

## Persistence and Amalgamation Types in Optical Spectra of Mixed Crystals

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The optical spectra of substitutional mixed crystal of the type  $AB_pC_{1-p}$  can be classified into two types, persistence and amalgamation types ( $p$ - and  $a$ -type). In the former, two structures corresponding to the two constituent substances do persist. In the latter, they are amalgamated in a single one. The exact criterion for the  $p$ -type behavior is given for the isotopic mixed crystal, Frenkel exciton model and Rosenstock-Nowell model in connection with the Saxon-Hutner theorem. The criterion for the  $a$ -type behavior is numerically investigated for the one-dimensional model of mixed crystals. The result is compared with the infrared experiments of various mixed crystals. Possible failure of the Saxon-Hutner theorem is pointed out in the non-isotopic mixed crystal. The importance of the change of optical band edges with concentration of constituents is emphasized for analyzing the nature of the force field.

### §1. Introduction

As early as in 1928 Krüger, Reinkober and Koch-Holm reported that the infrared spectrum of mixed crystals of alkali halides including NaCl + KCl, KCl + RbCl and KCl + TlCl contains only one reflection maximum, the frequency of which shifts gradually with concentration of constituents.<sup>1)</sup> Similar behaviors were also observed, for instance, in infrared spectrum of mixed crystals  $\text{NaNO}_3 + \text{KNO}_3$ <sup>2)</sup> and Raman spectrum of  $p\text{-C}_6\text{H}_4\text{Cl}_2 + p\text{-C}_6\text{H}_4\text{Br}_2$ .<sup>3)</sup> We call such behaviors of mixed crystals amalgamation type ( $a$ -type), since here the different constituents seem to produce an amalgamated effect.

In order to interpret this type of behavior Matossi<sup>4)</sup> calculated the normal modes of a unique periodic linear chain of the type ...ABACABAC... corresponding to the equal concentration of B and C, and pointed out that only one vibrational mode is strongly active enough to give a reflection band. Following this idea of the model of a unique periodic chain for mixed crystals, Aggarwal and Saksena<sup>5)</sup> fitted the normal frequency giving the maximum optical activity of such a periodic chain to the observed frequency shift for several concentration of the two constituents.

On the other hand, recent experiments on mixed crystals  $\text{GaAs}_x\text{P}_{1-x}$

( $0 < x < 1$ ) show that there exist two maxima in the infrared reflection spectrum and as  $x$  changes the intensities rather than the frequencies of these maxima change gradually.<sup>6),7)</sup> We call this type of behavior persistence type ( $p$ -type), because in the mixed crystal the two maxima characteristic of the two pure crystals GaAs and GaP persist to exist. It is interesting to note that whereas both mixed crystals GaAs <sub>$x$</sub> P <sub>$1-x$</sub>  and GaAs <sub>$x$</sub> Sb <sub>$1-x$</sub>  have the same crystal structure (zinc-blende-type), the infrared reflection spectrum of the latter is of  $a$ -type.\*)

Chen, Shockley and Pearson<sup>7)</sup> tried to interpret their data on GaAs <sub>$x$</sub> P <sub>$1-x$</sub>  by assuming that anions of like species vibrate in phase and with identical amplitudes against the cations which also vibrate together as a rigid unit. They concluded that the next-nearest neighbor interaction is very important to fit the theory to the experiment.

Verleur and Barker<sup>6)</sup> introduced an elaborate model for GaAs <sub>$x$</sub> P <sub>$1-x$</sub>  in which they gave 5 coordinates to each atomic species to distinguish the displacements of the same atomic species placed in the different environments. Taking also the effect of clustering of the atoms of the same species into account, they could excellently reproduce the experimental reflectivity by the calculation.

Although experiments seem to be fitted by all these theories, since the parameters were determined by the calculation based on intuitive assumptions it is not very clear to what extent one can attach the significance to these parameters. Moreover, they did not discuss the cause of the difference of the two types, amalgamation and persistence.

The two types are also observed in the exciton spectra of mixed crystals. Onodera and Toyozawa<sup>8)</sup> basing on the Frenkel exciton model of mixed crystals have introduced the approximation method which is exact in several limiting cases for obtaining both state density and optical density of the exciton band. The most important parameter which determines to which type any mixed crystal belongs is the ratio of the difference  $A$  of the energies of the two individual components to the width  $W$  of the energy band. They have approximately shown how the system passes from  $a$ -type over to  $p$ -type as the value of  $A/W$  increases.

On the other hand, one of the present authors (Matsuda) has given the exact sufficient condition for the Rosenstock-Newell model of harmonic oscillators for mixed crystals to be of  $p$ -type.<sup>10)</sup> This is a kind of so-called Saxon-Hutner theorem.<sup>11)</sup> In this model if the optical bands (frequency bands formed by optical modes) of the pure crystals AB and AC have no frequency

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\*)  $a$ -type and  $p$ -type are also referred to as "one-mode" and "two-mode" behaviors. The definition is qualitative rather than quantitative, so that the demarcation of the two types of behaviors cannot so sharply be defined as the existence or non-existence of a band gap. See reference 8).

in common, then the common band gap in the pure crystals remains as a band gap in the mixed crystal  $AB_xC_{1-x}$ , hence the mixed crystal behaves as  $p$ -type. This sufficient condition is also a necessary condition for the existence of the relevant band gap for random mixed crystals. Because in the mixed crystal there is a non-zero probability to have a part in which the atomic arrangement is almost either of pure crystal AB or AC, so that if the above condition fails then there can be no relevant band gap. The above condition has been generalized by Hori to include long-range interaction in the harmonic oscillation of isotopically mixed crystals by a so-called evaporation method.<sup>12)</sup>

In this paper we derive in §2 the exact criterion of the existence of band gaps in mixed crystals both for the Frenkel exciton and isotopically disordered harmonic oscillators in a unified way. Although this criterion is a sufficient condition for  $p$ -type behavior, it is not always a necessary condition, since without band gap the mixed crystal may behave still as  $p$ -type. In order to investigate this point we calculate in §3 the optical density of the one-dimensional model of mixed crystals by the method of ensemble average of periodic systems (MEAPS) developed by Matsuda and others.<sup>13)-15)</sup>

In §4 we compare our results with infrared experimental data. It is to be noted that the theory is based either on the Rosenstock-Newell model or on the isotopically substituted mixed crystals, although the criterion is given in a form independent of the further specification of the model. If the experimental result would not conform to the theory, it should directly indicate the failure of the above model for the mixed crystal. Thus we may obtain an insight to the type of the model representing the essential feature of the mixed crystal. We also compare our results with those previously obtained by other authors.

## §2. Criterion for the existence of band gaps

The Hamiltonian describing the Frenkel exciton in binary mixed crystal has the form

$$\mathcal{H} = \sum_n \epsilon_n a_n^* a_n + \sum_m \sum_n t_{mn} a_m^* a_n, \quad (2.1)$$

where  $a_n^*$  and  $a_n$  represent the excitation and de-excitation operators on the atom situated at the lattice point  $n$ , and satisfy boson commutation relations. The atomic excitation energy  $\epsilon_n$  takes on either  $\epsilon_A$  or  $\epsilon_B$  according as the atom located at  $n$  is A atom or B atom. The coefficient  $t_{mn}$  stands for the transfer energy of excitation between the atoms at  $m$  and  $n$ . Onodera and Toyozawa<sup>8)</sup> assumed that  $t_{mn}$  depends only on the relative position of the lattice points  $m$  and  $n$ , and does not depend on the types of the atoms. Here we generalize it and assume that  $t_{mn}$  may depend on the types of the atoms located at  $m$  and  $n$  but does not depend on the types of atoms located

at the other lattice points than  $m$  and  $n$ .

Let  $\sigma(n)$  denote the type of the atom located at  $n$ . Then according to our assumption Eq. (2.1) may be written as

$$\mathcal{H} = \sum_m \sum_n v_{mn}(\sigma(m), \sigma(n)) a_m^* a_n, \tag{2.2}$$

$$v_{mn}(\sigma(m), \sigma(n)) = v_{nm}(\sigma(n), \sigma(m)). \tag{2.3}$$

Therefore, the eigenvalue of  $\mathcal{H}$  for a single exciton is nothing but the eigenvalue of an Hermitian (in the present case symmetric) matrix

$$\mathbf{H} = \{v_{ms}(\sigma(m), \sigma(s))\}. \tag{2.4}$$

This type of the matrix is just what we have in the isotopically disordered harmonic oscillator. Indeed, the dynamical matrix whose eigenvalue is the squared normal frequency is  $\{\phi_{ij}/\sqrt{m_i m_j}\}$ , where  $\phi_{ij}$  is the force constant related to the displacement  $u_i$  and  $u_j$  and  $m_i$  is the mass of an atom making the displacement  $u_i$ . Here the  $(ij)$  element of the matrix can be assumed to depend only on the masses of atoms making the displacement  $u_i$  and  $u_j$ .

When the matrix has the type as represented by (2.4), which may be called isotopic type, we can directly use the following theorem in order to obtain the criterion:

Let  $E(k)$  be the  $k$ th eigenvalue of the  $N$ -dimensional Hermitian matrix  $\mathbf{H}$ , where the eigenvalues are ordered in a sequence of decreasing values,  $E(1)$  being the greatest eigenvalue,  $E(2)$  the next, and so on. Let  $\tilde{E}(k)$  be the  $k$ th eigenvalue of the  $N$ -dimensional Hermitian matrix  $\tilde{\mathbf{H}}$  which is obtained from  $\mathbf{H}$  by changing only the elements of  $r$  columns and corresponding  $r$  rows in what way so ever. Then, we have the inequality:

$$E(k+r) \leq \tilde{E}(k) \leq E(k-r). \tag{2.5}$$

The proof of this theorem is given in the Appendix.

Suppose that our system represented by (2.4) has  $N_A$  A-atoms and  $N_B$  B-atoms. Let now  $E(k)$  be the  $k$ -th eigenvalue of  $\mathbf{H}$  of our system. By changing  $N_A$  A-atoms into B-atoms we obtain the system (pure B-system) without A-atom. Let the  $k$ -th eigenvalue of the pure B-system be  $E_B(k)$ . By changing  $N_B$  B-atoms into A-atoms we obtain the system (pure A-system) without B-atoms. Let the  $k$ -th eigenvalue of the pure A-system be  $E_A(k)$ .

Using (2.5) we obtain

$$E(k) \geq E_A(k + N_B), \tag{2.6}$$

$$E(k+1) \leq E_B(k+1 - N_A). \tag{2.6'}$$

If there exists non-negative integer  $p$  such that

$$E_A(p + N_A + N_B) > E_B(p + 1), \tag{2.7}$$

then from (2.6) and (2.6') we have

$$E(p + N_A) \geq E_A(p + N_A + N_B) > E_B(p + 1) \geq E(p + N_A + 1), \tag{2.8}$$

so that there exists a gap including the interval  $(E_B(p + 1), E_A(p + N_A + N_B))$ .

By taking  $p=0$ , in the case of the Frenkel exciton model the condition (2.7) is just the criterion that the bands of pure A- and pure B-system does not overlap in energy. In the case of harmonic oscillation of mixed crystals of the type  $AB_xC_{1-x}$  in which only A occupies one set of alternate sites (anion site or cation site), the condition (2.7) is just the criterion that the optical bands of pure AB crystal and pure AC crystal does not overlap in frequency. The inequality (2.8) shows that when (2.7) holds  $N_A$  A-atoms and  $N_B$  B-atoms persist to contribute to the spectrum of their respective energy (frequency) region. This situation is suitable to be called persistence type.

If we re-define  $A$  and  $W$  such that  $A$  is the difference of the center of the relevant bands of two pure crystals and  $W$  is the mean of the width of the two bands, then from the above discussion  $A/W > 1$  is the criterion for the band gap in the mixed crystals. If  $A/W > 1$  the system surely behaves as  $p$ -type. In order to see how the system behaves for  $A/W < 1$  and somewhat in detail for  $A/W > 1$ , we study some one-dimensional examples in the following sections.

### §3. One-dimensional model for infrared absorption of mixed crystals

In order to investigate the infrared spectrum of mixed crystals of the type  $AB_xC_{1-x}$ , we consider a one-dimensional harmonic oscillator model the equations of motion of which are given by

$$m_j \ddot{u}_j = K(u_{j+1} + u_{j-1} - 2u_j), \tag{3.1}$$

$$m_j = \begin{cases} M_A & \text{for } j = 2s, \\ M_B \text{ or } M_C & \text{for } j = 2s + 1 \text{ (s: integer)}. \end{cases}$$

Here,  $m_j$  and  $u_j$  are the mass and the displacement of the  $j$ -th atom and  $K$  is the force constant. Putting the time factor as  $\exp(i\omega t)$ , Eq. (3.1) becomes

$$-\omega^2 m_j u_j = K(u_{j+1} + u_{j-1} - 2u_j). \tag{3.2}$$

We assume that the optical absorption strength of the  $\mu$ -th normal mode is proportional to the square of the dipole moment defined by

$$d_\mu = \sum_j (-1)^j u_{\mu,j}, \tag{3.3}$$

Here,  $u_{\mu,j}$  is the displacement of the  $j$ -th atom in the  $\mu$ -th normal mode with

frequency  $\omega_\mu$ , the normalization of  $u_{\mu,j}$  being given by

$$\sum_j m_j u_{\mu,j}^2 = 1. \tag{3.4}$$

The optical density is then given by the following expression:

$$f(\omega^2) = \sum_\mu d_\mu^2 \delta(\omega^2 - \omega_\mu^2). \tag{3.5}$$

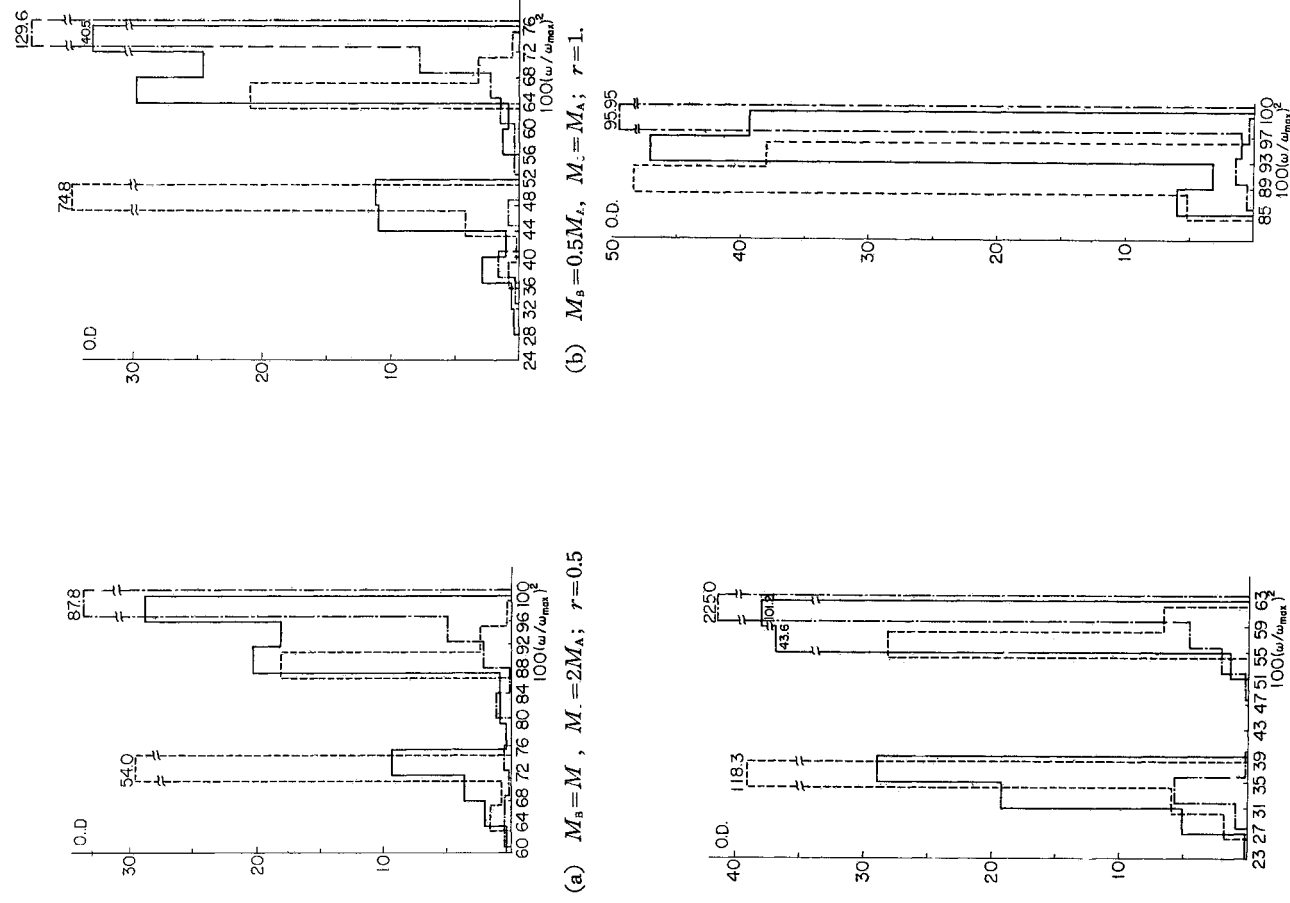
One of the present authors and others have developed the approximation method, which we call MEAPS, for obtaining coarse-grained physical quantities of aperiodic systems by an ensemble average of those of periodic systems.<sup>19-16</sup> The ensemble is a set of periodic chains each of which is constructed by the repetition of a pattern of each consecutive  $p$  atoms in a given aperiodic chain. The degree of coarse-graining may be represented by the width of the histogram. The larger the width of the histogram is chosen, the closer is the approximation by MEAPS to the true histogram of the aperiodic chain. The larger the value of the integer  $p$  is chosen, the smaller can be taken the width of the histogram without spoiling the approximation. It was numerically shown that by a suitable choice of the width of the histogram, MEAPS with  $p=8$  already gives good results for the frequency spectrum of aperiodic chains.<sup>14)</sup> The width of histogram may be so chosen that histogram is stable against the increment of the value of  $p$ .

We directly apply MEAPS to obtain the optical density. In this case we need only calculate the normal mode corresponding to the number  $k=0$  of periodic chains because of the selection rule. The maximum value of  $p$  taken in this calculation is 16.

Thus calculated histograms of optical densities for (a)  $M_B=M_A$ ,  $M_G=2M_A$ , (b)  $M_B=0.5M_A$ ,  $M_G=M_A$  and (c)  $M_B=0.25M_A$ ,  $M_G=0.5M_A$  are shown in Fig. 1. Here  $\omega_{\max}$  is the maximum frequency when the mass of all atoms are equal to the lightest mass. In Fig. 2 we illustrate some examples of the dependence of histograms on the change of size of unit cells.

It can easily be shown that the corresponding value of  $A/W$  is (a)  $1/3$ , (b) 1, (c) 2, respectively. As expected from the theory cases (b) and (c) belong to  $p$ -type. However, even in the case (a), where there can be no relevant band gap, Fig. 1 (a) indicates the  $p$ -type behavior of the optical density. The difference arises from the fact that only a few number of levels are strongly optically active, whereas all the levels equally contribute to the state density.

In order to see what value of  $A/W$  may produce  $a$ -type behavior we show in Fig. 1 (d) the histogram of optical density for  $M_B=M_A$ ,  $M_G=1.2M_A$ , for which we have  $A/W=1/11$ . We find the  $a$ -type behavior here. The result suggests that for  $A/W>1$  the system certainly is of  $p$ -type. For  $A/W<1$  the system is not necessarily of  $a$ -type. Even for  $A/W\approx 1/3$  the



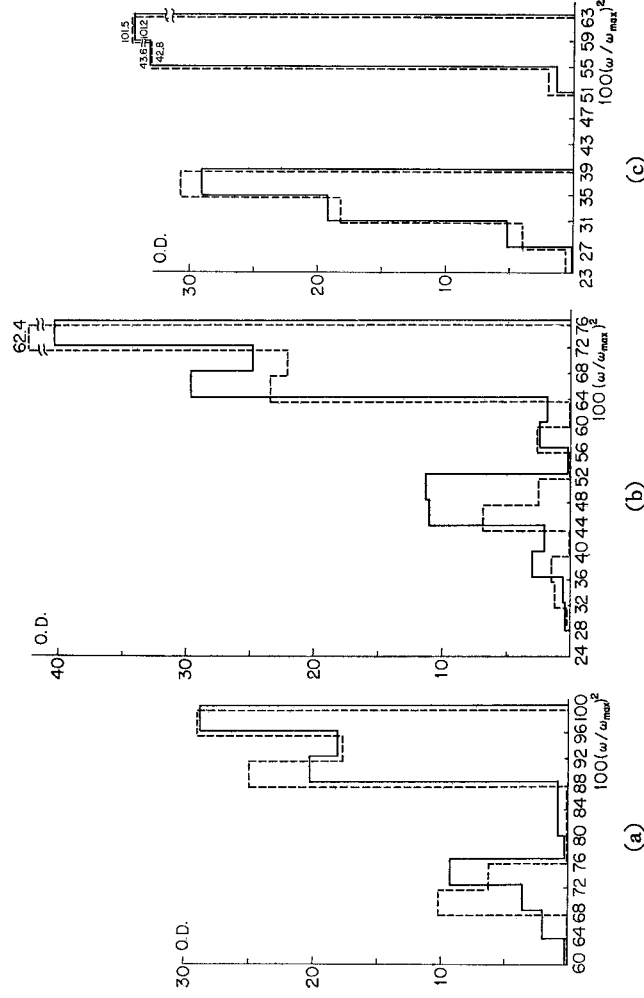


Fig. 2. Dependence of obtained histograms on the change of size of unit cells for the optical density of one-dimensional models of mixed crystals  $AB_{0.5}C_{0.5}$ , where (a) (b) (c) correspond to those of Fig. 1.

—: unit cell of 16 atoms, .....: unit cell of 8 atoms.

system may still behave as  $p$ -type. It can be of the order of  $1/10$  for the value of  $A/W$  that the  $a$ -type behavior sets in.

This situation may be connected with the dimensionality of the model. In one dimension if one atom is substituted by its lighter isotope localized mode always appears. Therefore, one may always expect two structures at least when the concentration of the lighter isotope is low. In three dimension this is not always the case. Therefore, one might expect in actual mixed crystals that the smaller value of  $A/W$  would give a  $a$ -type behavior than obtained here and the criterion of  $a$ -type might be close to the criterion for the appearance of localized modes. This point, however, is yet to be examined.

#### §4. Comparison with infrared experiments

It is shown in §2 that if atoms B and C are isotopes, that is, the difference of B and C is only in their masses, then the Saxon-Hutner theorem holds and the infrared spectrum of the mixed crystal  $AB_xC_{1-x}$  is of  $p$ -type when  $A/W \gg 1$ , irrespective of the nature of force constants. When the difference of force constants is also involved between B and C, then the Hamiltonian of the mixed crystal can no longer be written as (2.2), so that



the condition  $d/W \gg 1$  may not generally be a criterion for  $p$ -type. In order to see the qualitative feature of such a case, let us consider the so-called Rosenstock-Newell model<sup>16)</sup> of the simple cubic lattice for mixed crystals.

In this model the different components of the displacements of atoms are dynamically independent of each other, and the equation for one component, say  $x$ -component of the displacement  $u(\mathbf{n})$  of the atom at lattice point  $\mathbf{n}(n_1, n_2, n_3)$  is

$$-m(\sigma(\mathbf{n}))\omega^2 u(\mathbf{n}) = \sum_{\mathbf{e}} \kappa(\sigma(\mathbf{n}), \sigma(\mathbf{n}+\mathbf{e})) \{u(\mathbf{n}+\mathbf{e}) - u(\mathbf{n})\} + \sum_{\mathbf{e}'} \kappa'(\sigma(\mathbf{n}), \sigma(\mathbf{n}+\mathbf{e}')) \{u(\mathbf{n}+\mathbf{e}') - u(\mathbf{n})\}, \quad (4.1)$$

where  $n_1, n_2, n_3$  are integers. Here  $m(\sigma(\mathbf{n}))$  is a mass of an atom occupying the lattice point  $\mathbf{n}$ ; the species of the atom at  $\mathbf{n}$  is denoted by  $\sigma(\mathbf{n})$ . The force constants  $\kappa$  and  $\kappa'$  are central and non-central force constants. The vectors  $\mathbf{e}$  represent two unit vectors in the  $x$ -direction and  $\mathbf{e}'$  represent four unit vectors in the  $y$ - and  $z$ -direction.

For mixed crystal  $AB_2C_{1-x}$  we may assume that

$$\sigma(\mathbf{n}) = \begin{cases} 0 & \text{when } n_1+n_2+n_3 \text{ is even (E-sublattice),} \\ +1 & \text{for B-atom} \\ -1 & \text{for C-atom} \end{cases} \quad \text{when } n_1+n_2+n_3 \text{ is odd (O-sublattice),} \quad (4.2)$$

$$m(0) = M_A, \quad m(1) = M_B, \quad m(-1) = M_C; \quad (4.3)$$

$$\begin{aligned} \kappa(\sigma, \sigma') &= \kappa(\sigma', \sigma), \quad \kappa'(\sigma, \sigma') = \kappa'(\sigma', \sigma); \\ \kappa(0, 1) &= \kappa_B, \quad \kappa(0, -1) = \kappa_C, \end{aligned} \quad (4.4)$$

$$\kappa'(0, 1) = \kappa'_B, \quad \kappa'(0, -1) = \kappa'_C.$$

It can easily be shown in this model that for pure crystal AB and AC the optical band is the squared frequency interval  $[K_B \text{Max}(M_A^{-1}, M_B^{-1}), K_B(M_A^{-1} + M_B^{-1})]$ , and  $[K_C \text{Max}(M_A^{-1}, M_C^{-1}), K_C(M_A^{-1} + M_C^{-1})]$ , respectively, where  $K_B \equiv 2(\kappa_B + 2\kappa'_B)$  ( $\beta = B$  or C). Suppose that the two bands do not overlap in their frequency, or simultaneously that  $d/W \gg 1$ . Then we may assume without loss of generality that

$$K_C(M_A^{-1} + M_C^{-1}) < K_B \text{Max}(M_A^{-1}, M_B^{-1}). \quad (4.5)$$

If B and C are isotopes, that is,  $K_C = K_B$ , then in order to have the inequality (4.5),

$$M_A > M_B, \quad (4.6)$$

$$M_C > M_B; \quad (4.6')$$

and

$$r \equiv |M_B^{-1} - M_G^{-1}| / M_A^{-1} > 1. \tag{4.7}$$

Conversely, if the inequality (4.7) holds then the optical bands of the pure crystal AB and AC do not overlap in their frequency. Therefore, for Rosenstock-Newell-type isotopic mixed crystals if  $A/W > 1$ , so that if (4.7) holds then the mixed crystal should be of  $p$ -type.

In Table I we list the  $r$ -values for various mixed crystals together with the experimental verification of  $p$ - or  $a$ -type. It is interesting to note that experimentally  $r \approx 1$  seems to be a demarcation of  $p$ -type and  $a$ -type although these mixed crystals are not isotopic and the theory does not necessarily predict  $a$ -type behavior for  $r < 1$ .

Table I. AB<sub>B</sub>C<sub>1-x</sub>-type mixed crystal.

A ( $M_A^{-1}$ )	B ( $M_B^{-1}$ )	C ( $M_C^{-1}$ )	$r \equiv \frac{ M_B^{-1} - M_C^{-1} }{M_A^{-1}}$	type <sup>a)</sup>
Cl ( $\frac{1}{35.5} = 0.0282$ )	K ( $\frac{1}{39.1} = 0.0256$ )	Na ( $\frac{1}{23.0} = 0.0435$ )	0.635	$a$
Cl	K (0.0256)	Rb ( $\frac{1}{85.5} = 0.0117$ )	0.493	$a$
Cl	K (0.0256)	Tl ( $\frac{1}{204.4} = 0.0049$ )	0.735	$a$
O ( $\frac{1}{16.0} = 0.0625$ )	Ni ( $\frac{1}{58.7} = 0.0171$ )	Co ( $\frac{1}{58.9} = 0.0170$ )	0.002	$a$
F <sub>2</sub> ( $\frac{1}{19.2} = 0.0263$ )	Sr ( $\frac{1}{87.6} = 0.0114$ )	Ca ( $\frac{1}{40.1} = 0.0250$ )	0.517	$a$
F <sub>2</sub>	Sr (0.0114)	Ba ( $\frac{1}{137.4} = 0.0073$ )	0.156	$a$
S ( $\frac{1}{32.1} = 0.0312$ )	Cd ( $\frac{1}{112.4} = 0.0089$ )	Zn ( $\frac{1}{65.4} = 0.0153$ )	0.205	$a$
Ga ( $\frac{1}{69.7} = 0.0143$ )	As ( $\frac{1}{74.9} = 0.0133$ )	Sb ( $\frac{1}{121.8} = 0.0082$ )	0.357	$a$ or $p$
Ga	As (0.0133)	P ( $\frac{1}{31.0} = 0.0322$ )	1.32	$p$
Cd (0.0089)	S (0.0312)	Se ( $\frac{1}{79.0} = 0.0127$ )	2.08	$p$
In ( $\frac{1}{114.8} = 0.0087$ )	As (0.0133)	P (0.0322)	2.17	$p$
As (0.0133)	In (0.0087)	Ga (0.0143)	0.421	
Zn (0.0153)	S (0.0312)	Se (0.0127)	1.21	$p$

However, even if  $K_G \neq K_B$  so long as  $M_A$  is sufficiently larger than  $M_B$  such that the condition

$$K_B M_A^{-1} < K_G (M_A^{-1} + M_G^{-1}) < K_B M_B^{-1} \tag{4.8}$$

holds, the inequality  $A/W > 1$  still leads to the  $p$ -type behavior. Indeed,

remembering the technique of islandization introduced in reference 10) we at once note that the middle member of (4.8) is the highest frequency of the free island with C-atom at the center, which is lower than that of the free island with B-atom at the center but is higher than any other frequencies of the latter island, because of the first inequality in (4.8). The right side of (4.8) is the highest frequency of the fixed island with B-atom at the center. Therefore, in the mixed crystal  $N_B$  normal modes have the squared frequency not less than  $K_B M_B^{-1}$  whereas all the other normal modes must have the frequency not higher than  $K_C(M_A^{-1} + M_C^{-1})$ , so that in the mixed crystal the squared frequency interval  $[K_C(M_A^{-1} + M_C^{-1}), K_B M_B^{-1}]$  remains as a band gap in the mixed crystal leading to the  $p$ -type behavior.

Now let us consider the opposite extreme case, that is,  $M_A \ll M_B$ , and  $M_A \ll M_C$ . In this case for all the normal modes of the optical band of the crystal AB and AC the displacements of B- and C atoms are very small compared to those of A-atoms. Even in mixed crystals we may consider that for  $N_A$  normal modes B- and C-atoms are almost fixed at the lattice points. Therefore, in the mixed crystal there must be normal modes whose squared frequencies are close to  $\{2\kappa_C + \nu_B(\kappa_B - \kappa_C) + 4\kappa_C' + \nu_B'(\kappa_B' - \kappa_C')\} M_A^{-1}$ , where  $\nu_B = 0, 1, 2$  and  $\nu_B' = 0, 1, 2, 3, 4$ , corresponding various types of islands with A-atom at the center. Since these frequencies almost lie in the frequency interval between the upper edge and lower edge of the optical band of the pure crystal AC and AB, it indicates the failure of Saxon-Hutner theorem<sup>11)</sup> and possible  $\alpha$ -type behavior. This consideration of the failure of the Saxon-Hutner theorem can also be applicable to any other model than the Rosenstock-Newell model. It must be emphasized that the difference of force constants involving B- and C-atom plus the lightness of mass of A-atom is truly responsible for the failure of the Saxon-Hutner theorem; the range of the force field is rather irrelevant here.

Recently, Lucovsky et al. gave<sup>8)</sup> an excellent critical review on optical lattice modes of mixed polar crystals, in which they said, "It is tempting to try to tie the occurrence of one- $(\alpha$ -type) or two-mode ( $p$ -type) behavior to overlap of end number (pure AB or AC crystals) reststrahlen bands. Here we note that the occurrence of frequency overlap usually implies the existence of one mode behavior, however, the lack of frequency overlap is not always a clear indication of two-mode behavior". This is reasonable because the reststrahlen band only extends from the transverse optical to the longitudinal optical frequencies so that the non-overlap of the reststrahlen bands does not necessarily indicate the non-overlap of the end member optical bands as a whole.

Before conclusion let us compare our results of numerical calculation with the observed reflectivity<sup>9)</sup> of [mixed crystal GaAs, P<sub>1- $\nu$</sub> , shown in Fig. 3. As indicated in Table I the masses of Ga and As are nearly equal while the mass of P is about their half. This roughly corresponds to the case shown

in Fig. 1 (b), which is the histogram for the intensity of infrared absorption of one-dimensional mixed crystal  $AB_xC_{1-x}$  with  $M_B = 0.5M_A$  and  $M_C = M_A$ . Although we cannot expect any quantitative agreement between theory and experiment, since reflectivity and absorption intensity are different physical quantities, the qualitative aspects of the concentration de-

pendence agrees fairly well. As  $x=1-y$  increases the peak in the high frequency band shifts to the higher frequency side while the peak in the low frequency band shifts to the lower frequency side. The ratio of the frequencies of the two peaks is also of the right order of magnitude. In view of such agreements with nearest-neighbor interaction model, the importance of the inclusion of the second neighbor interaction as pointed out by Chen et al.<sup>17</sup> is of doubtful significance. The discrepancy may be due to the inadequacy of their assumption in the calculation rather than that of the nearest-neighbor interaction model. This indicates that here the careful calculation of the model is necessary before we draw any conclusion about the model from the experiment.

On the other hand, the ratio of atomic masses in the case of Fig. 1 (a) roughly corresponds to that in the mixed crystal  $KCl+RbCl$ . However, the observed reststrahlen band<sup>18</sup> is of  $a$ -type and quite different from Fig. 1 (a). Whether this is mainly due to the failure of the assumption of isotopic mixed crystal or due to the failure of the simple one-dimensional representation of the system is yet to be examined.

As we have remarked in the preceding sections the demarcation of  $a$ -type and  $p$ -type cannot be clearly defined. Moreover, optical spectra are rather complicated quantities depending on the charge distribution as well as force fields. On the other hand, the persistence and non-persistence of the band gap related to the Saxon-Hutner theorem is the phenomena closely connected with the difference of force fields related to B- and C-atoms. It is expected then that the study of the latter, including the change of optical band edges with concentration of constituents will give us rather direct informations about the nature of the force fields in the crystal.

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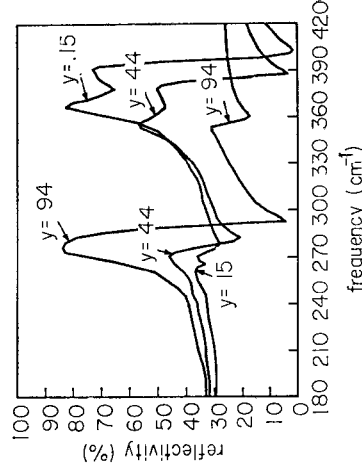


Fig. 3. Reflectivity spectra of three mixed crystals  $GaAs_xP_{1-x}$  ( $y=0.15$ ,  $y=0.44$ ,  $y=0.94$ ).<sup>19</sup>

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This paper is dedicated to Professor M. Kobayasi on the occasion of his sixtieth birthday.

**Appendix (Proof of (2.5))**

*Modification theorem of the Hermitian form*

Let  $\mathcal{H}$  and  $\tilde{\mathcal{H}}$  be Hermitian forms in  $N$  variables  $x_j$  ( $j=1, 2, \dots, N$ ) which are related by the equation

$$\tilde{\mathcal{H}} = \mathcal{H} + \sum_{h=1}^r (X_h Y_h + \bar{X}_h \bar{Y}_h). \tag{A.1}$$

Here  $X_h$  and  $Y_h$  are linear forms in  $N$  variables  $x_j$ ;  $\bar{X}_h$  and  $\bar{Y}_h$  are their complex conjugates. Let  $E(n)$  and  $\tilde{E}(n)$  be the  $n$ -th eigenvalue of  $\mathcal{H}$  and  $\tilde{\mathcal{H}}$ , the eigenvalues being labelled in a sequence of decreasing values such that  $E(n) \geq E(n+1)$  and  $\tilde{E}(n) \geq \tilde{E}(n+1)$ . Then we have the inequality

$$\tilde{E}(n-s) \geq E(n) \geq \tilde{E}(n+s). \tag{A.2}$$

By choosing  $X_h = x_h$  and  $s=r$ , (A.2) leads to (2.5).

**Proof:** First of all we note that the maximum value which the Hermitian form  $\mathcal{H}$  assumes under the condition

$$\sum_{i=1}^N |x_i|^2 = 1 \tag{A.2}$$

and

$$\sum_{i=1}^N C_{hi} x_i = 0, \quad (h=1, 2, \dots, n-1) \tag{A.3}$$

is the function of the set of constants  $C_{hi}$ , and the eigenvalue  $E(n)$  is the minimum of the maximum value for the set  $\{C_{hi}\}$ .<sup>17)</sup> Now apply the  $s$  fixed constraints

$$X_h = 0 \quad (h=1, 2, \dots, s) \tag{A.4}$$

and obtain from  $\mathcal{H}$  at least the  $(N-s)$ -dimensional Hermitian form  $\mathcal{H}'$  by eliminating at most  $s$  variables by (A.4). Let  $E'(n)$  be the  $n$ -th eigenvalue of  $\mathcal{H}'$ . Then the above minimum-maximum property tells us that

$$E(n) \geq E'(n) \geq E(n+s). \tag{A.5}$$

Here, the first inequality is the consequence of the imposition of the condition (A.4) besides (A.3) for  $E'(n)$ , and the second inequality is

because the  $s$  conditions are fixed constraints (A.4) among  $n+s$  conditions for  $E'(n)$ .

If we let  $\tilde{E}'(n)$  be the  $n$ -th eigenvalue of the Hermitian form  $\tilde{\mathcal{H}}$  obtained from  $\tilde{\mathcal{H}}$  by eliminating at most  $s$  variables by (A.4), then similarly one obtains

$$\tilde{E}(n) \geq \tilde{E}'(n) \geq \tilde{E}(n+s). \tag{A.6}$$

However, because of (A.4)  $\mathcal{H}'$  and  $\tilde{\mathcal{H}}$  must be identical. Therefore, we obtain from (A.5) and (A.6) the relation

$$\tilde{E}(n-s) \geq \tilde{E}'(n-s) = E'(n-s) \geq E(n) \geq E'(n) = \tilde{E}'(n) \geq \tilde{E}(n+s), \tag{A.7}$$

which proves our assertion.

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