol. 3, 1408 (1963).
4. Phonon Spectrum of CsI, (In Press).

A copy of each of the published papers has been attached at the end.

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