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Phonon Spectrum of Ternary Alloys

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Abstract

Recently measurements on the infrared and Raman scattering spectra of several quaternary alloy systems such as $Ga_{1-x}Al_xAs_{1-y}P_y$ have been reported. Depending on the concentration, this system can be thought of as either a GaAs-rich quaternary, where GaAs is the host containing the two kinds of impurity Al and P, or as a GaP-rich quaternary, where GaP is the host and Al and As are two impurities. Thus, the properties of such systems can be simulated by a ternary alloy. The coherent potential approximation (CPA) for ternary alloys proposed by Scarfone (1973) is used to analyse the experimental data, assuming a single Einstein oscillator model for the host crystal. The theory, consisting of both diagonal and off-diagonal randomness, agrees well with the observed values, but fails to predict the observed pair modes.

1. Introduction

The theory of excitation in substitutional alloys has been extensively developed in recent years notably by use of the coherent potential approximation (CPA) and related approaches (Taylor 1967; Soven 1967; Elliot *et al.* 1974, and references therein). Most of the work done in this area has been confined to the single site CPA (SSCPA), which has explained some of the observed properties; however, it has many shortcomings. Firstly, the SSCPA density of states cannot reproduce the structure in the impurity band, seen to be present from the exact computer calculations (Dean 1972), nor can it reproduce the band edges correctly. This is mainly because, being a single site theory, scattering from clusters of impurities is totally neglected. There have been many attempts (Elliot *et al.* 1974) to generalise the SSCPA to take into account clusters, the first for pairs being that by Aiyer *et al.* (1969) and then for n-impurity clusters by Nickel and Krumhansl (1971). However, these generalisations have been only of limited success. There have also been cellular CPA (CCPA) calculations for diatomic linear chains (Sen and Hartman 1974), where density of states as well as electrical susceptibility have been taken into account, and which give good agreement with experiment. All these calculations however have the drawback that they do not include off-diagonal randomness. Again, there have been many attempts (Berk 1970; Blackman *et al.* 1971; Tripathi and Behera 1974; Kaplan and Mostler 1974; Katayama and Kanamori 1978) to include off-diagonal disorder in an approximate way within single site theory. Nayak and Behera (1982) also attempted to include the off-diagonal disorder exactly and, although the calculations were done only in

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the low concentration limit, good agreement with experiment was found. Thus, the SSCPA calculations discussed so far are found to be a good approximation only for binary alloys. There have been attempts to generalise the SSCPA to ternary alloys (Scarfone 1973), but these calculations have been confined to a diagonal perturbation only. No general theory exists for taking into account off-diagonal randomness in the case of a cluster or standard CPA, for either a ternary or multicomponent alloy.

In this paper we give a systematic study of a ternary alloy using the method developed by Tripathi and Behera (1974) and by Nayak and Behera (1982). Tripathi and Behera (1974) proposed a self-consistent theory for phonons in mixed crystals taking into account both mass and force constant changes, while Nayak and Behera (1982) extended this work to study the concentration dependence of mixed crystal modes of vibrations for binary alloys. In the present paper we extend the Nayak–Behera theory to incorporate ternary alloys to explain the optical spectra observed in some quaternary semiconducting alloys such as $Ga_{1-x}Al_xAs_{1-y}P_y$ (Sen and Lucovsky 1975). Here the system is assumed, depending on the concentration, to be either GaAs-rich, where GaAs is the host containing the two kinds of impurity Al or P, or GaP-rich, where GaP is the host with Al and As as the two impurities. Thus, in such systems it is assumed that atoms A, B, C are randomly distributed in the form $A_{1-C_1-C_2}B_{C_1}C_{C_2}$ in regular sites, where C_1 and C_2 are the corresponding distributions of fractional concentration in the host sites of A. The results, thus obtained, are analysed in the Einstein model as given by Scarfone (1973) and found to give the correct density of states with appropriate strength.

Section 2 deals with the model theory of the binary alloy and the phenomenology of the concentration dependence. The model theory for a ternary alloy is given in Section 3, while the calculated results and a comparison with experiment are given in Section 4.

2. Model Theory and Phenomenology of Concentration Dependence

The self-consistent phonon self-energy in the generalised CPA, in the form of a 2×2 matrix and which takes into account changes in the nearest neighbour force constant approximately (Tripathi and Behera 1974), is given by

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

where

$$\hat{D}(\omega) = \sum_k U(k)\,\hat{D}_k(\omega)\,U(-k), \tag{2}$$

$$\hat{\Lambda} = \begin{pmatrix} \tau & 0 \\ 0 & \lambda \end{pmatrix}, \tag{3}$$

$$\hat{D}_k(\omega) = \{\hat{D}_k^{0\,-1}(\omega) - U(k)\,U(-k)\,\hat{M}(\omega)\}^{-1}, \tag{4}$$

$$U(k) = (4N)^{-\frac{1}{2}}\,e_\alpha(k)\,\omega_k^{\frac{1}{2}}\,\exp(\mathrm{i}\,\boldsymbol{k}\,.\,\boldsymbol{R}_l^0), \tag{5a}$$

$$\hat{D}_k^0(\omega) = \{\pi(\omega^2-\omega_k^2)\}^{-1}\begin{pmatrix} \omega_k & -\omega \\ \omega & -\omega_k \end{pmatrix}. \tag{5b}$$

Here $\tau = (\Phi - \Phi^0)/\Phi^0$ is the force constant change parameter, $\lambda = (M' - M)/M'$ is the mass change parameter associated with the impurity atoms, and C is the impurity concentration. In equations (1)–(5), R_l^0, $e_\alpha(k)$, ω_k and N stand for the distance of the impurity atom located at the lth site from the origin, the αth component of the polarisation, the phonon frequency of wavevector k and the total number of atoms respectively. In the Einstein model these equations are solved exactly and the (1, 1) element of the displacement–displacement Green function is evaluated. The poles of these Green functions give the modes which are concentration independent. A phenomenological concentration was attributed to the frequencies through the force constant change parameter. It is found that on fixing these parameters for the one, two and mixed mode system, a reasonably good agreement with the experimental data can be obtained (Nayak and Behera 1982), an idea which is incorporated in the following section to explain the optical spectra observed in some quaternary alloys.

3. Theory of Ternary Alloys

The self-consistent phonon self-energy for a ternary alloy is assumed to be the sum of two self-energies corresponding to both impurities and is given by

$$\hat{M}(\omega) = \sum_i \hat{M}_i(\omega) \quad \text{for} \quad i = 1, 2, \tag{6}$$

where

$$\hat{M}_i(\omega) = C_i \hat{\Lambda}_i [\hat{1} - \hat{D}(\omega)\{\hat{\Lambda}_i - \hat{M}(\omega)\}]^{-1}. \tag{7}$$

Here the τ_i and λ_i are given explicitly as per the prescription, where $\tau_1 = (\Phi_{AB} - \Phi_{AA})/\Phi_{AA}$ and $\tau_2 = (\Phi_{AC} - \Phi_{AA})/\Phi_{AA}$ are the nearest neighbour force constant change parameters and $\lambda_1 = (M_B - M_A)/M_B$ and $\lambda_2 = (M_C - M_A)/M_C$ are the impurity mass parameters associated with impurity atoms B and C respectively.

Rewriting equation (1) as

$$\hat{M}(\omega) = C[\hat{1} - \{\hat{\Lambda} - \hat{M}(\omega)\}\hat{D}(\omega)]^{-1}\hat{\Lambda}, \tag{8}$$

one can write equation (6) as

$$\begin{aligned} \hat{M}(\omega) = {} & C_1[\hat{1} - \{\hat{\Lambda}_1 - \hat{M}(\omega)\}\hat{D}(\omega)]^{-1}\hat{\Lambda}_1 \\ & + C_2[\hat{1} - \{\hat{\Lambda}_2 - \hat{M}(\omega)\}\hat{D}(\omega)]^{-1}\hat{\Lambda}_2, \end{aligned} \tag{9}$$

which gives the self-consistent value of $\hat{M}(\omega)$ as

$$\begin{aligned} \hat{M}(\omega) = {} & \omega_0^{-1}\hat{D}_0^{-1}(\omega,\omega_0)\{\hat{1} - \omega_0\hat{D}_0(\omega,\omega_0)\hat{\Lambda}_2\}^{-1}[C_1 \\ & \times\{\hat{1} - \omega_0\hat{D}_0(\omega,\omega_0)\hat{\Lambda}_2\}\omega_0\hat{D}_0(\omega,\omega_0)\hat{\Lambda}_1 + C_2\omega_0 \\ & \times\hat{D}_0(\omega,\omega_0)\hat{\Lambda}_2\{\hat{1} - \omega_0\hat{D}_0(\omega,\omega_0)\hat{\Lambda}_1\}][\hat{1} - (1 - C_1) \\ & \times\hat{D}_0(\omega,\omega_0)\omega_0\hat{\Lambda}_1 - (1 - C_2)\omega_0\hat{D}_0(\omega,\omega_0)\hat{\Lambda}_2 \\ & - (1 - C_1 - C_2)\omega_0^2\hat{D}_0(\omega,\omega_0)\hat{\Lambda}_2\hat{D}_0(\omega,\omega_0)\hat{\Lambda}_1\}^{-1} \\ & \times\{\hat{1} - \omega_0\hat{D}_0(\omega,\omega_0)\hat{\Lambda}_2\}, \end{aligned} \tag{10}$$

where

$$\hat{D}_0(\omega, \omega_0) = \omega_0\{\pi(\omega^2-\omega_0^2)\}^{-\frac{1}{2}}\begin{pmatrix}\omega_0 & -\omega \\ \omega & -\omega_0\end{pmatrix}, \tag{11}$$

and ω_0 is the Einstein frequency of the phonon to be identified later with transverse optic phonon frequency ω_{TO} of the host.

If we assume that the second impurity is absent, i.e. $C_2 = \lambda_2 = 0$, then equation (10) reduces to exactly the self-consistent self-energy equation for a single impurity in a binary alloy (Nayak and Behera 1982). The displacement–displacement Green function is calculated by substituting equation (10) in (4), to give

$$D^{11}(\omega, \omega_0) = \omega_0(P+Q)/R, \tag{12}$$

where

$$\begin{aligned} P = {} & (\omega^2-\omega_0^2)[(\omega^2-\omega_0^2)(1-\lambda_1-\lambda_2)-\omega_0^2(1-\lambda_1) \\ & \times(1-\lambda_2)\{(1-C_1)\tau_1+(1-C_2)\tau_2\}+\omega^2\{(1-C_1)\lambda_1 \\ & +(1-C_2)\lambda_2\}-\lambda_1\lambda_2\,\omega_0^2], \end{aligned} \tag{13a}$$

$$\begin{aligned} Q = {} & (1-C_1-C_2)[\omega_0^4(1-\lambda_1)(1-\lambda_2)\tau_1\,\tau_2+\omega^2\omega_0^2\lambda_1\lambda_2 \\ & \times(\tau_1+\tau_2)-\omega^2\omega_0^2(\lambda_1\,\tau_2+\lambda_2\,\tau_1+\omega^2\omega_0^2\lambda_1\lambda_2], \end{aligned} \tag{13b}$$

$$\begin{aligned} R = {} & (\omega^2-\omega_0^2)\{\omega^2-\omega_0^2(1-\lambda_1)(1+\tau_1)\} \\ & \times\{\omega^2-\omega_0^2(1-\lambda_2)(1+\tau_2)\}. \end{aligned} \tag{13c}$$

The frequencies of the vibrational modes are given by the poles of equation (12):

$$\omega^2 = \omega_0^2, \tag{14a}$$

$$= \omega_0^2(1-\lambda_1)(1+\tau_1), \tag{14b}$$

$$= \omega_0^2(1-\lambda_2)(1+\tau_2). \tag{14c}$$

The frequency given by (14a) is the transverse optic mode frequency for the host, while (14b) and (14c) are for the impurity local and gap modes. These frequencies are independent of concentration. However, we follow a similar procedure as in our earlier paper (Nayak and Behera 1982) for the concentration dependence through the force constant change parameter. Here τ and τ' are two such parameters at the two end members, which are fitted to the experimental values of the local (gap) and transverse optic frequencies for $C = 0$ and 1 for their determination. To state the prescription we write (14b) or (14c) as

$$\omega = \omega_0(1-\lambda)^{\frac{1}{2}}\{1+(1-C)\tau+C\tau'\}^{\frac{1}{2}}, \tag{15}$$

without subscripts. Once τ and τ' are obtained by fitting for the observed local or gap modes at $C = 0$ and for the transverse optic mode at $C = 1$, one can calculate the frequencies of the mode of vibration at any desired concentration.

The density of states for zero wavevector, which gives the infrared absorption spectrum, is proportional to the imaginary part of equation (12) and given by

$$\begin{aligned}\rho(\omega) &= -\pi^{-1}\mathrm{Im}\,D^{11}(\omega+\mathrm{i}\eta,\omega_0)\\ &= (1-C_1-C_2)\omega_0\,\delta(\omega^2-\omega_0^2)\\ &\quad + C_1(1-\lambda_1)\omega_0\,\delta(\omega^2-\omega_0^2(1-\lambda_1)(1+\tau_1))\\ &\quad + C_2(1-\lambda_2)\omega_0\,\delta(\omega^2-\omega_0^2(1-\lambda_2)(1+\tau_2)).\end{aligned} \tag{16}$$

Equation (16) coincides with that by Scarfone (1973) for $\tau = 0$. We find three δ-function absorption peaks with strengths $1-C_1-C_2$, $C_1(1-\lambda_1)$ and $C_2(1-\lambda_2)$. As the concentration increases the impurity strength increases, while the absorption of the first peak (i.e. the optic mode frequency) decreases, as observed in experiment. However, the strength of the impurity modes for a given concentration is enhanced by the factor $1-\lambda = M/M'$ for the local mode when $M' < M$, and is suppressed for gap modes when $M' > M$. This explains the observed impurity modes in the case of $\mathrm{Ga}_{1-x}\mathrm{Al}_x\mathrm{As}_{1-y}\mathrm{P}_y$ (Sen and Lucovsky 1975).

Table 1. Calculated and experimental impurity mode frequencies (in cm^{-1}) for the GaAlAsP system

System	Transverse optic mode	Impurity modes Calculated	Impurity modes Experimental[A]
GaAs: Al, P	260	360·5	≈350
		341·6	
GaP: Al, As	360	421·9	435
		269·0	270

[A] Sen and Lucovsky (1975).

4. Results and Discussion

In Table 1 we give the calculated impurity mode frequencies and compare them with the observed values for the $\mathrm{Ga}_{1-x}\mathrm{Al}_x\mathrm{As}_{1-y}\mathrm{P}_y$ system (Sen and Lucovsky 1975). The observed spectra of this system is for two different concentrations such as $\mathrm{Ga}_{0\cdot96}\mathrm{Al}_{0\cdot04}\mathrm{As}_{0\cdot88}\mathrm{P}_{0\cdot12}$ and $\mathrm{Ga}_{0\cdot92}\mathrm{Al}_{0\cdot08}\mathrm{As}_{0\cdot16}\mathrm{P}_{0\cdot84}$. The former is a GaAs-rich quaternary and we assume the system to be a GaAs host containing Al and P impurities; similarly, the latter is assumed to be a GaP host containing Al and As impurities. Again, these have been compared with their corresponding binary alloys $\mathrm{GaAs}_{0\cdot94}\mathrm{P}_{0\cdot06}$ ($\mathrm{GaAs}_{1-C}\mathrm{P}_C$), $\mathrm{Ga}_{0\cdot8}\mathrm{Al}_{0\cdot2}\mathrm{As}$ ($\mathrm{Ga}_{1-C}\mathrm{Al}_C\mathrm{As}$) and $\mathrm{GaAs}_{0\cdot25}\mathrm{P}_{0\cdot75}$ ($\mathrm{GaAs}_C\mathrm{P}_{1-C}$), $\mathrm{Ga}_{0\cdot8}\mathrm{Al}_{0\cdot2}\mathrm{P}$ ($\mathrm{Ga}_{1-C}\mathrm{Al}_C\mathrm{P}$) respectively. Considering first the GaAs-rich system, we see in the spectra a peak at 260 cm^{-1} dominant in all three alloys which is definitely due to the GaAs vibration of the host crystal. A broad peak near 350 cm^{-1} in the quaternary overlaps the local mode features observed both in $\mathrm{GaAs}_{1-C}\mathrm{P}_C$ and $\mathrm{Ga}_{1-C}\mathrm{Al}_C\mathrm{As}$, corresponding to the single impurity modes. A peak at 420 cm^{-1}, which is observed only in the quaternary, corresponds to the Al–P pair mode vibration. The calculated values for the impurity modes for Al and P are found to be 360·5 cm^{-1} and 341·6 cm^{-1} respectively. Therefore, on comparison it is observed that the broad peak occurring at 350 cm^{-1} is simply a merging of these two single impurity peaks. However, we failed to predict the Al–P pair impurity mode as observed in experiment. Similarly for the second system, we see single impurity peaks at 435 cm^{-1} for $\text{Ga}_{1-C}\text{Al}_C\text{P}$ and at 270 cm^{-1} for $\text{GaAs}_C\text{P}_{1-C}$, both of which are again present in the spectra of the GaP-rich quaternary. The calculated values of these single impurity modes are found to be at $421{\cdot}9\ \text{cm}^{-1}$ for $\text{Ga}_{1-C}\text{Al}_C\text{P}$ and $269{\cdot}0\ \text{cm}^{-1}$ for $\text{GaAs}_C\text{P}_{1-C}$, in excellent agreement with experiment. We fail to predict the pair impurity mode seen only for the quaternary system. Thus, from the above analysis, we find that the single impurity modes present in the ternary alloy give quantitative agreement with experiment.

5. Conclusions

We have attempted to explain the single impurity frequencies of the given ternary alloy system starting from the Einstein model analysis of the generalised CPA result by Tripathi and Behera (1974). In order to find the impurity mode at a given concentration, we introduced the concentration dependence through the force constant change parameter τ by demanding that it follow a virtual crystal-like behaviour. After determining the force constant change parameter by fitting to the behaviour at the end members, the impurity mode vibration of the alloy of desired concentration is calculated. Comparison of the calculated and observed values shows excellent agreement. However, we fail to predict the pair impurity modes such as Al–P and Al–As vibrations in the case of GaAs-rich and GaP-rich quaternaries respectively. This is a drawback of the present theory because at finite concentration it is quite likely that two or more impurities occupy sites close enough to produce impurity–impurity interaction. 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 cluster. However, the theory of Tripathi and Behera (1974) from which this extension is made excludes the inclusion of pair impurities. Again, since an impurity pair mode as identified from the characteristic concentration dependence of the strength of absorption has a quadratic dependence on impurity concentration, one can generalise the above theory by proper averaging over concentration to take such an effect into account. This study is in progress.

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