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A SELF CONSISTENT AVERAGE PHONON EQUATION OF STATE FOR SOLIDS

City University of New York PH.D. 1983

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A SELF CONSISTENT AVERAGE PHONON
EQUATION OF STATE FOR SOLIDS

BY

KANHIYA LAL SHUKLA

A dissertation submitted to the Graduate
Faculty in Physics in partial fulfilment of
the requirements for the degree of the Doctor
of Philosophy, The City University of New York.

1983

The manuscript has been read and accepted for the Graduate Faculty in Physics in satisfaction of the dissertation requirements for the degree of Doctor of Philosophy.

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ABSTRACT

A SELF CONSISTENT AVERAGE PHONON EQUATION OF STATE FOR SOLIDS

by

KANHIYA LAL SHUKLA

Advisor: Professor Arthur Paskin

In the present thesis the author has investigated the thermodynamical properties of solids and an equation of state for solids with particular reference to the rare gas solids and the ionic solids by developing a self consistent average phonon approximation scheme.

The self consistent phonon (SCP) formalisms have proved to be very useful in calculating the anharmonic contributions to the lattice properties. Replacing the sums over the frequencies in the SCP formalism by appropriate functions of the average phonon frequencies yields simple equations of state for solids. This method is referred to as the self consistent average phonon (SCAP) formalism.

In the first chapter the thermodynamical properties of Ne, Ar, Kr and Xe are presented. Using the Lennard-Jones potential, the lattice parameter, compressibility, coefficient of expansion etc., have been calculated. The SCAP results are compared with the experimental results as well as with ISCP. The agreement with the experiments is found to be very good.

In the second chapter, a first principle self consistent average phonon equation of state and the thermodynamical quantities of the ionic solids with reference to NaCl have been studied. Using the Gordon and Kim potential the equation of state lattice constant, compressibility etc., have been obtained in the SCAP formalism. It is found that in the low and medium temperature range the agreement between the experimental values and the SCAP results is good but in the high temperature region near the melting point the agreement is not good.

It is also found that at a critical temperature T_c , a lattice instability occurs when $B \Rightarrow 0.0$ at a physically unobservable temperature (above the melting point). Therefore such an instability does not have any physical significance relative to melting. In the quasiharmonic approximation such an instability occurs at a temperature close to the melting temperature. This closeness between the critical temperature and melting is a consequence of overestimating the vibrational pressure in the quasiharmonic approximation.

ACKNOWLEDGEMENT

I wish to express my gratitude to Professor Arthur Paskin for his keen interest, constant encouragement and inspiring guidance throughout the progress of this work.

I would like to thank Dr. George J. Dienes and Dr. David O. Welch of The Brookhaven National Laboratory for their encouragement and many thoughtful discussions about the work.

It is my great pleasure to express my gratefulness to my wife Uma for her patience, understanding and love during the progress of this work and also inspiring me to come to the United States of America. I am also thankful to my children Ashish and Arti.

It is also a great pleasure to thank Dr. Shailja Ratan and Smt.Urmila Shukla for their help and encouragement. I am also thankful to the members of my family and friends.

KANHIYA LAL SHUKLA

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1.1--INTRODUCTION

Lattice dynamical theory was initially developed by M.Born and T.von Karman[1] for insulating crystals. Failure of this theory when applied to the rare gas solid helium[2] forced theoretical physicist to look for new methods, particularly the many body techniques. Two distinct schemes were developed. In one of the schemes[3] the motion of the individual atom is considered in the self consistent potential of all other particles in the crystal. A phonon or lattice vibration mode is a collective mode of the crystal due to the disturbance. In the second scheme the crystal is considered to be in equilibrium with all the phonons and the system is described by a set of harmonic oscillators.

Exciting progress has been made in physics of the noble gas crystals Ne, Ar, Kr, and Xe during the past years both theoretically and experimentally. Preparation of very good single crystals of these solids made it possible to measure lattice parameter, compressibility, coefficient of expansion etc; from low to high tempratures up to the melting point.

Theoretically, with the development of high speed computer, many body techniques gave results which almost reproduces the experimental results. Several approximate formalisms are currently available. In the quasiharmonic approximation (QH), the interatomic potential is Taylor expanded in powers of the dynamical displacements and terms up to quadratic are kept. Properties of the crystal in the harmonic or quasiharmonic approximation are described in detail by A.A.Maradudin[4] et al., A fairly good account of the old work on the rare gas crystals is described in the review article by Pollack[5].

The effects of the terms other than the quadratic terms in the expansion of the interatomic potential are known as anharmonic effects. It is well known that the anharmonic effects are significant, particularly at high temperatures near the melting point. To investigate these anharmonic effects ordinary perturbation theory (PT), Self Consistent Phonon theory (SCP), Improved Self Consistent Phonon theory (ISCP), Cell Model (CM), and Self Consistent Cell Model (SCCM) etc; have been used.

A detailed account of these methods as applied to the rare gas solid crystals is given in a recent review article by Glyde and Klein[6]. The conclusion drawn from this work is that the quasiharmonic approximation is unreliable particularly at high temperatures. Feldman, Horton[7] and Feldman, Klein and Horton[8] carried out calculations using the quasiharmonic approximation. Recently Klein et al [9] applied the ordinary perturbation theory to evaluate the free energy of the system including the anharmonic effects. The perturbation theory gives good results up to one third of the melting temperatures when applied specifically to Ar, Kr, and Xe. Above one third of the melting temperatures, the anharmonic effects were unrealistically large.

To include the anharmonic effects due to large amplitude of the lattice vibrations several investigators[9-22] have developed many ideas. Choquard's[10] second order theory is the most comprehensive known theory for the anharmonic theory of crystals. Computationally it is very difficult to use the full second order theory of Choquard. Bocara and Sarma[11] used a variational approach. In this approach they replaced the true Hamiltonian by an effective Hamiltonian in which the force constants were considered to be variational parameters to minimize the free energy. Koehler[12-14] investigated the anharmonic properties using an approach similar to that of Bocara and Sarma. Hornor[15] combined the variational approach and the diagrammatic perturbation techniques applied by Ranninger[16]. The first order theory of Choquard, called Self Consistent Phonon theory has been used by Gillis, Werthamer and Koehler[17] for the rare gas solids Ne and Ar. In the Self Consistent Phonon (SCP) theory the odd order derivatives of the interatomic potential do not contribute to the free energy but all even order derivatives do contribute. SCP formalism calculates the frequencies of the normal modes and the dynamical displacement variables of atoms self consistently.

For the anharmonic effects, the contribution of the odd powers of the derivatives of the interatomic potential in the Taylor expansion are also important. Goldman, Horton and Klein[18-20] included the correction due to the odd powers(cubic) to the self consistent free energy using ordinary perturbation theory. These authors applied this Improved Self Consistent Phonon theory (ISCP) to Ar and Ne and later to Ar, Kr and Xe[21]. It is found that, in general, ISCP gives better agreement with the experimental results than SCP.

Welch, Dienes and Paskin[23] and Dienes, Welch and Paskin[24] have used a classical version of the Self Consistent Cell Model (SCCM) to obtain an equation of state for solids. The classical version of SCCM was found to be suitable at high temperatures as is usually the case. These authors improved the SCCM by an adhoc addition of quantum correction and found that the quantum corrected SCCM equation of state for solids Ne and Ar is in very good agreement with experiments both at high and low temperatures.

The SCP and ISCP theories have proved to be valuable in calculating the anharmonic properties of crystalline solids, such as phonon dispersion, lattice parameters, compressibility, specific heat etc.,[11-22]. This procedure requires extensive numerical calculation of the characteristic frequencies of the crystalline solids for each set of the volume and the temperature. In calculating the properties such as pressure, specific heat, compressibility etc., the results are obtained in numerical form after summing over all the normal modes. In such summations the overall effects of the detailed phonon spectrum are averaged out. This suggests that a self consistent theory formulated in terms of the average phonon frequency might be useful in predicting the thermodynamical properties as well as reducing the numerical work. Thus, an alternative approach to obtaining an equation of state is to replace the sum over of the various functions of the normal modes by appropriate functions of the average phonon frequency of the system.

Welch, Dienes, Paskin[23] and Dienes, Welch and Paskin[24] have used a classical version of the Self Consistent Cell Model (SCCM) to obtain an equation of state for solids in analytic form. Quantum corrected SCCM was found to be useful over the entire range of temperature from low to high up to the melting point. Because of the success of the quantum corrected SCCM equation of state, it was of interest to investigate the SCP formalism to see if replacing the sum over the normal modes of the crystal by appropriate functions of the average frequency of the solid will lead to accurate but relatively simple equations of state for solids. This approach will be referred to as the Self Consistent Average Phonon (SCAP) formalism.

SCAP has the advantage over the SCCM of being a quantum formalism and thus applicable at all temperatures. It has the advantage over the SCP formalism of being simple to use to calculate the thermodynamical properties of solids.

In this spirit a SCAP formalism has been developed and as a test the SCAP has been used to obtain an equation of state for the rare gas solids Ne, Ar, Kr and Xe. The thermodynamical properties such as lattice parameter, bulk modulus, average Gruneisen parameter, coefficient of expansion, specific heat etc. have also been calculated[25,26].

The calculated values of the lattice parameter, compressibility, specific heat, coefficient of expansion etc. are not only compared with the experiments but also with the detailed calculations of SCP and ISCP. The agreement is found to be good to excellent. In general the SCAP3 results are better than SCP results but somewhat less reliable when compared to ISCP.

1.2--INTER-ATOMIC POTENTIAL

Rare gas solids are simple to deal with. They have tightly bound complete electronic orbitals. The interatomic potential[27-29] in these solids is very complicated and not known with sufficient detail. It is reasonable to assume central pairwise interaction between these atoms. The most commenly used central pairwise potential in the study of the noble gas crystals are the Mie-Lennard-Jones and Exp-6 potentials. In the crystalline phase, there is some evidence(at least for Ar) that the contribution of the three body interaction is also important. The three body interaction is generally approximated by the 'Triple-dipole' interaction of Axilrod and Teller[30].

In the absence of a reliable interatomic potential, a phenomenological central pairwise potential of the Lennard-Jones type has been used,

$$v(R(NP)) = \epsilon \left[(R_0/R(NP))^{12} - 2\,(R_0/R(NP))^{6} \right] \quad \ldots 1.2.1$$

where ϵ and R_0 are two constants, R(NP) is the interatomic distance between the atom N and the atom P. The constants R_0 and ϵ are usually determined by fitting the zero temperature properties of the solid such as the lattice parameter and the sublimation energy[29]. These constants are listed in table--1.1 and are used in the SCAP calculation.

These parameters R_0 and ϵ are really the effective parameters for the additive pairwise central forces. Indirectly these parameters include some effects of the three body, non additive forces.

1.3-- SCAP FORMALISM

To obtain the SCAP equation of state for solids, the SCP approach is followed to obtain the temperature and the volume dependence of the phonon frequencies and the free energy of the system, but replace the sum over the normal modes by appropriate functions of the average phonon frequency.

A perfect crystal of point atoms with one atom per unit cell is considered. Let $R_i(N)$ be the i-th component of the position of the atom N in the static lattice in a cartesian system. The index N (capital letters) is used to denote a set of three integers n_1, n_2 and n_3 defining the position of the atoms with respect to the primittive lattice vectors a_1, a_2 and a_3 of a Bravais lattice. i.e.,

$$R(N) = n_1 a_1 + n_2 a_2 + n_3 a_3. \quad \ldots 1.3.1$$

Now if the crystal is disturbed, the displaced position of the atom r(N) can be written as

$$r(N) = R(N) + u(N) \quad \ldots 1.3.2$$

where u(N) is the dynamical displacement vector measured relative to the atom at the site N.

Considering only the central pairwise interaction, the potential energy of the crystal can be written as

$$\Phi = (1/2)\sum_{NP} v(r(NP)) \quad \ldots 1.3.3$$

where

$$r(NP) = R(NP) + u(NP)$$

$$= [R(P)-R(N)] + [\ u(P) - u(N)] \qquad \ldots 1.3.4$$

is the vector from the position of the atom N to the position of the atom P. In summation N and P are summed over all the possible triplets of the integers. The Hamiltonian H, of the system can be written as

$$H = \sum_{iN} [p_i{}^2(N)/2m)] + \Phi\ . \qquad \ldots 1.3.5$$

Expanding Φ using the static equilibrium conditions[31] one obtains

$$\Phi = \Phi_0 + (1/2)[(1/2!) \sum_{\substack{ij \\ NP}} \Phi_{ij}(NP)\ u_i(NP)\ u_j(NP)$$

$$+ (1/3!) \sum_{\substack{ijk \\ NP}} \Phi_{ijk}(NP)\ u_i(NP)\ u_j(NP)\ u_k(NP)$$

$$+ (1/4!) \sum_{\substack{ijkl \\ NP}} \Phi_{ijkl}(NP)\ u_i(NP)\ u_j(NP)\ u_k(NP)\ u_l(NP)$$

$$+ \text{--}\ ], \qquad \ldots\ldots\ldots 1.3.6$$

where

$$\Phi_{ij}(NP) = \partial^2 v / \partial u_i(NP)\, \partial u_j(NP), \qquad \ldots 1.3.7$$

$$\Phi_{ijk}(NP) = \partial^3 v / \partial u_i(NP) \partial u_j(NP) \partial u_k(NP), \qquad \ldots 1.3.8$$

$$\Phi_{ijkl}(NP) = \partial^4 v/\partial u_i(NP)\partial u_j(NP)\partial u_k(NP)\partial u_l(NP) \quad \ldots 1.3.9$$

In the harmonic or quasiharmonic approximation, the terms up to second order in u are kept and the other anharmonic terms depending upon u^3, u^4, --- are neglected. The coefficients $\Phi_{ij}(NP)$ are the harmonic force constants. The Hamiltonian in quasiharmonic approximation is

$$H_h = \sum_{iN}[\, p_i^2/2m] + (1/2)(1/2!)\sum_{\substack{ij\\NP}} u_i(NP)\,\Phi_{ij}(NP)\;u_j(NP). \quad \ldots 1.3.10$$

Using ordinary perturbation theory the effects of u^3 and u^4 terms are generally included to find the contributions of the anharmonic terms. In the self consistent phonon scheme, the trial Hamiltonian H_t is written as

$$H_t = H_h + (1/2)\sum_{NP}[v(r(NP)) - \sum_{ij}(1/2)\; u_i(NP)\,\Phi_{ij}(NP)u_j(NP)] \quad \ldots 1.3.11$$

and the trial free energy F_t can be written as

$$F_t = \mathrm{Tr}[\rho_h(\, H_t + \beta^{-1}\ln \rho_h)]$$

$$= \langle\, H_t + \beta^{-1}\ln\rho_h \,\rangle. \quad \ldots 1.3.12$$

The harmonic free energy F_h is given by

$$F_h = \mathrm{Tr}[\ \rho_h\ (\ H_h + \beta^{-1} \ln \rho_h\ )], \quad \ldots 1.3.13$$

$$= \langle\ H_h + \beta^{-1} \ln\ {}_h\ \rangle, \quad \ldots 1.3.13$$

where ρ_h is the harmonic density matrix and $\beta = 1/K_B T$ and K_B is the Boltzmann constant

$$\rho_h = [\exp(-\ \beta H_h)]/C_0, \quad \ldots 1.3.14$$

$$C_0 = \mathrm{Tr}[\exp(-\beta H_h)].$$

Angular bracket <----> denotes the harmonic or the thermal average defined by (1.3.12).

In fact for any Hamiltonian, H, the density matrix is given by $\rho = \exp(-\beta H)/C$,

$$C = \mathrm{Tr}(\exp(-\beta H)).$$

The free energy is given by

$$F = (-1/\beta)[\ln(\mathrm{Tr}(\exp(-\beta H)))]$$

$$= (-1/\beta C)[(\mathrm{Tr}(\exp(-\beta H)))\ln C]$$

$$= (-1/\beta)\ \mathrm{Tr}[(\ln C)(\exp(-\beta H))/C]$$

$$= (-1/\beta)\ \mathrm{Tr}[\ \rho(\ -\beta H - \ln\rho\ )]$$

$$= \mathrm{Tr}[\ \rho(\ H + (1/\beta)\ln\rho\ ].$$

Since the actual density matrix ρ is not known, the trial free energy is obtained by approximating the true density ρ by the harmonic density ρ_h.

The displacement-displacement correlation function[17] $d_{ij}(NP)$ is defined as

$$d_{ij}(NP) = < u_i(NP)u_j(NP) > \qquad \ldots 1.3.15$$

The essence of the SCP formalism lies in the fact that the force constants Φ_{ij} and displacement-displacement correlation function are determined by minimizing the trial free energy F_t with respect to the parameters $d_{ij}(NP)$ and $\Phi_{ij}(NP)$

$$\partial F_t/\partial \Phi_{ij} = 0,$$

$$\partial F_t/\partial d_{ij} = 0. \qquad \ldots .1.3.16$$

Now $< v(r(NP)) >$ is given by

$$\langle v(r(NP))\rangle = v(r(NP)) + \sum_i \Phi_i(NP)\langle u_i(NP)\rangle$$

$$+ (1/2!) \sum_{ij} \Phi_{ij}(NP) < u_i(NP)\ u_j(NP) > + --- \qquad \ldots 1.3.17$$

where

$$\Phi_i(NP) = (R_i/R)\ v'(R(NP)), \qquad \ldots 1.3.18$$

$$\Phi_{ij}(NP) = (R_iR_j/R^2)[v'' - v'/R] + (v'/R)\delta_{ij} \qquad \ldots 1.3.19$$

$$\Phi_{ijk}(NP) = (R_iR_jR_k/R^3)[v''' - 3v''/R + 3v'/R^2]$$

$$+ (R_i\delta_{jk} + R_j\delta_{ik} + R_k\delta_{ij})[(v'' - v'/R)/R^2)]$$

$$\Phi_{ijkl}(NP) = (R_iR_jR_kR_l/R^4)[v'''' - 6v'''/R$$

$$+ 15v''/R^2 - 15v'/R^3] + [(v''' - 3v''/R + 3v'/R^2)$$

$$\cdot(R_iR_j\,\delta_{kl} + R_iR_k\,\delta_{jl} + R_iR_l\,\delta_{jk} + R_jR_k\,\delta_{il} + R_jR_l\,\delta_{ik} + R_kR_l\,\delta_{ij})/R^3] + [(v'' - v'/R)(\delta_{ij}\,\delta_{kl} + \delta_{ik}\,\delta_{jl} + \delta_{il}\,\delta_{jk})/R^2],$$

where ' means the derivative with respect to the bond length R(NP).

In the harmonic averaging process, the average of the odd powers of the displacement vanishes, i.e.,

$$< u_i(NP) > = < u_i^3(NP) > = --- = 0.0,$$

$$<u_i^m \cdot u_j^n> = <u_i^m><u_j^n>. \quad ...1.3.21$$

Also in the harmonic approximation

$$<u_i^4> = 3<u_i^2>^2,$$

$$<u_i^6> = 15<u_i^2>^3, \text{ etc.}$$

Using equation(1.3.21) in equation (1.3.17) one finds that

$$<v(r(NP))> = \exp[(1/2)(\sum_{ij} d_{ij}(NP)\nabla_i\nabla_j)]\ v(r(NP)). \quad ...1.3.22$$

Thus the free energy F_t can be written as

$$F_t = F_h + (1/2) \sum_{NP} \langle v(r(NP)) \rangle - (1/4) \sum_{\substack{ij \\ NP}} \Phi_{ij}(NP) d_{ij}(NP). \qquad ...1.3.23$$

Now the free energy F_t is minimized by considering the force constant $\Phi_{ij}(NP)$ and $d_{ij}(NP)$ the variational parameters. Mininmizing the free energy with respect to these parameters one finds that

$$d_{ij}(NP) = 4\, \partial F_h / \partial \Phi_{ij}(NP), \qquad ...1.3.24$$

and

$$\Phi_{ij}(NP) = \langle \nabla_i \nabla_j v(r(NP)) \rangle. \qquad ...1.3.25$$

Equations (1.3.24) and (1.3.25) show that variationally (in the harmonic averaging process) the optimum values of Φ_{ij}, the force constants, are given by the harmonic or the thermal average of the second derivatives of the potential evaluated at the actual position of the atoms. In the quasiharmonic approximation the force constants are evaluated at the equilibrium positions. The SCP force constants Φ_{ij} and hence the characteristic frequencies of the system depend both on the volume and the temprature while the quasiharmonic force constants and normal mode frequencies are dependent only on the volume and independent of the temperature.

To obtain the SCP phonon normal modes, the Fourier representation is defined by

$$\Phi_{ij}(NP) = (1/N_0)\sum_{k}[1 - \exp(-ik\cdot R(NP))]\ \Phi_{ij}(k),$$

$$\Phi_{ij}(k) = \sum_{P}[1 - \exp(ik\cdot R(NP))]\ \Phi_{ij}(NP). \qquad \ldots 1.3.26$$

The phonon frequency $\omega(k\lambda)$ for a given wave vector k is obtained by the diagonalization condition

$$\Phi_{ij}(k) = m\sum_{\lambda} e_i(k\lambda)\ \omega^2(k\lambda)\ e_j(k\lambda), \qquad \ldots 1.3.27$$

where $e(k\lambda)$ are the polarization vectors. Using equation (1.3.26) equation (1.3.27) becomes

$$m\,\omega^2(k\lambda) = \sum_{ijP}[e_i(k\lambda)\ \Phi_{ij}(OP)\ e_j(k\lambda)][1 - \exp(ik\cdot R(OP))],$$

$$\ldots 1.3.28$$

where

$$R(OP) = R(P) - R(0)$$

i.e., the lattice separation with respect to the zeroth cell which is located at the origin. Also the harmonic free energy F_h can be written as

$$F_h = \sum_{k\lambda} \beta^{-1}[\ln(2\sinh(0.5\beta\hbar\omega(k\lambda)))] \qquad ...1.3.29$$

$$d_{ij}(NP) = \sum_{k\lambda}[(\hbar \coth(\xi(k\lambda))/mN_0\omega(k\lambda)][1 - \exp(ik\cdot R(NP))] \cdot e_i(k\lambda)\, e_j(k\lambda), \qquad ....1.3.30$$

where

$$\xi(k\lambda) = 0.5\beta\hbar\,\omega(k\lambda).$$

Equations (1.3.28) and (1.3.30) must be solved self consistently for each wave vector k and for several values of volumes to obtain the volume dependence of the phonon characteristic frequencies. Hence the volume and the temperature dependence of the free energy, which ultimately determines the thermodynamical properties of the system by summing over all the modes of the system.

The self consistent phonon formalism has proved to be valuable in the calculation of the anharmonic properties of the system, such as the phonon spectrum. The SCP formalism requires extensive numerical calculation. For each set of volume and temperature, one first calculates the normal modes of the crystal to get the phonon spectrum and then one finds the free energy from each of the modes and sums over all modes to get the total free energy of the crystal. Once the free energy of the crystal is obtained as a function of volume and temperature, all other thermodynamical properties such as pressure, bulk modulus, and the specific heat etc., can be obtained.

In such calculations of equation of state and the thermodynamical properties the details of the temperature and volume dependence of the phonon spectrum are averaged out when summed over all the phonon characteristic modes. In fact the thermodynamical properties of the system are the average properties of the system, therefore, it was of interest to investigate, and, obtain an equation of state of the system by an appropriate function of the average phonon frequency.

This procedure, replacing the sums over the normal modes by the functions of an average phonon frequency will be called "Self Consistent Average phonon" (SCAP) formalism. The SCAP formalism leads to simpler analytical expressions for the average squared frequency, mean square displacement, pressure etc. This procedure i.e., SCAP, is much simpler for the computation of the thermodynamical properties.

The SCAP procedure has the advantage over the SCP and ISCP formalisms of being simple to calculate the thermodynamical properties of the system. It has the advantage over the quasiharmonic approximation of being a self consistent and quantum calculation. The SCAP frequencies are functions of both the volume and the temperature due to the self consistancy while the quasiharmonic frequencies are independent of the temperature. It also has the advantage over the self consistent cell model of being a quantum formalism and thus applicable at all temperatures.

To proceed furthur, one needs the average squared frequency. To obtain the average squared frequency $< \omega^2 >$ the SCP expression for the normal modes[17] has been used.

$$m\, \omega^2(k\lambda) = \sum_{ijP} [1 - \exp(ik \cdot R(0P))]\, e_i(k\lambda)\, \Phi_{ij}(0P) e_j(k\lambda) \ldots 1.3.31$$

In the continuum approximation it may be assumed that all the modes are purely longitudinal or purely transverse. For each mode vector $k = k\, e_z$, one can write the polarization vectors as

$$e(k,l) = e_z,$$

$$e(k,t_1) = l_1 e_x + l_2 e_y,$$

$$e(k,t_2) = -l_2 e_x + l_1 e_y, \quad \ldots 1.3.32$$

where e_x, e_y and e_z are three mutually orthogonal unit vectors and l_1, l_2 and l_3 are the direction cosines. Thus, for each wave vector k, using (1.3.32), one can write

$$\sum_{ij\lambda} e_i(k\lambda)\,\Phi_{ij}(OP)\,e_j(k\lambda) = \sum_i \Phi_{ii}(OP). \quad \ldots 1.3.33$$

Now the average squared frequency $\langle\omega^2\rangle$ is defined by

$$\langle\omega^2\rangle = (3N_0)^{-1}\sum_{k\lambda}\omega^2(k\lambda)$$

$$=(1/3N_0 m)\sum_{ijPk\lambda}[1 - \exp(ik\cdot R(OP))]\,e_i(k\lambda)\,\Phi_{ij}(OP)\,e_j(k\lambda).$$

$$\ldots 1.3.34$$

Using equation (1.3.33) in equation (1.3.34) and the properties of the lattice Fourier series

$$(1/N_0)\sum_{k} \exp(ik\cdot R(OP)) = \delta_{OP},$$

where δ_{OP} is the kronecker delta function, the mean square frequency $\langle \omega^2 \rangle$ is given by

$$\langle \omega^2 \rangle = (1/3m)\sum_{iP} \Phi_{ii}(OP). \qquad \ldots 1.3.35$$

The essence of the SCAP formalism is to use the square root of $\langle \omega^2 \rangle$ as the phonon frequency i.e.,

$$\omega = \langle \omega^2 \rangle^{1/2} \qquad \ldots .1.3.36$$

of the crystal and approximate the summation over $k\lambda$ by the functions of the average phonon frequecy ω i.e.,

$$\sum_{k\lambda} f(\omega(k\lambda)) \cdot g((k\ R(NP), e(k\lambda)) = f(\omega)\sum_{k\lambda} g((k\cdot R(NP)), e(k\lambda)). \qquad \ldots 1.3.37$$

$$\langle u^2 \rangle = u^2 = \sum_{ij} e_i\ d_{ij}\ e_j$$

$$= \sum_{ik\lambda} (\hbar \coth(\xi(k\lambda))/mN_0\omega(k\lambda)][1 - \exp(ik\cdot R(OP))][e_i\cdot e_i(k\lambda)]^2$$

$$= (3\hbar/m\omega)\coth\xi, \qquad \ldots 1.3.38$$

where $\xi_1 = 0.5\,\hbar\beta\omega$. The average square frequency $\langle\omega^2\rangle = \omega^2$ is

$$\langle\omega^2\rangle = (1/3m)\sum_{iP}\langle \nabla_i^2\, v(r(0P))\rangle.$$

Taylor expanding v(r(0P)) and using the properties of the harmonic average one finds following expression for the average frequency

$$\omega^2 = (1/3m)[\, S_2 + (u^2/6)S_4 + (u^4/72)S_6 + \text{---}], \quad \ldots 1.3.39$$

$$S_2 = \sum_P [\, v''(R(0P)) + (2/R(0P))v'],$$

$$S_4 = \sum_P [v^{IV} + (4/R(0P))v'''],$$

in general for any n=even

$$S_n = \sum_P [(d^n v/dR^n) + (n/R)(d^{n-1}v/dR^{n-1})]_{R(0P)}. \quad \ldots 1.3.40$$

The equations (1.3.38) and (1.3.39) must be solved self consistently. These are the basic equations in the SCAP formalism. The values of ω^2 and u^2 that are obtained by solving equations (1.3.38) and (1.3.39) self consistently are used to calculate the free energy and the other properties like pressure, P, coefficient of linear expansion, α, specific heat, C_V, etc.

1.4-- THERMODYNAMICAL PROPERTIES

A-- FREE ENERGY

The Helmholtz free energy per atom, F_{SCP}, in the self consistent phonon formalism, of a crystal with N_0 atoms is given by

$$F_{SCP} = (1/N_0\beta)\sum_{k\lambda}\ln[2\sinh(\xi(k\lambda))] - \sum_{k\lambda}\hbar\omega(k\lambda)\coth\,\xi(k\lambda)/4N_0)]$$

$$+ (1/2N_0)\sum_{NP}< v(r(NP)) >. \qquad ....1.4.1$$

Using equation (1.3.37) and summing over $k\lambda$ one obtains the free energy, $F_{SCAP} = F$, in the SCAP formalism

$$F = (3/\beta)\ \ln[2\sinh(\xi)] - (3\hbar\omega/4)\coth\xi + f_0, \qquad ...1.4.2$$

where

$$f_0 = (1/2)[\ S_0 + (u^2/6)S_2 + (u^4/72)S_4$$

$$+ (u^6/1296)S_6 + --- \quad], \qquad ...1.4.3$$

$\xi = 0.5\beta\hbar\omega$.

In terms of the mean square displacement

$$\langle u^2\rangle = u^2 = 3\hbar \coth\xi/m\omega. \qquad ...1.4.4$$

The free energy of the system can be written as

$$F = (3/\beta)[\ln 2\sinh\xi] - (m/4)u^2\omega^2 + f_0. \qquad ...1.4.5$$

B--PRESSURE

The pressure, P, is obtained by differentiating equation (1.4.5) with respect to volume at constant temperature

$$P = (-\partial F/\partial V) = (-R_1/3V)(\partial F/\partial R_1). \qquad ...1.4.6$$

From equation (1.4.5) one can write

$$\partial F/\partial R_1 = -(m\omega^2/4)(\partial u^2/\partial R_1) + \partial f_0/\partial R_1. \qquad ...1.4.7$$

But

$$\partial f_0/\partial R_1 = (1/2)[(dS_0/dR_1) + (u^2/6)(dS_2/dR_1) + ---]$$

$$+ (m\omega^2/4)(\partial u^2/\partial R_1). \qquad ...1.4.8$$

Substituting the expression for $\partial f_0/\partial R_1$ into equation (1.4.6) the following expression for the pressure is obtained

$$P = (-R_1/6V)[(dS_0/dR_1) + (u^2/6)(dS_2/dR_1) +$$

$$+ (u^4/72)(dS_4/dR_1) + ---]. \qquad ...1.4.9$$

The pressure P can be calculated using expression (1.4.9) for a set of near neighbor distances R_1. The equilibrium near neighbor distance R_1 can then be obtained graphically by the intersection of the pressure versus near neighbor distance R_1 curves with P=0.0 curve. Actually zero pressure lattice parameter can be obtained directly from the computer but this requires a lot of computational time.

C BULK MODULUS

The isothermal bulk modulus, B_T, is obtained using the following thermodynamical expression

$$B_T = -V(\partial P/\partial V) = (-R_1/3)(\partial P/\partial R_1)$$

$$=(R_1{}^2/18V)[\ ((d^2S_0/dR_1{}^2) - (2/R_1)(dS_0/dR_1))$$

$$+\ (u^2/6)((d^2S_2/dR_1{}^2) - (2/R_1)(dS_2/dR_1))$$

$$+(u^4/72)((d^2S_4/dR_1{}^2) - (2/R_1)(dS_4/dR_1))]$$

$$+\ (R_1{}^2/108V)(\partial u^2/\partial R_1)[(dS_2/dR_1) + (u^2/6)(dS_4/dR_1)$$

$$+ \text{-----}\ ], \qquad \ldots 1.4.10$$

where

$$(\partial u^2/\partial R_1) = -A(\partial \omega^2/\partial R_1), \qquad \ldots 1.4.11$$

$$A = [u^2 + (3\hbar^2\beta/2m)(\coth^2\xi_1 - 1)]/2\omega^2\ . \qquad \ldots 1.4.12$$

The quantity A a function of order u^2. Differentiating ω^2 with respect to R_1

$$\partial\omega^2/\partial R_1 = (1/3mA_0)[(dS_2/dR_1) + (u^2/6)(dS_4/dR_1)$$

$$+\ (\ u^4/72)(dS_6/dR_1) + \text{---}\ ], \qquad \ldots 1.4.13$$

$$A_0 = [1 + (A/18m)(S_4 + (u^2/6)(S_6) + ---]. \qquad ...1.4.14$$

D. SPECIFIC HEAT

The internal energy per atom is obtained from the thermo dynamical expression

$$U = F + \beta\partial F/\partial\beta \,. \qquad ...1.4.15$$

Differentiating u^2 and ω^2 with respect to β ,

$$(\partial\,\omega^2/\partial\beta) = (1/18m)(\partial u^2/\partial\beta)[(S_4 + (u^2/6)(S_6) + ---] \qquad ...1.4.16$$

and

$$(\partial u^2/\partial\beta) = (3\,\hbar^2/2mA_0)[1 - \coth^2\xi]. \qquad ...1.4.17$$

and differentiating the expression for the free energy with respect to β

$$(\partial F/\partial\beta) = (-3/\beta^2)[\ln 2\sinh\xi] + mu^2\omega^2/2\beta, \qquad \ldots 1.4.18$$

gives the following expression for the internal energy

$$U = m\,u^2\omega^2/4 + f_0. \qquad \ldots 1.4.19$$

The specific heat, C_V, of the system is obtained by differentiating U with respect to the temperature T

$$C_V = (dU/dT) = -K_B\beta^2(\partial U/\partial\beta)$$

$$=(-K_B\beta^2\, m/4)[u^2(\partial\omega^2/\partial\beta) + 2\,\omega^2(\partial u^2/\partial\beta)]. \qquad \ldots 1.4.20$$

E. COEFFICIENT OF EXPANSION

The coefficient of linear expansion, α , at constant pressure (P=0.0) is obtained by the differentiation of the pressure with respect to temperature, T,

$$dP/dT = \partial^2F/\partial V\partial T - (dV/dT)(\partial^2F/\partial V^2) = 0.0$$

or

$$\alpha = -[(\partial^2F/\partial V\partial T)/3B_T]$$

$$= (R_1 K_B \beta^2/9VB_T)[\partial^2F/\partial\beta\partial R_1]. \quad ...1.4.21$$

Differentiating equation (1.4.18) with respect to R_1 and using the expression for A from equation (1.4.12) one finds that

$$\partial^2F/\partial\beta\partial R_1 = (3\hbar^2/8)(\partial\omega^2/\partial R_1)[1 - \coth^2\xi]. \quad ...1.4.22$$

Thus the expression for the coefficient of expansion, α , can be written as

$$\alpha = (K_B R_1 \beta^2 \hbar^2/24B_T V)(1 - \coth^2\xi)(\partial\omega^2/\partial R_1). \quad ...1.4.23$$

Alternatively the coefficient of expansion, α , may also be obtained by differentiating the expression (1.4.7) for the pressure with respect to the temperature, T or β ,

$$\alpha = (K_B R_1 \beta^2/108VB_T)(\partial u^2/\partial\beta)[(dS_2/dR_1)+(u^2/6)(dS_4/dR_1) + ---]. \quad ...1.4.24$$

These two expressions for α are equivalent.

F. GRUNEISEN PARAMETER

The Gruneisen parameter, γ , arises naturally in the discussion of the thermal and elastic properties of the solids. The simplest Gruneisen parameter $\gamma(k\lambda)$ describes the isothermal volume dependence of individual normal mode frequency $\omega(k\lambda)$, and is usually defined as

$$\gamma(k\lambda) = -\partial \ln[\omega(k\lambda)]/\partial(\ln V). \qquad \ldots.1.4.25$$

An average Gruneisen parameter, γ, is defined by

$$\gamma = (1/3N_0)\sum_{k\lambda}[-\partial \ln(\omega(k\lambda))/\partial(\ln V)]$$

$$= (-R_1/6\omega^2)(\partial\omega^2/\partial R_1).$$

The mean square frequency ω^2 can be calculated self consistently and then the thermodynamical quantities such as pressure, P, internal energy U, specific heat, C_V, etc. can be calculated with SCAP formalism. Up to now no approximation has been made to what order of u the thermodynamical properties must be evaluated.

1.5-- Various SCAP Approximations

In the SCAP(1) formalism all the expressions are evaluated to order u^2. The quantities A and $\partial u^2/\partial R_1$ are of the order of u^2 the self consistent expressions for ω^2 and u^2 can be written as

$$\omega^2 = [\ S_2 + (u^2/6)S_4]/3m, \quad \ldots 1.5.1$$

$$u^2 = (3\hbar \coth\xi\ )/m\omega. \quad \ldots 1.5.2$$

The expressions for the free energy, F, pressure, P, and the bulk modulus, B_T in the SCAP(1) approximation can be written as

$$F = (3/\beta)[\ln 2\sinh\xi\ ] - (m/4)u^2\omega^2 + f_0, \quad \ldots 1.5.3$$

where

$$f_0 = (1/2)[\ S_0 + (u^2/6)S_2 + (u^4/72)S_4]. \quad \ldots 1.5.4$$

$$P = (-R_1/6V)[(dS_0/dR_1) + (u^2/6)(dS_2/dR_1)] \quad \ldots 1.5.5$$

$$B_T = (R_1{}^2/18V)[\ ((d^2S_0/dR_1{}^2) - (2/R_1)(dS_0/dR_1))$$

$$+ (u^2/6)((d^2S_2/dR_1{}^2) - (2/R_1)(dS_2/dR_1))$$

$$+ (R_1{}^2/108V)(\partial u^2/\partial R_1)[(dS_2/dR_1)] \quad ...1.5.6$$

where

$$(\partial u^2/\partial R_1) = -A(\partial \omega^2/\partial R_1),$$

$$A = [u^2 + (3\hbar^2\beta/2m)(\coth^2\xi - 1)]/2\,\omega^2. \quad ...1.5.7$$

The quantity A is of the order of u^2. Differentiating ω^2 with respect to R_1

$$\partial\omega^2/\partial R_1 = (1/3mA_0)[(dS_2/dR_1) + (u^2/6)(dS_4/dR_1)]. \quad ...1.5.8$$

$$A_0 = [1 + (A/18m)(S_4)] \quad ...1.5.9$$

To order u^2, the expressions for the internal energy, U, specific heat, C_V, are given by

$$U = mu^2\omega^2/4 + (1/2)[S_0 + (u^2/6)S_2 + (u^4/72)S_4]...1.5.10$$

$$C_V = (-K_B \beta^2 m/4)[u^2(\partial \omega^2/\partial\beta) + 2\omega^2(\partial u^2/\partial\beta)]. \quad \ldots 1.5.11$$

$$(\partial u^2/\partial\beta) = (3\hbar^2/2mA_0)[1 - \coth^2\xi]. \quad \ldots 1.5.12$$

$$\partial \omega^2/\partial\beta = (\hbar^2/12A_0m^2)(1 - \coth^2\xi)S_4. \quad \ldots 1.5.13$$

The average Gruneisen parameter, γ, and the coefficient of linear expansion, α , are

$$\gamma = (-R_1/6A_0)[(dS_2/dR_1) + (u^2/6)(dS_4/dR_1)]$$

$$\cdot [S_2 + (u^2/6)S_4]^{-1} \quad \ldots 1.5.14$$

and

$$\alpha = (K_B R_1 \beta^2 \hbar^2/24B_T V)(1 - \coth^2\xi)(\partial\omega^2/\partial R_1). \quad \ldots 1.5.15$$

B -- SCAP(2)

In the SCAP(2) approximation all the expressions are evaluated to order u^4. To order u^4, the self consistent consistent expressions for u^2 and ω^2 are

$$u^2 = (3\hbar/m\omega)\coth\xi . \qquad ....1.5.16$$

$$\omega^2 = (1/3m)[S_2 + (u^2/6)S_4 + (u^4/72)S_6] \qquad ...1.5.17$$

Thermodynamical quantities such as the Helmohltz free energy, F, pressure, P, and the bulk modulus, B_T, are given by the following expressions:

$$F = (3/\beta)[\ln 2\sinh\xi] - (m/4)u^2\omega^2 + f_0. \qquad ...1.5.18$$

$$f_0 = (1/2)[\ S_0 + (u^2/6)S_2 + (u^4/72)S_4$$

$$+ (u^6/1296)S_6] \qquad ...1.5.19$$

$$P = (-R_1/6V)[(dS_0/dR_1) + (u^2/6)(dS_2/dR_1) +$$

$$+ (u^4/72)(dS_4/dR_1)] \qquad ...1.5.20$$

$$B_T = (R_1^2/18V)[\ ((d^2S_0/dR_1^2) - (2/R_1)(dS_0/dR_1))$$

$$+ (u^2/6)((d^2S_2/dR_1^2) - (2/R_1)(dS_2/dR_1))$$

$$+(u^4/72)((d^2S_4/dR_1{}^2) - (2/R_1)(dS_4/dR_1))]$$

$$+ (R_1{}^2/108V)(\partial u^2/\partial R_1)[(dS_2/dR_1) + (u^2/6)(dS_4/dR_1)] \qquad \ldots 1.5.21$$

where

$$(\partial u^2/\partial R_1) = -A(\partial \omega^2/\partial R_1),$$

$$A = [u^2 + (3\,\hbar^2\beta/2m)(\coth^2\xi_1 - 1)]/2\,\omega^2. \qquad \ldots 1.5.22$$

The quantity A is a function of order u^2. Differentiating ω^2 with respect to R_1

$$\partial \omega^2/\partial R_1 = (1/3mA_0)[(dS_2/dR_1) + (u^2/6)(dS_4/dR_1)$$

$$+ (u^4/72)(dS_6/dR_1)] \qquad \ldots 1.5.23$$

$$A_0 = [1 + (A/18m)(S_4 + (u^2/6)(S_6)]. \qquad \ldots 1.5.24$$

The internal energy, U, and the specific heat, C_V, are obtained by the following expressions:

$$U = mu^2\omega^2/4 + f_0 \qquad \ldots 1.5.25$$

and

$$C_V = (-K_B\beta^2\ m/4)[u^2(\partial\omega^2/\partial\beta) + 2\omega^2(\partial u^2/\partial\beta), \qquad ..1.5.26$$

$$(\partial\omega^2/\partial\beta) = (1/18m)(\partial u^2/\partial\beta)(S_4 + (u^2/6)(S_6)) \quad \ldots 1.5.27$$

and

$$(\partial u^2/\partial\beta) = (3\hbar^2/2mA_0)[1 - \coth^2\xi]. \qquad \ldots 1.5.28$$

The average Gruneisen parameter, γ, and the coefficient of linear expansion, α , are given by

$$\gamma = (R_1/6)[\ (\partial\omega^2/\partial R_1)/\ \omega^2\ ],$$

$$\alpha = (K_BR_1\,\beta^2\hbar^2\ /24B_TV)(1 - \coth^2\xi\ )(\partial\omega^2\ /\partial R_1)\ldots 1.5.29$$

C--SCAP(3) OR HYBRID SCAP

All the thermodynamical quantities in SCAP(1) and SCAP(2) are evaluated to order u^2, and u^4, respectively. The free energy F has to be evaluated to one higher order in u^2 to evaluate other quantities such as the pressure, P, compressibility χ , specific heat, C_V, to correct order.

Thermodynamical quantities can be evaluated which in a sense are mixture of the two approximations, the SCAP(1) and the SCAP(2). This approximation is refered as 'SCAP(3)' or 'Hybrid SCAP'. The average square frequency ω^2 and the mean square displacement are evaluted as in the SCAP(1) approximation i.e. ,

$$u^2 = (3\hbar/m\omega)\coth\xi , \quad \ldots 1.5.30$$

$$\omega^2 = (1/3m)[S_2 + (u^2/6)S_4]. \quad \ldots 1.5.31$$

But all other thermodynamical quantities such as the pressure, P, bulk modulus, B_T, specific heat, C_V, coefficient of linear expansion, α , etc., are evaluated from the expressions (1.5.20), (1.5.21), (1.5.26) and (1.5.29) of the SCAP(2) formalism.

Average Quasiharmonic Approximation

In the average quasiharmonic approximation the average frequency ω^2 does not depend upon u^2. The average square frequency ω^2 and mean square displacement u^2 are given by

$$\omega^2 = S_2/3m, \quad \ldots 1.5.32$$

$$u^2 = (3\hbar \coth(0.5\hbar\beta\omega))/m\omega . \quad \ldots 1.5.33$$

The expression for the free energy, F, pressure, P, are

$$F = (3/\beta)[\ln(2\sinh \xi_1)] + S_0/2, \qquad \ldots 1.5.34$$

$$P = (-R_1/6V)[\,(dS_0/dR_1) + (u^2/6)(dS_2/dR_1)]. \qquad \ldots 1.5.35$$

Knowing the expression for the free energy, F, all other thermodynamical quantities can be evaluated by usual thermodynamical relations:

$$B_T = -V(\partial P/\partial V),$$

$$U = F + \beta \partial F/\partial \beta,$$

$$C_V = \partial U/\partial T.$$

1.6-- COMPARISION OF VARIOUS SELF CONSISTENT AVERAGE PHONON FORMALISMS

In the SCAP(1) approximation equations (1.5.1),(1.5.2) have been used to calculate the average square frequency and mean square displacement. Equations (1.5.3), (1.5.5), (1.5.6), (1.5.11), (1.5.14) and (1.5.15) have been used to calculate the free enrgy, pressure, bulk modulus, constant volume specific heat, Gruneisen parameter and coeficient of expansion respectively.

Equations (1.5.16), (1.5.17), (1.5.18), (1.5.20), (1.5.21), (1.5.26), (1.5.29) have been used to calculate the mean square displacement, average square frequency, free energy, pressure, bulk modulus, specific heat and coefficient of expansion respectively in the SCAP(2) approximation.

In the SCAP(3) approximation equations (1.5.1) and (1.5.2) have been used to calculate the frequeny and mean square displacement self consistently. Equations (1.5.16), (1.5.17), (1.5.18), (1.5.20), (1.5.21), (1.5.26) and (1.5.29) of SCAP(2) approximation have been used to calculate the free energy, pressure, bulk modulus, specific heat and coefficient of expansion respectively.

In table--1.2 the parameters R_0 and ϵ are given that have been used for calculating the various thermodynamical properties of Ar in SCAP, SCP and ISCP formalisms. The parameters of potential in the SCAP approximation have been chosen to fit zero pressure, zero temperature lattice parameter and the classical energy.

The SCP [17,18] and ISCP[21] formalisms use interatomic potentials extending to near neighbor or all neighbors. SCAP treatment restricts the interaction to two neighbors only. This requires a change in the values of the parameters R_0 and ϵ compared to the values used in the SCP and ISCP formalisms.

The SCP formalism takes into account the contributions from all the even derivatives of the interatomic potential. Due to the harmonic averaging process, the contribution from the odd derivatives of the interatomic potential vanishes. The improved self consistent phonon scheme includes the contributions from the odd derivatives particularly the third derivative of the interatomic potential through three phonon processes. It is known from the work of Klein, Horton and Feldman[9] and Feldman, Klein and Horton[7] that the odd derivatives are of importance and have significant effect on the results. Thus a meaningful theory must try to include the effects of the odd derivatives of the interatomic potential. The inclusion of the contribution of the odd derivatives to the free energy shows an improved agreement with the experimental data, compared to the self consistent phonon

(SCP) theory, in magnitude as well as in the volume and temperature dependence[21]. Significant discrepancies still exist[21] but in general ISCP gives better fit to the experiments both at low and high temperatures. For this reason ISCP curves have been used as the "Standard Curve" to be fit by the other theoretical calculation such as SCP and the SCAP.

Figures 1.1, 1.2 and 1.3 show for Ar, respectively, the zero pressure isothermal bulk modulus, B_T, zero pressure volume expansitivity and the zero pressure constant volume specific heat, C_V, using the SCP , ISCP, SCAP(1), SCAP(2), SCAP(3) or the hybrid SCAP. Since it is known that ISCP gives best fit to the observed experimental data, therefore, it was appropriate to compare SCAP(1), SCAP(2), SCAP(3) and SCP calculations to ISCP calculation. Observations of figures 1.1 to 1.3 clearly show that the hybrid SCAP is the best fit of the SCP, SCAP(1) and SCAP(2) schemes. For this reason in all the other calculations the author has compared hybrid self consistent average phonon calculation with the experimental results and also with ISCP. It is observed that the SCP and SCAP(1) and SCAP(2) schemes give almost the same results in the low to medium range of temperatures. ISCP shows deviations from these results in the medium range and high temperature ranges from these approximations.

It is concluded that the hybrid self consistent average phonon formalism compares well with the improved self consistent phonon formalism and it will be seen that it gives very good agreement with the experimental data.

1.7--RESULTS

The calculated results(SCAP3) for the lattice parameter, bulk modulus (compressibility), specific heat, coefficient of expansion, melting curves etc., are presented. Equations (1.5.1) and (1.5.2) have been used to obtain the average square frequency ω^2 and the mean square displacement self consistently. Equations (1.5.18), (1.5.20), (1.5.21), (1.5.26) and (1.5.29) have been used, respectively, to obtain the free energy, pressure, bulk modulus, specific heat at constant pressure and coefficient of expansion.

A-Lattice Parameter

The nearest neighbor distance $R_1(T)$ or the lattice constant a(T) as a function of temperature for the rare gas solids Ne, Ar, Kr and Xe has been obtained by calculating the pressure, P, for a set of nearest neighbor distance. In the present calculation a set of sixteen such values of $R_1 = 0.98R_0$ to $1.13R_0$ has been used. The nearest neighbor distance R_1 was obtained by the intersection of and the pressure versus R_1 curves with the P=0.0 curve.

Computationally, the zero pressure thermodynamical properties were also obtained when the total pressure P was less than one bar.

The calculated zero pressure, zero temperature lattice parameter for argon is a =5.3124Å while the experimental value is a =5.31125Å. In table--1.3 the calculated and the experimental lattice constant and the relative expansion ($\Delta a/a$), where Δa = (a(T)-a) are given. Figure 1.4 shows the calculated nearest neighbor distance R_1 , in the SCAP, the SCP and ISCP formalisms along with the experimental data. The experimental data has been taken from the work of Peterson, Batchelder and Simmons[33] The lattice constant was measured using a massive single crystal of argon by means of X-ray diffraction and a large oscillating back reflection camera. The accuracy of the experimental results was 15 parts per million.

From figure--1.4 and table--1.3 it can be seen that the hybrid self consistent average phonon formalism results are in excellent agreement with the experimental data[33]. Figure--1.4 also indicates that the SCAP results are better than those of the SCP and ISCP.

The calculated zero presure, zero temperature lattice constant for Kr is a =5.6461Å, while the X-ray measured extrapolated value is a =5.64587Å. Figure--1.10 shows the results for the nearest neighbor distance R_1 in the hybrid SCAP, ISCP and also the experimental values. In table--1.4 the calculated and the experimental lattice constant and the relative expansion ($\Delta a/a$) are given. The experimental data has been taken from the paper of Losee and Simmons[34], who measured the lattice parameter on a large single crystal by X-ray diffraction techniques. Both SCAP and ISCP predict a higher lattice constant compared to the experimental result but the SCAP values are slightly closer to the experimental data compared to ISCP.

Figure--1.16 shows the predictions about the nearest neighbor distance R_1 for the Xe as calculated from the lattice dynamical theories, ISCP and SCAP and also the experimental data. Table--1.5 shows the lattice constant a(T) and the volume per mole of the solid. The calculated and the experimental zero pressure and the zero temperature lattice constant are a = 6.132Å and 6.132Å respectively. From figure--1.16 and table--1.5 it may be concluded that the SCAP calculated values are in excellent agreement with the experimental results given in the article of Trefny and Serin[35], over the entire range of temperature, low to high up to the melting point.

In figure--1.22 the ISCP and the SCAP results for nearest neighbor distance $R_1(T)$ for Ne has been compared with the experiments. The experimental values have been taken from the article of Batchelder, Losee and Simmons[36]. In table--1.6 calculated and the experimental results for the lattice constant and the relative expansion ($\Delta a/a$) are given. Table--1.6 and figure--1.22 show that, as with other rare gas solids Ar, Kr and Xe, the calculated values for Ne are in very good agreement with the experimental work[36].

The nearest neighbor distance or the lattice parameter obtained by the self consistent average phonon formalism are in much better agreement with the experiments over the entire temperature range, compared to the SCP results for neon. It appears that the SCP results were not matched to the low temperature data. If they were, perhaps the results would not be very much different.

Neon being the lightest of all the rare gas solids which have been considered here, therefore, it is expected that it will have large quantum effects. This is indeed the case. The quantum corrections are more important at high temperature and expanded volumes. It is observed that the deviation between the SCAP calculation and the experimental values increases as the temperature rises. For neon there is poorest fit of all the rare gas solid crystals consisdered here.

B-BULK MODULUS

Calculated values of the isothermal bulk modulus, B_T , using SCAP(1), SCAP(2), SCAP(3), the SCP and ISCP formalisms are shown in figure--1.1. From figure--1.1 it is observed that the hybrid SCAP values are quite close to the ISCP values which are chosen as a standard to be fit.

Figure--1.5 shows the zero pressure bulk modulus, B_T, obtained by SCAP(3) and the ISCP formalisms along with the experimental data for Ar. The experimental data has been taken from the paper of Peterson, Batchelder and Simmons[33] who measured the compressibility $\chi = 1/B_T$ by X-ray diffraction techniques. In table--1.7 the calculated and the experimental compressibility for Ar are given. At low to middle range of temperatures, SCAP results are in very good agreement with the experiments. At high temperatures near the melting point, the results are about 10-15% lower than the measured values.

From figure--1.5 it may be observed that ISCP values are close to the experimentally observed values at low and high temperature ranges. ISCP results are about 10% off in the middle range of temperature.

At high temperatures the SCAP bulk modulus is about 10-15% higher than the observed values. This suggests that at high temperature the hybrid SCAP scheme does not take anharmonicity into account properly. This may be considered as a failure of the SCAP approximation to account for the anharmonicity satisfactorily of a perfect crystal or it is just possible that the deviation from the high temperature experimental data may be due to the imperfections in the crystal. Imperfections, particularly vacancies modify the interatomic potential. Thus the volume and the temperature dependence of the average phonon frequency and hence the free energy is modified. SCAP formalism does not include the effects of an imperfection. A physically meaningful theory, near the melting point must try to include the effects of the imperfections.

For Kr, the zero pressure isothermal bulk modulus, B_T, calculated by the SCAP and the ISCP approximations along with the X-ray measured data of Uras, Losee and Simmons[32] are shown in figure--1.11. Table--1.8 shows the calculated and experimental data for Kr. The results are similar to that for Ar. The calculated values are about 10% off the experimental values. At low and high temperatures the ISCP results are better than the SCAP results, on the other hand, in the middle temperature range SCAP results are sligtly better. Over all, the self consistent average phonon scheme gives very good agreement with the observed values.

At high temperatures, near the melting point there is experimental evidence that vacancies are formed as reported by Losee and Simmons[34]. If the vacancies are present, the bulk compressibility differs from the perfect crystal isothermal compressibility:

$$\chi = \chi_0 + n(v^f)^2/v_a K_B T$$

where n is the concentration of the vacancies, v^f is the volume of formation of a vacancy, v_a is the volume per atom. If $v^f = v_a$,

$$\chi = \chi_0 + n\, v_a/K_B T$$

and at temperatures near the melting point, the vacancies contribute as much as 10% to the isothermal compressibility. This contribution is due to the pressure dependence of the vacancy enthalpy. If this contribution is taken into account, the corrected bulk modulus will be in very good agreement with the experiments.

A physical description of the lattice dynamics must try to include a prescription to deal with the anharmonic effects arising from the imperfections in the crystal. It will be a worth while effort to include the corrections to thermodynamical properties due to the imperfections. These imperfections will modify the average phonon frequency and therefore the disagreement between SCAP and the measured values must be taken with some reservation.

Figure--1.17 shows the predictions about the bulk modulus (compressibility) for xenon using SCAP and the SCP theories and also the experimental data from the article of the Trefny and Serin[35].

They actually took the compressibility data from the paper of Packard and Swenson[37]. At low and high temperatures ISCP gives better results compared to SCAP and in the middle range of temperature SCAP does better than ISCP. This has been the case with Ar and Kr also. From table--1.10 it can be seen that the SCAP bulk modulus is 36.34 kbar and is in excellent agreement with the measured value 36.0 kbar but at higher temperatures, near the melting point, the SCAP values are poor.

In the case of krypton there is experimental evidence of vacancy formation[34] and the law of corresponding states[34] suggests that the contribution from such imperfections is not only important for Kr but also for other rare gas crystals, namely, Ne, Ar and Xe. At high temperatures the measurements are really performed on imperfect crystal. Hence the high temperature disagreement between the calculated values and the experiments may be due to lack of taking into account the contribution from the vacancies etc., to the free energy.

Figure--1.23 shows the isothermal bulk modulus, B_T, for Ne, obtained by the use of the lattice dynamical theories such as SCAP and SCP . Due to lack of the experimental data, complete comparison between theories and the experiments could not be made. Figure--1.23 shows the experimental results of Stewarts[38] at 4.2 K. Within experimental deviation both SCAP and the SCP match the experimental data. In table--1.11 the calculated values of the compressibility (bulk modulus) are given.

C-SPECIFIC HEAT

Figure--1.3 shows the constant volume specific for Ar in SCAP(1), SCAP(2), SCAP(3), the SCP and ISCP approximation schemes. SCAP(1), SCAP(2), SCAP(3) and the SCP results are almost the same and lower than that of ISCP. Figures --1.7 and 1.8 show the specific heat at constant volume and pressure respectively. Table--1.12 shows the constant volume specific heat for Ar. From these figures one can see that in general ISCP results are better than those of SCAP and the SCP compared to the experiments. The experimental values were taken from the article of Beaumont, Chihara and Morrison[37] and Flaubacher Leadbetter and

Morrison[38] respectively. The discrepency between SCAP and the experiments increases with the temperature.

Figures --1.13 and 1.14 show the predictions of the SCAP and the ISCP formalisms about the specific heat at constant volume and constant pressure for Kr respectively. These results are compared to the experimental data of Losee and Simmons[34] and Uras, Losee and Simmons[32] Again both the SCAP and the ISCP agree qualitatively with the experiments with ISCP doing a slightly better job.

In figures --1.18 and 1.19 C_V versus T and C_P versus T curves for xenon are shown. The experimental values are from the work of Crawford and Daniel[41] and Trefny and Serin[35]. Again the behavior is similar to that for Ar and Kr. The values are about 10-15% off the experimental values.

Values of the constant volume and constant pressure specific heat for Ne from the present work i.e., SCAP are shown in figures 1.24 and 1.25 respectively. The values of C_v are also tabulated in table--1.14 .The experimental data for Ne has been taken from the paper of Fenichel and Serin[42]. As can be seen from these figures and table--1.14 neon gives the poorest fit of all the rare gases solids. This poorest agreement between the SCAP and the experiments for neon is not surprising because of the light mass of the neon atom. The lighter the mass the larger is the quantum correction. Thus the SCAP approximation does not provide a very accurate description of "very quantum crystals" such as Ne and He.

D-COEFFICIENT OF EXPANSION

In figure--1.6 the SCAP, the SCP and ISCP results for argon are compared to the experimental results of Peterson, Batchelder and Simmons[33]. The calculated coefficient of volume expansion and the experimental values are listed in table--1.15 for argon. From figure--1.6 it may be noted that ISCP gives good results at low and high temperatures where SCAP does not give results as good as ISCP. On the other hand ISCP results deviate from the experiments in the middle range of temperature where SCAP gives some what better results.

At high temperature there is experimental evidence of vacancy formation. The formation of vacancies increases the volume expansitivity. For Kr Losee and Simmons[34] have estimated that the compressibility increases by 10% near the melting point. On the basis of law of corresponding states it is expected that similar results hold good for Ar and the other rare gas crystals. Thus the high temperature disagreement between the SCAP calculated values of expansitivity and the experiments may be due to the neglect of accounting for the contribution of the vacancies and the other imperfections.

Figures --1.12, 1.20, 1.26 and tables --1.16, 1.17, 1.18 show the results of the present work for the volume expansivity of Kr, Xe and Ne respectively. The results are similar to that for Ar i.e., at low and high temperatures ISCP gives better results and in the middle range of temperature SCAP results are some what better. For neon the fit is found to be poorest of all the rare gas crystals considered here which reflects the very quantum nature of neon.

GRUNEISEN PARAMETER

The Gruneisen parameter, γ, has been calculated for the rare gas solid crystals Ne, Ar, Kr and Xe. The calculated values for Ne at 0 K and 23 K are 2.459 and 2.079 respectively are in very good agreement with the SCP values 2.465 and 2.086 respectively The SCAP calculated Gruneisen parameter for Ar at 0 K and 80 K are 2.925 and 2.167 respectively. These values are also in very good agreement with the SCP[22] results 2.853 and 2.083 respectively.

The agreement between the SCAP results and the experimental data for Kr and Xe is very good as can be seen from tables--1.19 and 1.20 except at very low temperatures.

MELTING CURVES

The pressure along the melting line is a useful relationship for testing an equation of state for a solid. Excellent results have been obtained for Ar and Kr as can be seen from figures 1.9 and 1.15. The ratio, root mean square displacement to the nearest neighbor, the Lindemann parameter was assumed to be independent of pressure at the melting point. The Lindemann parameter has been chosen from the zero pressure value at the known melting point. It was found that for Ar, Kr and Xe the Lindemann parameter $L=0.081$, described the experimental data very well. For Ne $L=0.091$ was a good choice.

For Ar and Kr the agreement between the experiments and the calculated values was found to be excellent as can be seen from figures 1.9 and 1.15. A recent study of melting curves on Xe[43] shows that the experimental values are in very good agreement with the values predicted by SCAP formalism. But for Ne the agreement with the experiments is not as good as with Ar and Kr.

It is of interest to see how well the Simon equation[43] can be written in the form

$$P + a = a(T/T_0)^c,$$

where a and c are constants to be chosen and T_0 is the temperature of the triple point.

To compare with the Simon equation, curves were plotted in the form P+a versus T. The values of a were chosen to give an approximately linear curve on a log-log plot. The chosen values are given in table 1.1, which gave linear graph over the available data.

CONCLUSION

Starting with the self consistent phonon formalism, which has proved to be very useful in describing the anharmonic contributions to the lattice dynamical properties of solids, a self consistent average phonon formalism has been developed.

The crystalline solid is described in terms of an average frequency which has to be calculated self consistently. The self consistent condition was obtained between the average square frequency ω^2 and the mean square displacement u^2. Considering the system to be descriable in terms of an average frequency ω^2, the free energy F, and all other thermodynamical properties of the system such as pressure, compressibility, lattice constant, specific heat, melting curves etc., were calculated for the rare gas solids Ne, Ar, Kr and Xe.

Using the emperical potential of the Lennard - Jones type the equation of state and the other thermodynamical properties of the inert gas crystalline solids were calculated. The SCAP calculated results have been compared not only with the experiments but also with the more detailed calculation such as the improved self consistent phonon approximation, since in general ISCP, which utilizes the full phonon spectrum, gives better agreement with the experimental data over a wide range of temperatures. The agreement with the experimental data and the SCAP calculated results has been found to be very good in general.

The SCAP formalism describes thermodynamical properties of the inert gas crystals very well in the low and medium range of temperatures. At high temperatures there are still discrepancies which may be taken as a failure of the SCAP formalism for not accounting for the anharmonicity of a perfect crystal or it may be due to the imperfections in the solids or it may be due to the lack of knowledge of the crystal poential. In pratice the crystal is imperfect at temperatures near the melting temperatures. The contribution due to the vacancies, dislocations, fractures and the surfaces are important. The effects of the imperfections have not been taken into considerations in the present analysis.

This investigation clearly shows the usefulness of the simplicity of the self consistent average phonon formalism developed here. It was worthwhile to extend the SCAP formalism to more complicated solids. An attempt has been made to study an ionic solid. This is discussed in next chapter.

2.1--INTRODUCTION

The theoretical study of ionic crystals was initiated by M.Born[44]. M.Born proposed that the ions could be regarded as point charges. The cohesion of the system is by the coulomb interaction between the ions and the crystal is stabilized by the short range interaction. Such a rigid ion model has been used by several authors.

In 1940 Kellerman[45] applied Born's rigid ion model to obtain the phonon frequencies of the ionic crystals, particularly NaCl. The rigid ion model was further eloborated by Fumi and Tosi[46] and Tosi and Fumi[47]. Cowley[48,49] applied quasiharmonic and perturbation theory to a model of NaCl, and from this study it may be concluded that[50] the quasiharmonic approximation was useful up to 30% of the melting temperature and that perturbation theory gave good results up to 80% of the melting temperature. Later Karo[51] calculated the dynamics of the alkali halides when the experimental data became available. The theoretical results were in qualitative agreement with the experiments. Inadequacies of the rigid ion model lead to the proposal of two simple models, namely, the shell model and the deformation dipole model. The displacement of the ions from the equilibrium position destroys the high symmetry at the lattice sites. This leads to the appearance of dipole and quadrupole moments at the lattice sites. A shell model was used by Dick and Overhauser[53] to calculate the phonon frequencies of NaI. Wood et al.,[54] studied NaI and KBr. Later Cowley et. al.,[55] incorporated the non central forces into the shell model.

Hardy and Karo[56] proposed a deformation dipole model. Karo and Hardy[57] applied this deformation dipole model to an investigation of the phonon spectrum and other properties of the alkali halides. The agreement was found to be very good with the experiments. The detailed description of the model and its applications are given in a recent book by Hardy and Karo[59].

The equation of state of the crystal such as NaCl has been investigated by several reseachers. Barrons[60] and Blackman[61] used the Kellerman model to calculate the low and the high temperature Gruneisen parameters. Using the quasiharmonic model and the Born-Mayer repulsive energy Decker[62] obtained an equation of state valid up to high pressures. Robert and Ruppin[63] calculated the Gruneisen parameters form the thermodynamical data.

By expanding the free energy in terms of a strain parameter Hardy and Karo[58] have made a self consistent calculation of the thermal expansion, heat capacity and the Gruneisen parameters of the alkali halides(NaCl, KCl, RbCl). Also Boyer[64-66] obtained an equation of state for NaCl and KCl using the expansion of the free energy in the quasiharmonic approximation. His predictions about the relative expansion and the compressibility(at room temperature 293 K) are quite good. But the lattice parameter is consistently higher than the experimental values and the discrepancy increases at higher temperatures. Boyer has predicted a lattice instability $B_T ==> 0$ as a possible cause of the melting. The critical temperature T_c at which $B_T ==> 0$ is quite near the melting temperature T_m of NaCl and KCl. It is this closeness between the critical temperature and the melting temperature which lead him to suggest such an instability as a possible cause the melting.

Self consistent phonon(SCP) and the improved self consistent phonon (ISCP) formalisms have proved to be valuable in predicting the anharmonic contributions to the thermodynamical properties of the rare gas crystals[17-22]. This procedure requires a great deal of numerical calculation for each mode k and a set of volumes and temperatures. In the calculation of the thermodynamical properties such as the pressure, P, etc., the details of the phonon dispersion is averaged out. Therefore an attempt was made to develop the self consistent phonon formalism in terms of an average phonon frequency and such a self consistent average phonon formalism turned out to be successful in predicting the properties of the rare gas crystals Ne,Ar, Kr and Xe[25,26].

The unit cell of a rare gas solid crystal is a primitive cell i.e., it contains one atom per unit cell. The self consistent average phonon formalism was extended to nonprimitive lattices. If the unit cell contains two atoms per unit cell then there are six modes for each wave vector k. Three of the phonon modes are the acoustic modes and the other three are the optical modes. For a crystal with N_0 cells two kinds of averaging processes are defined:

(a) An average phonon frequency $<\omega^2>$ over all the $6N_0$ modes can be defined as

$$<\omega^2> = (1/6N_0)\sum_{k\lambda}\omega^2(k\lambda), \qquad \ldots 2.1.1$$

where $\lambda=1$, 2, 3 (acoustic modes) and $\lambda=4$, 5, 6(optical modes).In this case it is found that the coulomb interaction does not contribute to the average phonon frequency $<\omega^2>$ the sole contribution comes from the short range part of the interaction[67]. The coulomb interaction of course contributes to the free energy through the average interaction energy.

(b) The averaage acoustic frequency $\langle \omega^2 \rangle_a$ and the average optical frequency $\langle \omega^2 \rangle_p$ can be defined separately:

$$\langle \omega^2 \rangle_a = \omega_a^2 = (3N_0)^{-1} \sum_{k\lambda=1}^{3} \omega^2(k\lambda) \quad \ldots 2.1.2$$

$$\langle \omega^2 \rangle_p = \omega_p^2 = (3N_0)^{-1} \sum_{k\lambda=4}^{6} \omega^2(k\lambda) \quad \ldots 2.1.3$$

Now the free energy has contributions from the acoustic and the the optical phonon frequencies separately.

A first principle calculation has been performed to obtain an equation of state and the other thermodynamical properties for sodium chloride, using the Gordon and Kim potential^{72}. Several years ago Gordon and Kim developed a theory from which reliable pair potential for a closed shell systems can be calculated from the charge densities of the free ions. Gordon and Kim expressed the ground state energy in terms of the charge density of the system, as if it were a free electron gas. This is a parameter free calculation in the sense that no experimentally determined thermodynamical quantities such as the lattice parameter, cohesive energy, compressibilty etc., have been used to find the parameters in the repulsive part of the interaction energy.

To the author's knowldge this is the first self consistent phonon, first principle, extensive calculation of equation of state for NaCl. The self consistent average phonon equation of state results are compared with the experiments as well as with the quasiharmonic (non self consistent) calculation of Boyer[64-66]. It is found that the self consistent average phonon equation of state for NaCl is quite different from the quasiharmonic equation of state. It is found that B_T===>0 instability occurs at temperatures much higher than the experimental melting temperature and thus lies in the unphysical region. Applying of the quasiharmonic and perturbation theories to NaCl, Cowley[48,49] has found that the quasiharmonic approximation overestimates the vibrational pressure. Therefore it is difficult to believe that such a lattice instability B_T===>0 is the cause of the melting. Further, at the experimental melting temperature T_m the compressibility $\chi=1/B_T$ is finite, not infinite as suggested by the lattice instabillity, in agreement with Jackson and Liebermann[73] who argued that the shear modulus is finite at the melting.

Inclusion of the anharmonic effects lowers the thermal (or vibrational) pressure. This in turn will raise the critical temperature T_c, the temperature where the lattice instabilty B_T===>0 occurs and will be higher than the prediction of the quasiharmonic results. Thus, the lattice instability will set in at a temperature higher than the actual melting, a region which can not be reached experimentally.

For a complete analysis of the system's thermodynamical properties anharmonic effects must be included. The cause of the melting is still an open question, whether the lattice instability B_T===>0 or any other lattice instability or the imperfections in the solids such as the vacancies, dislocations, cracks etc., are really responsible for the melting of the solid.

2.2--INTERATOMIC POTENTIAL

The ions of a crystal interact with one another through the long range coulomb interaction and the short range repulsive interaction. According to the Born theory[44] of ionic crystals, the lattice sites are the ions with unit charge positive or negative. The binding of the crystal is due to the long range coulomb interaction between the ions and the crystal is stabilized by the short range interaction which arises due to the distortion of the electronic states of the ion. In the rigid ion model the potential energy of the crystal system is

$$\Phi = (1/2) \sum_{\substack{\nu\pi \\ NP}} e_\nu e_\pi/(r(N\nu,P\pi)) + v_{sr}, \qquad \ldots 2.2.1$$

where the first term is due to the coulomb interaction and the second term is due to the short range interaction and $r(N\nu,P\pi)$ is the distance between the ions $N\nu$, $P\pi$.

Several years ago Gordon and Kim[72] developed a theory from which a realiable pair potential for a closed shell system could be calculated from the charge densities of the ions. Such a charge density was calculated without any experimental data of thermodynamical nature. Recently Boyer[64-66] obtained an equation of state of the alkali halides in the quasiharmonic approximation using the Gordon and Kim potential. Boyer has emphasized the first principle nature of his calculation because the input data used in calculating the potential were of a fundamental nature such as the electronic charge, mass and the Planck constant etc. No experimentally measured quantities such as the lattice parameter, cohesive energy etc., were used. Boyer expressed the short range potential in the form

$$v_{sr}(r) = \sum_{\alpha=1}^{4} A_\alpha \exp(-B_\alpha r). \qquad .....2.2.2$$

This short range potential has contributions from the (a) short range coulomb, (b) kinetic, (c) exchange and (d) the correlation interactions. The values of the constants A and B have been listed in the reference[66].

The potential energy per molecule of the crystal is

$$\Phi = -\alpha_0 e^2/R_1 + 6\sum_{\alpha=1}^{4} A_\alpha \exp(-B_\alpha R_1) + 6\sum_{\sigma=1}^{4} A_\sigma \exp(-B_\sigma R_2), \qquad ...2.2.3$$

where R_1 and R_2 are the near neighbor and the next near neighbor distances, respectively and α_0 is the Madulung constant. Here the interaction between the Na-Na ion has been neglected but the NaCl(near neighbor) and Cl-Cl(next neighbor) interactions are included.

The purpose of the present work is to obtain an equation of state for the ionic crystals, particularly sodium chloride using the method of self consistent average phonon approximation, which was developed and applied successfully to obtain equation of state for the rare gas solids Ne, Ar, Kr and Xe[25,26].

Use of the Gordon and Kim potential gives the author an opportunity to compare the self consistent average phonon results not only with the experiments but also with the quasiharmonic results. It is observed that there are some significant differences between the quasiharmonic and the self consistent average phonon equations of state.

2.3--SCP FORMALISM

A perfect crystal of point ions is considered with two ions per unit cell and N cells. Let $R(N\nu)$ be the equilibrium position of the ion $(N\nu)$,

$$R(N\ ) = R(N) + R(\nu), \qquad \ldots\ 2.3.1$$

where $R(N)$ is the position vector of the cell N and $R(\nu)$ is the position of the νth type of the ion within the unit cell. Now if the ion is displaced from the equilibrium position, the displaced position of the ion is given by

$$r(N\nu) = R(N\nu) + u(N\nu), \qquad \ldots\ 2.3.2$$

where $u(N\nu)$ is the dynamical displacement of the ion from the equilibrium position $R(N\nu)$.

For a central pairwise interaction, the potential energy of the crystal can be written as

$$\Phi = (1/2)\sum_{\substack{NP \\ \nu\pi}} v(r(N\nu,P\pi)), \qquad \ldots.2.3.3$$

$$r(N\nu,P\pi) = r(P\pi) - r(N\nu). \qquad \ldots\ 2.3.4$$

The Hamiltonian, H, of the system can be written as

$$H = \sum_{iN\nu} (1/2m_\nu)[p_i(N\nu)]^2 + \Phi\ , \qquad \ldots\ 2.3.5.$$

where m_ν is the mass of the νth type of ion ($\nu = 1$ for sodium and $\nu = 2$ for chlorine) and $p_i(N\nu)$ is the i-th component of the momentum of the ν-th ion in the N-th cell. Expanding Φ, using the static equilibrium conditions[31]

$$\Phi = \Phi_0 + [(1/2!) \sum_{\substack{\nu\pi \\ NP}} \sum_{ij} \Phi_{ij}(N\nu,P\pi)\ u_i(N\nu)\ u_j(P\pi)$$

$$+ (1/3!) \sum_{\substack{ijk \\ \nu\pi\rho \\ NPQ}} \Phi_{ijk}(N\nu,P\pi,Q\rho) u_i(N\nu)\ u_j(P\pi)\ u_k(Q\rho)$$

$$+ \text{etc.} \qquad], \qquad \ldots .2.3.6$$

where

$$\Phi_{ij}\ (N\nu,P\pi) = \partial^2 v/\partial u_i(N\nu)\partial u_j(P\pi), \qquad \ldots 2.3.7$$

$$\Phi_{ijk}(N\nu,P\pi,Q\rho) = \partial^3 v/\partial u_i(N\nu)\partial u_j(P\pi)\partial u_k(Q\rho), \qquad \ldots 2.3.8$$

etc.

In the harmonic approximation, the second order terms in the displacement are kept and the other so called anharmonic terms depending upon u^3, u^4, etc. are neglected. The coefficients $\Phi_{ij}(N\nu,P\pi)$ are called the harmonic force constants.

The effective harmonic energy θ is introduced and the Hamiltonian can be written as

$$H = H_h + (\Phi - \theta), \qquad \text{...2.3.9}$$

where

$$\theta = (1/2) \sum_{\substack{ij \\ \nu\pi \\ NP}} \theta_{ij} (N\nu,P\pi)\ u_i(N\nu)u_j(P\pi) \qquad \text{...2.3.10}$$

is the effective harmonic energy and the effective harmonic Hamiltonian, H_h , is

$$H_h = \sum_{i\nu P}(1/2m_\nu)[p_i(N\nu)]^2 + (1/2) \sum_{\substack{ij \\ \nu\pi \\ NP}} \theta_{ij}(N\nu,P\pi)u_i(N\nu)u_j(P\pi). \qquad \text{...2.3.11}$$

In the harmonic approximation the thermal or harmonic average of free energy F is defined by

$$< F > = Tr(\rho_h (H + \beta^{-1} \ln \rho_h)), \qquad \text{...2.3.12}$$

where the angular braket <-----> denotes the harmonic average and ρ_h is the harmonic density matrix

$$\rho_h = C_0^{-1}(\exp(-\beta H_h)), \qquad \text{... 2.3.13}$$

$$C_0 = \mathrm{Tr}\,[\exp(-\beta H_h)], \qquad \ldots\ 2.3.14$$

where $\beta = 1/K_BT$, K_B is the Boltzmann constant.

The displacement - displacement correlation function d_{ij} is defined by

$$d_{ij}(N\nu,P\pi) = \langle\, u_i(N\nu)\; u_j(P\pi)\, \rangle. \qquad \ldots\ 2.3.15$$

To find the effective harmonic force constants $\theta_{ij}(N\nu,P\pi)$ a variational principle is used in which the force constants $\Phi_{ij}(N\nu,P\pi)$ and the displacement-displacement correlation function $d_{ij}(N\nu,P\pi)$ are regarded as the variational parameters. The minimization of the free energy with respect to $\Phi_{ij}(NP)$ and d_{ij} determines the effective or optimum force constants. The effective force constants $\theta_{ij}(N\nu,P\pi)$ may also be obtained by the use statistical perturbation theory[68] such that the effect of perturbation on $\Phi - \theta$ is negligible. In both cases it is found that the optimum values of the force constants must be determined by the harmonic or the thermal average of the second derivatives of the crystal potential i.e.,

$$\theta_{ij}(N\nu,P\pi) = < \partial^2 v/\partial u_i(N\nu)\,\partial u_j(P\pi) >. \quad \ldots\ 2.3.16$$

Due to the thermal averaging of the second derivative of the crystal potential, the force constants $\theta_{ij}(N\nu,P\pi)$ are temperature dependent. On the other hand the quasiharmonic force constants $\Phi_{ij}(N\nu,P\pi)$ are temperature indpendent. This results in a significant difference between the self consistent phonon and the quasiharmonic approximations. The SCP frequencies are temperature and volume dependent. Because of the self consistancy between the frequency $\omega^2(k\lambda)$ and the mean square displacement $<u^2(N\nu)>$, the SCP frequencies $\omega^2(k\lambda)$ are higher compared to the quasiharmonic frequencies. The effect of the temperature is particularly important at temperatures near the melting point. At high temperatures in the quasiharmonic approximation very large ionic excursion from the mean position are obtained but in the SCP formalism the ionic excursion is limited due to self consistancy. This results in important differences between the two approaches.

In the harmonic approximation, the partition function Z_h is

$$Z_h = \mathrm{Tr}[\exp(-\beta H_h)], \quad \ldots 2.3.17$$

the harmonic free energy F_h is

$$F_h = -\beta^{-1} \ln Z_h$$

$$= \langle H_h + \beta^{-1} \ln \rho_h \rangle. \qquad \ldots 2.3.18$$

The crystal free energy F, in the harmonic averaging approximation is

$$F = F_h + \langle \Phi - \theta \rangle_h. \qquad \ldots 2.3.19$$

To diagonalize the harmonic Hamiltonain H_h the transformations are defined as

$$u_i(N\nu) = \sum_{k\lambda} (\hbar/2N_0 m_\nu \omega(k\lambda))^{1/2} \exp(i\, k\cdot R(N\nu))$$

$$[A(k\lambda) + A^\dagger(-k\lambda)]\, w_i(\nu k\lambda) \quad \ldots 2.3.20$$

and

$$\dot{u}_i(N\nu) = (\hbar/2N_0 m_\nu \omega(k\lambda))^{1/2} \exp(i\, k\cdot R(N\nu))$$

$$\cdot\, \omega(k\lambda)[A^\dagger(-k\lambda) - A(k\lambda)]\, w_i(\nu k\lambda), \quad \ldots 2.3.21$$

where $A^{\dagger}(k\lambda)$ and $A(k\lambda)$ are the creation and the destruction operators of the phonons of mode $k\lambda$. The position and the momentum operators satisfies the usual commutation relations

$$[u_i(N\nu),\ u_j(P\pi)] = [\dot{u}_i(N\nu),\ \dot{u}_j(P\pi)] = 0, \quad ...2.3.22$$

$$[u_i(N\nu),\ \dot{u}_j(P\pi)] = (i\hbar/m_{\pi})\,\delta_{ij}\,\delta_{NP}\delta_{\nu\pi} \quad ..2.3.23$$

Using the transformations (2.3.20) and (2.3.21) the harmonic Hamiltonian reduces to

$$H_h = \sum_{k\lambda} \hbar\omega(k\lambda)[\ A^{\dagger}(k\lambda)\ A(k\lambda) + 1/2\ ]. \quad ...\ 2.3.24$$

The eigenvalues are obtained by the diagonalization condition

$$[\ \omega^2\ (k\lambda)\delta_{\lambda\lambda'} - w_i^*(\nu k\lambda)M_{ij}(\nu k\pi)\ w_j(\pi k\lambda')]=0.0, \quad ...2.3.25$$

where

$$M_{ij}(\ \nu k\ \pi) = (m_{\nu}m_{\pi})^{-1/2}[\ \sum_{P} \phi_{ij}(0\,\nu,P\pi)\exp(ikR(0\nu,P\pi))]. \quad ...2.3.26$$

The dynamical matrix $M_{ij}(\nu k\pi)$ is a 6 X 6 hermitian matrix For each wave vector k there are six characteristic modes (

λ=1, 2, -- 6). Three of the modes are the acoustic phonon modes (λ= 1, 2, 3) and the other three modes are the optical modes (λ= 4, 5, 6). The phonon occupation number is

$$\langle A^{\dagger}(k\lambda)A(k'\lambda') \rangle = [\exp(\beta\hbar\omega(k\lambda)) - 1]^{-1} \delta_{kk'}\delta_{\lambda\lambda'}, \quad ...2.3.27$$

$$\langle A(k\lambda)A(k'\lambda') \rangle = \langle A^{\dagger}(k\lambda)A^{\dagger}(k'\lambda') \rangle = 0. \quad ... 2.3.28$$

Using equations (2.3.27) and (2.3.28) it is found that in the self consistent phonon approximation, the displacement- displacement correlation function $d_{ij} = \langle u_i(N\nu)\, u_j(P\pi)\rangle$ is

$$d_{ij} = (N_0^2 m_\nu m_\pi)^{-1/2} \sum_{k\lambda} [\hbar \coth(\xi(k\lambda))/2\omega(k\lambda)]$$

$$\cdot [\exp(ik\cdot R(N\nu,P\pi))]\, w_i^{*}(\nu k\lambda) w_j(\pi k\lambda) \quad ...2.3.29$$

In the self consistent phonon approximation the mode frequencies $\omega^2(k\lambda)$ from equation (2.3.25), the force constants $\theta_{ij}(N\nu, P\pi)$ from equation (2.3.16) are evaluated self consistently through the use of equation (2.3.29). This procedure requires extensive numerical iterative calculation of $\omega^2(k\lambda)$, $\theta_{ij}(N\nu,P\pi)$ and d_{ij} for each wave vector k and a set of values of volume and temperature to obtain volume and temperature dependence of the eigenmodes which ultimately determine the dependence of the free energy on volume and temperature.

To evaluate the thermodynamical quantities such as the pressure, P, of the system a sum over the phonon characteristic modes has to be performed. In such a summation the details of the phonon dispersion are averaged out. This suggested that a self consistent theory may be developed in terms of the average phonon frequency. Such an approach was useful in predicting an equation of state for the rare gas solid crystals Ar, Kr, Xe and Ne[25,26] and the other thermodynamical properties.

The self consistent average phonon formalism is now extended to solids which are non primitive. The thermodynamical properties of the ionic crystals, particularly sodium chloride, will be studied. For NaCl the self consistent average phonon scheme may be formulated in two ways. In one of the schemes a single average square frequency ω^2 is defined over all the six modes, acoustic as well as the optical modes i.e.,

$$\langle \omega^2 \rangle = \omega^2 = (6N_0)^{-1} \sum_{k\lambda} \omega^2(k\lambda). \qquad \ldots 2.3.30$$

This scheme will be referred as the single frequency self consistent average phonon approximation. In the second of the schemes, two average square frequencies are defined corresponding to two distinct kinds of phonon modes, the acoustic and the optical modes. The average square acoustic frequency ω_a^2 is defined by

$$\langle \omega^2 \rangle_a = \omega^2{}_a = \sum_{k} (3N_0)^{-1} \sum_{\lambda=1}^{3} \omega^2(k\lambda) \quad \ldots 2.3.31$$

and the average square optical mode frequency ω_p^2 is defined by

$$\langle \omega^2 \rangle_p = \omega^2{}_p = \sum_{k} (3N_0)^{-1} \sum_{\lambda=4}^{6} \omega^2 (k\lambda). \quad \ldots 2.3.32$$

The second of the schemes will be called the two frequencies self consistent average phonon formalism.

The free energy F_{SCP} in the self consistent phonon formalism is

$$F_{SCP} = \beta^{-1} \sum_{k\lambda} [\ln[2\mathrm{Sinh}\, \xi_1(k\lambda)] - [(\hbar\omega(k\lambda)/4)\coth(\xi_1(k\lambda))]]$$

$$+ \langle \Phi \rangle_h, \quad \ldots 2.3.33$$

where

$\xi_1(k\lambda) = 0.5\beta\hbar\,\omega(k\lambda).$

The internal energy U of the crystal system is

$$U = \sum_{k\lambda} (\hbar\,\omega(k\lambda)/4)\coth \xi(k\lambda) \quad + \quad \langle \Phi \rangle_h . \qquad \ldots 2.3.34$$

The self consistent phonon free energy F_{SCP} has contributions from the even derivatives of the interatomic potential. Due to the harmonic averaging with respect to the effective phonon modes, the contribution from the odd derivatives of the interatomic potential vanishes. In this way the self consistent phonon formalism only partially takes into account the anharmonicity. Improvement to F can be made by including the contribution from the odd derivatives by ordinary perturbation theory.

2.4-- ONE FREQUENCY SELF CONSISTENT AVERAGE PHONON APPROXIMATION

The average square frequency ω^2 over all the $6N_0$ modes is defined by

$$\omega^2 = (6N_0)^{-1} \sum_{k\lambda} \omega^2(k\lambda). \qquad ...2.4.1$$

The sum of the eigenvalues of the dynamical matrix $M_{ij}(\gamma\pi k)$ is the trace of the matrix M i.e.,

$$\sum_{\lambda} \omega^2(k\lambda) = \text{Tr } M. \qquad ...2.4.2$$

Using (2.3.26) one obtains

$$\text{Tr } M = \sum_{i} M_{ii}(\gamma\pi k) = (m_\nu m_\pi)^{-1/2} \sum_{iP} \theta_{ii}(0\nu, P\pi)$$

$$[\exp(ik \cdot R(0\nu, P\pi)]. \qquad ...2.4.3$$

The equation (2.4.1) can be written as

$$\omega^2 = (1/6) \sum_{i\gamma} \theta_{ii}(0\gamma, 0\nu)/m_\gamma$$

$$= (-1/6)\sum_{i\nu P\pi}{}' \theta_{ii}(0\nu,P\pi)/m_\nu . \qquad \ldots 2.4.4$$

For a central pairwise interaction the potential energy of the system is

$$\Phi = (1/2)\sum_{\substack{\nu\pi \\ NP}} v(r(N\nu,P\pi)). \qquad \ldots 2.4.5$$

For such a potential, the mean square frequency ω^2 is

$$\omega^2 = (1/6)\sum_{i\nu P\pi}{}' <\nabla_{ii}(r(0\nu,P\pi))>/m_\nu , \qquad \ldots 2.4.6$$

where the derivatives are to be evaluated with respect to the bond length $r(0\nu,P\pi) = r(P\pi) - r(0\nu)$. There are six near neighbors and twelve next near neighbors in the sodium chloride structure. The equation (2.4.6) reduces to

$$\omega^2 = (1/m_1+1/m_2)<\nabla^2 v(Na,Cl)>+2/m_2<\nabla^2 v(Cl,Cl)>, \qquad \ldots 2.4.7$$

where v(Na,Cl) is the interaction between the sodium and the chlorine ions, v(Cl,Cl) represents the interaction between the Cl-Cl ions. The potential energy of interaction for a crystal with N_0 unit cells (or per molecule) may be written as

$$v= N_0[-(\alpha_0 e^2/R_1) +\sum_{\alpha=1}^{4} A_\alpha 6\exp(-B_\alpha R_1) +\sum_{\sigma=1}^{4} A_\sigma 6\exp(-B_\sigma R_2)],$$

where α_0 is the Madelung constant and R_1 is the near neighbor distance i.e., the distance between the sodium and the chloride ions. The displacement-displacement correlation function d_{ij} is given by equation (2.3.29)

$$d_{ij} = (N_0^2 m_\nu m_\pi)^{1/2} \sum_{k\lambda} [\hbar \coth(\xi(k\lambda))/2\ \omega(k\lambda)]$$

$$[\exp(ik \cdot R(N\nu, P\pi))]\ w_i^*(\nu k\lambda) w_j(\pi k\lambda). \qquad \ldots 2.4.9$$

In the self consistent average phonon formalism all the mode frequencies are replaced by the average frequency ω . Further using the orthonormality and the completeness relations of the polarization coefficients

$$\sum_{i\nu} w_i^*(\nu k\lambda)\ w_i(\nu k\lambda') = \delta_{\lambda\lambda'}, \qquad \ldots 2.4.10$$

$$\sum_{\lambda} w_i^*(\nu k\lambda)\ w_j(\pi k\lambda) = \delta_{ij}\ \delta_{\nu\pi}, \qquad \ldots 2.4.11$$

one obtains

$$\langle u_i(N\nu)\ u_j(P\pi)\rangle = (\ \hbar \coth\xi\ /2m_\nu\ \omega\ )\ \delta_{ij}\ \delta_{NP}\ \delta_{\nu\pi}. \qquad \ldots 2.4.12$$

The displacement-displacement correlation function between sodium and chlorine ions can be written as

$$U^2(\mathrm{NaCl})=\sum_{i}\langle(u_i(0,\mathrm{Na}) - u_i(P,\mathrm{Cl}))^2\rangle$$

$$= U^2(\mathrm{Na}) + U^2(\mathrm{Cl})$$

$$= (3\hbar \coth\xi_1/2\mu\omega), \quad \ldots 2.4.13$$

where μ is the reduced mass

$\mu^{-1} = m_1^{-1} + m_2^{-1}$,

m_1 = mass of the sodium ion,

m_2 = mass of the chlorine ion,

$U^2(\mathrm{Na})$ = mean square displacement of sodium ion,

$U^2(\mathrm{Cl})$ = mean square displacement of chlorine ion.

and the mean square displacement of the chlorine ion is given by

$$U^2(\mathrm{Cl})=\sum_{i}(1/2)\langle(u_i(0,\mathrm{Cl}) - u_i(P,\mathrm{Cl}))^2\rangle$$

$$= (3\hbar \coth\xi_1/2m_2\omega). \quad \ldots 2.4.14$$

The harmonic average of the interatomic potential energy between the ions (0ν) and $(P\pi)$ is

$$\langle v(r(0\gamma,P\pi))\rangle = [\ v(r(0\gamma,P\pi)) + 1/2 \sum_{i} \langle u_i^2(0\gamma,P\pi)\rangle$$

$$\cdot\ \partial^2 v/\partial u_i^2(0\gamma\ ,P\pi) + \text{--} \qquad \ldots 2.4.15$$

Now the derivatives are evaluated with respect to the bond length $r(0\gamma,P\pi)$. The effective interaction between the Na and Cl ions (near neighbor, short range) may be written as

$$\langle v(\mathrm{Na,Cl})\rangle = [\ S_0 + (U^2(\mathrm{NaCl})/6)S_2 + (U^4(\mathrm{NaCl})/72)S_4$$

$$+ (U^6(\mathrm{NaCl})/1296)S_6 + \text{---}], \qquad \ldots 2.4.16$$

where

$$S_0 = v(\mathrm{Na,Cl}) = \sum_{\alpha=1}^{4} A_\alpha \exp(-B_\alpha R_1),$$

$$S_2 = \nabla^2 v(\mathrm{Na,Cl})$$

$$= \sum_{\alpha=1}^{4} A_\alpha (B_\alpha^2 - 2\ B_\alpha/R_1)\exp(-B_\alpha R_1),$$

$$S_4 = (\nabla^2)^2\ v(\mathrm{Na,Cl})$$

$$= \sum_{\alpha=1}^{4} A_\alpha (B_\alpha^4 - 4B_\alpha^3/R_1)\exp(-B_\alpha R_1).$$

The thermal average of the interaction energy between the chlorine- chlorine ions (second neighbor interaction) is

$$\langle v(Cl,Cl)\rangle = [\ F_0 + (U^2(Cl)/3)F_2 + (U^4(Cl)/18)F_4$$

$$+ (U^6(Cl)/162)F_6 + ---], \qquad ...2.4.17$$

where

$$F_0 = v(Cl,Cl) = \sum_{\sigma=1}^{4} A_\sigma \exp(-B_\sigma R_2),$$

$$F_2 = \nabla^2 v(Cl,Cl)$$

$$= \sum_{\sigma=1}^{4} A_\sigma (B_\sigma^2 - 2B_\sigma/R_2) \exp(-B_\sigma R_2),$$

$$F_4 = (\nabla^2)^2 v(Cl,Cl)$$

$$= \sum_{\sigma=1}^{4} A_\sigma (B_\sigma^4 - 4B_\sigma^3/R_2)\exp(-B_\sigma R_2).$$

Now the harmonic average of the potential energy of the crystal becomes

$$\langle \Phi \rangle_h = N_0[-(\alpha_0 e^2/R_1) + 6\langle v(Na,Cl)\rangle + 6\langle v(Cl,Cl)\rangle]. \quad ..2.4.18$$

In the harmonic averaging approximation

$$F_h = \beta^{-1} \sum_{k\lambda} \ln[2\sinh(\xi(k\lambda))]. \quad \ldots 2.4.19$$

Using equations (2.4.18) and (2.4.19), neglecting the Na-Na interaction, it is found that

$$F_{SCP} = \beta^{-1} \sum_{k\lambda} [\ln 2\sinh(\xi(k\lambda))] + \langle \Phi \rangle_h$$

$$- (\hbar\omega(k\lambda)\ (\coth \xi(k\lambda))/4). \quad \ldots 2.4.20$$

Replacing the mode frequency $\omega(k\lambda)$ by the average frequency and summing over all the modes $k\lambda$, from F_{SCP}, the SCAP free energy F can be obtained

$$F = 6N_0\ \beta^{-1}[\ln 2\sinh \xi\,] - (3N_0\hbar\ \omega/2)\ \coth \xi + \langle \Phi \rangle_h. \quad \ldots 2.4.21$$

The internal energy U is obtained from equation (2.3.34) in a similar way

$$U = (3N_0\ \hbar\ \omega/2)\ \coth \xi + \langle \Phi \rangle_h. \quad \ldots 2.4.22$$

The equations (2.4.7) for the average frequency ω^2, and (2.4.21) for the free energy, (2.4.13) and (2.4.14) for the mean square displacements are the basic set of equations in the self consistent average phonon formalism. The values of ω^2 and $U^2(Cl)$ and $U^2(NaCl)$ are obtained self consistently and then the free energy is evaluated. The pressure, P, is obtained by differentiating the free energy (Equation 2.4.21) respect to volume at constant temperature,

$$P = (- R /3V)(\partial F/\partial R_1), \qquad \ldots.2.4.23$$

$$(\partial F/\partial R_1) = 6N_0[S_0' + (U^2(NaCl)/6)S_2' + (U^4(NaCl)/72)S_4']$$

$$+ 6\sqrt{2}\ N_0[F_0' + (U^2(Cl)/3)F_2' + (U^4(Cl)/18)F_4']$$

$$+ N_0 \alpha_0\ e^2/R_1^2.$$

where ' means the differentiation with respect to the argument i.e.,

$$S_0' = (dS_0/dR_1),$$

$$F_0' = (dF_0/dR_2).$$

The bulk modulus B_T is obtained by the thermodynamical identity

$$B_T = -V(\partial P/\partial V)$$

$$= (R_1{}^2/9V)[(\partial^2F/\partial R_1{}^2) - (2/R_1)(\partial F/\partial R_1)], \quad ...2.4.24$$

where

$$(\partial^2F/\partial R_1^2) =$$

$$6N_0[S_0'' + (U^2(\mathrm{NaCl})/6)S_2'' + (U^4(\mathrm{NaCl})/72)S_4'']$$

$$+ 12N_0[F_0'' + (U^2(\mathrm{Cl})/3)F_2'' + (U^4(\mathrm{Cl})/18)F_4'']$$

$$+ N_0(\partial U^2(\mathrm{NaCl})/\partial R_1)[S_2' + (U^2(\mathrm{NaCl})/6)S_4'$$

$$+ (U^4(\mathrm{NaCl})/72)S_6'] + N_0(2\sqrt{2})(\partial U^2(\mathrm{Cl})/\partial R_1)$$

$$[F_2' + (U^2(\mathrm{Cl})/3)F_4' + (U^4(\mathrm{Cl})/18)F_6']$$

$$- 2\alpha_0N_0 e^2/R_1{}^3,$$

where

$$(\partial U^2(\mathrm{NaCl})/\partial R_1) = - A_{NC}(\partial \omega^2/\partial R_1), \quad ...2.4.25$$

$$A_{NC} = (3\hbar/4\mu\omega^2)[(\coth\xi/\omega) + (\hbar\beta/2)(\coth^2\xi - 1)], \quad ...2.4.26.$$

$$(\partial U^2(\mathrm{Cl})/\partial R_1) = - A_{Cl}(\partial \omega^2/\partial R_1), \quad ...2.4.27$$

$$A_{Cl} = (3\hbar/4m_2\omega^2)[(\coth\xi/\omega)+(\beta\hbar/2)(\coth^2\xi - 1)], \quad \ldots 2.4.28$$

$$(\partial\omega^2/\partial R_1) =$$

$$(A_0^{-1})[(1/\mu)[S_2' + (U^2(\mathrm{NaCl})/6)S_4' + (U^4(\mathrm{NaCl})/72)S_6']$$

$$+ 2\sqrt{2}\,(1/m_2)[F_2' + (U^2(\mathrm{Cl})/3)F_4' + (U^4(\mathrm{Cl})/18)F_6']],$$

$$A_0 = 1 + (A_{NC}/6\mu)[S_4 + (U^2(\mathrm{NaCl})/6)S_6]$$

$$+ (A_{Cl}/3m_2)[F_4 + (U^2(\mathrm{Cl}))/F_6].$$

The internal energy U of the crystal is

$$U = F + \beta\partial F/\partial\beta,$$

$$= \mu\omega^2\,U^2(\mathrm{NaCl}) + \langle \Phi \rangle. \quad \ldots 2.4.30$$

The specific heat C_V is obtained by differentiating the internal energy U with respect to temperature

$$C_V = -K_B\,\beta^2(\partial U/\partial\beta)$$

$$= -K_B\,\mu\,\beta^2[2\omega^2(\partial U^2(\mathrm{NaCl})/\partial\beta)$$

$$+ U^2(\mathrm{NaCl})(\partial\omega^2/\partial\beta)], \quad \ldots 2.4.31$$

where

$$(\partial U^2(\mathrm{NaCl})/\partial\beta) = (3\hbar^2/4\mu)(1 - \coth\xi_1)$$

$$- (3\hbar/4\mu\omega^2)(\partial\omega^2/\partial\beta)[(\coth\xi_1/\omega) + (\hbar\beta/2)(\coth^2\xi_1 - 1)], \quad \ldots 2.4.32$$

$$A_0(\partial\omega^2/\partial\beta) =$$

$$[(3\hbar^2/4\mu^2)(1 - \coth^2\xi_1)][S_4/6 + (U^2(\mathrm{NaCl})/36)S_6)]$$

$$+ [(3\hbar^2/2m_2^2)(1 - \coth^2\xi_1)(F_4/3 + (U^2(\mathrm{Cl})/9)F_6)]. \quad \ldots 2.4.33$$

The coefficient of linear expansion α is obtained from the relation

$$\alpha = -(\partial^2F/\partial V\partial T)/3B_T$$

$$=[(R_1/3V)(K_B\beta^2/3B_T)(\partial^2F/\partial R_1\partial\beta), \quad \ldots 2.4.34$$

where

$$(\partial^2F/\partial R_1\partial\beta) = (3\hbar^2/4)(1 - \coth^2\xi_1)[\partial\omega^2/\partial R_1].$$

The specific heat at constant pressure is obtained from the thermodynamical identity

$$C_P = C_V + 9TVB_T \alpha^2. \quad ...2.4.35$$

2.5-- TWO FREQUIENCIES SELF CONSISTENT AVERAGE PHONON FORMALISM

Sodium chloride has two interpenetrating Bravais lattices. For a crystal with two ions per unit cell there are six characteristic modes for each k, the wave vector. Three of the modes are the acoustic modes and the other three are the optical modes. The average frequency ω^2, defined over all the $6N_0$ modes, where N_0 is the number of units cells in the crystal, does not depend upon the long range coulomb interaction. In such an averaging process only the short range interaction contributes to the average frequency. For sodium chloride there are two possibilities One can define the average square frequency ω_a^2 of the acoustic phonons as follows:

$$\omega_a^2 = (1/3N_0) \sum_{k\lambda=1}^{3} \omega^2(k\lambda) \quad \ldots 2.5.1$$

and the average square frequency ω_p^2 of the optical phonons as follows:

$$\omega_p^2 = (1/3N_0) \sum_{k\lambda=4}^{6} \omega^2(k\lambda). \quad \ldots 2.5.2$$

In the self consistent phonon formalism, the characteristic phonon frequency $\omega^2(k\lambda)$ is obtained by the diagonalization condition (2.3.25).

$$[\sum_{ij\nu\pi} w_i^*(\nu k\lambda)\, M_{ij}(\nu\pi k)\, w_j(\pi k\lambda) - \omega^2(k\lambda)] = 0, \quad \ldots 2.5.3$$

where the dynamical matrix M is given by (2.3.26)

$$M_{ij}(\nu\pi k) = (m_\nu\, m_\pi)^{-1/2} \sum_P [\ \theta_{ij}(0\nu,P\pi)\exp(ik\cdot R(0\nu,P\pi))]. \quad \ldots 2.5.4$$

The polarization coefficients satisfies the orthonormality and the completeness relations:

$$\sum_{\nu i} w_i^*(\nu k\lambda)\, w_i(\nu k\lambda') = \delta_{\lambda\lambda'}, \quad \ldots 2.5.5$$

$$\sum_{\lambda} w_i^*(\nu k\lambda)\, w_j(\pi k\lambda) = \delta_{ij}\, \delta_{\nu\pi}. \quad \ldots 2.5.6$$

The new polarization coefficients are defined as

$$e_i(\nu k\lambda) = w_i(\nu k\lambda)\exp(ik\cdot R(\nu)). \quad \ldots 2.5.7$$

Now the diagonalization condition can be written as

$$\omega^2 - [\sum_{ij\nu\pi} e_i^*(\nu k\lambda)\, G_{ij}(\nu\pi k)\, e_j(\pi k\lambda)] = 0. \quad \ldots 2.5.8$$

The dynamical matrix G is a 6X6 matrix and therefore there are six characteristic modes for each wave vector k. The dynamical matrix can be written as

$$G = \begin{bmatrix} f_1 & g_1 \\ g_2 & f_2 \end{bmatrix}$$

where f_1, f_2, $g_1=g_2^*$ are 3X3 matrices.

$$f_1 = \begin{bmatrix} G_{xx}(11k) & G_{xy}(11k) & G_{xz}(11k) \\ G_{yx}(11k) & G_{yy}(11k) & G_{yz}(11k) \\ G_{zx}(11k) & G_{zy}(11k) & G_{zz}(11k) \end{bmatrix} \quad ...2.5.10$$

and

$$g_1 = \begin{bmatrix} G_{xx}(12k) & G_{xy}(12k) & G_{xz}(12k) \\ G_{yx}(12k) & G_{yy}(12k) & G_{yz}(12k) \\ G_{zx}(12k) & G_{zy}(12k) & G_{zz}(12k) \end{bmatrix} ...2.5.11$$

The dynamical matrix G is a hermitian matrix

$$G_{ij}(\nu\bar{\nu}k) = G_{ji}^{*}(\bar{\nu}\nu k) = G_{ji}(\bar{\nu}\nu -k). \quad \ldots 2.5.12$$

The eigen value equation may be written as

$$\begin{bmatrix} f_1 & g_1 \\ & \\ & \\ g_2 & f_2 \end{bmatrix} \begin{bmatrix} W_1 \\ \\ \\ W_2 \end{bmatrix} = \omega^2 \begin{bmatrix} W_1 \\ \\ \\ W_2 \end{bmatrix} \quad \ldots 2.5.13$$

where W_1 and W_2 are 3X1 polarization matrices. The diagonalization condition requires that

$$\begin{vmatrix} f_1 - \omega^2(k\lambda) & g_1 \\ g_2 & f_2 - \omega^2(k\lambda) \end{vmatrix} = 0. \quad \ldots 2.5.14$$

The equation (2.5.14) is a quadratic equation in $\omega^2(k\lambda)$ giving two roots corresponding to the acoustic and the optical modes. Summing over k and λ=(1, 2, 3 or 4, 5, 6) and replacing the frequency $\omega^2(k\lambda)$ by the average frequency ω^2, equation (2.5.14) reduces to

$$3N_0\,\omega^4 - \omega^2\sum_{K}\mathrm{Tr}(f_1 + f_2) + \sum_{K}\mathrm{Tr}(f_1 f_2 - g_1^{*} g_1)] = 0$$

...2.5.15

The roots of equation (2.5.15) are

$$\omega_a^2 = [\, b_0 - (b_0^{\,2} - 12a_0)^{1/2}]/6, \quad ...2.5.16$$

$$\omega_p^2 = [\, b_0 + (b_0^{\,2} - 12a_0)^{1/2}]/6, \quad ...2.5.17$$

where

$$b_0 = N_0^{-1}[\sum_{K}\mathrm{Tr}(f_1 + f_2)], \qquad ...2.5.18$$

$$a_0 = N_0^{-1}[\sum_{K}\mathrm{Tr}(f_1 f_2 - g_1^{*} g_1)]. \qquad ...2.5.19$$

Summing over all k-modes one finds that

$$b_0 = -\sum_{i\,p\pi}{}^{\prime}[\;\theta_{ii}(01,p\pi) + \theta_{ii}(02,p\pi)]. \qquad ...2.5.20$$

Keeping only the Na-Cl and Cl-Cl interactions equation (2.5.20) reduces to

$$b_0 = 6[S_2 + (U^2(\mathrm{NaCl})/6)S_4 + (U^4(\mathrm{NaCl})/72)S_6 + --]/\mu$$

$$+ 12[F_2 + (U^2(\mathrm{Cl})/3)F_4 + (U^4(\mathrm{Cl})/18)F_6 + --]/m_2 \qquad \ldots 2.5.21$$

Also

$$\sum_{K} N_0^{-1}[\mathrm{Tr}(f_1 f_2)] =$$

$$\sum_{ijP}[\ \theta_{ij}(01,P1) \cdot \theta_{ij}(02,P2)]/m_1 m_2 \qquad \ldots 2.5.23$$

and

$$\sum_{K} N_0^{-1}[\mathrm{Tr}(g_1^{*} g_1)] =$$

$$\sum_{ijP}[\ \theta_{ij}(01,P2)]^2/m_1 m_2. \qquad \ldots .2.5.24$$

The value of a_0 depends upon the non diagonal elements $\theta_{ij}(01,P1)$, $\theta_{ij}(02,P2)$ and $\theta_{ij}(01,P2)$ and therefore has contributions from the long range coulomb interaction also. Further it is also dependent on the product of the short range force constants and the long range force constants. In general long range force constant (due to coulomb interaction) varies as R^{-3} and the product of the force constants will vary as R^{-6}. Thus the contribution to a_0 varies as R^{-6} and the lattice sums may be terminated after a few neighbors. For this reason the lattice sums have been evaluated for a crystal whose extension was -3R to 3R. Evaluating the sums it is found that

$$a_0 = 12[S_a(S_a + 2F_a) + (6e^2/R_2^3)(\theta^s_{zz}(R_2)$$

$$- \theta^s_{xx}(R_2) - 3\theta^s_{xy}(R_2)) + (\theta^s_{xx}(R_1) - e^2/R_1^3)^2$$

$$+ 0.5(\theta^s_{zz}(R_1) - 2e^2/R_1^3)^2 - 1.566e^4/R_1^6],$$

....2.5.25

where

$$S_a = S_2 + (U^2(\mathrm{NaCl})/6)S_4 + (U^4(\mathrm{NaCl})/72)S_6,$$

$$F_a = F_2 + (U^2(\mathrm{Cl})/3)F_4 + (U^4(\mathrm{Cl})/18)F_6,$$

$$\theta^s_{xx}(R_1) = \Phi_{xx}(R_1) + (U^2(\mathrm{NaCl})/6)\sum_K \Phi_{xxkk}(R_1)$$

$$+ (U^4(\mathrm{NaCl})/72)\sum_{Kl} \Phi_{xxkkll}(R_1)], \quad \text{...2.5.26}$$

$$\Phi_{xx}(R_1) = \sum_{\alpha=1}^{4} [A_\alpha \mathrm{EXP}(-B_\alpha R_1)][(B_\alpha/R_1)], \quad \text{...2.5.27}$$

$$\sum_K \Phi_{xxkk}(R_1) = \sum_{\alpha=1}^{4}[A_\alpha \exp(- B_\alpha/R_1)][(B_\alpha^3/R_1)$$

$$- 2(B_\alpha^2/R_1^2) - 2(B_\alpha/R_1^3)], \quad \text{...2.5.28}$$

$$\Phi_{zz}(R_1) = \sum_{\alpha=1}^{4} [A_\alpha \exp(-B_\alpha R_1)] B_\alpha^2 \, , \qquad \ldots 2.5.29$$

$$\sum_k \Phi_{zzkk}(R_1) = \sum_{\alpha=1}^{4} [- B_\alpha^{4} + 2(B_\alpha^{3}/R_1) + 4(B_\alpha^{2}/R_1^{2})$$

$$+ 4(B_\alpha/R_1^{3})] A_\alpha \exp(-B_\alpha R_1), \qquad \ldots . 2.5.30$$

$$\theta^{s}_{zz}(R_2) = [\Phi_{zz}(R_2) + (U^2(Cl)/3) \sum_K \Phi_{zzkk}(R_2)$$

$$+ (U^4(Cl)/18) \sum_{Kl} \Phi_{zzkkll}(R_2)], \qquad \ldots 2.5.31$$

$$\theta^{s}_{xx}(R_2) = [\Phi_{xx}(R_2) + (U^2(Cl)/3) \sum_K \Phi_{xxkk}(R_2)$$

$$+ (U^4(Cl)/18) \sum_{Kl} \Phi_{xxkkll}(R_2)]. \qquad \ldots 2.5.32$$

The mean square displacement $U^2(0\gamma, P\pi)$ can be written as

$$U^2(0\gamma,P\pi) = \sum_{i} \langle (u_i(0\gamma) - u_i(P\pi))^2 \rangle . \qquad \ldots 2.5.33$$

The polarization coefficients $e_i(\nu k\lambda)$ satisfies the normalization condition,

$$\sum_{i\nu} e_i^{*}(\nu k\lambda) \, e_i(\nu k\lambda') = \delta_{\lambda\lambda'} . \qquad \ldots 2.5.34$$

For the acoustic modes the ions may vibrate in phase and the center of mass $m_c = m_1 + m_2$ plays an important role. Apart from the phase factor one may choose

$$e_i(\nu k\lambda) = (m_\nu / m_c)^{1/2} \qquad \ldots 2.5.35$$

such that the normalization condition is satisfied. For the optical phonons the ions may vibrate in opposit phase and the reduced mass μ, $\mu^{-1} = m_1^{-1} + m_2^{-1}$ plays an important role. Apart from the phase factor the polarization coefficient may be chosen as

$$e_i(\nu k\lambda) = (\mu/m_\nu)^{1/2}, \qquad \ldots 2.5.36$$

so as to satisfy the normalization condition and also the completeness relations.

In the continuum approximation, it is assumed that the phonon modes are purely longitudinal or purely transverse. For each wave vector k, the polarization coefficients are written as

$$e_1(\nu k\lambda) = [(m_\nu/m_c)^{1/2} \text{ OR } (\mu/m_\nu)^{1/2}]\ e_z,$$

$$e_{t_1}(\nu k\lambda) = [(m_\nu / m_c)^{1/2} \text{ OR } (\mu/m_\nu)^{1/2}]\; e_x,$$

$$e_{t_2}(\nu k\lambda) = [(m_\nu / m_c)^{1/2} \text{ OR } (\mu/m_\nu)^{1/2})]\; e_y.$$

Using these polarization coefficients and replacing the mode frequency $\omega^2(k\lambda)$ by ω_a^2 or ω_p^2, equation (2.3.29) gives

$$\langle u_i(0\nu)\; u_j(P\pi)\rangle = (\hbar \coth \xi_a/2m_c \omega_a)\; \delta_{ij}\delta_{\nu\pi}, \quad \ldots 2.5.37$$

$$\langle u_i(0\nu)\; u_j(P\pi)\rangle = (\mu \hbar \coth \xi_p/2m_\nu^2\; \omega_p)\; \delta_{ij}\delta_{\nu\pi}, \ldots 2.5.38$$

where

$$\xi_a = 0.5\hbar\, \beta \cdot \omega_a,$$

$$\xi_p = 0.5\, \hbar\; \beta\, \omega_p.$$

Using Eqs. (2.5.37) and (2.5.38), the mean square displacements U^2(NaCl) and U^2(Cl) are found to be

$$U^2(\mathrm{NaCl}) = \sum_i \langle\, u_i(0,\mathrm{Na};P,\mathrm{Cl})^2\rangle$$

or

$$U^2(\mathrm{NaCl}) = (3\hbar\, /m_c\, \omega_a^2)\, \coth \xi_a$$

$$+ (3\hbar/2\ \omega_p)(\mu/m_1^2 + \mu/m_2^2)\coth \xi_p, \quad ...2.5.39$$

$$U^2(Cl) = (1/2) \sum_i \langle (u_i(0,Cl;\ P,Cl))^2 \rangle$$

$$= (3\hbar/2m_c\omega_a)\coth \xi_a + (3\mu\hbar/2m_2^2\omega_p)\coth \xi_p. \quad ..2.5.40$$

Replacing the mode frequency $\omega^2(k\lambda)$ by ω_a^2 or ω_p^2 as the case may be into equation (2.3.33) for F_{SCP}, it is found that the free energy in the two frequecies self consistent average phonon formalism can be written as

$$F = (3N_0/\beta)[\ \ln(2\sinh(\xi_a) + \ln(2\sinh(\xi_p))]$$

$$- (3\hbar N_0/4)[\ (\omega_a \coth \xi_a) + (\omega_p \coth \xi_p)]$$

$$+ \langle \Phi \rangle_h, \quad ....2.5.41$$

where $\langle \Phi \rangle_h$ is given by equation (2.4.18). The internal energy U is obtained from equation (2.3.34),

$$U = (3N_0\hbar/4)[\ \omega_a \coth \xi_a + \omega_p \coth \xi_p] + \langle \Phi \rangle_h. \quad ...2.5.42$$

Having obtained the free energy and the internal energy all other thermodynamical quantities such as the pressure, bulk modulus, specific heat etc., can be obtained by the usual thermodynamical relations.

$$P = -(\partial F/\partial V), \qquad ...2.5.43$$

$$B_T = -V(\partial P/\partial V). \qquad ...2.5.44$$

2.6--ONE FREQUENCY AVERAGE QUASIHARMONIC APPROXIMATION

In the one frequency AQH, the average square freeequency does not depend on the mean square displacement. The frequency ω^2 and the mean square displacement are given by

$$\omega^2 = (1/m_1 + 1/m_2)S_2 + (2/m_2)F_2,$$

$$U^2(\mathrm{NaCl}) = 3\hbar \coth \xi /2\mu\omega,$$

$$U^2(\mathrm{Cl}) = 3\hbar \coth \xi /2 m_2 \omega .$$

The expressions for the free energy, F, and pressure, P, are

$$F = (6 N_0/\beta)[\ln(2\sinh \xi)] - (3N_0 \hbar \omega/2) \coth \xi + \Phi ,$$

$$\Phi = N_0[-\alpha_0 e^2/R_1 + 6S_0 + 6F_0],$$

$$P = (-R_1/3V)(\partial F/\partial R_1)$$

$$\partial F/\partial R_1 = 6N_0[S_0' + (U^2(\mathrm{NaCl})/6)S_2']$$

$$+ \sqrt{2}\cdot 6N_0[F_0' + (U^2(\mathrm{Cl})/3)F_2'] + N_0 \alpha_0 e^2/R_1{}^2.$$

2.7--TWO FREQUENCIES AVERAGE QUASIHARMONIC APPROXIMATION

The average acoustic frequency ω_a^2 and the average optic frequency ω_p^2 are still given by equations (2.5.16) and (2.5.17), but b_0 and a_0 are now indepedent of $U^2(NaCl)$ and $U^2(Cl)$. The mean square displacements are given by equations (2.5.39) and (2.5.40).

The free energy, F, and pressure, P, are given by

$$F = (3N_0/\beta)[\ln(2\sinh\xi_a) + \ln(2\sinh\xi_p)] + \Phi ,$$

$$P = (-\partial F/\partial V).$$

2.8--RESULTS

EQUATION OF STATE

In the one frequency SCAP approximation equations (2.4.7), (2.4.13) and (2.4.14) were used to calculate the frequency ω^2 and the displacements $U^2(NaCl)$ and $U^2(Cl)$ self consistently. The thermodynamical quantities such as the pressure, P, bulk modulus, specific heat, coefficient of expansion were calculated using equations (2.4.23), (2.4.24), (2.4.31) and (2.4.34) respectively.

In the two frequencies approximation equations (2.5.16), (2.5.17), (2.5.39) and (2.5.40) were used to calculate the average square acoustic and optical frequencies and ionic displacements self consistently. Equations (2.5.43) and (2.5.44) were used to calculate the pressure and bulk modulus.

The total pressure, P, is the sum of the static pressure $P_{st} = \partial \Phi / \partial V$ and the vibrational pressure or the thermal pressure P_{th}. When the thermal pressure just balances the static pressure the crystal is in equilibrium and one finds the equilibrium lattice constant by the condition that the total pressure is zero.

The isothermal curves of P versus the nearest neighbor distance R_1 are plotted in figure--2.1. The figure --2.1 also includes the isothermal cuves in the average quasiharmonic approximation.

The critical temperature, T_c, is the temperature at which the isothermal curve just touches the curve P=0 i.e. above this temperature the isothermal curves do not intersect the curve P=0 and therefore the zero pressure lattice constant can not be determined and the crystal is unstable. From figure 2.1 it is clear that in the average quasiharmonic approximation the critical temperature T_c is about 1400K (above the melting point) and in the self consistent approximation the critical temperature is much above the melting temperature T_m = 1073K. At the critical temperature the bulk modulus B_T tends to zero.

Recently Boyer[64-66] using, the Gordon and Kim potential reported the quasiharmonic equation of state for sodium chloride and the other alkali halide crystals. Boyer found that the critical temperature T_c for NaCl was 1100K, which was very close to the melting temperature 1073K. This closeness between the melting temperature and the critical temperature lead him to suggest that the lattice instability B_T ===> 0 is a possible important cause of the melting of the alkali halide solids and solids in general.

The quasiharmonic approximation overestimates the vibrational pressure or the phonon pressure because the phonon frequencies are independent of the temperature explicitly but depend only on the volume. The overestimation of the phonon pressure by the quasiharmonic approximation has previously been commented upon and discused by E.R.Cowley[48,49] and H.H.Demarest[74]. Because of the overestimation of the vibrational pressure the lattice instability B_T ===> 0 occurs at a lower temprature and gives lower critical temperature.

In the self consistent average phonon approximation considered here the phonon frequencies are functions of both the temperature and the volume. As the temperature rises the vibrational amplitude of the ions increases and the vibrating ions are able to sample a region of high repulsion. This sampling of the high repulsive region increases the effective force constants which in turn increases the characteristic frequencies and reduces the amplitude of the vibration of the ions. This feedback mechanism between the ion's amplitude and the phonon frequencies of the system lowers the thermal pressure. Also this feedback mechanism between the normal mode frequencies and the mean square displacement prevents the amplitude of oscillation to be unphysically large in the self consistent formalism but in the quasiharmonic approximation ion displacement can be unphysically large giving rise to high vibrational pressure.

Thus for the same interaction potential the critical temperature would be higher in the self consistent average phonon formalism (also in any self consistent phonon formalism) compared to the quasiharmonic approximation. The analysis in the self consistent average phonon formalism shows that the critical temperature is higher than the normal melting temperature. Thus the lattice instability B_T===>0 occurs in a physically unobservable region. Therefore in the author's opinion it is reasonable to say that the lattice instability B_T===>0 does not play a significant or important role in the melting of the solids. Further experimentally the bulk modulus or the compressibility is observed to be finite at the melting temperatures, not unphysically large as predicted by the quasiharmonic approximation.

What causes the solid to melt is still an open question? Whether the lattice instabilities such as B_T===>0 or other lattice instabilities or the imperfections in the crystals such as the vacancies, dislocations, fractures and the surfaces or both cause the solid to melt. In fact theories have been formulated in terms of the lattice imperfections[75-77]. One may say that near the melting temperature the properties of the solid are largely governed by the lattice imperfections.

The experimental data and the SCAP calculated results of the coefficient of expansion are given in table--2.4. From this table--2.4 one can see that the SCAP results are much lower than the experimental results. The discrepancies increase with the rise in the temperature. The quasiharmonic values are also lower than the experimental values but sligtly greater than the SCAP values. Although quasiharmonic results are questionable in the high temperature and low density regions the agreement with the experiments is very good.

LATTICE PARAMETER

The lattice parameter a(T) as a function of the temperature has been calculated by calculating the total presure, P, for a set of near distances. The zero pressure thermodynamical properties were also obtained numerically when the total pressure was less than 10^6 dyne/cm^2.

The table--2.1 and figure --2.3 show the variation of the lattice constant a(T) as a function of the temperature. In table--2.1 the experimental data[79] along with the calculated results in the one and the two frequencies formalisms and the quasiharmonic (non self consistent) formalism(Boyer's) are given. From table--2.1 it is concluded that:

(a) Lattice constant a(T) in the one and the two frequencies SCAP formalisms is practically the same almost over the entire temperature region.

(b) The agreement between the calculated and the experimental data is very good in the low to the medium range of the temperatures but in the high temperature region the results are low compared to the experiments. The discrepancy between the calculated and the experimental data increases with the rise in the temperature. The zero pressure, zero temperature value of the lattice constant of NaCl in the one and the two frequencies approximations are 5.6247Å and 5.6257Å respectively compared to the experimental value 5.5967Å. At room temperature (300K) the calculated values are 5.6589Å and 5.6632Å compared to the experimental value 5.6402Å.

(c) Boyer's quasiharmonic results are in very good agreement with the experiments. At high temperatures the quasiharmonic values are greater than the SCAP results for the same interaction potential. This result is not surprising since the quasiharmonic frequencies are functions of the volume only while the SCAP frequencies are function of both the volume and the temperature because of a self consistancy condition between the mean square displacement and the mean square frequency. This feedback mechanism lowers the thermal pressure giving rise to lower lattice constant and higher bulk modulus and therefore higher critical temperature, the temperature where the isothermal bulk modulus tends to zero.

The discrepancies between the SCAP results and the experimental results may be due to the failure of the SCAP approximation to account for the anharmonicity of the perfect crystal properly or may be due to the imperfections in the crystal which become increasingly important with the rise in the temperature or may be due to the incomplete information about the interaction potential or the several approximations involved in estimating the interaction energy such as pair wise interaction approximation and the free ion charge density approximation in the Gordon and Kim potential etc.

COMPRESSIBILITY

The calculated values of the isothermal compressibility using the one frequency and the two frequencies SCAP formalisms are shown in table--2.2 and figure--2.4 along with the experimental data of Hunter and Siegel[80] and of Stepanov and Eidus[81].

At low temperature the agreement between the experiments and the SCAP calculated results is very good. But at high temperatures the calculated results are in poor agreement with the measured values. Near the melting temperature the calculated results are about 30% off compared to the experimental data of Hunter and Siegel and about 40% off compared to the experimental results of Stepanov and Eidus.

These lower values of the compressibility are perhaps due to the lower estimation of the lattice constant. If the lattice constant were predicted correctly the agreement would have been better.

SPECIFIC HEAT

In the one frequency SCAP approximation the constant pressure specific heat for NaCl are shown in table--2.3 along with the experimental data of Leadbetter and Settatree[82]. The agreement between the experimental and the calculated values of specific heat is very good. The calculated values are low compared to the measured values. The discrepancy is probably due to the underestimation of the coefficient of expansion and the neglect of the polarizability in the rigid ion model. Neglect of the polarizability leads to overestimation of the phonon frequency which in turn underestimates the specific heat.

2.9--CONCLUSION

The self consistent average phonon formalism has been developed and has been applied successfully to study the equation of state and other thermodynamical properties of the primitive solids with reference to the rare gas solid crystals, Ne, Ar, Kr and Xe. The SCAP formalism has also been extended to the nonprimitive solids and has been used to obtain an equation of state for solids such as the ionic solids, particularly sodium chloride.

A first principle, self consistent average phonon equation of state for NaCl has been obtained using the Gordon and Kim potential. The Gordon and Kim potential is a parameter free potential since such a potential was derived without making use of any physically measurable quantities such as the lattice constant, compressibility, cohesive energy etc. Further a quasiharmonic equation of state (a non self consistent) is also available for comparison.

Using the Gordon and Kim potential, in the quasiharmonic approximation, Boyer obtained an equation of state for NaCl and emphasized the importance of the lattice instability B_T===>0 to the melting of the solid. Boyer found that the critical temperature T_c, at which B_T===>0 sets in, is very close to the melting point of NaCl. Because of this closeness between the critical temperature and the melting temperature, he suggested such an instability B_T===>0 with a possible cause of the melting of a solid.

In the self consistent average phonon formalism the average phonon frequency ω^2, which is the characteristic frequency of the crystal system, has to be determined self consistently, because of a self consistent condition between the mean square displacement and the mean square frequency ω^2. Due to this self consistancy condition it is found that:

(a) The self consistent frequency is a function of both the volume and the temperature. On the other hand the quasiharmonic frequencies are depedent only on the volume.

(b) At a given temperature and volume the self consistent frequencies are higher than the corresponding quasiharmonic frequencies. This effect inceases with the rise in temperature and, thus, the anharmonic effects are significant near the melting temperature of the solid.

(c) The amplitude of oscillations can be arbitrarily large in the quasiharmonic approximation, which may even be unphysical. Also, at high temperatures and expanded volumes the vibrational amplitude is large enough so that the contribution of the anharmonic effects is important. When the ionic displacement is large enough, the ion is able to sample a region of high repulsion which in turn increases the effective force constant and hence the effective frequencies of vibration. An increase in the mode frequency tends to decrease the ionic displacement and thus the vibrational amplitude cannot be unphysically large. This feedback is more important at high temperatures and the ionic displacement is greatly reduced. A reduction in the ionic displacement reduces the thermal pressure and the coulomb interaction is able to stabilize the crystal at a lower value of the interatomic distance. Thus in general the self consistent lattice constant will be smaller compared to the quasiharmonic lattice constant. In other words the quasiharmonic approximation overestimates the thermal or the phonon pressure. Because of the overestimation of the vibrational pressure the lattice instability B_T===>0 occurs at a lower temperature which may even be less than the actual melting temperature. Such an effect has also been observed in the study of equation of state of Ar.

The isothermal curves of P versus nearest neighbor distance for Ar are plotted in figure--2.2. From this figure one can see that in the SCAP approximation the critical temperature for Ar is about 135K which is much above the melting temperature 83K. Due to overestimation of the vibrational pressure in the average quasiharmonic approximation the critical temperature is lowered to about 70K. Thus in the average quasiharmonic approximation the critical temperature at which the lattice instability B_T===> 0 sets in, is a physically unobservable region. Hence such an instability is unlikely to be related to the melting of a solid. The self consistent study of the equation of state for Ar and NaCl points out that the lattice instability B_T ===> 0 does not play a significant role in the melting of a solid.

The study of equation of state for NaCl in the SCAP formalism reveals that the lattice instability B_T===>0 sets in at a temperature which is much higher than the normal melting point. In other words the solid destabilizes before the lattice instability actually sets in. Further, the compressibility of the solid is finite at the experimental melting temperature not infinitely large as suggested by the lattice instability under consideration. As a result it may be concluded that the lattice instabilization of the crystal is in fact an effect of the use of the quasiharmonic approximation in the calculation of equation of state. Since the critical temperature is in the physically unobservable region in the self consistent approximation, it may be reasonable to conclude that the lattice instability is not very important as far as the melting of the solid is concerned.

In the SCAP formalism the lattice constant, compressibility, the coefficient expansion etc. have been calculated. It is found that the agreement is very good at low and the medium range of temperatures. At high temperatures the agreement is not as good as was expected.

The present calculation is a parameter free calculation and the success of the SCAP approximation is very good. It is found that the agreement could be improved by taking a model potential and adjust the parameters. It will be worth while effort to develop a full self consistent phonon theory and apply it to the ionic solids. In full self consistent phonon theory the long range coulomb interaction may give rise to some difficulties in finding the lattice sums and may require a large number of iterations to obtain the self consistent values.

The poor agreement between the experiments and the SCAP calculated results may be due to: (a) Failure of the SCAP formalism not to account for the anharmonicity of the perfect crystal properly. (b) Not taking into the imperfections in the real crystals. Such imperfections are very important near the melting. A theory can be formulated in terms of imperfections. (c) Insufficient knowledge about the interaction between the ions. (d) Approximations, such as pair wise additive interaction, free ion charge density approximation used in deriving the Gordon and Kim potential etc.

TABLE--1.1

Values of the constants ϵ (10^{-16} ergs) and R_0 (10^{-10}m) in the Lennard-Jones potential. Values of the Lindemann parameter, $L = \langle u^2 \rangle^{1/2}/R_1$ and the constant a used in Simon's equation are also given.

	Ne	Ar	Kr	Xe
ϵ	67.735	212.007	290.632	409.149
R_0	3.0536	3.7410	3.9940	4.3553
L	0.091	0.081	0.081	0.081
a(kbar)	1.2	2.11	2.5	3.0

TABLE--1.2

The parameters R_0 and ϵ used in calculating the various thermodynamical properties of Ar. R_0 (10^{-10}m) and ϵ (10^{-16} ergs).

Formalism	R_0	ϵ	Interaction
SCAP	3.7410	212.007	Two neighbors[25,26]
SCP	$(3.407)\cdot 2^{1/6}$	165	All neighbors[17]
SCP	3.707	236.2	Near neighbors[22]
ISCP	3.709	236	Near neighbor[21]

TABLE--1.3

Lattice parameter(10^{-10}m) and the relative expansion(10^{-5}/K) for Ar.

Temp. K	Lattice parameter Calculated	Lattice parameter Experimental	Relative expansion Calculated	Relative expansion Experimental
1.0	5.3124	5.3113	0.0000	0.0000
10.0	5.3126	5.3118	0.4461	1.06
20.0	5.3188	5.3180	11.23	12.79
25.0	5.3243	5.3236	22.33	23.31
30.0	5.3317	5.3306	36.33	36.45
35.0	5.3403	5.3387	52.55	51.73
40.0	5.3499	5.3478	70.52	68.84
45.0	5.3603	5.3577	90.08	87.52
50.0	5.3714	5.3686	111.0	107.9
55.0	5.3832	5.3802	133.3	129.9
60.0	5.3957	5.3930	156.8	153.5
65.0	5.4089	5.4063	181.6	179.0
70.0	5.4229	5.4210	210.0	206.9
75.0	5.4376	5.4371	235.7	236.7
80.0	5.4533	5.4547	265.3	270.1

TABLE--1.4

The lattice parameter (10^{-10}m) and the relative expansion (10^{-5}/K) for Kr.

Temp. K	Lattice parameter Calc.	Lattice parameter Expt.	Relative expansion Calc.	Relative expansion Expt.
1.0	5.6461	5.6459	0.00000	0.0000
10.0	5.6467	5.6469	1.033	1.74
20.0	5.6535	5.6531	13.20	12.8
30.0	5.6657	5.6639	34.67	32.0
40.0	5.6805	5.6773	60.85	55.7
50.0	5.6968	5.6923	89.78	82.3
60.0	5.7144	5.7105	120.9	114.4
70.0	5.7332	5.7268	154.2	143.3
80.0	5.7531	5.7465	189.6	178.2
90.0	5.7745	5.7680	227.3	216.3
100.0	5.7954	5.7914	267.9	257.8
110.0	5.8219	5.8181	311.5	305.1

TABLE--1.5

The lattice parameter (10^{-10}m) and the molar volume in cm^3 for Xe.

Temp. K	Lattice parameter Calc.	Lattice parameter Expt.	Molar volume Calc.	Molar volume Expt.
0.000	6.132	6.132	34.72	34.72
8.0	6.132	6.133	34.72	34.73
20.0	6.139	6.137	34.83	34.80
32.0	6.151	6.142	35.04	34.89
40.0	6.160	6.154	35.20	35.10
48.0	6.170	6.164	35.36	35.26
60.0	6.185	6.181	35.63	35.55
72.0	6.201	6.196	35.91	35.86
80.0	6.213	6.210	36.10	36.07
88.0	6.224	6.223	36.31	36.29
100.0	6.242	6.242	36.60	36.63
108.0	6.255	6.256	36.84	36.87
120.0	6.274	6.277	37.19	37.25
128.0	6.288	6.292	37.43	37.51
140.0	6.309	6.314	37.82	37.91
148.0	6.324	6.328	38.09	38.15
160.0	6.348	6.340	38.52	38.40

TABLE--1.6

The calculated and the experimental values of the lattice parameter (10^{-10}m) and the relative expansion (10^{-5}/K) for Ne.

Temp. K	Lattice parameter Calc.	Lattice parameter Expt.	Relative expansion Calc.	Relative expansion Expt.
0.5	4.4654	4.4644	0.0000	0.0000
2.0	4.4654	4.4644	0.0000	0.0000
4.0	4.4654	4.4645	0.0000	0.12
6.0	4.4654	4.4649	0.0000	1.1
8.0	4.4657	4.4662	0.6718	3.72
10.0	4.4669	4.4685	3.359	9.07
12.0	4.4693	4.4722	8.734	17.53
14.0	4.4732	4.4776	17.47	29.62
16.0	4.4787	4.4847	29.78	45.50
18.0	4.4860	4.4935	46.13	65.29
20.0	4.4949	4.5045	66.06	89.79
22.0	4.5054	4.5178	89.58	119.6
24.0	4.5177	4.5338	117.1	155.4

TABLE--1.7

The calculated and the experimental values of the compressibility (10^{12} cm^2/dyne) for Ar.

Temp. K	Compressibility Calculated	Compressibillity Experimental
0.000	3.801	3.75
10.0	3.812	3.7
15.0	3.874	3.8
20.0	3.987	3.9
25.0	4.135	4.0
30.0	4.307	4.2
35.0	4.500	4.3
40.0	4.712	4.5
45.0	4.943	4.8
50.0	5.195	5.1
55.0	5.471	5.4
60.0	5.773	5.8
65.0	6.104	6.2
70.0	6.472	6.8
75.0	6.878	7.4
80.0	7.338	8.2

TABLE--1.8

The calculated and the experimental values of the compressibility (10^{12} cm^2/dyne) for Kr.

Temp. K	Compressibility Calculated	Compressibility Experimental
0.000	3.117	2.9
10.0	3.136	2.9
20.0	3.278	2.9
30.0	3.483	3.1
40.0	3.718	3.3
50.0	3.981	3.5
60.0	4.274	3.9
70.0	4.603	4.3
80.0	4.972	4.8
90.0	5.395	5.4
100.0	5.884	6.1
110.0	6.455	7.0

TABLE--1.9

The calculated and the experimental values of the compressibility (10^{12} cm^2/dyne) for Xe.

Temp. K	Compressibility Calculated	Compressibility Experimental
0.000	2.752	2.778
8.0	2.758	2.809
20.0	2.867	2.857
32.0	3.023	2.933
40.0	3.136	3.000
48.0	3.257	3.106
60.0	3.451	3.333
72.0	3.662	3.623
80.0	3.813	3.831
88.0	3.974	4.032
100.0	4.236	4.348
108.0	4.426	4.608
120.0	4.737	5.051
128.0	4.967	5.405
140.0	5.349	6.024
148.0	5.632	6.494
160.0	6.115	7.299

TABLE--1.10

The calculated and the experimental values of the compressibilty (10^{12} cm^2/dyne) for Ne.

Temp. K	Compressibility Calculated	Compressibility Experimental
0.5	9.834	------
2.0	9.834	------
4.0	9.834	9.0 ± 0.2
6.0	9.837	9.1 ± 0.4
8.0	9.889	9.2 ± 0.4
10.0	10.03	9.4 ± 0.6
12.0	10.27	9.6 ± 0.8
14.0	10.64	10.0 ± 0.8
16.0	11.13	10.7 ± 1.0
18.0	11.73	12.4 ± 1.5
20.0	12.47	16.2 ± 1.5
22.0	13.35	----------
24.0	14.40	----------

TABLE--1.11

The calculated and the experimental values of the constant volume specific heat (J/mol/K) and the calculated values of the average frequency (10^{12} Hz) and the mean square displacement ($10^{-18} cm^2$).

Temp. K	Specific heat	Specific heat	$\langle \omega^2 \rangle^{1/2}$	$\langle u^2 \rangle$
0.000	0.0000	0.0000	8.446	5.641
10.0	1.641	3.294	8.445	5.660
20.0	10.97	12.16	8.417	6.135
30.0	16.40	17.49	8.350	7.253
40.0	18.68	20.25	8.254	8.782
50.0	19.66	21.54	8.136	10.61
60.0	19.85	22.19	7.988	12.70
70.0	19.81	22.60	7.836	15.07
80.0	19.59	23.34	7.655	17.78

TABLE--1.12

The calculated and the experimental values of the constant volume specific heat (J/mol/K) and the calculated values of the average frequency (10^{12} Hz) and the mean square displacement (10^{-18} cm^2) for Kr.

Temp. K	Specific heat Calculated	Specific heat Experimental	$\langle \omega^2 \rangle^{1/2}$ Calc.	$\langle u^2 \rangle$ Calc.
0.000	0.0000	0.0000	6.499	3.500
10.0	4.343	5.907	6.497	3.550
20.0	14.97	15.95	6.476	4.159
30.0	19.11	19.75	6.367	6.547
40.0	20.61	21.59	6.329	8.003
50.0	21.13	22.35	6.264	9.582
60.0	21.23	22.83	6.192	11.28
70.0	21.14	23.05	6.113	13.11
80.0	20.95	22.07	6.026	15.08
90.0	20.69	23.12	5.931	17.22
100.0	20.41	23.18	5.827	19.55
110.0	20.09	22.70	5.710	22.36

TABLE--1.13

The calculated and the experimental values of the constant volume specific heat and the calculated values values of the average frequency (10^{12} Hz) and the mean square displacement ($10^{-18} cm^2$) for Xe.

Temp. K --------	Specific heat Calculated	Specific heat Experimental	$\langle \omega^2 \rangle^{1/2}$ Calc.	$\langle u^2 \rangle$ Calc.
0.00	0.0000	0.0000	5.702	2.552
8.0	3.22	4.93	5.701	2.574
20.0	16.75	17.49	5.686	3.217
32.0	20.66	21.00	5.657	4.349
40.0	21.55	22.1	5.635	5.253
48.0	21.95	23.2	5.[illegible]9	6.193
60.0	22.12	23.2	5.568	7.680
72.0	22.04	23.4	5.522	9.249
80.0	21.93	23.5	5.490	10.34
88.0	21.80	23.5	5.455	11.48
100.0	21.56	23.5	5.400	13.25
108.0	21.38	23.5	5.361	14.49
120.0	21.10	23.6	5.296	16.44
128.0	20.91	23.8	5.254	17.81
140.0	20.61	24.0	5.182	19.99
148.0	20.41	24.1	5.132	21.53
160.0	20.10	30.4	5.050	24.02

TABLE--1.14

The calculated and the experimental values of the constant volume specific heat (J/mol/K) and the calculated values of the average frequency (10^{12} Hz) and the mean square displacement ($10^{-18} cm^2$) for Ne.

Temp. K	Specific heat	Specific heat	$\langle \omega^2 \rangle^{1/2}$	$\langle u^2 \rangle$
-------	Calculated	Experimental	Calc.	Calc.
0.5	0.0000	0.0000	7.394	12.89
2.0	0.0000	0.039	7.394	12.89
4.0	0.002371	0.345	7.394	12.89
6.0	0.1802	1.35	7.394	12.89
8.0	1.069	3.04	7.390	12.91
10.0	2.813	5.04	7.383	13.00
12.0	5.031	7.73	7.365	13.18
14.0	7.294	10.04	7.336	13.47
16.0	9.354	11.91	7.295	13.89
18.0	11.11	13.54	7.241	14.44
20.0	12.54	14.95	7.176	15.12
22.0	13.68	16.50	7.097	15.92
24.0	14.55	17.32	7.006	16.88

TABLE--1.15

The calculated and the experimental values of the coefficient of volume expansion (10^{-4}/K) for Ar.

Temp. K	Calculated	Experimental
0.000	0.0000	0.0000
10.0	0.8145	1.38
15.0	3.211	3.48
20.0	5.657	5.55
25.0	7.564	7.14
30.0	8.992	8.54
35.0	10.09	9.69
40.0	10.98	10.68
45.0	11.74	11.64
50.0	12.41	12.54
55.0	13.05	13.49
60.0	13.66	14.50
65.0	14.29	15.63
70.0	14.93	16.99
75.0	15.61	18.55
80.0	16.34	20.31

TABLE--1.16

The calculated and the experimental values of the coefficient of volume expansion (10^{-4}/K) for Kr.

Temp. K	Calculated	Experimental
0.000	0.0000	0.0000
10.0	1.513	1.68
20.0	5.403	4.71
30.0	7.215	6.54
40.0	8.159	7.54
50.0	8.791	8.26
60.0	9.310	9.04
70.0	9.803	9.791
80.0	10.30	10.87
90.0	10.84	12.05
100.0	11.45	13.76
110.0	12.14	16.40

TABLE--1.17

The calculated and the experimental values of the coefficient of volume expansion ($10^{-4}/K$) for Xe.

Temp. K	Calculated	Experimental
0.000	0.00000	0.000
8.0	0.7807	0.74
20.0	4.186	2.80
32.0	5.361	4.35
40.0	5.738	4.91
48.0	6.000	5.39
60.0	6.299	6.00
72.0	6.551	6.35
80.0	6.712	6.53
88.0	6.876	7.10
100.0	7.13	7.52
108.0	7.307	7.80
120.0	7.597	8.30
128.0	7.811	8.72
140.0	8.162	9.50
148.0	8.419	10.3
160.0	8.862	11.2

TABLE--1.18

The calculated and the experimental values of the coefficient of volume expansion (10^{-4}/K) for Ne.

Temp. K	Calculated	Experimental
0.5	0.0000	0.0000
2.0	0.0000	------
4.0	0.0048	0.48
6.0	0.3659	2.42
8.0	2.181	5.91
10.0	5.815	10.23
12.0	10.63	15.27
14.0	15.92	20.81
16.0	21.24	26.54
18.0	26.46	32.85
20.0	31.51	40.17
22.0	36.48	48.39
24.0	41.49	57.69

TABLE--1.19

The calculated and the experimental values of the Gruneisen parameter for Ar and Kr.

Argon			Krypton		
Temp. K	Calc.	Expt.	Temp. K	Calc.	Expt.
0.0	2.94	-----	0.00	3.01	-----
10.0	2.94	2.50	10.0	3.00	-----
20.0	2.86	2.63	20.0	2.92	2.778
30.0	2.75	2.66	30.0	2.83	2.894
40.0	2.64	2.67	40.0	2.74	2.911
50.0	2.54	2.67	50.0	2.66	2.878
60.0	2.45	2.66	60.0	2.59	2.834
70.0	2.36	2.65	70.0	2.52	2.783
80.0	2.28	2.59	80.0	2.45	2.733
			90.0	2.39	2.700
			100.0	2.33	2.711
			110.0	2.27	-----

TABLE--1.20

The calculated and the experimental values of the Gruneisen parameter for Xe and Ne.

Temp. K	Calc.	Expt.	Temp. K	Calc.	Expt.
0.00	3.05	-----	0.00	2.77	-----
8.0	3.05	-----	2.0	2.77	-----
20.0	2.98	2.33	4.0	2.77	-----
32.0	2.89	----	6.0	2.77	-----
40.0	2.84	2.52	8.0	2.76	-----
48.0	2.79	-----	10.0	2.74	-----
60.0	2.72	2.73	12.0	2.71	-----
72.0	2.65	-----	14.0	2.66	------
80.0	2.61	2.80	16.0	2.61	-----
88.0	2.57	-----	18.0	2.56	------
100.0	2.51	2.68	20.0	2.50	-----
108.0	2.47	-----	22.0	2.45	-----
120.0	2.41	2.98	24.0	2.39	-----
128.0	2.36	-----			
140.0	2.33	3.10			
148.0	2.30	-----			
160.0	2.27	-----			

TABLE--2.1

The calculated and the experimental values of the lattice parameter(10^{-10}m) in the one and the two frequencies SCAP and the quasiharmonic approximation(Boyer's)

Temp. K	Expt.	QH	One freq. SCAP	Two freq. SCAP
0.00	5.5967	5.6180	5.6247	5.6257
100.0	5.6023	5.6320	5.6286	5.6304
200.0	5.6201	5.6484	5.6425	5.6456
300.0	5.6402	5.6660	5.6589	5.6332
400.0	5.6650	5.6875	5.6763	5.6816
500.0	5.6901	5.7092	5.6942	5.7004
600.0	5.7169	5.7334	5.7127	5.7192
700.0	5.7456	------	5.7316	5.7382
800.0	5.7767	5.7929	5.7509	5.7571
900.0	5.8112	------	5.7707	5.7750
1000.0	5.8472	5.8561	5.7910	5.7948
1070.0	------	------	5.8054	5.8048

TABLE--2.2

The calculated and the experimental values of the compressibility (10^{12} cm^2/dyne) for NaCl.

Temp. K	Expt. (Ref. 80)	Expt . (Ref.81)	One freq. SCAP	Two freq. SCAP
1.0	------	------	3.536	3.540
100.0	------	------	3.585	3.593
200.0	-----	-----	3.709	3.726
300.0	4.14	4.40	3.847	3.873
400.0	4.31	4.30	3.994	4.027
500.0	4.56	4.16	4.148	4.187
600.0	5.01	4.37	4.309	4.352
700.0	5.48	4.98	4.479	4.519
800.0	5.93	6.00	4.656	4.687
900.0	6.31	7.35	4.847	4.853
1000.0	6.57	8.80	5.046	5.014
1070.0	6.72	----	5.191	5.122

TABLE--2.3

The calculated and the experimental values of the constant pressure specific heat (cal/mol/K) for NaCl. The calculated values of the average phonon frequency (10^{13}Hz) and the Gruneisen parameter are also given.

Temp. K	Expt.	Calc.	$< \omega^2 >^{1/2}$	γ
0.0000	0.00000	0.0000	3.215	1.405
100.0	-----	7.402	3.212	1.395
200.0	-----	10.60	3.202	1.372
300.0	12.40	11.40	3.190	1.351
400.0	12.50	11.73	3.176	1.330
500.0	12.88	11.92	3.162	1.309
600.0	13.26	12.04	3.148	1.290
700.0	13.66	12.13	3.132	1.271
800.0	14.23	12.22	3.117	1.253
900.0	-----	12.30	3.110	1.235
1000.0	-----	12.38	3.083	1.218
1070.0	-----	12.43	3.070	1.206

TABLE--2.4

The calculated and the experimental values of the coefficient of linear expansion (10^{-6}/K) for NaCl in one frequency SCAP formalism.

Temp. K	Experimental	Calculated
0.0000	0.0000	0.0000
100.0	------	19.2
200.0	33.8(173K)	27.2
300.0	36.9(273K)	30.0
400.0	39.7(373K)	31.1
500.0	42.3(473K)	31.9
600.0	48.3(573K)	32.5
700.0	51.9(673K)	33.1
800.0	56.1(773K)	33.6
900.0	60.9(873K)	34.6
1000.0	67.3(973K)	34.7
1070.0	----------	-----

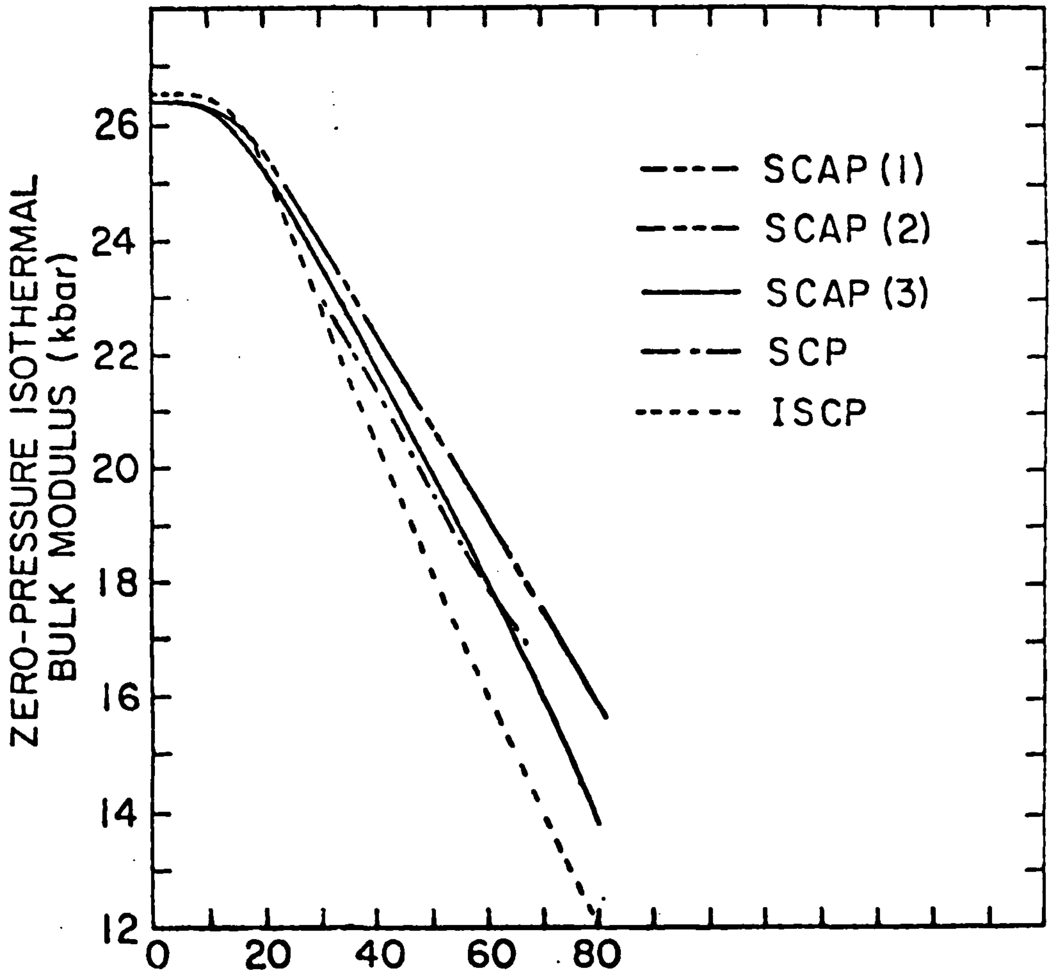

ZERO-PRESSURE ISOTHERMAL BULK MODULUS (kbar)
26
24
22
20
18
16
14
12
0
20
40
60
80
TEMPERATURE, °K
SCAP (1)
SCAP (2)
SCAP (3)
SCP
ISCP

FIGURE 1.1

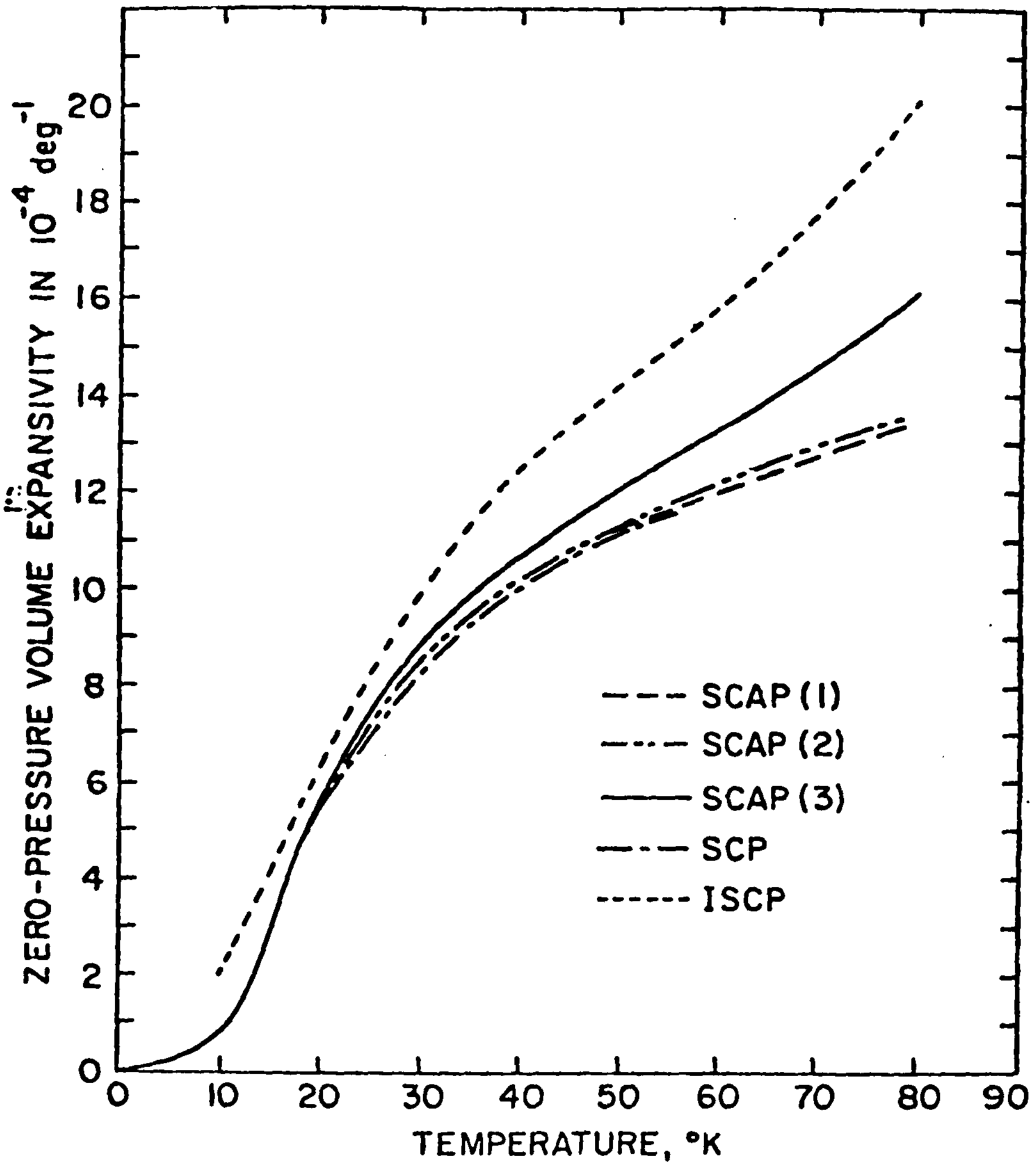

ZERO-PRESSURE VOLUME EXPANSIVITY IN 10^{-4} deg^{-1}
0
2
4
6
8
10
12
14
16
18
20
0
10
20
30
40
50
60
70
80
90
TEMPERATURE, °K
SCAP (1)
SCAP (2)
SCAP (3)
SCP
ISCP

FIGURE 1.2

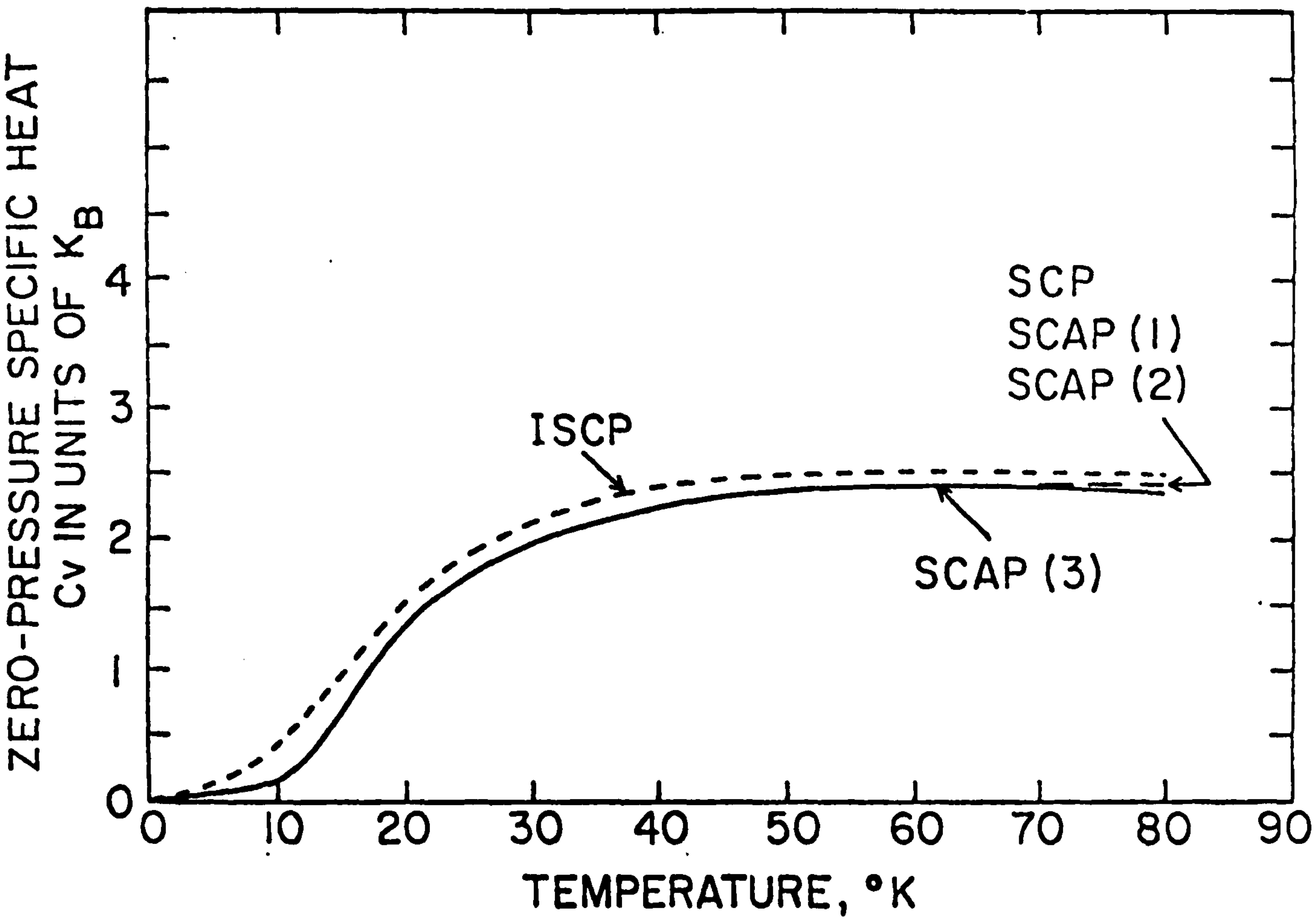

ZERO-PRESSURE SPECIFIC HEAT
Cv IN UNITS OF K_B
0
1
2
3
4
0
10
20
30
40
50
60
70
80
90
TEMPERATURE, °K
ISCP
SCP
SCAP (1)
SCAP (2)
SCAP (3)

FIGURE 1.3

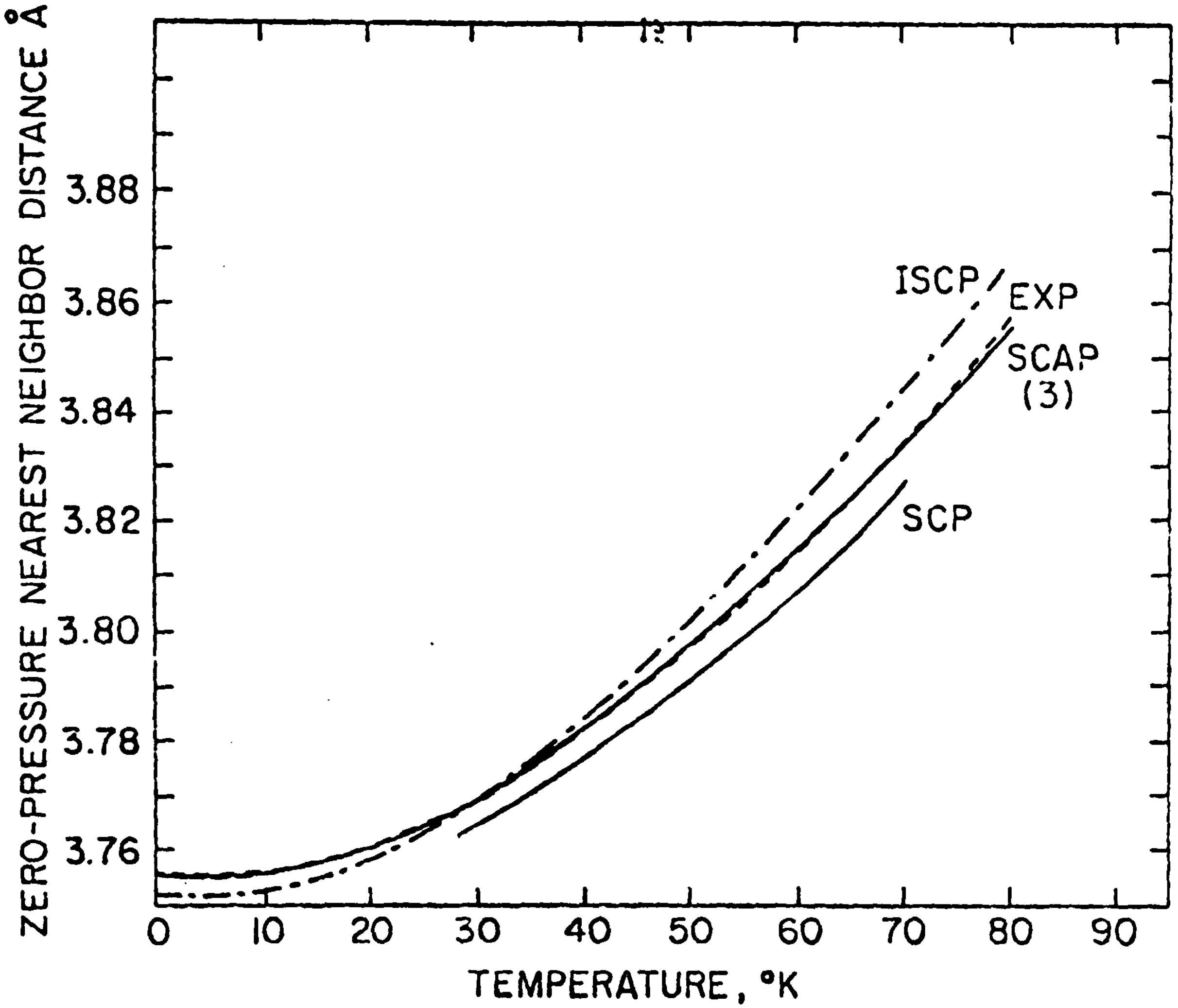

ZERO-PRESSURE NEAREST NEIGHBOR DISTANCE Å
3.76
3.78
3.80
3.82
3.84
3.86
3.88
0
10
20
30
40
50
60
70
80
90
TEMPERATURE, °K
ISCP
EXP
SCAP
(3)
SCP

FIGURE 1.4

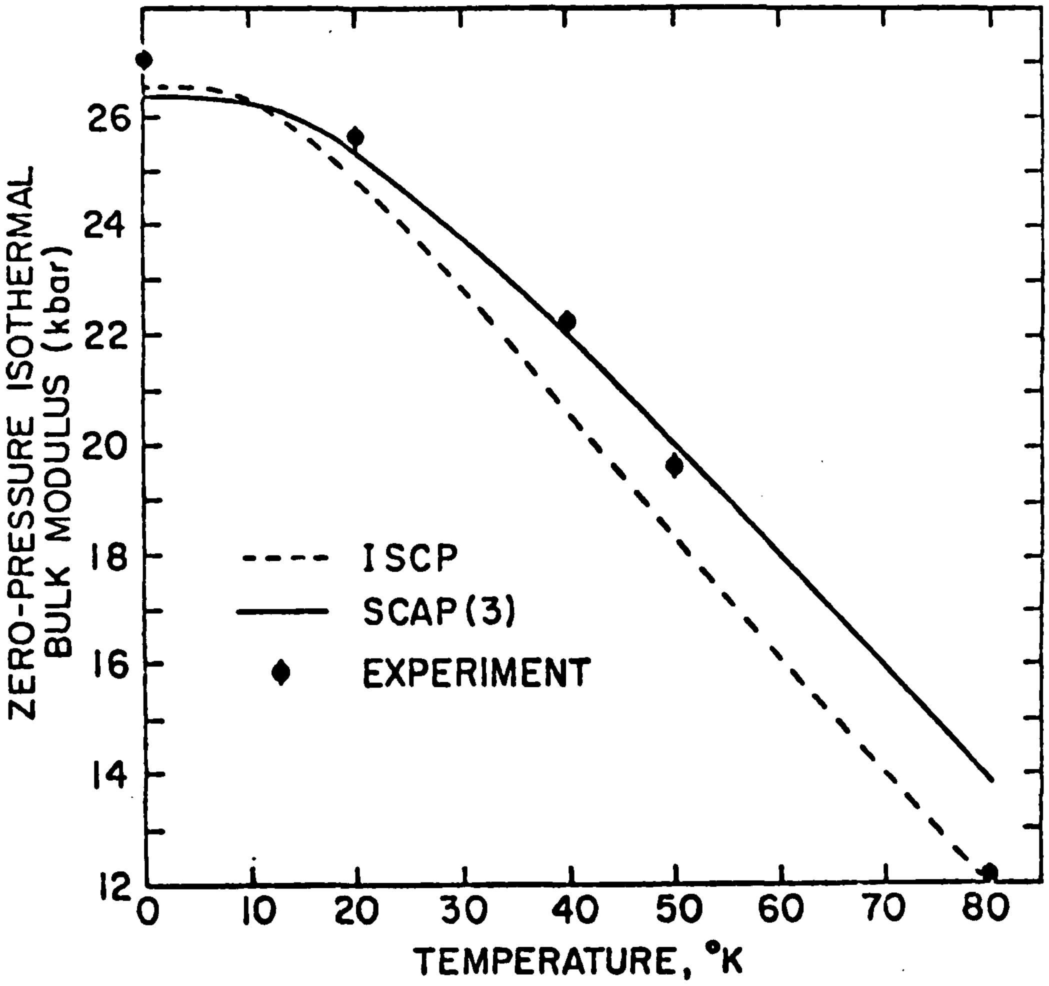

ZERO-PRESSURE ISOTHERMAL
BULK MODULUS (kbar)
12
14
16
18
20
22
24
26
0
10
20
30
40
50
60
70
80
TEMPERATURE, °K
ISCP
SCAP(3)
EXPERIMENT

FIGURE 1.5

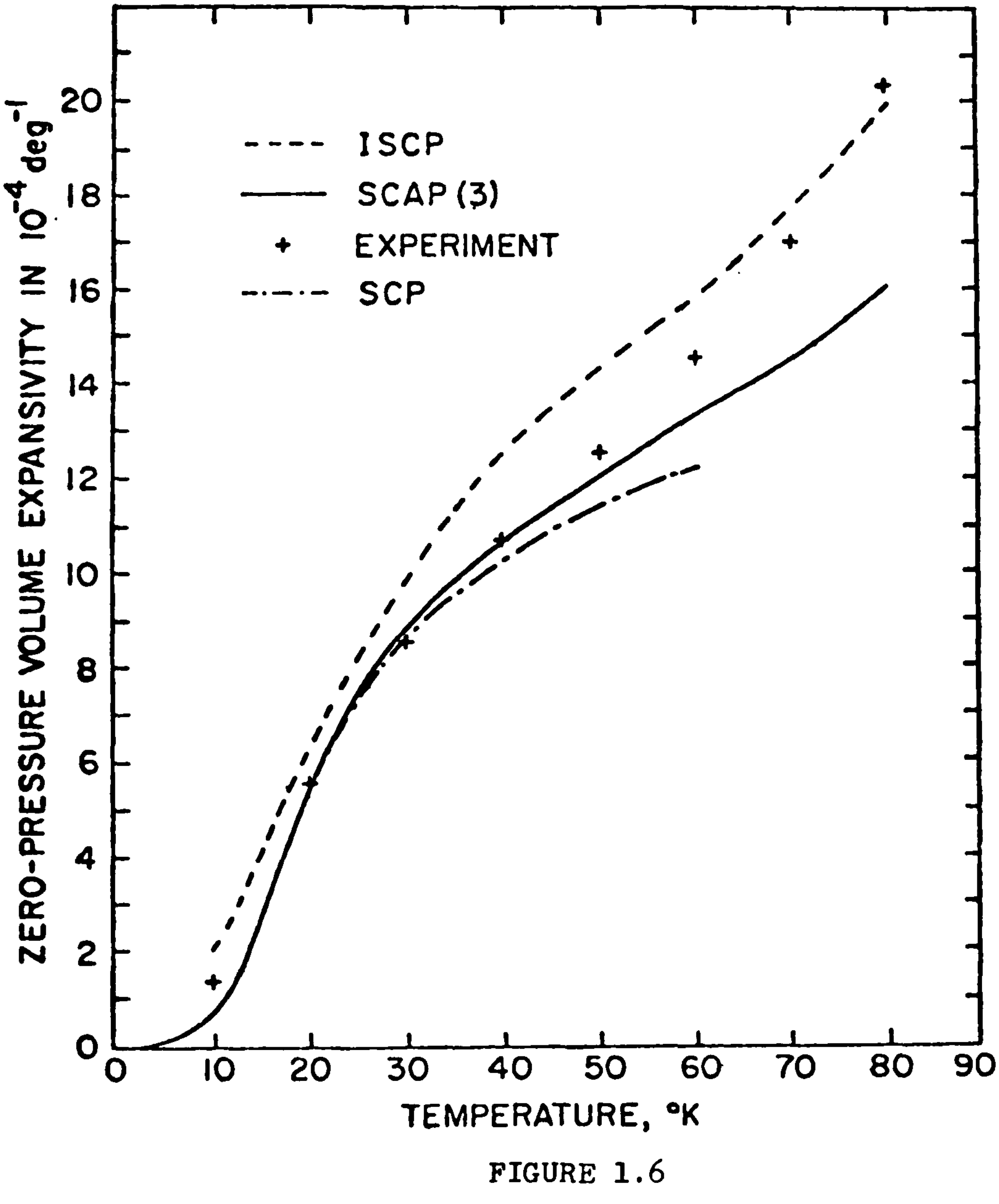

ZERO-PRESSURE VOLUME EXPANSIVITY IN 10^{-4} deg^{-1}
TEMPERATURE, °K
ISCP
SCAP (3)
EXPERIMENT
SCP
0
2
4
6
8
10
12
14
16
18
20
0
10
20
30
40
50
60
70
80
90

FIGURE 1.6

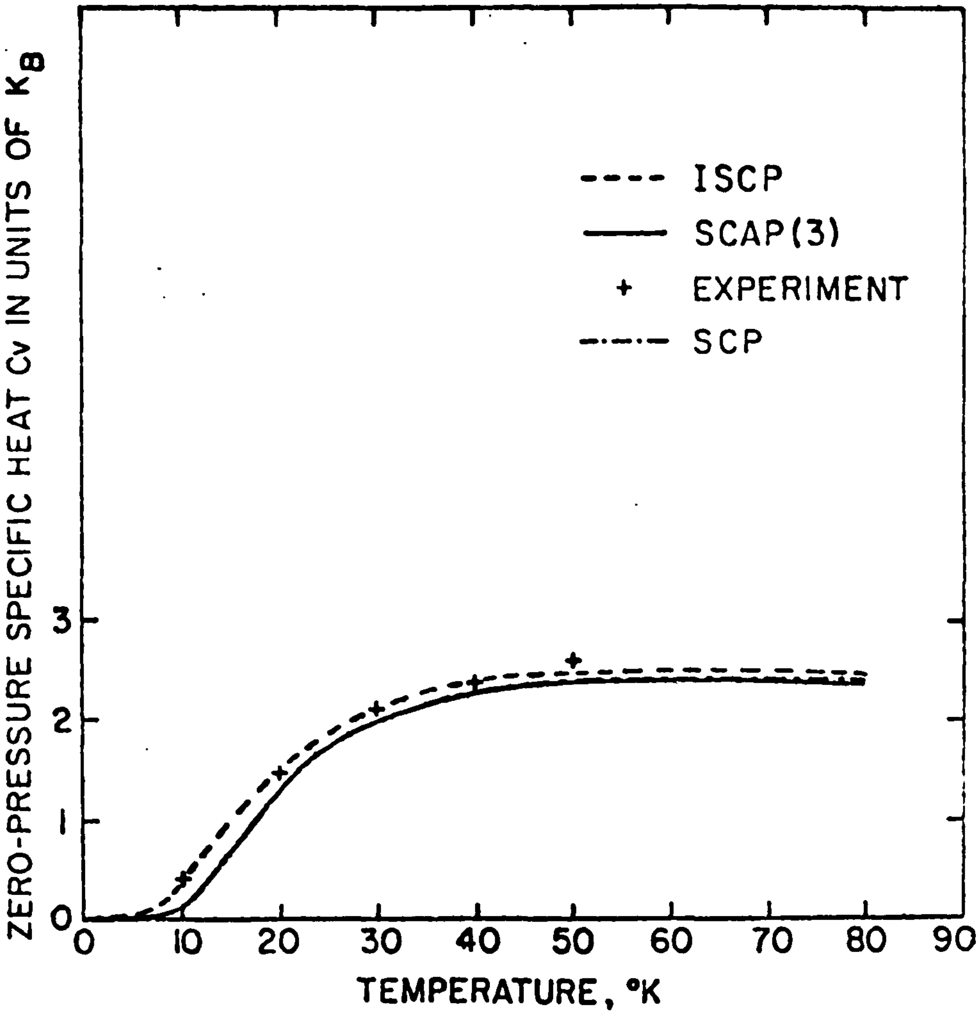
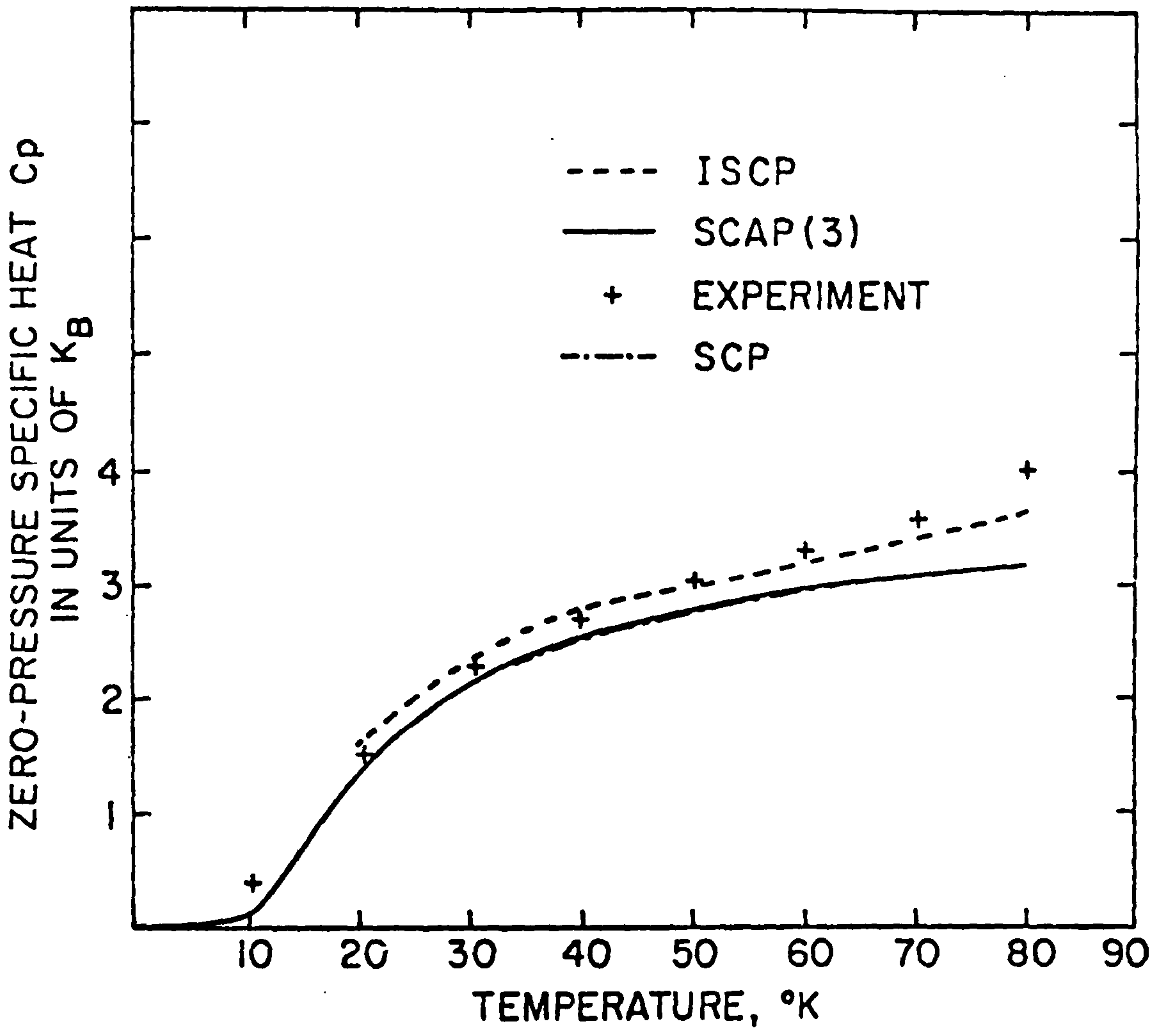

ISCP
SCAP(3)
EXPERIMENT
SCP
ZERO-PRESSURE SPECIFIC HEAT Cv IN UNITS OF K$_B$
0
1
2
3
0
10
20
30
40
50
60
70
80
90
TEMPERATURE, °K

FIGURE 1.7



ISCP
SCAP(3)
EXPERIMENT
SCP
ZERO-PRESSURE SPECIFIC HEAT Cp IN UNITS OF K$_B$
1
2
3
4
10
20
30
40
50
60
70
80
90
TEMPERATURE, °K

FIGURE 1.8

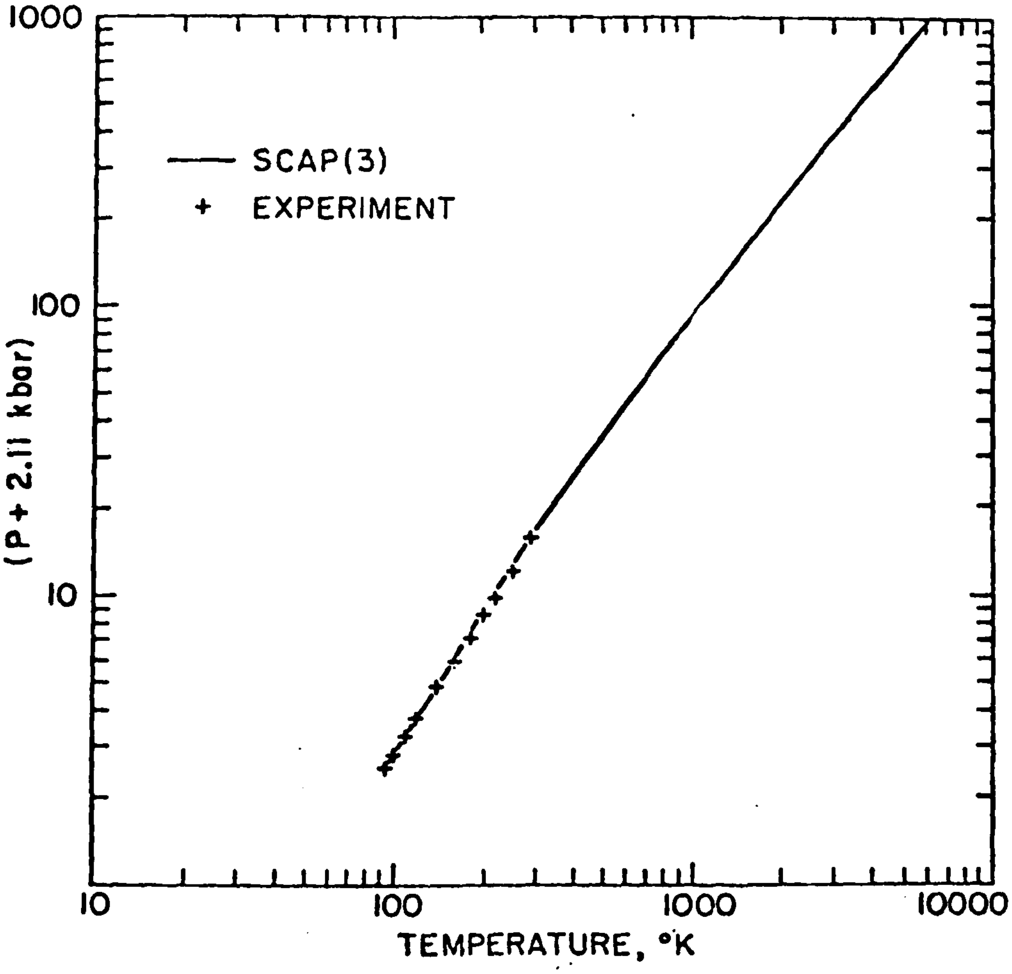

1000
100
10
(P + 2.11 kbar)
10
100
1000
10000
TEMPERATURE, °K
SCAP(3)
+ EXPERIMENT

FIGURE 1.9

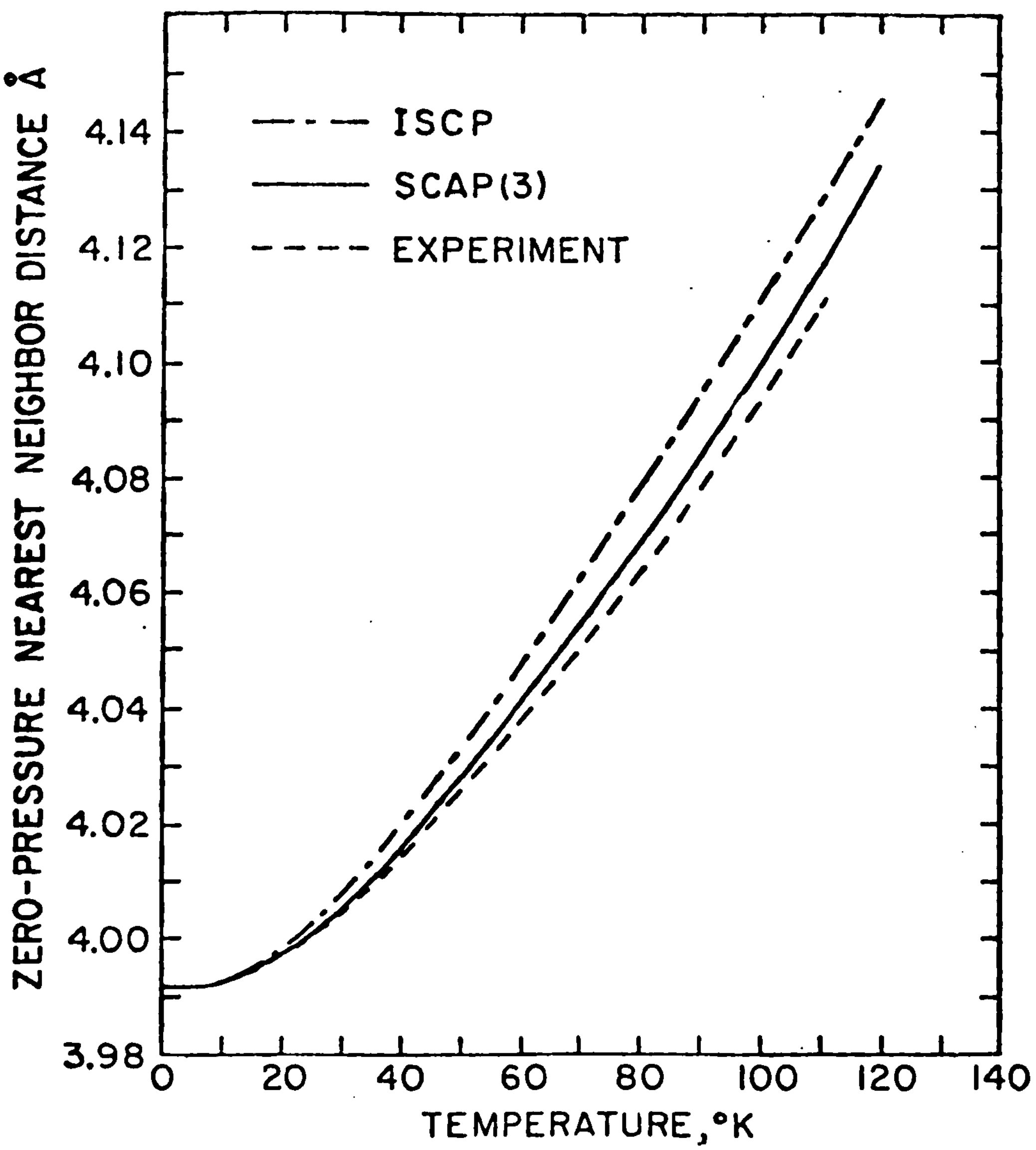

ZERO-PRESSURE NEAREST NEIGHBOR DISTANCE Å
3.98
4.00
4.02
4.04
4.06
4.08
4.10
4.12
4.14
0
20
40
60
80
100
120
140
TEMPERATURE,°K
ISCP
SCAP(3)
EXPERIMENT

FIGURE 1.10

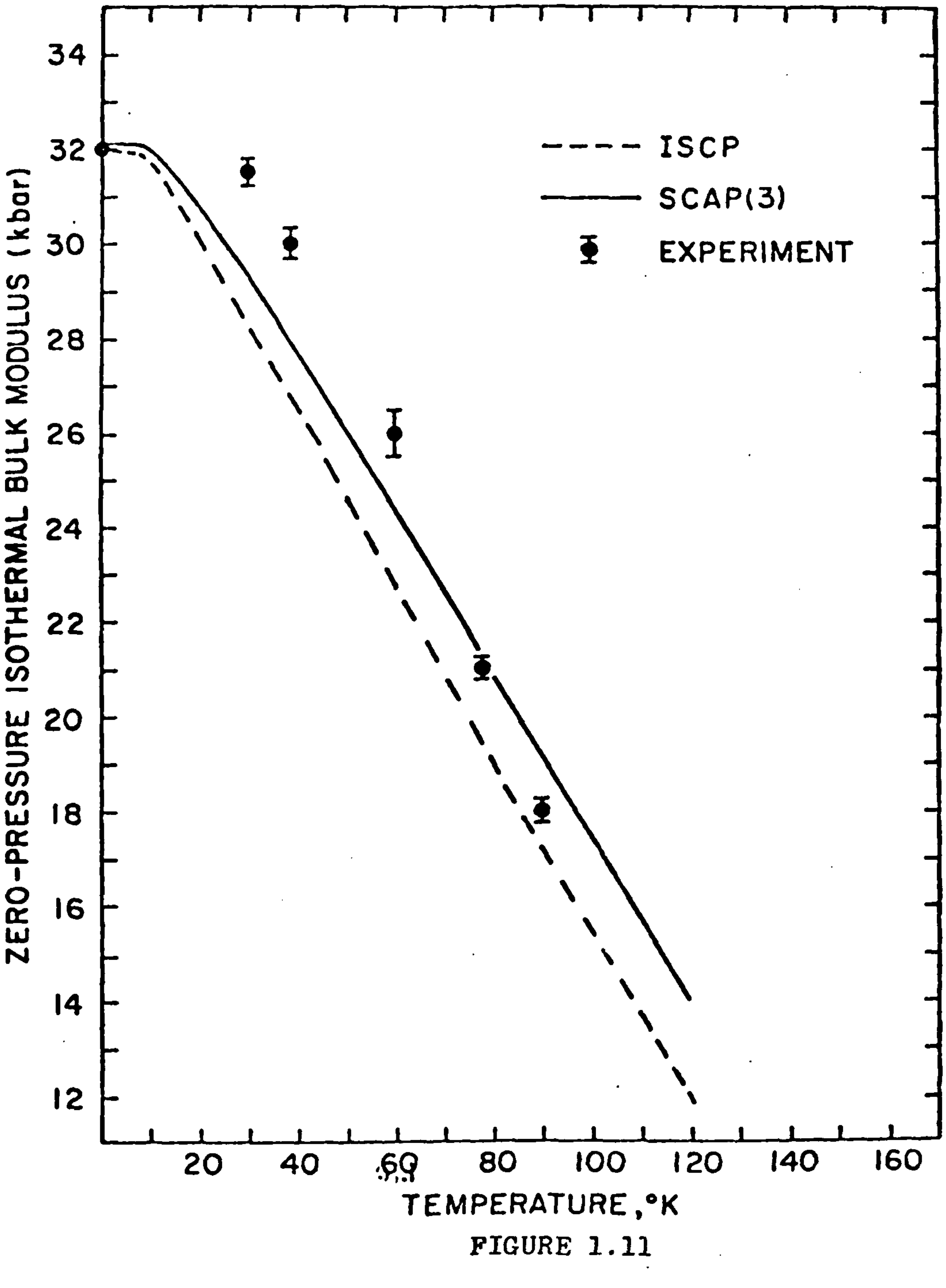

ZERO-PRESSURE ISOTHERMAL BULK MODULUS (kbar)
34
32
30
28
26
24
22
20
18
16
14
12
20
40
60
80
100
120
140
160
TEMPERATURE, °K
ISCP
SCAP(3)
EXPERIMENT

FIGURE 1.11

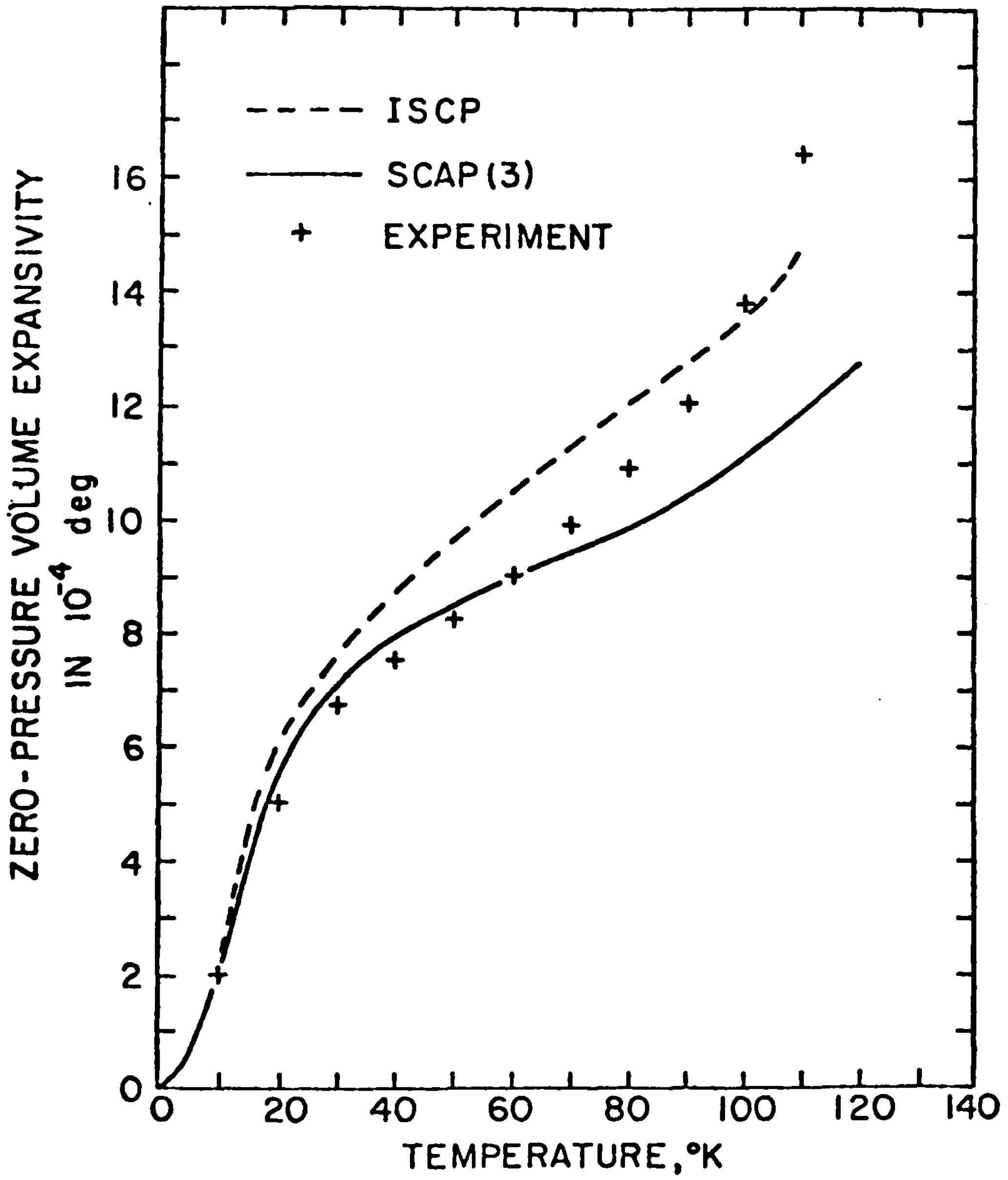

ISCP
SCAP(3)
EXPERIMENT
ZERO-PRESSURE VOLUME EXPANSIVITY IN 10^-4 deg
0
2
4
6
8
10
12
14
16
0
20
40
60
80
100
120
140
TEMPERATURE, °K

FIGURE 1.12

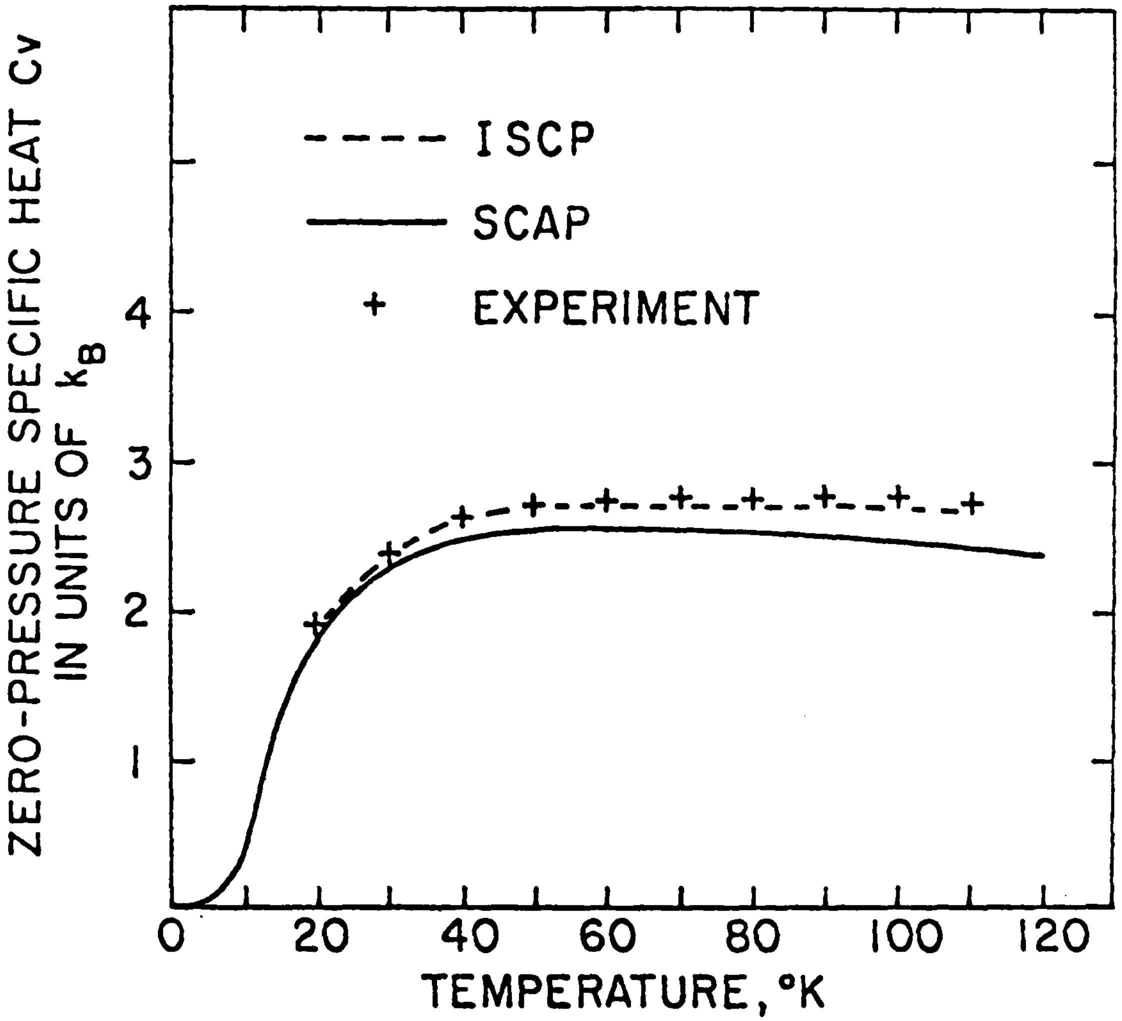

ZERO-PRESSURE SPECIFIC HEAT Cv
IN UNITS OF k_B
4
3
2
1
0
20
40
60
80
100
120
TEMPERATURE, °K
- - - - ISCP
SCAP
+ EXPERIMENT

FIGURE 1.13

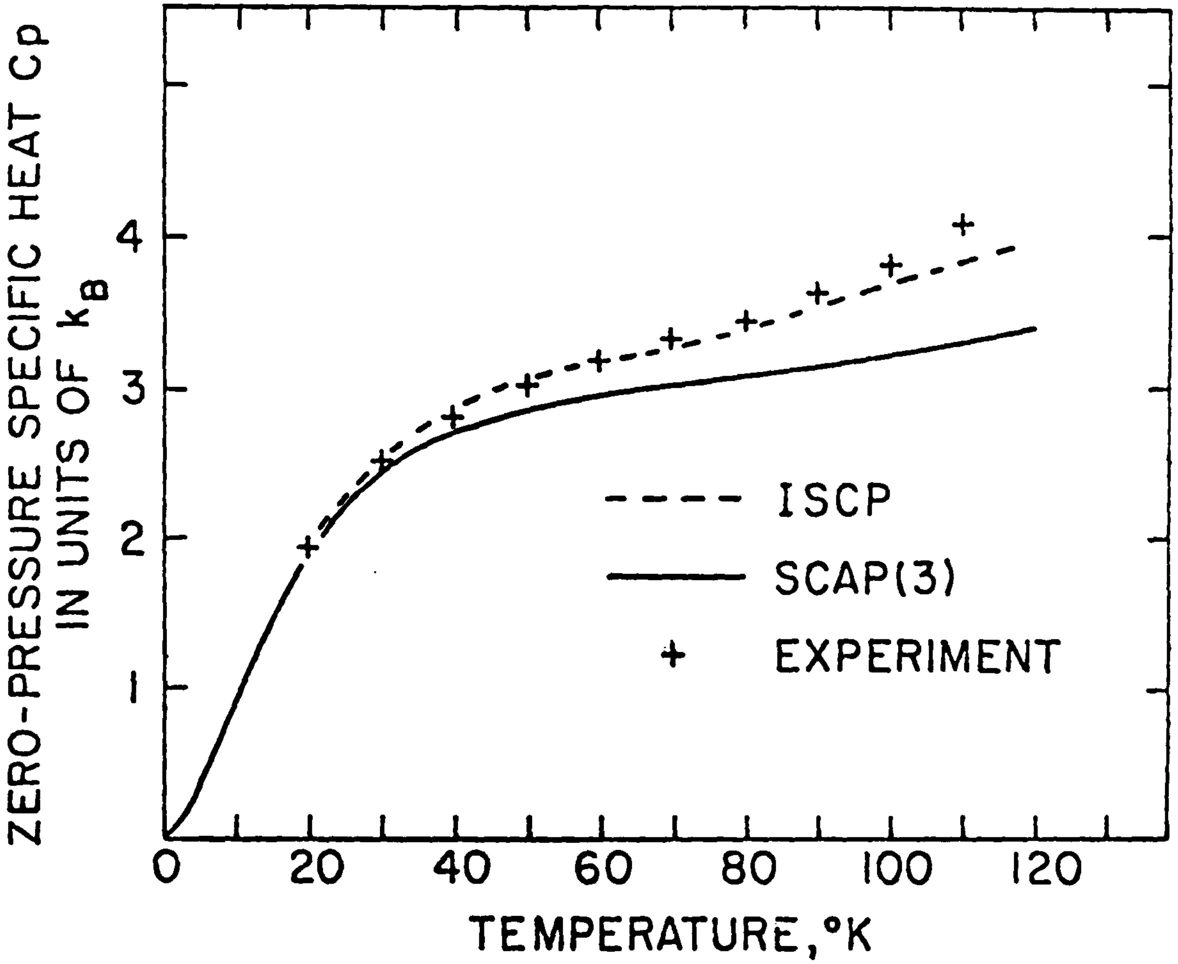

ZERO-PRESSURE SPECIFIC HEAT Cp
IN UNITS OF k_B
4
3
2
1
0
20
40
60
80
100
120
TEMPERATURE, °K
ISCP
SCAP(3)
EXPERIMENT

FIGURE 1.14

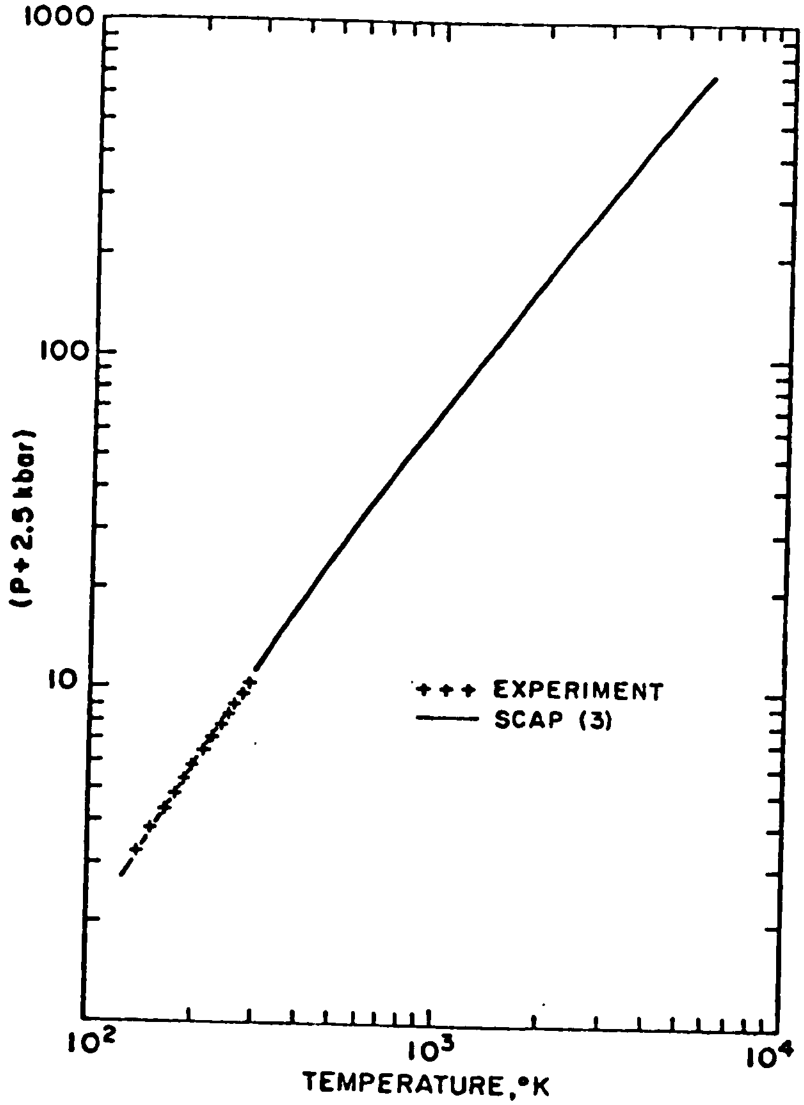

1000
100
10
(P + 2.5 kbar)
10^2
10^3
10^4
TEMPERATURE, °K
+ + + EXPERIMENT
—— SCAP (3)

FIGURE 1.15

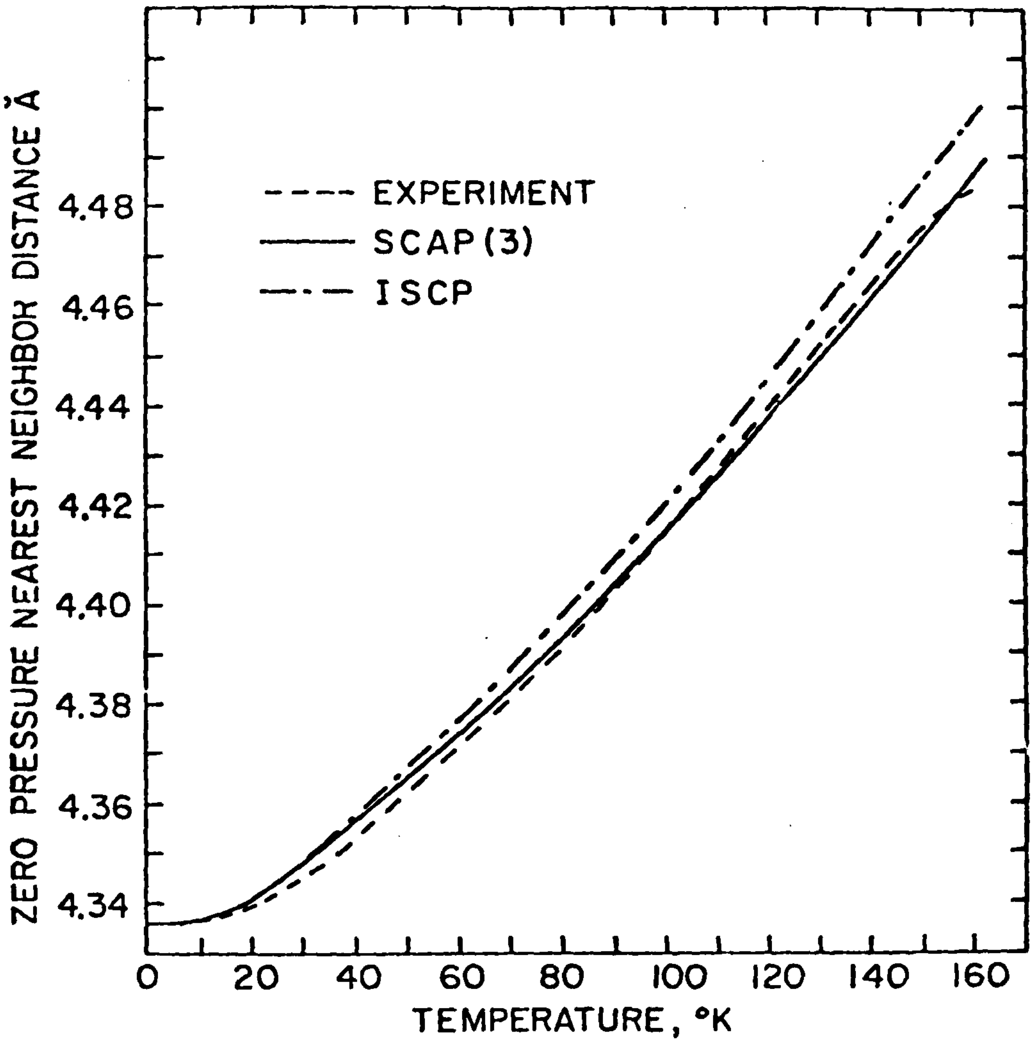

ZERO PRESSURE NEAREST NEIGHBOR DISTANCE Å
4.34
4.36
4.38
4.40
4.42
4.44
4.46
4.48
0
20
40
60
80
100
120
140
160
TEMPERATURE, °K
---- EXPERIMENT
—— SCAP(3)
—·— ISCP

FIGURE 1.16

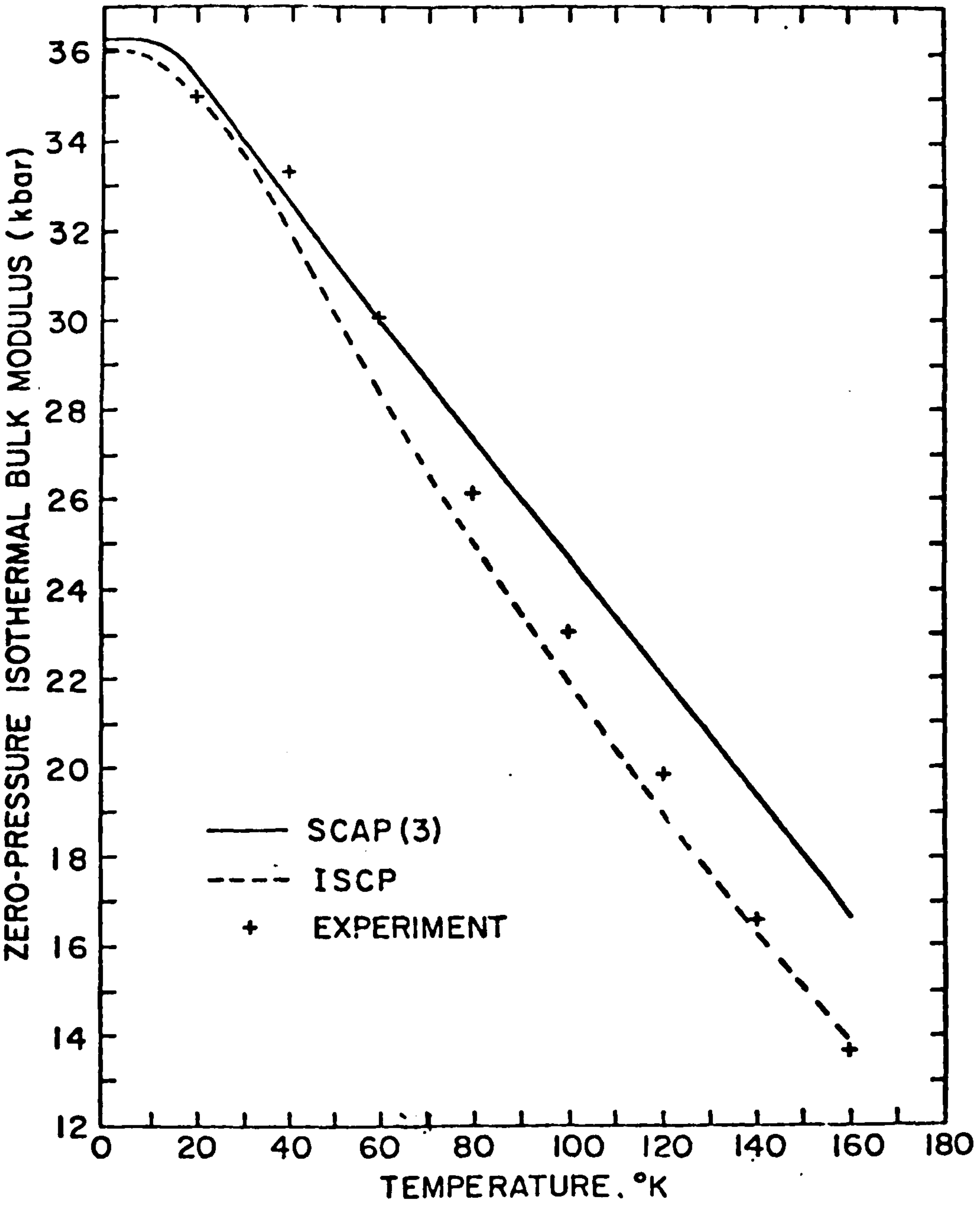

ZERO-PRESSURE ISOTHERMAL BULK MODULUS (kbar)
36
34
32
30
28
26
24
22
20
18
16
14
12
0
20
40
60
80
100
120
140
160
180
TEMPERATURE, °K
SCAP(3)
ISCP
EXPERIMENT

FIGURE 1.17

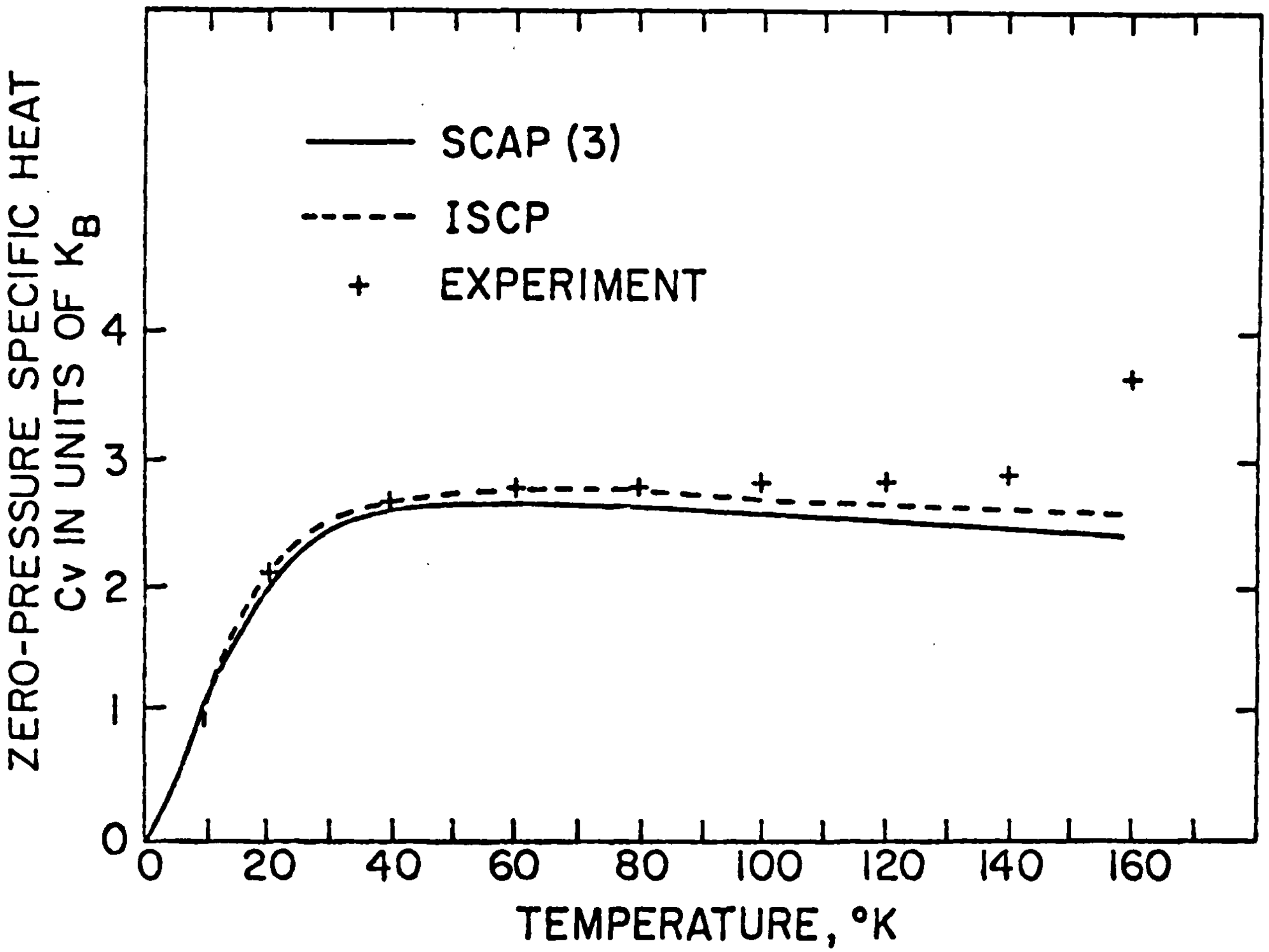

SCAP (3)
ISCP
EXPERIMENT
ZERO-PRESSURE SPECIFIC HEAT
Cv IN UNITS OF K_B
0
1
2
3
4
0
20
40
60
80
100
120
140
160
TEMPERATURE, °K

FIGURE 1.18

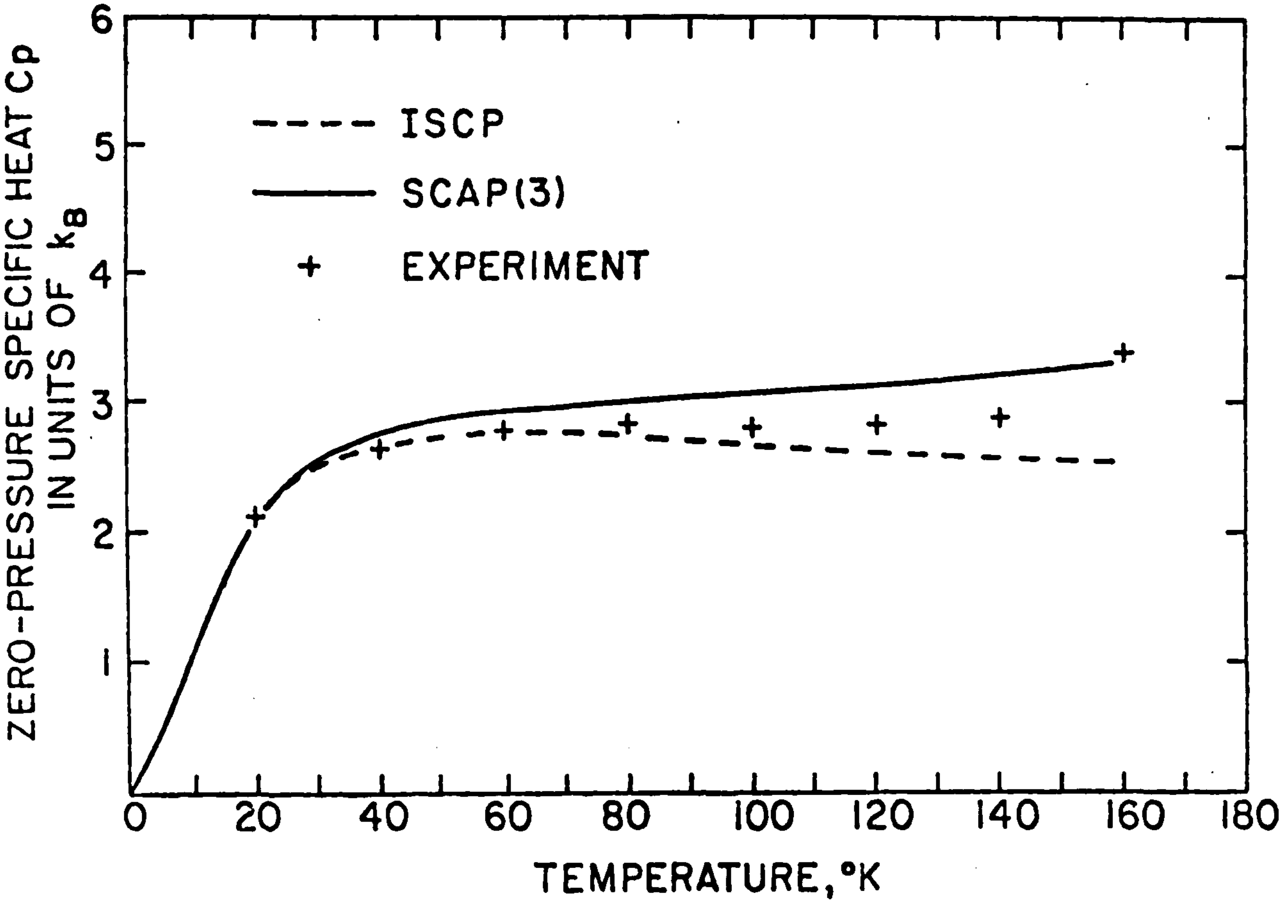

ZERO-PRESSURE SPECIFIC HEAT Cp IN UNITS OF k_B
TEMPERATURE, °K
ISCP
SCAP(3)
EXPERIMENT
0
1
2
3
4
5
6
20
40
60
80
100
120
140
160
180

FIGURE 1.19

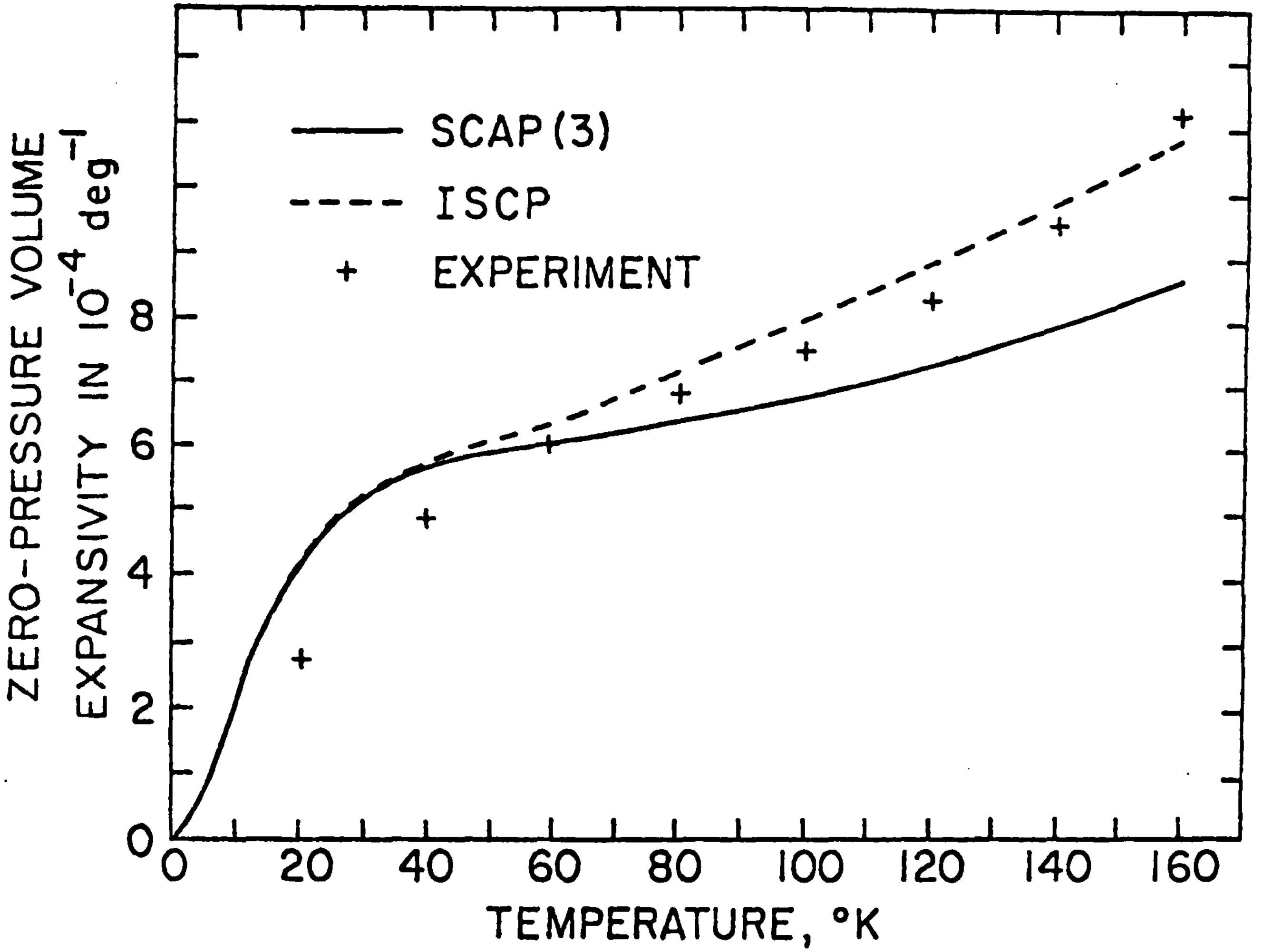

SCAP(3)
ISCP
+ EXPERIMENT
ZERO-PRESSURE VOLUME EXPANSIVITY IN 10^{-4} deg^{-1}
0
2
4
6
8
0
20
40
60
80
100
120
140
160
TEMPERATURE, °K

FIGURE 1.20

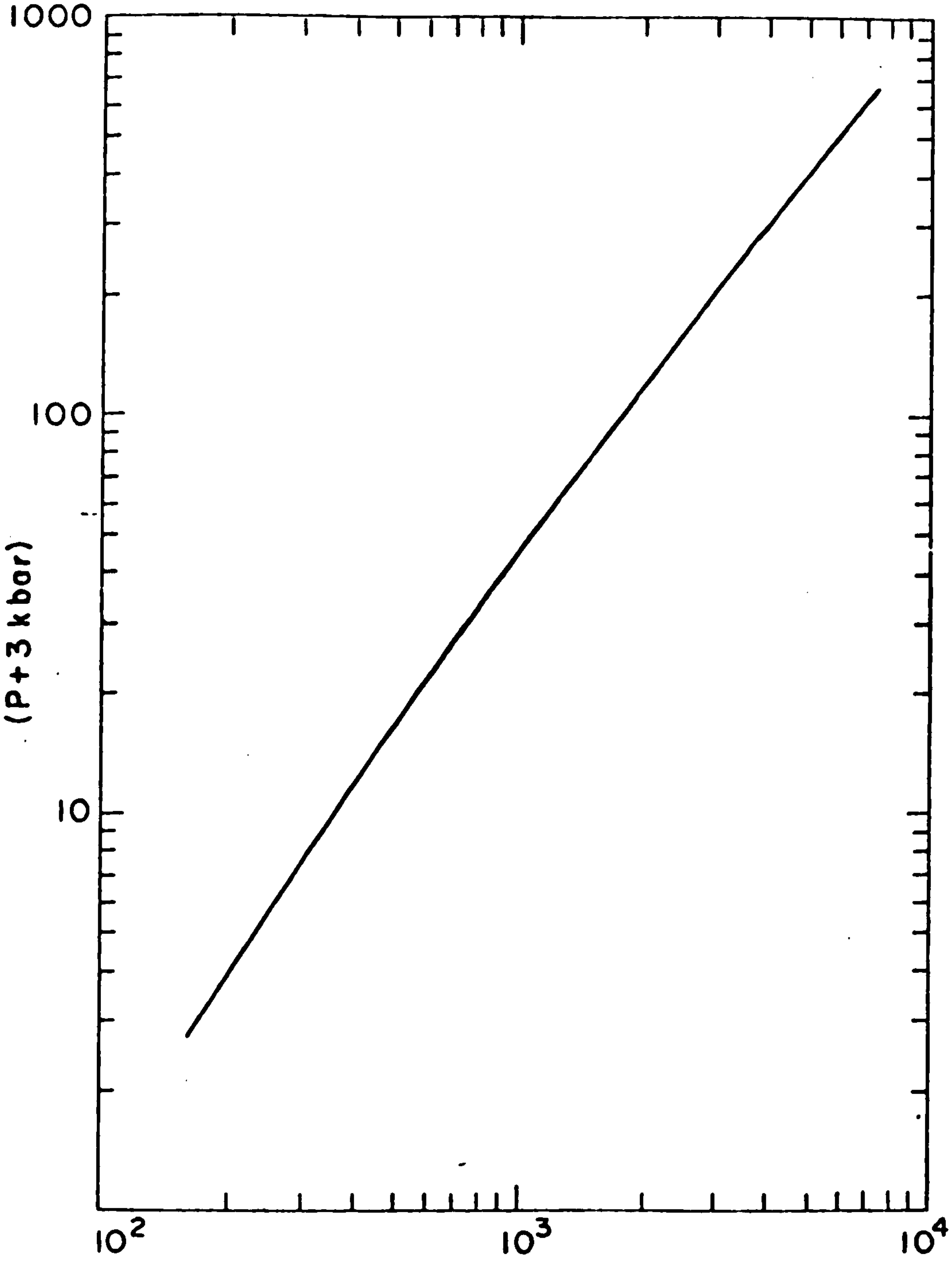


FIGURE 1.21

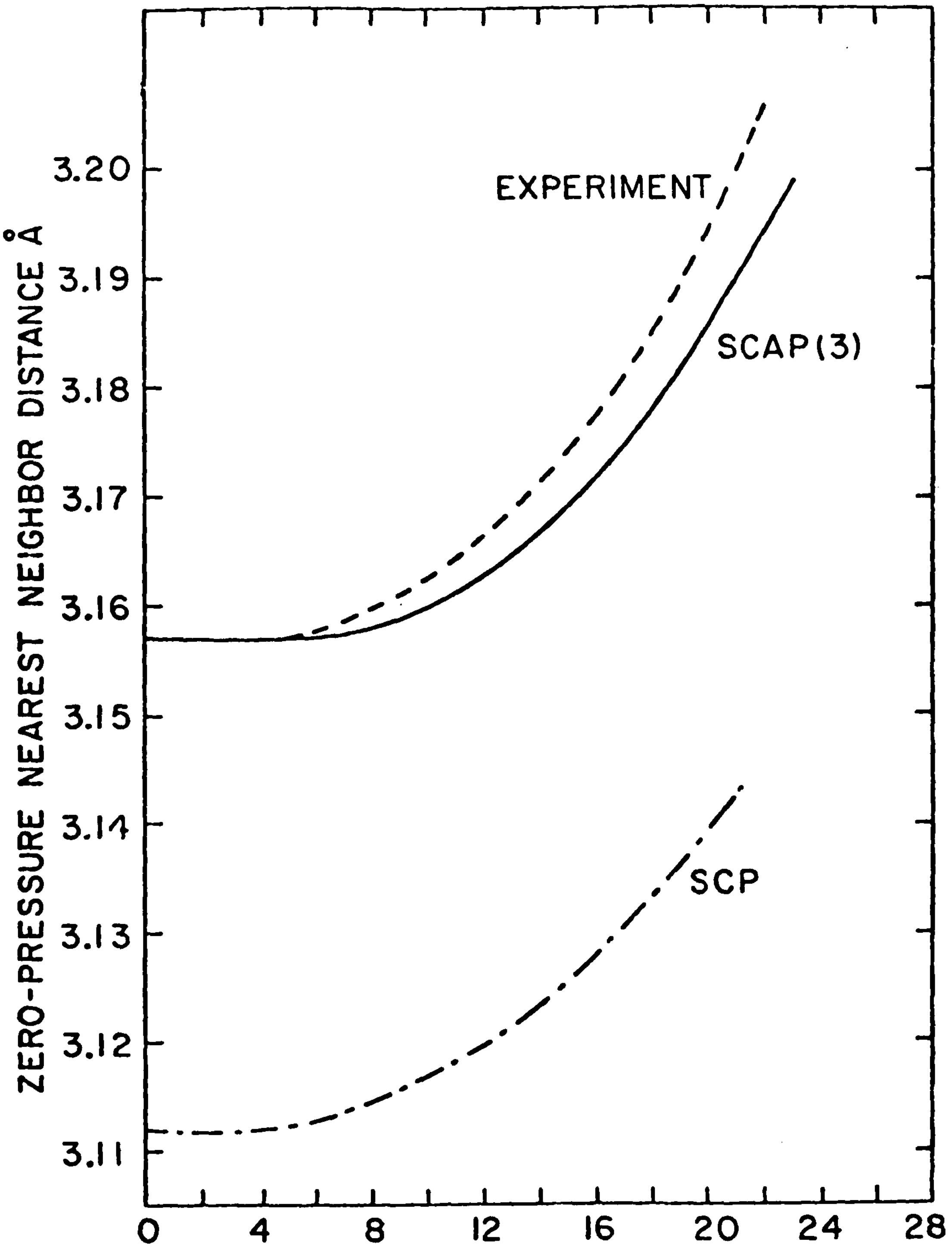

ZERO-PRESSURE NEAREST NEIGHBOR DISTANCE Å
3.20
3.19
3.18
3.17
3.16
3.15
3.14
3.13
3.12
3.11
0
4
8
12
16
20
24
28
EXPERIMENT
SCAP(3)
SCP

FIGURE 1.22

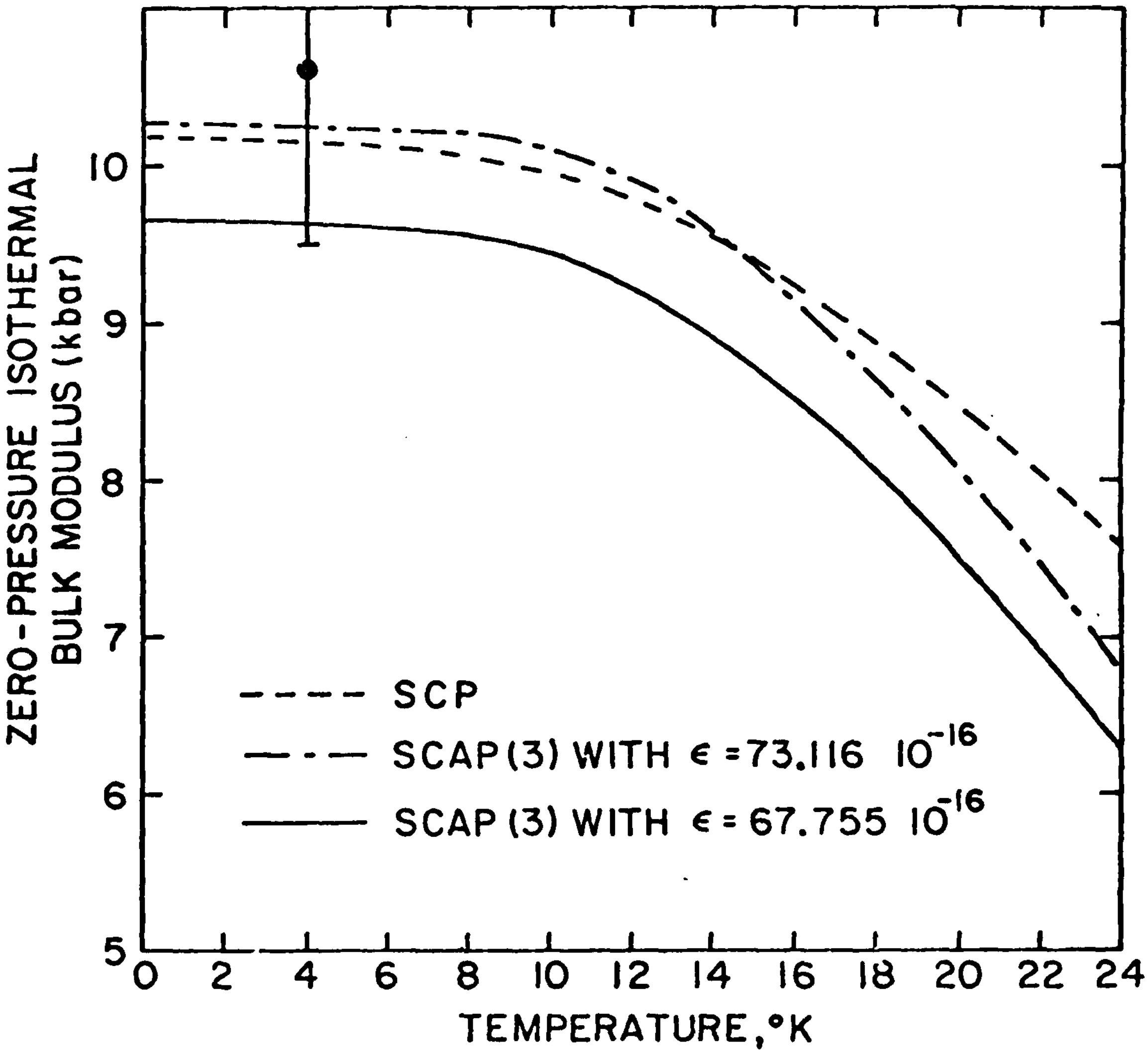

ZERO-PRESSURE ISOTHERMAL BULK MODULUS (kbar)
5
6
7
8
9
10
0
2
4
6
8
10
12
14
16
18
20
22
24
TEMPERATURE, °K
SCP
SCAP(3) WITH ϵ = 73.116 10⁻¹⁶
SCAP(3) WITH ϵ = 67.755 10⁻¹⁶

FIGURE 1.23

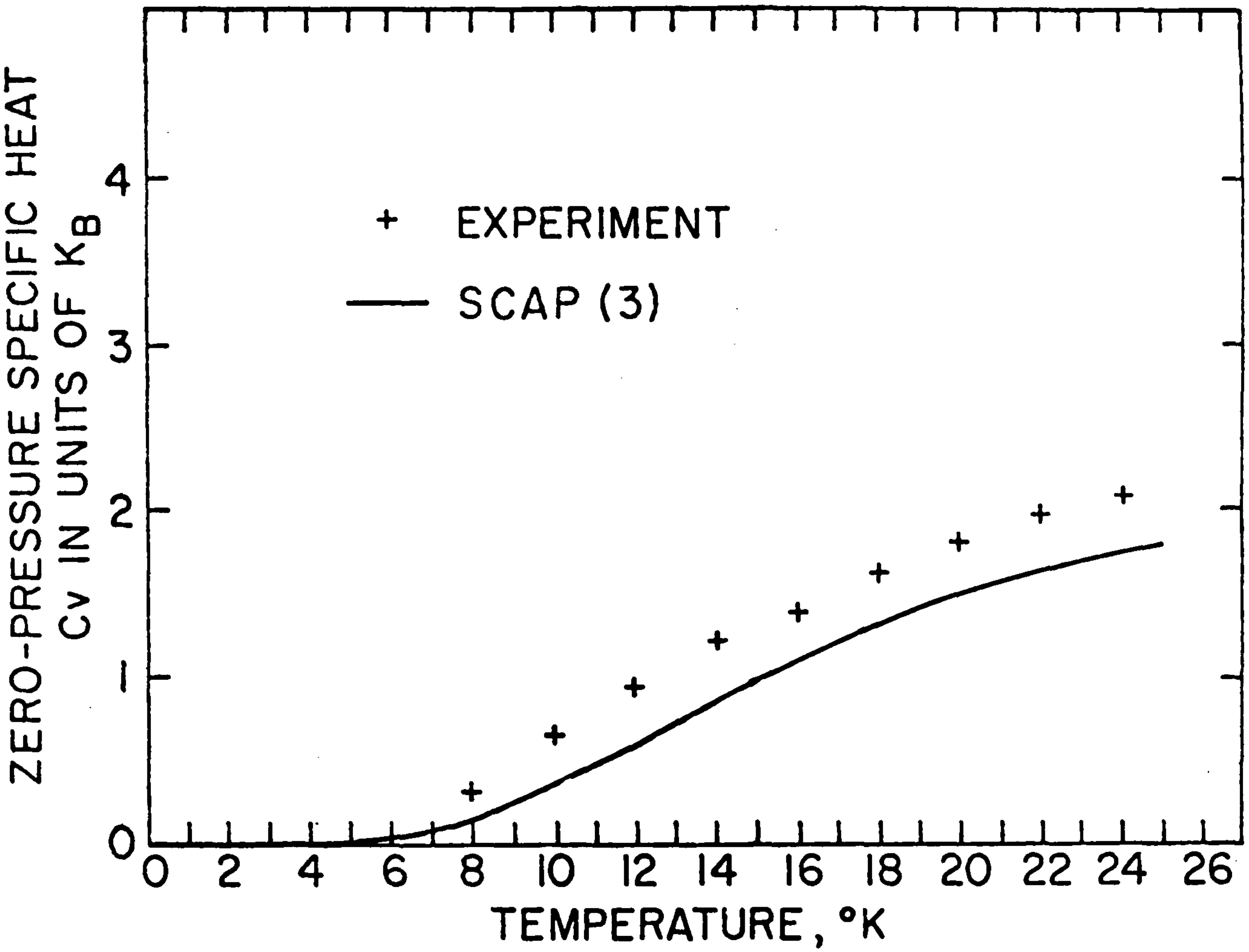

ZERO-PRESSURE SPECIFIC HEAT
Cv IN UNITS OF K_B
0
1
2
3
4
+ EXPERIMENT
— SCAP (3)
0
2
4
6
8
10
12
14
16
18
20
22
24
26
TEMPERATURE, °K

FIGURE 1.24

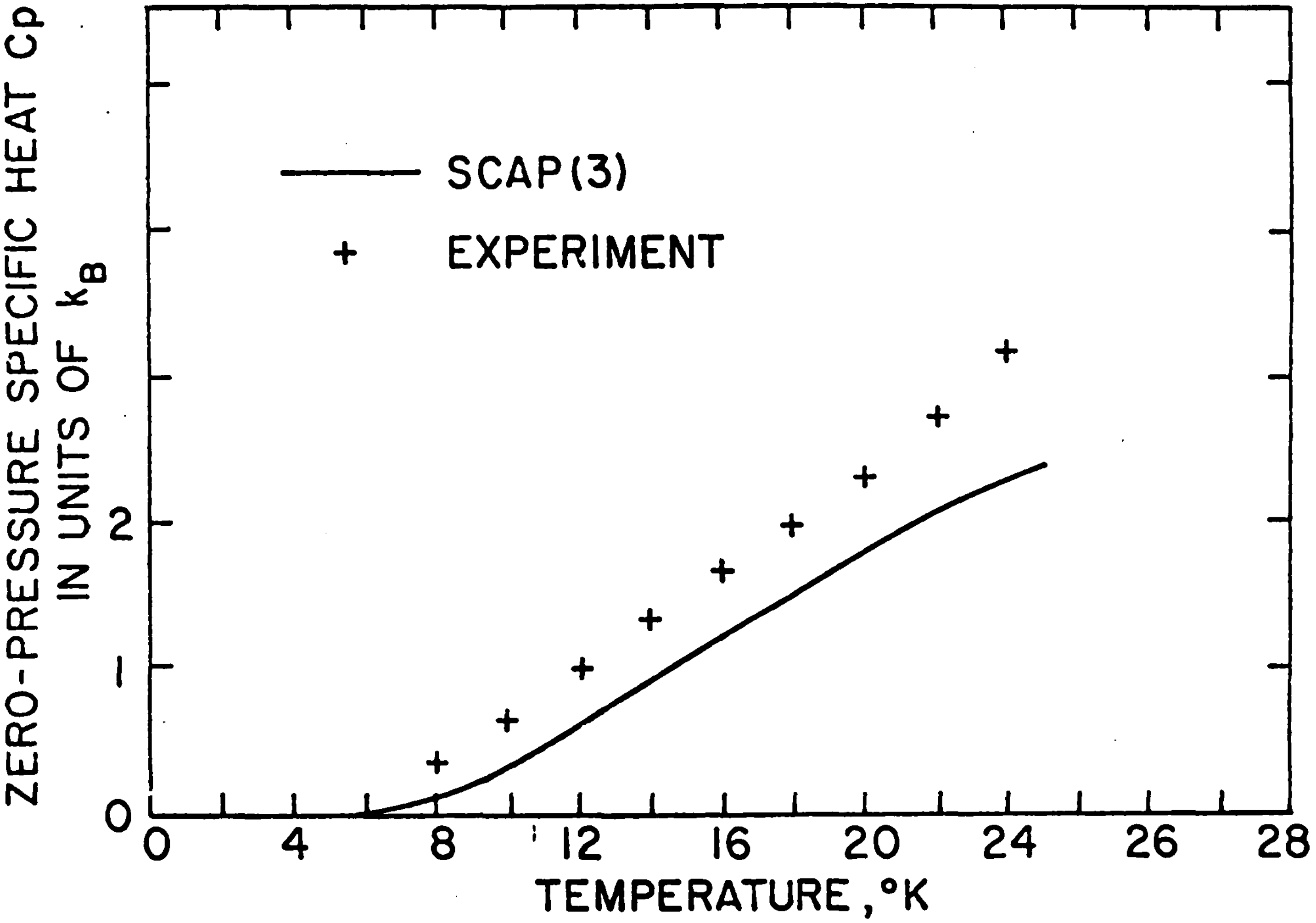

ZERO-PRESSURE SPECIFIC HEAT Cp
IN UNITS OF k_B
0
1
2
0
4
8
12
16
20
24
26
28
TEMPERATURE, °K
SCAP(3)
EXPERIMENT

FIGURE 1.25

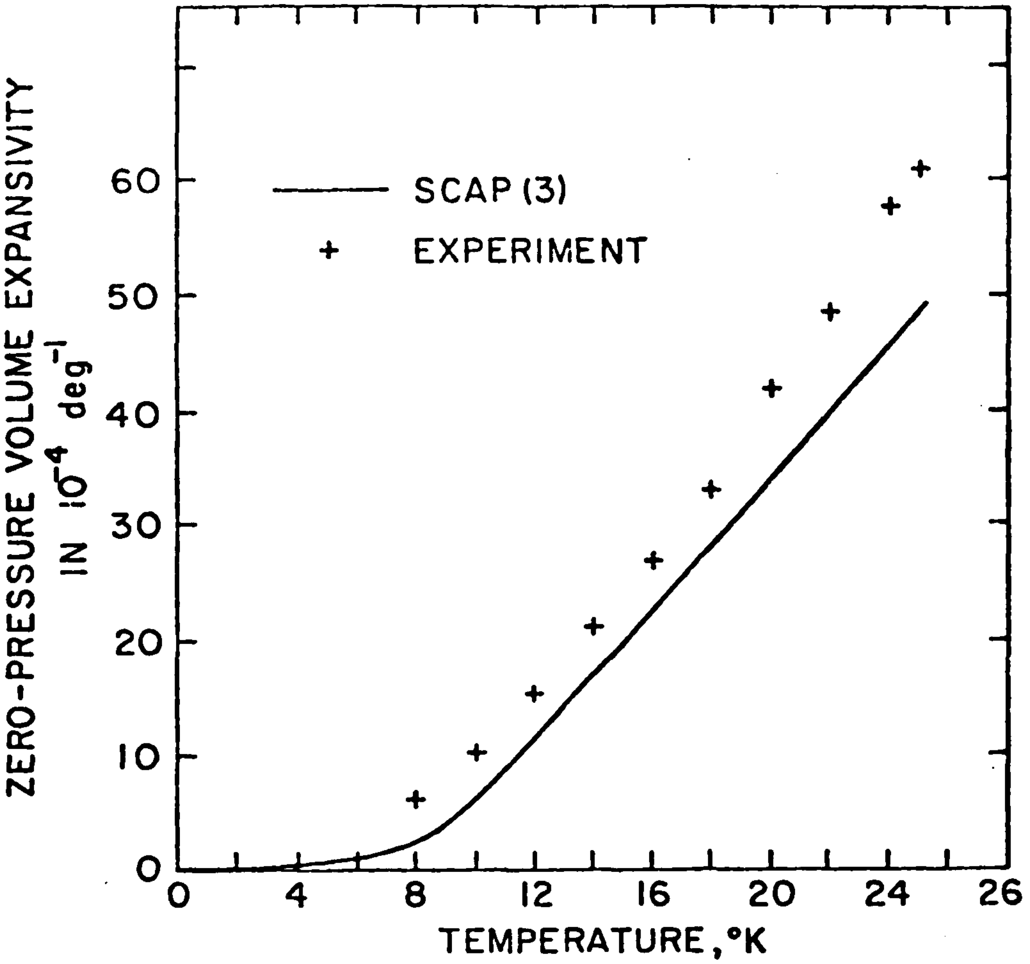
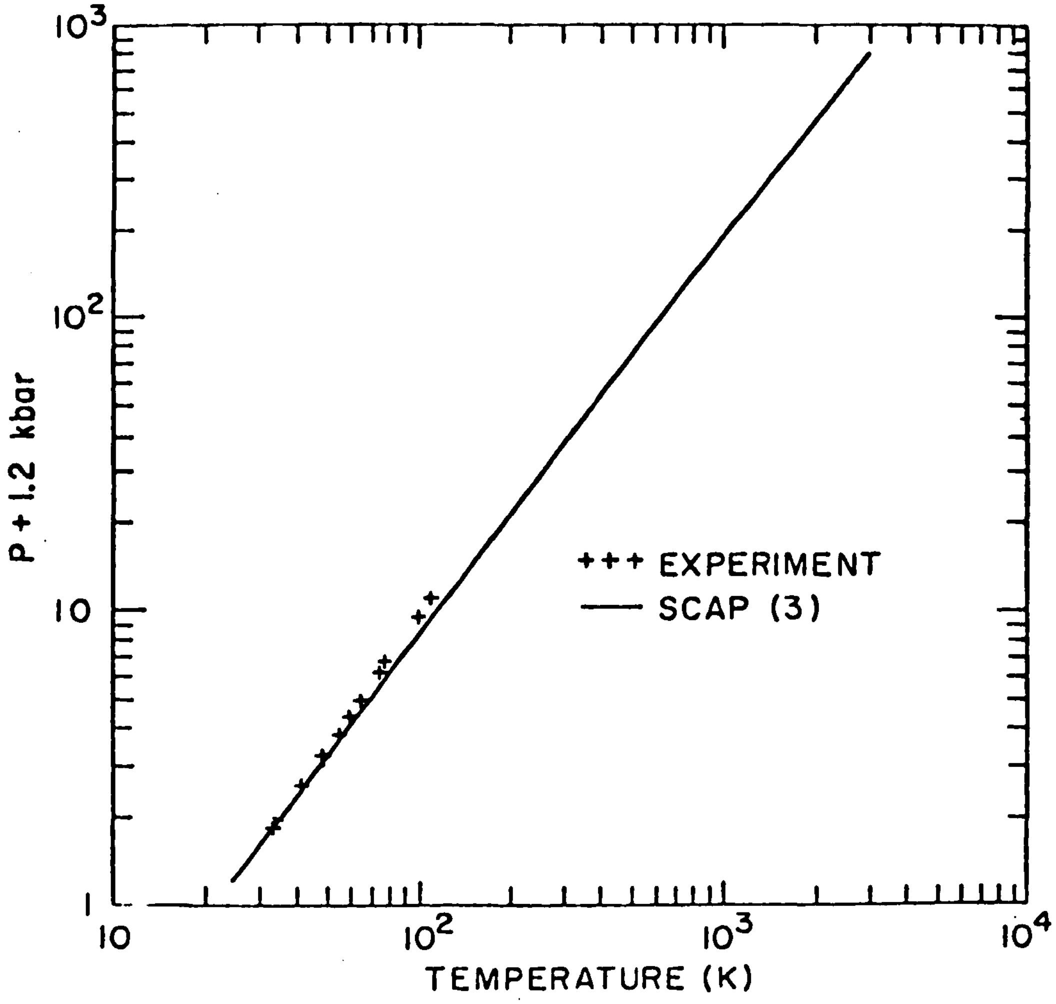
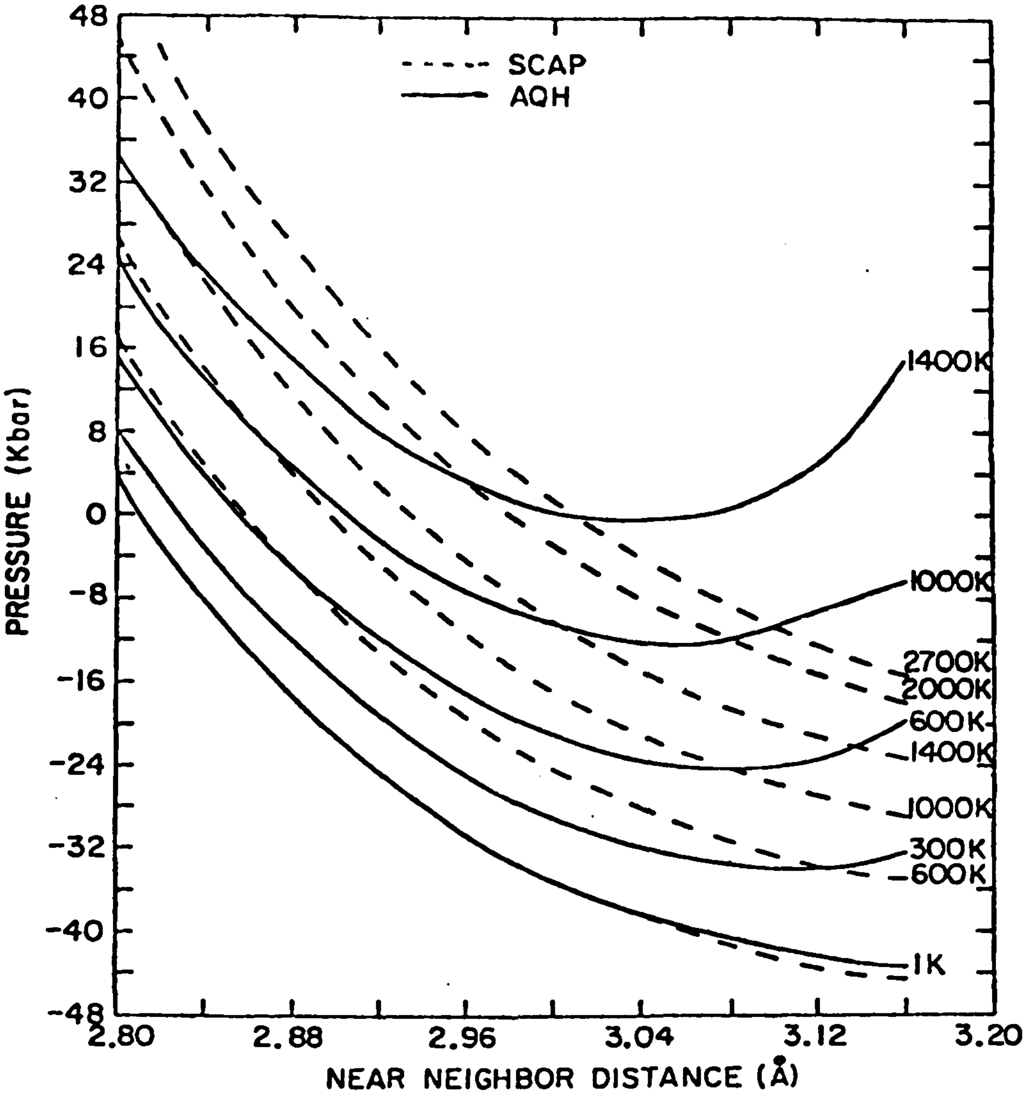

ZERO-PRESSURE VOLUME EXPANSIVITY
IN 10^{-4} deg^{-1}
0
10
20
30
40
50
60
0
4
8
12
16
20
24
26
TEMPERATURE, °K
SCAP (3)
+ EXPERIMENT

FIGURE 1.26



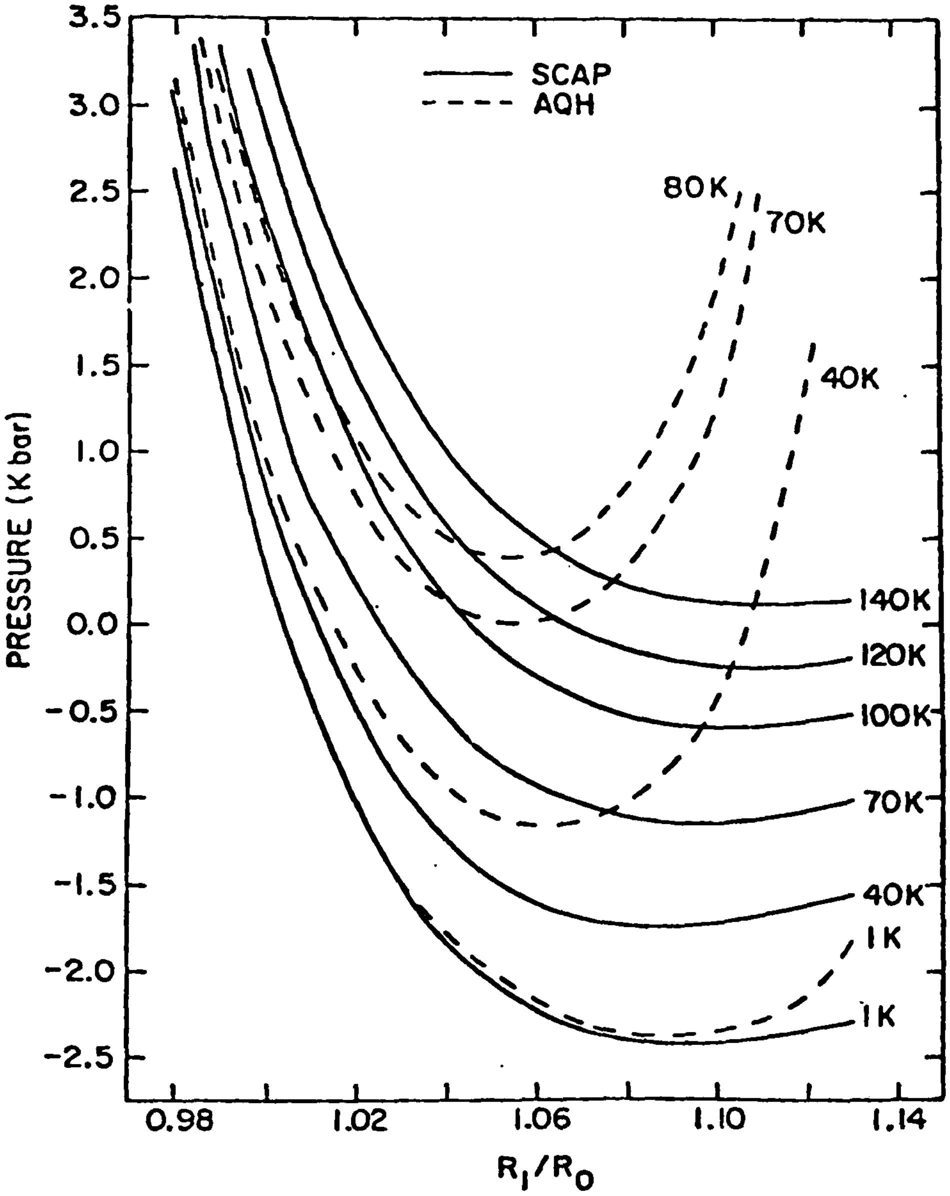
10^3
10^2
10
1
P + 1.2 kbar
10
10^2
10^3
10^4
TEMPERATURE (K)
+++ EXPERIMENT
—— SCAP (3)

FIGURE 1.27



48
40
32
24
16
8
0
-8
-16
-24
-32
-40
-48
PRESSURE (Kbar)
SCAP
AQH
1400K
1000K
2700K
2000K
600K
1400K
1000K
300K
600K
1K
2.80
2.88
2.96
3.04
3.12
3.20
NEAR NEIGHBOR DISTANCE (Å)

FIGURE 2.1



SCAP
AQH
PRESSURE (K bar)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
0.98
1.02
1.06
1.10
1.14
R_I/R_O
80K
70K
40K
140K
120K
100K
70K
40K
1K
1K

FIGURE 2.2

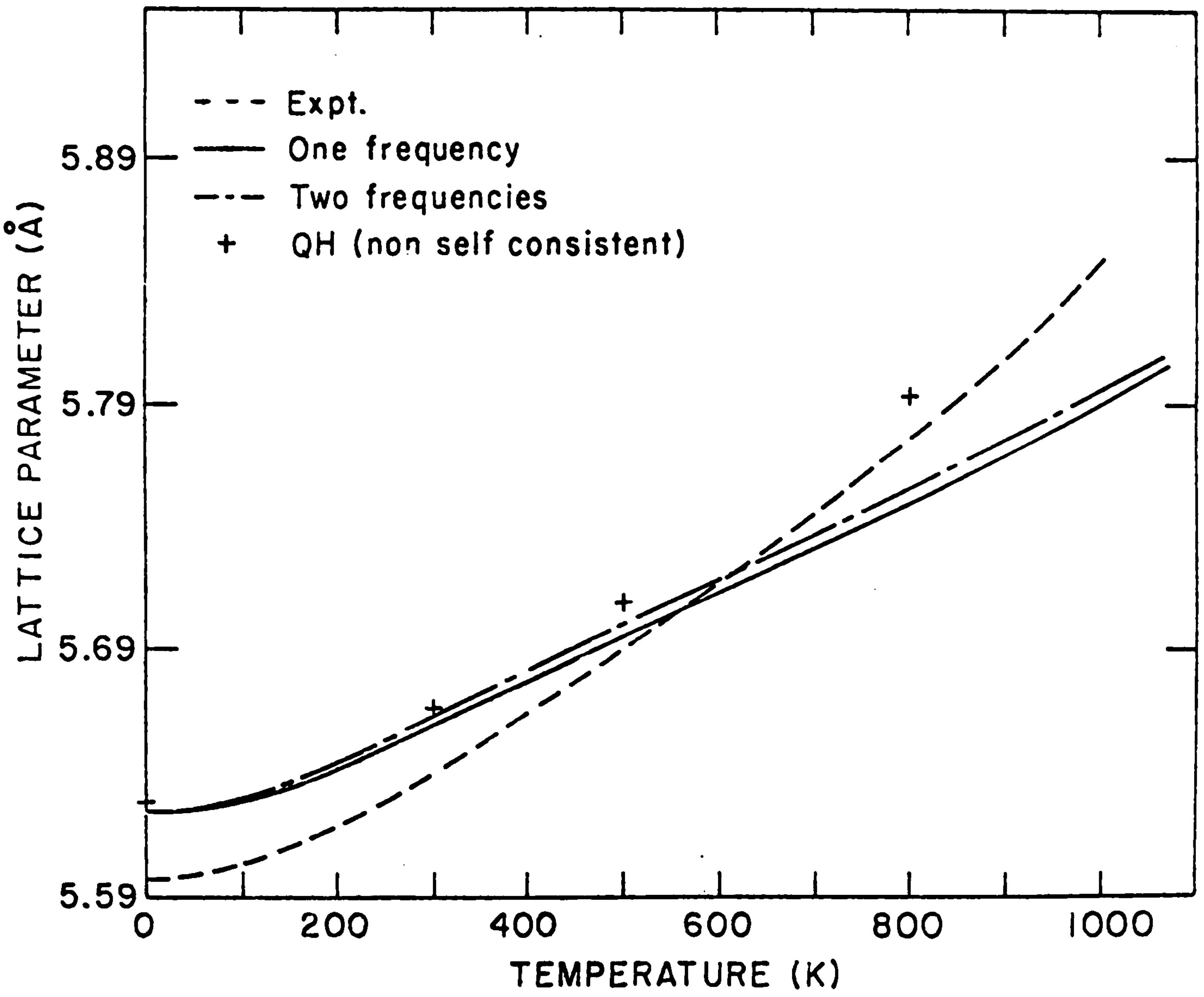

Expt.
One frequency
Two frequencies
+ QH (non self consistent)
LATTICE PARAMETER (Å)
5.89
5.79
5.69
5.59
0
200
400
600
800
1000
TEMPERATURE (K)

FIGURE 2.3

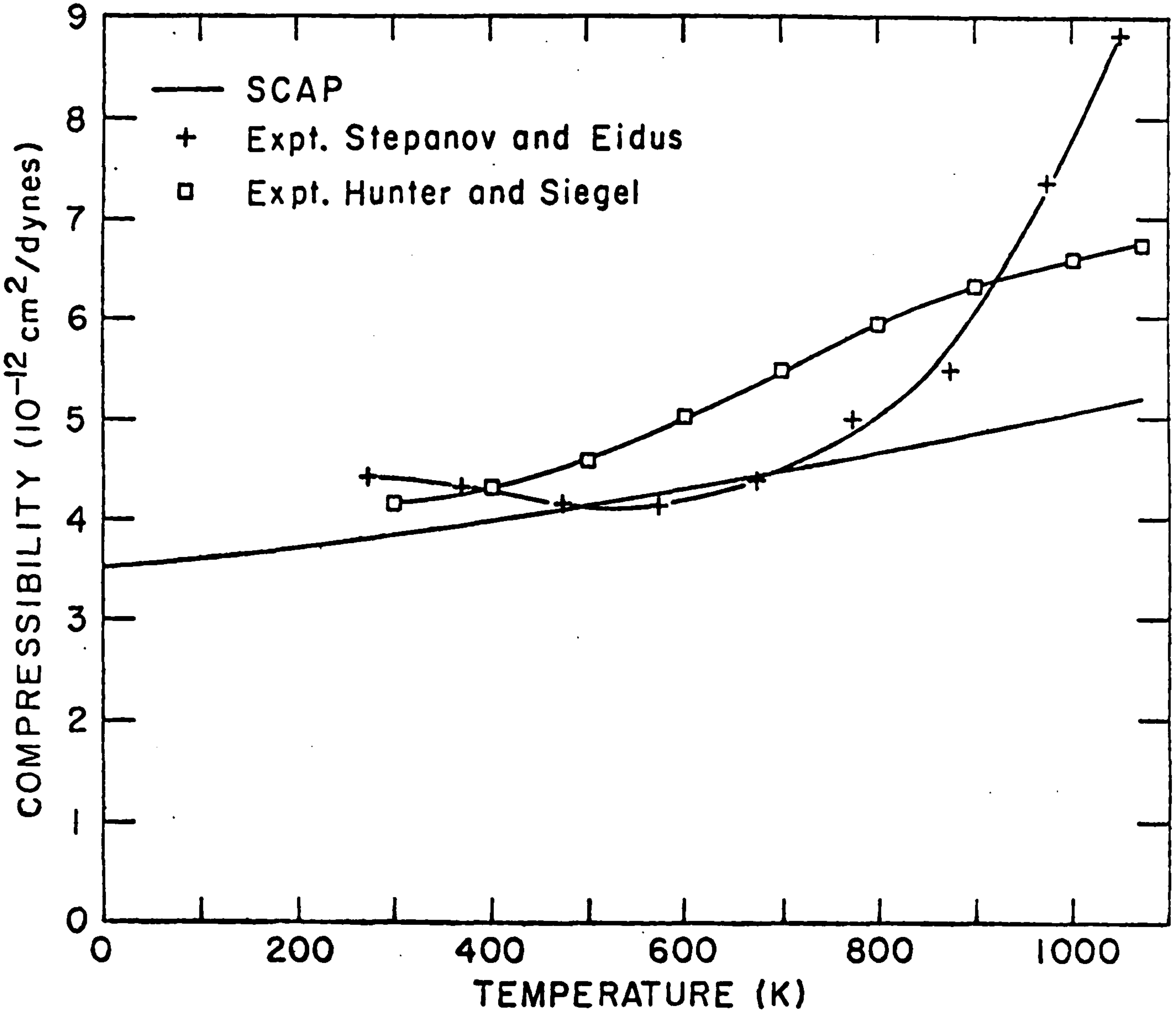

SCAP
+ Expt. Stepanov and Eidus
□ Expt. Hunter and Siegel
COMPRESSIBILITY (10^{-12} cm^2/dynes)
0
1
2
3
4
5
6
7
8
9
TEMPERATURE (K)
0
200
400
600
800
1000

FIGURE 2.4

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