

The localised modes due to P defects in cadmium telluride

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Abstract. Dutt and Spitzer experimentally observed the localised vibrational modes related to the phosphorus defects in CdTe and reported that P would go either to substitutional or interstitial site. In this paper we have theoretically investigated the P defect behaviour in CdTe for those two possible sites by Green's function technique and we believe from our calculations that P goes interstitially rather than substitutionally.

Keywords. localised vibrational modes; substitutional modes; interstitial modes; Green's function technique; cadmium telluride.

1. Introduction

Although a number of papers appeared on the vibrational studies of disordered solids and defect crystals, the II-VI compounds did not receive adequate attention until 1974. After the review of Barker and Sievers (1975), these compounds were studied both experimentally and theoretically and most of the studies to date involved iso-electronic substitutions in these compounds. Hayes and Spray (1969) measured the infrared absorption of CdTe doped with Be and in this case the fundamental local mode was at 391 cm^{-1} at 4°K . Meanwhile Sennet *et al* (1969), in addition, found a resonant mode at 61 cm^{-1} which they explained using the Green's function method.

Recently Dutt and Spitzer (1977a) measured the infrared localised vibrational modes (LVM) in CdTe when defects like P, Al, In and Ga are substituted. They reported two major P defect centres, an acceptor with a T_a symmetry and an electrically inactive P complex having trigonal symmetry. Their measurements of double doped CdTe showed LVM absorption suggesting the presence of the isolated acceptors and P impurity pairs.

It is generally known that the group V impurities behave as acceptors in II-VI compounds although the nature of the defects and the self compensation mechanism are not that clear. But phosphorus is known to exhibit both electropositive and electronegative character in forming the compounds (Apple 1959). It is thus possible that P is an amphoteric impurity in CdTe. Dutt and Spitzer (1977a) predicted that the observed self compensation could arise in a number of alternate ways (i) by different P centres compensating themselves; *a priori* one expects P on a Te site P_{Te} to be a single acceptor, P on an interstitial site P_i ; a multiple donor (ii) by some of the defects forming neutral or chemically inactive associates (iii) by native defects with or without complexing with P acceptor centres.

From symmetry considerations, an isolated substitutional or an interstitial P atom in II-VI compounds, both have the same T_d point symmetry and hence from LVM observations alone it is rather difficult to isolate these two possibilities since in either case we expect a triply degenerate localised modes. Further P, being an amphoteric impurity, can replace either Cd or Te substitutionally and also can occupy interstitial site surrounded by either Cd or Te as first neighbours. Thus to explore all the possibilities, some theoretical investigations are also simultaneously desirable apart from experimental measurements, and with this in mind we have investigated theoretically all these possibilities using Green's function technique. Further, we have also investigated the impurity pair problem associated with the additive impurities of Ga, In and Al.

2. Theory

Cadmium telluride has the zinc blende structure. Therefore, the Cd, Te as well as the two common types of interstitial sites are all tetrahedrally coordinated with a T_d point group symmetry. If P is located at any of these sites one would expect each type of defect to give rise to a triply degenerate vibrational absorption band in the infrared.

We employ the general theory of impurities to work out the impurity modes both at substitutional and interstitial sites.

2.1 Substitutional studies

When a substitutional impurity atom is introduced into the crystal, the equation of motion becomes

$$(L - \partial L) U = 0, \quad (1)$$

where L is the force constant matrix of perfect crystal and ∂L is the perturbation brought about by the impurity. The elements of the matrix ∂L are

$$\partial L_{\alpha\beta} \begin{pmatrix} l & l' \\ k & k' \end{pmatrix} = -\epsilon M_k \omega^2 \partial_{ll'} \partial_{\alpha\beta} \partial_{kk'} + \Delta \phi_{\alpha\beta} \begin{pmatrix} l & l' \\ k & k' \end{pmatrix},$$

where ϵ is the mass defect parameter $\epsilon = (M_h - M_d)/M_h$ and M_k is the mass of the k th atom; M_h is the mass of the host atom and M_d is that of the defect atom.

$$\phi_{\alpha\beta} \begin{pmatrix} l & l' \\ k & k' \end{pmatrix}$$

represents the force in the α -direction on the atom $\begin{pmatrix} l \\ k \end{pmatrix}$ when the atom $\begin{pmatrix} l' \\ k' \end{pmatrix}$ undergoes unit displacement along the β direction.

∂L has the dimensionality $3m$ where m is the number of atoms interacting with the impurity including it. G is the inverse of L and it can be shown to be equal to

$$\frac{1}{N(M_k M_{k'})^{1/2}} \sum_{qj} \frac{e_\alpha(k|qj) e_\beta^*(k|qj)}{\omega^2 - \omega_j^2(q)} \times \exp \left[2\pi i \bar{q} \cdot \bar{r} \begin{pmatrix} l & l' \\ k & k' \end{pmatrix} \right],$$

where $e_a(k|qj)$ is the a th component of the eigen vector corresponding to the k th atom for $\omega_j(q)$, the eigen frequency. \bar{q} is the phonon vector and j is the branch index (G is known as the Green's functions of the perfect lattice).

Following the method of Maradudin *et al* (1971) we find that the condition to give all the perturbed modes is

$$|I - g\partial l| = 0,$$

where g and ∂l are the partitioned parts of the matrices G and ∂L in the defect space and have the order of $(3m \times 3m)$.

In all determination of impurity modes, both the real and imaginary parts of the function $G_{a\beta} \begin{pmatrix} l & l \\ k & k \end{pmatrix}; \omega^2$ are found to be useful. For LVM calculations, however, we encounter only the real part of the Green's functions.

2.2 Application to CdTe

As is known, CdTe is tetrahedrally bonded crystal and the position of the atoms is given in figure 1.

As a first approximation, the contribution from the second neighbours is neglected. It is found when Te is substituted with phosphorous the symmetry did not get altered. *i.e.* it retained the T_d symmetry.

When Te is taken as the origin, we have four Cd neighbours and so the defect space will be of dimension (15×15) and the Green's function matrix for the host lattice in the defect space will also be (15×15) .

One can make use of group theoretical arguments to block diagonalise the g and ∂l matrices. To facilitate block diagonalisation of the matrix, we have to find a matrix U which partitions $g\partial l$ by the process $(U^+ | g\partial l | U)$. The U matrix can be worked out from the symmetry coordinates of the normal modes. With that U matrix, block diagonalisation of g and ∂l matrices was separately carried out.

The symmetry coordinates for this symmetry are available from the work of Brice (1965).

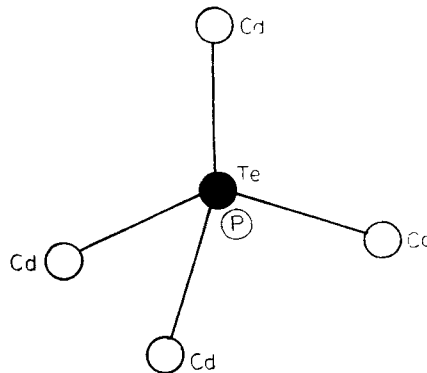


Figure 1. Isolated substitutional case with Te at origin and Cd as first neighbours; phosphorus is substituted at Te site.

The (15×15) matrix will reduce into blocks in the following representations.

$$\Gamma_{15} = A_1 + E + F_1 + 3F_2,$$

$$A_1 \rightarrow (1 \times 1) \text{ matrix}$$

$$E \rightarrow (2 \times 2) \text{ matrix}$$

$$F_1 \rightarrow (3 \times 3) \text{ matrix}$$

$$F_2 \rightarrow (3 \times 3) \text{ matrix}$$

The blocks are given in Appendix 1.

The position of the atoms and the definition of various Green's functions are given below

No.	Atom	Position
1	Te	0 0 0
2	Cd	$\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$
3	Cd	$\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$
4	Cd	$\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$
5	Cd	$\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$

The Green's functions are

$$g_{xx} \begin{pmatrix} 0 & 0 \\ \text{Te} & \text{Te} \end{pmatrix} = B; \quad g_{xx} \begin{pmatrix} 0 & 0 \\ \text{Cd} & \text{Cd} \end{pmatrix} = A_1;$$

$$g_{xx} \begin{pmatrix} 0 & \frac{1}{2} \frac{1}{2} \frac{1}{2} \\ \text{Cd} & \text{Te} \end{pmatrix} = Y; \quad g_{xy} \begin{pmatrix} 0 & \frac{1}{2} \frac{1}{2} \frac{1}{2} \\ \text{Cd} & \text{Te} \end{pmatrix} = Z;$$

$$g_{xx} \begin{pmatrix} 0 & 110 \\ \text{Cd} & \text{Cd} \end{pmatrix} = P_1; \quad g_{zz} \begin{pmatrix} 0 & 110 \\ \text{Cd} & \text{Cd} \end{pmatrix} = Q_1;$$

$$g_{xy} \begin{pmatrix} 0 & 110 \\ \text{Cd} & \text{Cd} \end{pmatrix} = R_1; \quad g_{xz} \begin{pmatrix} 0 & 110 \\ \text{Cd} & \text{Cd} \end{pmatrix} = S_1.$$

The Green's functions are evaluated for CdTe in a modified rigid ion approximations, using the parameters given by Plumble and Vandevyuer (1976). This modified rigid ion model though simple indeed reproduces the dispersion relations fairly well and hence can be used as a good model for interpolating frequencies at the different mesh points of the Brillouin zone. More refined lattice dynamical model when available in future would not give widely different values for these Green's functions since these functions are obtained as average over the number of wavevector points in the entire Brillouin zone. Hence, the Green's functions are now available from $X = 0.01$ to 2.99 where $X = \omega/\omega_{\max}$ and ω is the vibrational frequency and ω_{\max} is the maximum allowed frequency for this host crystal.

Since our main interest is on the LVM, we concentrate on the Green's functions after $X = 1.00$.

To start with, let us consider P at Te site, which is at the origin. The proper Green's functions are fed in the computer along with a prescribed value of change in force constant (i.e. ΔA and ΔB which are change in force constants in terms of

Kellerman's constants A and B , between the host lattice and defect lattice). The force constant is actually varied from 10% to 100% and corresponding to each value, $|I-g \partial I|$ is worked out for nearly 50 values of X . The value of X which gives $|I-g \partial I|$ zero was picked corresponding to each ΔA value and a graph is plotted with this X versus ΔA . The X value corresponding to the experimentally suggested LVM value is taken and was used to fit the corresponding ΔA value in the F_1 representation.

The value of ΔA obtained from the graph is 4.4451×10^4 dynes/cm. The ΔA obtained corresponds to increase in force constant when a P atom is substituted in the place of Te.

The molecular model was also worked out (Ramachandran and Haridasan 1977) to study this unusual behaviour. We found that there was an increase in force constant for the case of P_{Te} . The actual change obtained was $\Delta A = 4.6066 \times 10^4$ dynes/cm which is very close to our presently calculated value. Dutt and Spitzer (1977a) also predicted an increase in force constant in their experimental results. Thus, one sees an unusual increase of about 74% in the nearest neighbour force constant, even when a lighter impurity like P is substituted in Te site.

Past experience in other solids indicate that when a lighter atom is substituted, only a reduction in force constant is expected (Fritz *et al* 1965), unlike in the present situation. One is therefore tempted to eliminate the possibility of P going into Te site substitutionally.

The second configuration, *i.e.* Cd at origin and Te as neighbours, can also be tried, because both sites are possible and we have worked out the ΔA for this case also; *i.e.* when Cd is replaced by phosphorus. Here again, an increase in force constant was seen and for the same reason mentioned with regard to P at Te site, it is felt that one should eliminate this possibility as well.

3. Isolated interstitial—Theory

Brice (1965) gave a basic theory when an atom occupies an interstitial site with particular reference to Si and Ge.

It is to be understood that by the introduction of an interstitial the number of degrees of freedom of the system is increased by three. Brice introduced a new Green's function of the host crystal, combined with that of the interstitial, as

$$g = g(\text{interstitial}) \oplus g(\text{lattice})$$

where $g_{\alpha\beta}(\text{interstitial})$ is a (3×3) matrix given by $(m \omega^2)^{-1} \partial_{\alpha\beta}$ and $g(\text{lattice})$ is defined as usual (equation (1)).

The interstitial is taken to be at the origin and if the interstitial interacts with m host atoms around, the g and ∂I matrix would be of dimension $3(m+1) \times 3(m+1)$. So, it is now brought in the line of regular dynamics of crystals with substitutional defects.

Brice (1965) assumed that the coupling between the interstitial and the host atoms is weak and here when g matrix is written, it has two blocks, a (3×3) block for the interstitial and a $(3m \times 3m)$ block for the host atoms surrounding it. There is no matrix element in g , coupling the interstitial and any of the host atoms. In ∂I ,

the first three rows and first three columns contain the actual interaction of the interstitial with the surrounding atoms. The remaining part of the ∂I matrix however would represent the force constant changes at the host atom sites due to the interstitial defect.

For the CdTe lattice, the interstitial site is at $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ for the configuration described earlier. A phosphorus atom occupying the interstitial site is surrounded either by 4 Cd atoms as immediate neighbours or 4 Te atoms as first neighbours. It is assumed that charge compensation is achieved by some other foreign atoms situated much farther away from the P site.

If the interstitial P is taken as the origin then the positions of other atoms are given below.

(for the first configuration with Cd as neighbours)

No.	Atom	Position (in units of $a = 2r_0$)
1	P	0 0 0
2	Cd	$\bar{1} \frac{1}{2} \frac{1}{2}$
3	Cd	$\frac{1}{2} \bar{1} \frac{1}{2}$
4	Cd	$\frac{1}{2} \frac{1}{2} \bar{1}$
5	Cd	$\bar{1} \bar{1} \bar{1}$
6	Te	$\bar{1} 0 0$
7	Te	0 $\bar{1} 0$
8	Te	0 0 $\bar{1}$
9	Te	1 0 0
10	Te	0 1 0
11	Te	0 0 1

We can look for both localised modes as well as resonant modes, but as we explained earlier, we do not go into detail for the resonant modes, as there are no experimental results yet available.

If we consider the first neighbours alone g and ∂I matrix will have dimension (15×15) whereas when second neighbours are included it will be (33×33) . To begin with, we consider the second neighbours also and construct the g and ∂I matrix.

When an atom occupies an interstitial site in a crystal, then one has to consider the lattice relaxation also *i.e.* the nearest neighbour Cd atoms and the next nearest neighbour Te atom are displaced from their normal positions and due to this mechanical relaxation, assume new equilibrium positions. Norgett (1974) developed a programme to work out the new position, to estimate the relaxation, by a self-consistent calculations with lattice potential as input. Haridasan *et al* (1979) worked out this part when they studied the impurity modes due to interstitial in CaF_2 . Such relaxation calculations are possible only when the interatomic pair potential is well known. But in CdTe the analytic form of such a potential is less clear at the moment and hence relaxation calculation for these crystals would have to wait till such potentials become available. However the effect of relaxation is to alter the nearest neighbour force constants and in our present calculations we try to fit this force

constant from the experimental LVM frequencies. Thus the effect of relaxation is indirectly brought out in our theory through these force constant changes.

Now let us construct the g matrix for the present case. Again at the interstitial site, we have the T_d symmetry.

The symmetry coordinates have been obtained for the tetrahedron plus interstitial by Brice (1965). The set of coordinates spans the representation Γ_e of the group T_d given by

$$\Gamma_e = 2A_1 + 2E + 3F_1 + 6F_2.$$

The block diagonalisation of the (33×33) matrix will now give

(2×2) matrix for A_1 block,

(2×2) matrix for E block,

(3×3) matrix for F_1 block,

(6×6) matrix for F_2 block.

Looking at the (33×33) defect space, one finds that g matrix contains the following independent lattice Green's functions, which are labelled below for convenience of discussion.

$$\begin{array}{ll} g_{xx} \begin{pmatrix} 0 & 0 \\ \text{Cd} & \text{Cd} \end{pmatrix} = A_1, & g_{xx} \begin{pmatrix} 0 & \frac{1}{2} \frac{1}{2} \frac{1}{2} \\ \text{Cd} & \text{Te} \end{pmatrix} = Y, \\ g_{xx} \begin{pmatrix} 0 & 0 \\ \text{Te} & \text{Te} \end{pmatrix} = B, & g_{xy} \begin{pmatrix} 0 & \frac{1}{2} \frac{1}{2} \frac{1}{2} \\ \text{Cd} & \text{Te} \end{pmatrix} = Z, \\ g_{xx} \begin{pmatrix} 0 & 110 \\ \text{Cd} & \text{Cd} \end{pmatrix} = P_1, & g_{xx} \begin{pmatrix} 0 & \frac{3}{2} \frac{1}{2} \bar{1} \\ \text{Cd} & \text{Te} \end{pmatrix} = C_1, \\ g_{xy} \begin{pmatrix} 0 & 110 \\ \text{Cd} & \text{Cd} \end{pmatrix} = R_1, & g_{xy} \begin{pmatrix} 0 & \frac{3}{2} \frac{1}{2} \bar{1} \\ \text{Cd} & \text{Te} \end{pmatrix} = D_1, \\ g_{xz} \begin{pmatrix} 0 & 110 \\ \text{Cd} & \text{Cd} \end{pmatrix} = S_1, & g_{yx} \begin{pmatrix} 0 & \frac{3}{2} \frac{1}{2} \bar{1} \\ \text{Cd} & \text{Te} \end{pmatrix} = E_1, \\ g_{zz} \begin{pmatrix} 0 & 110 \\ \text{Cd} & \text{Cd} \end{pmatrix} = Q_1, & g_{yy} \begin{pmatrix} 0 & \frac{3}{2} \frac{1}{2} \bar{1} \\ \text{Cd} & \text{Te} \end{pmatrix} = G_1, \\ g_{xx} \begin{pmatrix} 0 & 110 \\ \text{Te} & \text{Te} \end{pmatrix} = P, & g_{yz} \begin{pmatrix} 0 & \frac{3}{2} \frac{1}{2} \bar{1} \\ \text{Cd} & \text{Te} \end{pmatrix} = J_1, \\ g_{xy} \begin{pmatrix} 0 & 110 \\ \text{Te} & \text{Te} \end{pmatrix} = R, & g_{xx} \begin{pmatrix} 0 & 200 \\ \text{Te} & \text{Te} \end{pmatrix} = A_2, \\ g_{xz} \begin{pmatrix} 0 & 110 \\ \text{Te} & \text{Te} \end{pmatrix} = S, & g_{yy} \begin{pmatrix} 0 & 200 \\ \text{Te} & \text{Te} \end{pmatrix} = B_2, \\ g_{zz} \begin{pmatrix} 0 & 110 \\ \text{Te} & \text{Te} \end{pmatrix} = Q, & \end{array}$$

The form of the (33×33) g matrix, in terms of the above labelled Green's functions, is shown in appendix 2.

Now let us see the ∂l matrix. It has to naturally contain two parts (i) arising from the Coulombian interaction which is essentially a long range interaction (ii) and the other, short range in nature.

The ∂l matrix will have elements representing the various interactions and changes of interactions, in terms of the parameters $a, b, c, d, \Delta E_1$ and ΔF_1 , etc.

Interactions between k and k' atoms are represented as $(k - k')$; then 1-2 for example (1 is the interstitial) can be written as

$$\begin{bmatrix} a & -b & -b \\ -b & a & b \\ -b & b & a \end{bmatrix},$$

1-3, 1-4, 1-5 can be obtained from this 1-2 by symmetry considerations; 1-6 for example can be written as

$$\begin{bmatrix} c & 0 & 0 \\ 0 & d & 0 \\ 0 & 0 & d \end{bmatrix},$$

1-7, 1-8, 1-9, 1-10, 1-11 are all derived from this.

The 2-6 matrix (now is Cd-Te interaction) can be given in terms of change of interaction, as

$$\begin{bmatrix} \Delta E_1 & \Delta F_1 & \Delta F_1 \\ \Delta F_1 & \Delta E_1 & \Delta F_1 \\ \Delta F_1 & \Delta F_1 & \Delta E_1 \end{bmatrix},$$

where ΔE_1 and ΔF_1 represent the change in force constant between Cd and Te as the result of the P at interstitial site. All the force constants are defined in terms of the Kellerman's parameter. i.e.

$$a = (A_{\text{CdTe}} + 2B_{\text{CdTe}})/3,$$

$$b = (A_{\text{CdTe}} - B_{\text{CdTe}})/3.$$

The other possible interactions are derived from the above from symmetry considerations. The whole structure of the $(\partial l)_{\text{short range}}$ is given in appendix 2.

The long range contribution can be straightaway obtained from the Coulombic potential.

4. Group theoretical simplifications

Symmetry coordinates have already been worked out for this configuration (Brice 1965) and are therefore not repeated here. With the U matrix constructed from the

symmetry coordinates and properly orthonormalised, we did $U^{+(\partial I)_{\text{SR}}}$, $U^{+(\partial I)_{\text{LR}}}$, U , $U+gU$ separately in the 33×33 space. (LR denotes long range; SR denotes short range). However long range contribution is neglected for our present calculations.

The block diagonalised form of the g and ∂I matrices obtained using the symmetry coordinates are given in appendix 3.

5. Results

To start with, we took just first neighbours alone and neglected the second neighbour contributions. Group theory considerations reduce g and ∂I to blocks. For this case, LVM comes under F_2 representation which is only (3×3) matrix. The reduced blocks of g and ∂I are given in appendix 4.

Just as we have done in the substitutional case, we calculated the $|I-g\partial I|$ for nearly 50 values of X , for various values of force constants. Actually we tried both the configurations (i) Cd as neighbours and (ii) Te as neighbours. A graph was drawn connecting the force constant and x , where the sign of the determinant changes. The force constant is fixed corresponding to the localised mode frequency of 322 cm^{-1} (phosphorus mode), we found

$$a = 3.8468 \times 10^4 \text{ dynes/cm.}$$

The situation is not very different when configuration (ii) is taken (*i.e.* Te as neighbours).

This shows that in the interstitial configuration (either (i) or (ii)) we get a smaller force constant between the interstitial and its first neighbours as we ordinarily expect.

The effect of second neighbours is also worked out in the same fashion as we had done in the first neighbour case. Here F_2 mode is a (6×6) matrix. The block diagonalised form of g and ∂I are given in appendix 3. The case of Cd being neighbours is tried first. All the 19 independent Green's functions are used in this second neighbours case. The force constant we estimated from the graph (force constant versus X) fitted to the experimental frequency of 322 cm^{-1} is

$$a = 3.9314 \times 10^4 \text{ dynes/cm.}$$

The contribution from the second neighbours is less than 5% (phosphorus-tellurium interaction was estimated by making proper scaling). It appears therefore more plausible that P goes rather interstitially and not substitutionally.

In order to substantiate the conclusions reached from isolated substitutional and isolated interstitial cases we extended the study to the LVM calculations for these P impurities paired with substitutional impurities like Ga, In and Al at the nearest neighbour sites of the P center. Apart from charge compensations these additional defects reduce the site symmetry of the P center giving more LVMs.

6. Substitutional pair modes

Dutt and Spitzer (1977a) studied such pair modes and hence a comparison with their experimental results is possible, if theoretical investigations are made. The configu-

ration of atoms to indicate the above situation in the case of substitutional P center is as follows (figure 2). We have experimentally measured LVMs only for this configuration.

Let us try to explain the LVMs for the situation as in figure 2. The original dimension of the g and ∂l matrix are of the order 15×15 and group theoretical considerations would not reduce the order to a convenient one so easily, as we have done in the isolated substitutional impurity case, since the site symmetry is now further reduced to C_{3v} .

There are therefore two impurities namely phosphorus at Te site and Ga (In or Al) at one of the Cd sites. The interaction matrix will have now two ϵ factors

$$\epsilon_1 = \frac{(\text{Te})_m - P_m}{(\text{Te})_m},$$

and
$$\epsilon_2 = \frac{(\text{Cd})_m - (\text{Ga})_m}{(\text{Cd})_m},$$

where suffix m denotes the mass of the corresponding atoms.

Now ΔA in the interaction matrix will have two parts, ΔA_1 arising from Te replaced by P and A_2 from Cd by Ga. The former is actually evaluated separately as in the isolated substitutional case and the latter is evaluated as follows.

ΔA_2 is the change in force constant between A_{CdTe} and A_{GaP} ; so,

$$\Delta A_2 = \frac{A_{\text{CdTe}} + 2B_{\text{CdTe}}}{3} - \frac{A_{\text{GaP}} + 2B_{\text{GaP}}}{3},$$

$$\Delta B_2 = \frac{A_{\text{CdTe}} - B_{\text{CdTe}}}{3} - \frac{A_{\text{GaP}} - B_{\text{GaP}}}{3}.$$

To a very good approximation we treat in almost all the cases $\Delta A = \Delta B$ which is quite valid for negligible relaxation.

A_{GaP} , A_{CdTe} , B_{GaP} and B_{CdTe} are taken from the respective crystal data of the corresponding host lattice.

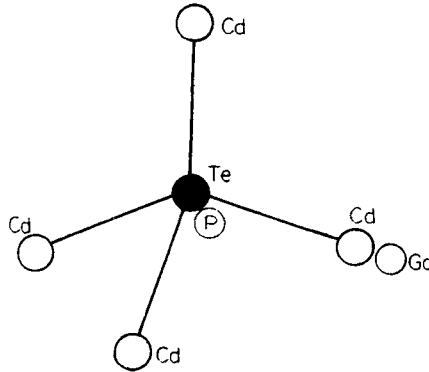


Figure 2. Substitutional pair case with P defect at origin and one of the Cd neighbours is replaced by Ga or In or Al.

The Green's function matrix g is unaltered whereas perturbation matrix ∂I gets slightly modified as mentioned above. The modified ∂I matrix for the present situation is given in appendix 5.

Due to the presence of two defects, we get 2 LVM frequencies corresponding to the reduced symmetry of C_{3v} for the P center. Thus the determinant $|I - g \partial I|$ gives zero at two X values and the corresponding LVM frequencies obtained are given in table 1.

The cases like $P_{Te} - Ga_{Cd}$ and $P_{Te} - In_{Cd}$ could reproduce the experimental results to a reasonable accuracy by our present calculations and $P_{Te} - Al_{Cd}$ could not now be compared with as there is no experimental observations of LVMs in the pair mode case.

The reason why Dutt and Spitzer could not find LVM in the case of $P_{Te} - Al_{Cd}$ is perhaps due to the fact that they did experiment only in the range upto 400 cm^{-1} whereas our calculation shows the range to be more than 400 cm^{-1} for at least one of the modes. They predicted that there should be a very high increase in the force constant for the cases CdTe:P and CdTe:Al. This conclusion derived from the fact that the recent experimental observations showed the ω_{LVM} of Al_{Cd} to be 299 cm^{-1} (Dutt and Spitzer 1977b) and to explain this, an increase in force constant was required even in our calculations. Here again is an anomalous case of a lighter impurity demanding simultaneously an increase in force constant to reproduce the LVM.

We calculated the change in force constant in CdTe:Al as 50% increase which is not very great compared to the case of CdTe:P, where it is more than 74%.

The CdTe:P, In spectrum is the simplest one to consider. Substitution of In for Cd results in no significant size or mass changes. We may therefore expect the LVM as a first approximation, still to involve primarily the motion of P, but now in a potential having a point group symmetry of C_{3v} with the trigonal axis being along the In-P pair direction. Thus for the pairs, the 322 cm^{-1} band should split into two bands.

But CdTe:P, Ga is a bit complicated; here again $Ga_{Cd} - P_{Te}$ pairs have a point group symmetry of C_{3v} . But Ga is lighter than Cd and the pair bands might involve the localised vibrational motion of both Ga and P.

Table 1. Localised frequencies in the case of substitutional pair modes (Cd as neighbours)

No.	System	Calculated LVMs		Experimental LVMs
		Molecular model	Green's function technique	
1	$P_{Te} - Ga_{Cd}$	319.654	318.97	301.5
		365.613	349.21	352.5
				357.5
2	$P_{Te} - In_{Cd}$	308.93	315.59	305
		320.32	345.97	331.5
3	$P_{Te} - Al_{Cd}$	322.51	399.98	—
		368.51	430.36	

The LVM frequencies are in units of cm^{-1}

There are two configurations in this pair modes case (i) phosphorus paired with Ga as given in figure 2 (ii) Ga paired with phosphorus.

Since both the above configurations are possible for infrared absorption measurements for the pair mode case, the intermixing of the two cases may give rise to three bands.

When we try one configuration (figure 2) separately we could get only two bands in accordance with group theoretical principles.

7. Interstitial pair modes

Although we could explain the pair modes reasonably well, it demands an increase in force constant between the group III substitutional defects and their neighbours. Further we could not rule out whether the 322 cm^{-1} band corresponds to P_{T_e} or P_i and so, we proceeded to work out in detail the localised modes when phosphorus occupies interstitial site, surrounded with Ga, In or Al in one of the neighbouring Cd site.

The Cd-P interaction is already computed in the previous case of isolated interstitial. Since one Ga atom presents at the Ga site, the new interaction of Ga-P is taken from the interaction of GaP crystal. With the presence of two defects the Td symmetry of the host lattice is again reduced to C_{3v} as in the substitutional case. The modified form of the ∂I matrix (second neighbours neglected) is shown in appendix 6.

The pair modes are now calculated for three cases (Al, Ga, In) and they are compared with the experimental measurements of Dutt and Spitzer as can be seen in table 2.

8. Conclusions

The LVM study of CdTe with particular reference to the phosphorus impurity is carried out as most of the relevant experimental infrared results are now available.

Table 2. Localised frequencies when P at interstitial site and one of the Cd neighbours is replaced by Ga or Al or In.

No.	System	Calculated LVMs		Experimental LVMs
		Cd neighbours	Te neighbours	
1	(Ga) _{Cd} -Te	318.92	339.22	301.5
	P interstitial	345.97	346.43	352.5 357.5
2	(In) _{Cd} -Te	322.4	322	305
	P interstitial	352.7	352.72	331.5
3	(Al) _{Cd} -Te	352.72	322	
	P interstitial	420.23	345.97	—

The LVM frequencies are in units of cm^{-1}

Dutt and Spitzer in their principal experimental investigations pointed out that phosphorus can go into any one of the possible two sites (i) substitutional site (ii) interstitial site. We have analysed the two possibilities by using Green's function formalism.

Apart from looking into the localised modes due to isolated substitutional and interstitial P centers we also investigated the effect on LVM due to pairing when Ga, In or Al is substituted in the nearest Cd site for both configurations. The study reveals an unusual increase in force constants even for lighter impurities when the substitutional P center is assumed. On the other hand for the interstitial configurations one gets considerable reduction in force constants between the impurity (P_i) and its nearest neighbours. This is the behaviour one expects for lighter impurity. This fact as also the fair agreement for the pair modes for interstitial case with experiment gives us a feeling that the P defect have more affinity to occupy the interstitial site rather than substitutional site in CdTe. Since the site symmetries are identical in both cases, it would be advisable to do more experiments especially by the application of P defects to throw more light on the nature of the LVM associated with these P centers.

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Appendix 1. Isolated substitutional case with first neighbours alone.

Block diagonalised ∂' matrix

$$A_1 = -(\Delta A + 2\Delta B),$$

$$E = \begin{bmatrix} -(\Delta A - \Delta B) & 0 \\ & -(\Delta A - \Delta B) \end{bmatrix},$$

$$F_1 = \begin{bmatrix} -(\Delta A - \Delta B) & 0 & 0 \\ 0 & -(\Delta A - \Delta B) & 0 \\ 0 & 0 & -(\Delta A - \Delta B) \end{bmatrix}$$

$$F_2 = \begin{bmatrix} \frac{1}{20} (16\epsilon m\omega^2 - 100\Delta A) & -\frac{4}{10} \epsilon m\omega^2 & \frac{40}{\sqrt{160}} \Delta B \\ & \frac{\epsilon m\omega^2}{5} & 0 \\ & & -(\Delta A + \Delta B) \end{bmatrix}$$

Block diagonalised g matrix:

$$A_1 = (A_1 - 4S_1 - 2P_1 + Q_1 - R_1),$$

$$E = \begin{bmatrix} (A_1 - 2P_1 + Q_1 - R_1 + 2S_1) & 0 \\ & (A_1 + Q_1 - R_1 + 2S_1 - 2P_1) \end{bmatrix},$$

$$F_1 = \begin{bmatrix} (A_1 - 2P_1 + Q_1 + R_1 + 2S_1) & 0 & 0 \\ 0 & (A_1 - 2P_1 + Q_1 + R_1 + 2S_1) & 0 \\ 0 & 0 & (A_1 - 2P_1 + Q_1 + R_1 + 2S_1) \end{bmatrix}$$

$$F_2 = \begin{bmatrix} \frac{1}{20} (-16(2Y - B) + 4A_1 + 8P_1 + 4Q_1) & \frac{4}{10} (-(B + 3Y) + A_1 + 2P_1 + Q_1) & \frac{8}{\sqrt{160}} (-R_1 + 4Z) \\ & \frac{1}{5} (B + 8Y + 4(A_1 + P_1 + Q_1)) & \frac{-(R_1 + Z)}{\sqrt{40}} \\ & & (A_1 - Q_1 - R_1) \end{bmatrix}$$

In all appendices only the upper half of the matrices are given, as all of them are symmetric.

Appendix 3

Isolated interstitial case with second neighbours included

Block diagonalised g matrix

$$A_1 = \begin{bmatrix} (B-A_2-4R) & \frac{12}{\sqrt{72}} (Y-C_1-2E_1-2Z) \\ & \frac{6}{12} (A_1+Q_1-2P_1-2R_1+4S_1) \end{bmatrix}$$

$$E_1 = \begin{bmatrix} (B-A_2+2R) & \frac{24}{\sqrt{288}} (Y-C_1+E_1+Z) \\ & (A_1-2P_1-2S_1+R_1+Q_1) \end{bmatrix}$$

$$F_1 = \begin{bmatrix} -(B-B_2+2Q) & -2S & -\frac{8}{\sqrt{32}} (D_1-J_1-2Z) \\ & -(-B+B_2-2R) & \frac{8}{\sqrt{32}} (Y+Z+D_1-G_1) \\ & & -(A_1+Q_1-R_1-2S_1) \end{bmatrix}$$

$$F_2 = \begin{bmatrix} A & B & C & D & E & F \\ & G & H & I & J & K \\ & & L & M & N & O \\ & & & P & Q & R \\ & & & & S & T \\ & & & & & U \end{bmatrix}$$

where

$$A = \frac{1}{3}(2\alpha + B + A_2); \quad B = 8(\alpha - B - A_2 + 3P)/\sqrt{504}$$

$$C = [8\alpha + 28(Y + C_1) - 8(B + A_2) - 32P]/\sqrt{1848}$$

$$D = [-2\alpha + 4(Y + C_1) + 2(B + A_2) + 8P]/\sqrt{66};$$

$$E = -8S/\sqrt{24}$$

$$F = 8(Z - E_1)/\sqrt{48}$$

$$G = (16\alpha + 68B + 32A_2 - 192P + 36B_2 + 72Q)/84$$

$$H = (16\alpha + 56(Y + 3G_1 - 2C_1) - (2B - 4A_2 + 6B_2 - 4P + 12Q))/\sqrt{25872}$$

$$I = (-4\alpha + 8(Y + 3G_1 - 2C_1) + 20B + 8A_2 - 56P + 12B_2 + 24Q)/\sqrt{924}$$

$$J = 56S/\sqrt{336}$$

$$K = 8(4E_1 - 4Z - 3D_1 - 3J_1)/\sqrt{672}$$

$$L = (16\alpha + 196(A_1 + Q_1 + 2P_1) - 224(3Y + 2G_1 + C_1) + 64(2Q + B_2 + 4P) + 32(A_2 + 3B))/308$$

$$M = (-4\alpha + 28(A_1 + 2P_1 + Q_1) + 12(2G_1 + 3Y + C_1 - 2B) - 8(A_2 + 8P + 2B_2 + 4Q))/\sqrt{3388}$$

$$N=56(Z-E_1)/\sqrt{1232}$$

$$O=-8(7R_1+4(Z-D_1-J_1-E_1))/\sqrt{2464}$$

$$P=(a+4(A_1+Q_1+B+B_2)+8(P_1+Q+C_1+3Y+2G_1+2P)+2B+2A_2))/11$$

$$Q=8(Z-E_1-J_1+E_1)/\sqrt{44}$$

$$R=8(Z-R_1-D_1-J_1-E_1)/\sqrt{88}$$

$$S=(B-B_2-2R)$$

$$T=8(D_1+G_1+Z-Y)/\sqrt{32}$$

$$U=8(A_1-Q_1-R_1-2S_1)/8$$

Block diagonalised form of δI matrix

$$A_1 = \begin{bmatrix} N & \frac{12}{\sqrt{72}} (\Delta E_1 - 2 \Delta E_1) \\ & (L-2M) \end{bmatrix}$$

$$E_1 = \begin{bmatrix} \frac{1}{3} N & \frac{8}{\sqrt{288}} (\Delta E_1 + \Delta F_1) \\ & \frac{1}{3} (L+M) \end{bmatrix}$$

$$F_1 = \begin{bmatrix} V & U & 16 \Delta F_1 / \sqrt{32} \\ & V & 8 (\Delta E_1 + \Delta F_1) / \sqrt{32} \\ & & (L+M) \end{bmatrix}$$

$$F_1 = \begin{bmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ & 7 & 8 & 9 & 10 & 11 \\ & & 12 & 13 & 14 & 15 \\ & & & 16 & 17 & 18 \\ & & & & 19 & 20 \\ & & & & & 21 \end{bmatrix}$$

where

$$1=(4(k-2c)+2N)/6$$

$$2=8(k+c-N-3d)/\sqrt{504}$$

$$3=(8(k+4d-N-7a+c)+28 \Delta E_1)/\sqrt{1848}$$

$$4=2(-c-k+2 \Delta E_1-4a-4d+N)/\sqrt{66}$$

$$5=0$$

$$6=8(2b+\Delta E_1)/\sqrt{48}$$

$$7=(16(k-6d+4c+2N)+36V)/84$$

$$8=(16(k+4c+d-3V+2N)-56(2a+\Delta E_1))/\sqrt{25872}$$

$$9=(-(k+d+4c-2 \Delta E_1+4a-3V+2N))/\sqrt{924}$$

$$10=-12U/\sqrt{336}$$

$$\begin{aligned}
 11 &= 32(b - \Delta F_1)/\sqrt{672} \\
 12 &= (16(k - 14a + 4c + 8d + 4V + 2N) + 28(7L - 24 \Delta E_1))/308 \\
 13 &= -4(k - 3a + 8d + 4c - 7L - 90 \Delta E_1 + 4V + 2N)/\sqrt{3388} \\
 14 &= 8(2U - 7 \Delta F_1)/\sqrt{1232} \\
 15 &= 8(4b + 7M - 4 \Delta F_1)/\sqrt{2464} \\
 16 &= (k + 8a + 4c + 4L + 24 \Delta E_1 + 4V + 2N)/11 \\
 17 &= -4(U + 2 \Delta F_1)/\sqrt{44} \\
 18 &= -8(b - M - \Delta F_1)/\sqrt{88} \\
 19 &= V \\
 20 &= 8(\Delta E_1 - \Delta F_1)/\sqrt{32} \\
 21 &= L - M
 \end{aligned}$$

Appendix 4

Isolated interstitial case with first neighbours alone

Block diagonalised g matrix

$$\begin{aligned}
 A_1 &= [(A_1 - 2P_1 + Q_1 - 2R_1 + 4S_1)] \\
 E_1 &= \begin{bmatrix} (A_1 - 2P_1 + Q_1 + R_1 - 2S_1) & 0 \\ & (A_1 + Q_1 - 2P_1 + R_1 + 2S_1) \end{bmatrix} \\
 F_1 &= \begin{bmatrix} (A_1 - Q_1 + R_1 + 2S_1) & 0 & 0 \\ & (A_1 - Q_1 + R_1 + 2S_1) & 0 \\ & & (A_1 - Q_1 + R_1 + 2S_1) \end{bmatrix} \\
 F_2 &= \begin{bmatrix} \frac{4}{20}(4a + A_1 + 2P_1 + Q_1) & -\frac{4}{10}(-a + A_1 + 2P_1 + Q_1) & \frac{-8R_1}{\sqrt{160}} \\ & \frac{1}{5}(a + 4 + (2P_1 + Q_1 + A_1)) & \frac{-8R_1}{\sqrt{40}} \\ & & (A_1 - Q_1 - R_1 - 2S_1) \end{bmatrix}
 \end{aligned}$$

Block diagonalised ∂I matrix

$$\begin{aligned}
 A_1 &= [(a + 2b)] & E_1 &= \begin{bmatrix} -(a-b) & 0 \\ & -(a-b) \end{bmatrix} \\
 F_1 &= \begin{bmatrix} -(a-b) & 0 & 0 \\ & -(a-b) & 0 \\ & & -(a-b) \end{bmatrix} \\
 F_2 &= \begin{bmatrix} -5a & 0 & \frac{40b}{\sqrt{160}} \\ & 0 & 0 \\ & & (a+b) \end{bmatrix}
 \end{aligned}$$

Appendix 6. $\partial 1$ matrix for interstitial defect paired with a substitutional defect.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
K	0	0	a	$-b$	$-b$	a	$-b$	b	a	b	b	a	b	b
	K	0	$-b$	a	b	$-b$	a	b	b	a	b	b	a	b
		K	$-b$	b	a	b	$-b$	a	b	b	a	b	b	a
			L'	0	0									
				L'	0		0		0	0			0	
						L'								
							L	M						
								M						
									L	0			0	
										M				
										L	M			
											M			
												L	M	
													L	M
														L

where
 $L' = \epsilon m \omega^2$
 $L = -a$
 $M = b$
 $K = -4a$

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