

Multiplying Eq. (26) by U_{ni}^0 , since the vectors U_{ni}^0 are real, and summing over i , making use of the orthogonality of the unperturbed eigenvectors U_{ni}^0 we obtain

$$\lambda_m^1 \delta_{mn} + (\lambda_m^0 - \lambda_n^0) g_n^m = \sum_{i,j} U_{ni}^0 b_{ij}^1 U_{jm}^0 = B_{nm}^1. \quad (27)$$

If $m=n$ we obtain

$$\lambda_m^1 = \sum_{i,j} U_{mi}^0 b_{ij}^1 U_{jm}^0 = B_{mm}^1. \quad (28)$$

Thus, we may write for the perturbed circular frequencies,

$$\omega^2 = \frac{V_0}{V} \omega_0^2 + \frac{e^2}{V} B_{mm}^1. \quad (29)$$

Equations (28) and (29) are valid for degenerate eigenvalues only if $B_{nm}^1 = 0$. In this event the perturbed eigenvalues are again degenerate. For the NaCl crystal the degeneracy is due to the symmetry of the crystal itself. The degeneracy would not be removed by going to higher order terms in the perturbation series. Hence, the above equations may also be used to find the perturbed frequencies for the degenerate case.

For the Kellermann model of NaCl we have

$$B_{mm}^1 = \Delta R \left\{ \frac{1}{m_1} [(U_{1m}^0)^2 + (U_{3m}^0)^2 + (U_{5m}^0)^2] + \frac{1}{m_2} [(U_{2m}^0)^2 + (U_{4m}^0)^2 + (U_{6m}^0)^2] + \frac{2}{(m_1 m_2)^{1/2}} (U_{1m}^0 U_{2m}^0 \cos \pi q_x + U_{3m}^0 U_{4m}^0 \cos \pi q_y + U_{5m}^0 U_{6m}^0 \cos \pi q_z) \right\}, \quad (30)$$

where ΔR is the change in R as defined in Eq. (14):

$$\Delta R = 12r^4/e^2\chi - 12r_0^4/e^2\chi_0, \quad (31)$$

where r and χ are the new lattice constant and compressibility, respectively.

For the modified Kellermann model of NaCl we have

$$B_{mm}^1 = b_{11}^1 \left\{ (U_{1m}^0)^2 + (U_{3m}^0)^2 + (U_{5m}^0)^2 + \frac{m_1}{m_2} [(U_{2m}^0)^2 + (U_{4m}^0)^2 + (U_{6m}^0)^2] + 2[b_{12}^1 U_{1m}^0 U_{2m}^0 + b_{34}^1 U_{3m}^0 U_{4m}^0 + b_{56}^1 U_{5m}^0 U_{6m}^0] \right\}, \quad (32)$$

where

$$b_{11}^1 = \frac{1}{m_1} [R(r) + 2S(r) - R(r_0) - 2S(r_0)], \quad (33)$$

$$R(r_0) = 4B^2 A r_0^3 e^{-Br_0}/e^2, \quad (34)$$

$$S(r_0) = -4BA r_0^2 e^{-Br_0}/e^2,$$

and

$$b_{12}^1 = -\frac{1}{(m_1 m_2)^{1/2}} [(R(r) - R(r_0)) \cos \pi q_x + (S(r) - S(r_0)) (\cos \pi q_y + \cos \pi q_z)], \quad (35)$$

with similar terms for b_{34}^1 and b_{56}^1 .

IV. THE γ_i 'S

For the Kellermann model we obtain

$$\omega^2 = \frac{r_0^3 \omega_0^2}{r^3} + \frac{e^2}{2r^3} \left[\frac{12r^4}{e^2\chi} - \frac{12r_0^4}{e^2\chi_0} \right] \Gamma, \quad (36)$$

where

$$\Gamma = \frac{1}{m_1} [(U_{1m}^0)^2 + (U_{3m}^0)^2 + (U_{5m}^0)^2] + \frac{1}{m_2} [(U_{2m}^0)^2 + (U_{4m}^0)^2 + (U_{6m}^0)^2] + \frac{1}{(m_1 m_2)^{1/2}} (U_{1m}^0 U_{2m}^0 \cos \pi q_x + U_{3m}^0 U_{4m}^0 \cos \pi q_y + U_{5m}^0 U_{6m}^0 \cos \pi q_z). \quad (37)$$

We have then from Eq. (2)

$$\gamma_i = \frac{-V}{2\omega_i^2} \frac{dr}{dV} \frac{d\omega_i^2}{dr}. \quad (38)$$

and

$$\frac{d\omega_i^2}{dr} = \frac{-3r_0\omega_0^2}{r^4} - \frac{3e^2}{2r^4} \left[\frac{12r^4}{e^2\chi} - \frac{12r_0^4}{e^2\chi_0} \right] \Gamma + \frac{e^2}{2r^3} \left[\frac{48r^3}{e^2\chi} - \frac{12r^4}{e^2\chi^2} \left(\frac{\partial\chi}{\partial r} \right)_T \right] \Gamma. \quad (39)$$

Thus, we write for γ_{ik} at $r=r_0$

$$\gamma_{ik} = \frac{1}{2} \left\{ 1 - \frac{2}{\omega_0^2} \left[\frac{4r_0}{\chi_0} - \frac{r_0^2}{\chi_0^2} \left(\frac{\partial\chi}{\partial r} \right)_T \right] \right\} \Gamma. \quad (40)$$

This formula for γ_{ik} can be used in an equation of state and a self-consistent technique developed to get the compressibility, the thermal expansion, and the other quantities of physical interest at different temperatures.

It is of interest to compare this γ_{ik} to Slater's γ_s . Thus, γ_s can be written as

$$\gamma_s = -\frac{1}{2} \frac{d \ln \chi V^{-1/3}}{d \ln V} = -\frac{1}{2} \left\{ 1 - \frac{\chi_0}{3r_0} \left[\frac{4r_0}{\chi_0} - \frac{r_0^2}{\chi_0^2} \left(\frac{\partial\chi}{\partial r} \right)_T \right] \right\}. \quad (41)$$

If we assume that γ_s equals γ_i at some particular frequencies, the condition for equality is

$$2\Gamma/\omega_0^2 = \chi_0/3r_0. \quad (42)$$