

Phonon density of states of an n -component alloy

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Abstract. We have generalized the coherent potential approximation (CPA) of Tripathi and Behera to the case of an n -component alloy. It is seen that the n -component CPA density of states reproduces the binary, ternary quaternary alloys etc when the appropriate limits are adopted.

Keywords. Coherent potential approximation; density of states; Green function; self-energy.

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1. Introduction

In recent years, the theory of excitations in substitutional alloy has been developed substantially to explain the experimental data available from infra-red absorption and Raman scattering. Though many theoretical models as well as the technique of Green function have been used, the best theoretical calculation is possible by the coherent potential approximation (CPA) method (Elliot *et al* 1974; Taylor 1967; Soven 1967). Most of the studies so far using this approach seem to confine to single site CPA (SSCPA) which has many shortcomings. One of them is that it does not consider scattering from clusters of two or more impurities. The importance of accounting these effects would be quit clear if one compares the differences between the calculated density of states (Taylor 1967) and the fine structure appearing in the numerical studies of Payton and Visscher (1967) below a certain critical concentration. There have been many attempts to generalize the SSCPA (Elliot *et al* 1974 and references therein) to take into account the effect of clusters and to include the off-diagonal disorder in order to explain the fine structure appearing in the impurity band. Notable among these attempts are those of Nakamura and Yonezawa (1972), who carried out a numerical study of the effect of pairs, Aiyer *et al* (1969) who carried out calculations for pairs and higher clusters and Foo *et al* (1971) who tried to explain the effect of off-diagonal disorder and the formation of clusters in the lattice vibrational problems. However, these generalizations have proved to be of limited success. There also exist some cellular CPA (CCPA) calculations for diatomic linear chain (Sen and Hartman 1974) as well as a generalization of the SSCPA to ternary alloys (Scarfione 1973). But these calculations are confined to diagonal perturbation only. Nayak (1986) has generalized SSCPA to the ternary case taking into account both diagonal and off-diagonal randomness. However, to the best of our knowledge, no theory exists which considers changes in both mass and force constant in the case of a multicomponent alloy.

In this paper, we have generalized the CPA work of Tripathi and Behera (1974) to an n -component alloy following the line of approach adopted earlier (Nayak and Behera 1982; Nayak 1986). In doing so, we have assumed that the system consists of n impurities, B, C, \dots, N ; where the atoms A, B, C, \dots, N are randomly distributed in the form of $A_{1-C_1-C_2-\dots-C_n}, B_{C_1}, C_{C_2}, \dots, N_{C_n}$ with C_1, C_2, \dots, C_n being the corresponding distribution of fractional concentrations in the host sites of A . The results have been analysed on the basis of the Einstein model and it is found that they reduce exactly to those for other alloys of lower order, when appropriate limits are adopted. In §2 we briefly discuss the theory of the model, §3 gives the theory for n -component alloy with its application and our conclusions in §4.

2. The model theory

The two-component binary alloy model of Tripathi and Behera (1974) considers a mixed crystal $A_{1-C}B_C$ where A is the atom of host crystal having a concentration $(1 - C)$ and B is the solute atom with a concentration C . The Hamiltonian for such a system can be written as

$$H = H_0 + H_1 + H_2, \quad (1)$$

where

$$H_0 = \sum_{l\alpha} \frac{P_\alpha^2(l)}{2M_A} + \frac{1}{2} \sum_{l'l'\alpha\beta} \Phi_{\alpha\beta}(ll') u_\alpha(l) u_\beta(l') \quad (2)$$

$$H_1 = \frac{1}{2} \left(\frac{1}{M_B} - \frac{1}{M_A} \right) \sum_{\alpha, l=1}^n P_\alpha^2(l) \quad (3)$$

and

$$H_2 = \frac{1}{2} \sum_{l\alpha} \sum_{l'\beta} \Delta\Phi_{\alpha\beta}(l, l') u_\alpha(l) u_\beta(l') \quad (4)$$

where

$$\Delta\Phi_{\alpha\beta}(l, l') = \Phi_{\alpha\beta}(l, l') - \Phi_{\alpha\beta}^{(0)}(l, l'). \quad (5)$$

From equations (1) to (5) it is evident that H_0 is the Hamiltonian of the perfect crystal, H_1 is due to the change in mass on introduction of impurities and H_2 is for the changes in force constant as a result of introduction of impurities. In the above equations, the summations over l, l' correspond to the sum over entire lattice, α, β are the cartesian co-ordinates (x, y, z) , U_α and P_α are respectively the displacement and momentum, M_A is the mass of the host atom, $\Phi_{\alpha\beta}^{(0)}$ and $\Phi_{\alpha\beta}$ correspond to the force constants for the host and mixed crystals respectively. The above Hamiltonian can be rewritten in the second quantized notation using the well-known normal mode transformation.

$$u_\alpha(l) = \left(\frac{1}{2NM} \right)^{1/2} \sum_{K_j} \frac{e_\alpha(K_j)}{\sqrt{\omega_{K_j}}} A_{K_j} \exp(iK \cdot R_l) \quad (6a)$$

and

$$P_\alpha(l) = \frac{1}{i} \left(\frac{M}{2N} \right)^{1/2} \sum_{K_j} e_\alpha(K_j) \sqrt{\omega_{K_j}} B_{K_j} \exp(iK \cdot R_l) \quad (6b)$$

where

$$A_{Kj} = a_{Kj} + a_{Kj}^\dagger \quad (7a)$$

and

$$B_{Kj} = a_{Kj} - a_{Kj}^\dagger \quad (7b)$$

a_{Kj} , a_{Kj}^\dagger are the annihilation and creation operators for phonons with wave vector K , branch index j , and frequency ω_{Kj} and $e_\alpha(Kj)$ is the α th component of the polarization vector. With the help of (6a) and (6b) (1) can be written as

$$H = \sum_{K,j} \omega_K (a_{Kj}^\dagger a_{Kj} + \frac{1}{2}) + \sum_{Kq} V(K, q) B_K B_q + \sum_{Kq} W(K, q) A_K A_q \quad (8)$$

where

$$V(Kq) = \frac{\lambda}{4N} \sum_{l=1,\alpha}^n e_\alpha(K) e_\alpha(q) (\omega_K \omega_q)^{1/2} \exp [i(K+q) \cdot R_l] \quad (9)$$

and

$$W(Kq) = \frac{\tau}{4N} \frac{\Phi^{(0)}}{M} \sum_{l=1}^N \sum_{m=1}^n \frac{(e(K) \cdot r_0^{lm})(e(q) \cdot r_0^{lm})}{(\omega_K \omega_q)^{1/2}} \times \exp [i(K+q) \cdot R_0^m] [\exp (iK \cdot r_0^{lm}) - 1] [\exp (iq \cdot r_0^{lm}) - 1] \quad (10)$$

with $K = (K, j)$ and r_0^{lm} as the nearest neighbour lattice separation. λ , τ stand for the mass and force constant change parameter and are defined by

$$\lambda = (M_B - M_A)/M_B \quad (11a)$$

and

$$\tau = (\Phi^{AB} - \Phi^{AA})/\Phi^{AA}, \quad (11b)$$

where Φ^0 and Φ are replaced by Φ^{AA} and Φ^{AB} , respectively.

The model Hamiltonian given by (1) is now solved using various double time Green functions (Zubarev 1960). Since the introduction of force constant mixes up all the possible four Green functions during its solution through equations of motion, the authors, therefore, adopted a 2×2 matrix Green function involving all the functions defined through the operators A and B and this is defined as

$$\hat{D}_{Kq}(t) = \begin{pmatrix} D_{Kq}^{11}(t) & D_{Kq}^{12}(t) \\ D_{Kq}^{21}(t) & D_{Kq}^{22}(t) \end{pmatrix}, \quad (12)$$

where

$$D_{Kq}^{11}(t) = \langle\langle A_K(t); A_q(0) \rangle\rangle, \quad (13a)$$

$$D_{Kq}^{12}(t) = \langle\langle A_K(t); B_q(0) \rangle\rangle, \quad (13b)$$

$$D_{Kq}^{21}(t) = \langle\langle B_K(t); A_q(0) \rangle\rangle, \quad (13c)$$

$$D_{Kq}^{22}(t) = \langle\langle B_K(t); B_q(0) \rangle\rangle. \quad (13d)$$

One can write down the equations of motion for the individual Green function whose Fourier transforms with a little manipulation can be put into a matrix form and is given by

$$\hat{D}_{Kq}(\omega) = \delta_{K,-q} \hat{D}_K^0(\omega) + \hat{D}_K^0(\omega) \sum_P \hat{\chi}(-K, P) \hat{D}_{Pq}(\omega), \quad (14)$$

where

$$\hat{D}_{\mathbf{k}}^{(0)}(\omega) = \frac{1}{\pi(\omega^2 - \omega_{\mathbf{k}}^2)} \begin{pmatrix} \omega_{\mathbf{k}} & -\omega \\ \omega & -\omega_{\mathbf{k}} \end{pmatrix}, \quad (15)$$

and

$$\hat{\chi}(-K, P) = \hat{\Lambda}u(-K)u(P) \sum_{i=1}^n \exp[-i(\mathbf{K} - \mathbf{P}) \cdot \mathbf{R}_i], \quad (16)$$

where

$$\hat{\Lambda} = \begin{pmatrix} \tau & 0 \\ 0 & \lambda \end{pmatrix} \quad (17)$$

is the interaction strength matrix. Thus it is seen that all the quantities entered in (14) are now 2×2 matrices. The configurational averaging of the Green function defined through (14) is performed over impurity sites and the configurationally averaged Green function so obtained is given by

$$\langle \hat{D}_{\mathbf{k}q}(\omega) \rangle = \delta_{\mathbf{k}, -q} [\hat{D}_{\mathbf{k}}^{(0)-1}(\omega) - \hat{M}(\mathbf{K}, \omega)]^{-1}, \quad (18)$$

where $M(\mathbf{K}, \omega)$ is the matrix self-energy which is also in the 2×2 matrix form. The self-consistent value of this self-energy determined through diagrammatic analysis is given by

$$\hat{M}(\omega) = C\hat{\Lambda}[\hat{1} - \hat{D}(\omega)(\hat{\Lambda} - \hat{M}(\omega))]^{-1}, \quad (19)$$

where

$$\begin{aligned} \hat{D}(\omega) &= \sum_{\mathbf{K}} u(\mathbf{K})\hat{D}_{\mathbf{K}}(\omega)u(-\mathbf{K}) \\ &= \sum_{\mathbf{K}} u(\mathbf{K})[\hat{D}_{\mathbf{K}}^{(0)-1}(\omega) - u(\mathbf{K})u(-\mathbf{K})\hat{M}(\omega)]^{-1}u(-\mathbf{K}). \end{aligned} \quad (20)$$

On the basis of the Einstein model equations (19) and (20) are solved which ultimately result in a simple expression (Nayak and Behera 1982) given by

$$\hat{M}(\omega) = C\hat{\Lambda}[\hat{1} - (1 - C)\hat{D}^0(\omega, \omega_0)\hat{\Lambda}]^{-1}. \quad (21)$$

The displacement–displacement Green function (1, 1 element of the matrix Green function) which is associated with the properties of far infra-red absorption is calculated. The poles of this Green function give the impurity modes of vibration.

3. Theory of n -component alloy

Here, we have tried to generalize the above two-component alloy of Tripathi and Behera (1974) to an n -component alloy. In doing so, we have assumed that the atoms B, C etc are randomly distributed with fractional concentrations C_1, C_2 etc respectively on the regular sites of the host atom A . Further, we assume that the concentrations of these impurities are sufficiently low so that no two impurities can come closer to produce an impurity–impurity interaction. Under the above assumptions, we can write the total self-energy to be the sum of the individual self-energy corresponding to each of the impurities, such that each individual self-energy involves the total n -component self-energy. Thus, the self consistent phonon self-energy $\hat{M}_{ab}(\omega)$ for n -component alloy is given by

$$\hat{M}_{ab}(\omega) = \sum_i \hat{M}_{ab}^{(i)}(\omega) \quad \text{where } i = 1, 2, 3 \dots n \quad (22)$$

and

$$\hat{M}_{ab}^{(i)}(\omega) = C_i [\hat{\Gamma} - (\hat{\Lambda}_{ab}^{(i)} - \hat{M}_{ab}(\omega)) \hat{D}_{ab}^0(\omega)]^{-1} \hat{\Lambda}_{ab}^{(i)}. \quad (23)$$

Here each impurity self-energy $\hat{M}_{ab}^{(i)}(\omega)$ involves the total self-energy $\hat{M}_{ab}(\omega)$, a, b are the elements of the 2×2 matrix.

$$\hat{\Lambda}_{ab}^{(i)} = \begin{pmatrix} \tau_i & 0 \\ 0 & \lambda_i \end{pmatrix}. \quad (24)$$

In the light of the Einstein model, the self-consistent equations (20) and (22) are solved following the same procedure adopted in our earlier paper (Nayak and Behera 1982). With a careful handling of matrices and little manipulation, the self-consistent self-energy reduces to the following simple form

$$\hat{M}_{ab}(\omega) = \sum_i C_i \hat{\Lambda}_{ab}^{(i)} [\hat{\Gamma} - (1 - C_i) \hat{D}_{ab}^0(\omega) \hat{\Lambda}_{ab}^{(i)} \omega_0]^{-1} \quad (25)$$

or

$$\hat{M}_{ab}^{(i)} = C_i \hat{\Lambda}_{ab}^{(i)} [\hat{\Gamma} - (1 - C_i) \hat{D}_{ab}^{(i)}(\omega) \hat{\Lambda}_{ab}^{(i)} \omega_0]^{-1}, \quad (26)$$

where ω_0 is the Einstein frequency of the phonon which is the same as the transverse optic phonon frequency (ω_{T0}) of the host. The displacement–displacement Green function, which is the (1, 1) element of the matrix Green function, is calculated by substituting (26) in (20) and the expression so obtained, is given by

$$D_{11}^{(i)}(\omega, \omega_0) = \frac{(\delta_{i1} - M_{22}^{(i)}) \omega_{T0}}{\pi [(\omega \delta_{i1} - \omega_{T0} M_{12}^{(i)})^2 - \omega_{T0}^2 (\delta_{i1} + M_{11}^{(i)}) (\delta_{i2} - M_{22}^{(i)})]}, \quad (27)$$

where

$$D_{11}(\omega, \omega_0) = \sum_i D_{11}^{(i)}(\omega, \omega_0). \quad (28)$$

Equation (27) is further solved to give

$$D_{11}^{(i)}(\omega, \omega_0) = \frac{\omega_{T0} \{ (\omega^2 - \omega_{T0}^2) (\delta_{i1} - C_i \lambda_i) + (\delta_{i1} - C_i) (\lambda_i - \tau_i + \lambda_i \tau_i) \omega_{T0}^2 \}}{\pi (\omega^2 - \omega_{T0}^2) [\omega^2 - \omega_{T0}^2 (1 - \lambda_i) (1 + \tau_i)]}. \quad (29)$$

The density of states for the zero wave vector, which give the infra-red absorption spectra will be proportional to the imaginary part of (28) and is given by

$$\begin{aligned} \varphi(\omega) &= -\frac{1}{\pi} \text{Im } D_{11}(\omega + i\eta, \omega_0) \\ &= \sum_i [(\delta_{i1} - C_i) \omega_0 \delta(\omega^2 - \omega_0^2) \\ &\quad + C_i (1 - \lambda_i) \omega_0 \delta(\omega^2 - \omega_0^2 (1 - \lambda_i) (1 + \tau_i))]. \end{aligned} \quad (30)$$

Thus (30) gives $(n + 1)$ number of δ -absorption peaks. The one at $\omega = \omega_0$ and the rest n number of δ -function peaks appear at $\omega = \omega_0 (1 - \lambda_i)^{1/2} (1 + \tau_i)^{1/2}$ for each impurity. The first peak corresponds to the transverse optic mode frequency of the host and the other frequencies correspond to the impurity modes.

The above expression can be easily reduced to binary, ternary and other alloys by

putting the appropriate limits. Equation (30) will be reduced to binary (Nayak and Behera 1982) if we put $i = 1$ and this gives

$$\begin{aligned} \varphi(\omega) = & [(1 - C_1)\omega_0\delta(\omega^2 - \omega_0^2) \\ & + C_1(1 - \lambda_1)\omega_0\delta(\omega^2 - \omega_0^2(1 - \lambda_1)(1 + \tau_1))] \end{aligned} \quad (31)$$

and for ternary alloy (Nayak 1986) for $i = 2$ where

$$\begin{aligned} \varphi(\omega) = & (1 - C_1 - C_2)\omega_0\delta(\omega^2 - \omega_0^2) \\ & + C_1(1 - \lambda_1)\omega_0\delta[\omega^2 - \omega_0^2(1 - \lambda_1)(1 + \tau_1)] \\ & + C_2(1 - \lambda_2)\omega_0\delta[\omega^2 - \omega_0^2(1 - \lambda_2)(1 + \tau_2)]. \end{aligned} \quad (32)$$

4. Conclusion

Here, we have derived the general expression for the density of states for an n -component alloy. The general expression so obtained gives the impurity modes for different alloys by putting its appropriate limit and agrees well with the observed values. For $i = 1$, it takes the form of a binary alloy (Nayak and Behera 1982) and explains the concentration dependence of some twenty mixed crystals by introducing a phenomenological concentration dependence in the force constant changes. Similarly for $i = 2$, it takes the form of a ternary alloy (Nayak 1986) and successfully explains the observed spectra of $\text{Ga}_{1-x}\text{Al}_x\text{As}_{1-y}\text{P}_y$ (Sen and Lucovsky 1975). Several mixed crystals of complex nature can also be similarly studied. However, there does not seem to be too many reflectivity studies on these complex mixed crystals. As pointed out earlier, there are certain drawbacks which have not been incorporated in the theory. For example the impurity-impurity interaction which plays an important role in the disordered problems is not considered. In reality, as the concentration of impurity atoms increases, it is likely that two or more impurities occupy sites close enough to produce impurity-impurity interactions. As a result, the degeneracy of the single impurity modes will be lifted and split into a number of components depending on the number of atoms in the clusters and thereby the cluster modes such as pair, triplet etc. modes have not been predicted although they have been observed experimentally. However, one can generalize this by taking a proper average over concentration so as to take these effects into account. The latter is under investigation and will be reported separately.

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