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Calculation of the Raman spectra in compositional and topologically disordered semiconductors

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Abstract. A calculation of the Raman spectrum of a highly impurified tetrahedral semiconductor is presented. This sort of alloy gives rise to compositional and topological disorder. The theory used for the calculation of the vibrational modes is based on the coherent potential approximation (CPA). Very simple self-consistent equations are obtained if a Born-type Hamiltonian is used. The corresponding calculation of the polarised Raman spectrum is made using a simple model for the local polarisability of the bonds. The observed softening of the Raman mode is discussed in terms of the combined effects of the impurities, of the disorder introduced by vacancies and of force constant changes.

1. Introduction

Heavily doped semiconductors are of great interest regarding their basic optical and electronic properties, which make them useful in a wide range of technological applications. The preparation of these materials requires special techniques, like dopant diffusion or ion implantation, followed by appropriate annealing. The high impurity concentration gives rise to crystalline disorder, hence one can consider these systems as semiconducting disordered alloys.

It is important to have a microscopic understanding of the basic physical properties of these materials; therefore we have concentrated on the vibrational properties of ultraheavily doped Ge, which have been thoroughly investigated experimentally through Raman spectroscopy. Heavily doped Ge is particularly interesting due to its technological applications, like in tunnel diodes, strain gauges or in magnetoresistance stable probes under nuclear radiation (Fistul 1969). New crystalline semiconductor heterostructures based on Ge–Si alloys have been used for tailoring the band gap with the aim of engineering novel photodetectors.

In the case of Ge with light mass dopant impurities, like P, B or Al, a new vibrational mode appears at a frequency higher than that of the Γ-point optical phonon of Ge. The vibrational amplitude of this new mode is completely localised around the impurity, hence it is called an impurity local vibrational model (I-LVM). This I-LVM is observed in Raman as well as in infrared experiments. In the case of ultraheavily doped Ge with P, in addition to the observed P-LVM, a softening of the Raman optical phonon in the Ge

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band is detected in the experiments reported by Contreras *et al* (1985) (referred to hereafter as CTSC). This last effect is attributed to disorder in the material.

In a previous paper (Castillo-Alvarado *et al* 1988), referred to hereafter as I, there is a microscopic theory to calculate the vibrational density of states (DOS) of a $Ge_{1-x}P_x$ alloy. The possible local surroundings of the various atoms in the alloy are treated exactly and the rest of the lattice is simulated by an effective medium (Bethe lattice), which is found self-consistently using the coherent potential approximation (CPA). The calculated shift of the P-LVM was found to be in good agreement with the experiment. However the softening of the Ge-band mode predicted by the theory was not sufficient to explain the total effect observed. This disagreement could be attributed to three causes.

(1) The lack of a model for the Raman response makes it difficult to follow the Raman activity of the modes in a band. The DOS is not the best information to follow the variation of the Raman active modes in the band with the concentration of impurities.

(2) The introduction of vacancies in the network modifies the local symmetry of the atoms around them; therefore it is expected that these defect atoms become Raman active and it is necessary to investigate the defect mode distribution in the spectrum.

(3) The force constants could change around the defects and this could produce softening of the modes if the atoms become loose around the impurities or the vacancies.

The aim of this paper is to present a theory to examine these three effects, so one could compare it with the experimental Raman spectra.

2. Theory

In order to model the vibrations in the solid, a Born-type Hamiltonian was used, in which the interaction potential between atoms is

$$\frac{(\alpha-\beta)}{2}\sum_{i,j}[(\boldsymbol{u}_i-\boldsymbol{u}_j)\cdot\boldsymbol{\delta}_{ij}]^2+\frac{\beta}{2}\sum_{i,j}|\boldsymbol{u}_i-\boldsymbol{u}_j|^2 \qquad (1)$$

where i and j are neighbour sites and δ_{ij} is a unit vector in the direction of the bond. There is a central force constant α and a non-central one β. This type of model for phonons in semiconductors has been used extensively in the past (Torres and Stoneham 1985), instead of the Keating potential, or more complicated valence force models, due to its inherent simplicity and the accuracy attained to reproduce high-frequency modes. There is a problem in the acoustic region, because the way to model real angular restoring forces produces a fictitious restoring force under long-wave rotations. Since in the present study we are interested in the optical branch the Born Hamiltonian is appropriate.

The dynamical problem can be solved through the Green function formalism by considering the Dyson equation

$$G=G_0+G_0VG \qquad (2)$$

where G_0 is the Green function for the pure system and V is the perturbation. If the impurity or defect introduces very local perturbations, one can define an effective medium and take V to be the deviation of a true bond from the effective medium value. On averaging over configurations one obtains the following CPA equations (Tagüeña-Martinez *et al* 1987):

$$\langle G_G\rangle=P_{GG}\langle G_{GG}\rangle+P_{GP1}\langle G_{GP1}\rangle+P_{GP2}\langle G_{GP2}\rangle+P_{GV}\langle G_{GV}\rangle \qquad (3)$$

where the indices refer to a particular bond configuration. These are the fundamental equations in I, modified in order to include vacancies.

The conditioned probabilities P_{GB} of having a bond with an atom of type B if one is certain that there is a Ge atom at a given site are

$$P_{GP_1} = 6x_1/[4 - (x + x_v) + x_2] \tag{4a}$$

$$P_{GP_2} = 8x_2/[4 - (x + x_v) + x_2] \tag{4b}$$

$$P_{GV} = 6x_v/[4 - (x + x_v) + x_2] \tag{4c}$$

$$P_{GG} = 1 - P_{GP_1} - P_{GP_2} - P_{GV} \tag{4d}$$

where $x = x_1 + x_2$, $x_1 = N_{P1}/N$ (N_{P1} is the number of electrically inactive ions P_1 in trigonal sites), $x_2 = N_{P2}/N$ (N_{P2} is the number of electrically active ions P_2 in tetrahedral sites), and $x_v = N_v/N$ (N_v is the number of vacancies in G sites), with N being the total number of atoms in the alloy. The quantity linked with the vacancy in (3) has the explicit form

$$\langle G_{GV}\rangle = \left(M\omega^2 I - R_{GV} - \sum_{j=2,4} \sigma_j\right)^{-1} \tag{5}$$

where I is the 3×3 identity matrix, R_{GV} is the average interaction between the vacancy and the Ge atom and M is the mass of Ge. Finally the self-consistent equations are

$$\sigma_{\parallel} = E_{\parallel} - A_{\parallel} \tag{6a}$$

$$\sigma_{\perp} = E_{\perp} - A_{\perp} \tag{6b}$$

and

$$E_{\perp} = M\omega^2 - \gamma - \tfrac{1}{3}(4\sigma_{\parallel} + 5\sigma_{\perp}) + P_{GV}\beta \tag{7a}$$

$$E_{\parallel} = M\omega^2 - \gamma - \tfrac{1}{3}(\sigma_{\parallel} + 8\sigma_{\perp}) + P_{GV}\alpha \tag{7b}$$

$$\gamma = \tfrac{4}{3}[(P_{GG} + P_{GV})(\alpha + 2\beta) + (P_{GP1} + P_{GP2})(\alpha' + 2\beta')] \tag{7c}$$

where the primed force constants refer to the impurity bonds. The As are also dependent on the E, since they are simply the diagonal elements of $\langle G_G\rangle^{-1}$, as given on the right-hand side of equation (3). Self-consistency is obtained by iteration with respect to the mean field self-energies σ of equations (7). When the central site is a P_1 (P_2) atom one can calculate $\langle G_{P1}\rangle$ ($\langle G_{P2}\rangle$) by solving equations similar to (3).

From the above equations we obtain the total Green function as

$$\mu\langle G\rangle = m(x_1\langle G_{P1}\rangle + x_2\langle G_{P2}\rangle) + M(1-x)\langle G_G\rangle \tag{8}$$

where m is the phosphorus mass and μ is the reduced mass $[mM/(m + M)]$. The total density of states is

$$N(\omega) = -(2/\pi)\omega\mu \,\mathrm{Im\,Tr}\,\langle G\rangle. \tag{9}$$

The Raman spectrum is obtained from the Green function $\langle G\rangle$ by using a simple model developed by Elliott *et al* (1982), based on a model by Alben *et al* (1975), in which the atomic polarisability is expected to be proportional to bond stretching. The Raman polarisability is then written as

$$\sum_{i,j} (\boldsymbol{E} \cdot \boldsymbol{\delta}_{ij})(\boldsymbol{E}' \cdot \boldsymbol{\delta}_{ij})(\boldsymbol{u}_i - \boldsymbol{u}_j) \cdot \boldsymbol{\delta}_{ij}$$

where $\boldsymbol{E}$ and $\boldsymbol{E}'$ are the electric vectors of the incoming and outgoing light. The Raman

intensity is proportional to the imaginary part of the square of the Raman polarisability, if all the sites in the lattice are equivalent this quantity can be written in terms of the Green function for the displacements as

$$R(\omega) = -\frac{\omega}{\pi}(\boldsymbol{E}\cdot\boldsymbol{\delta}_0)(\boldsymbol{E}'\cdot\boldsymbol{\delta}_0)\,\mathrm{Im}\,\boldsymbol{\delta}_0\cdot\sum_l\sum_\delta(\boldsymbol{E}\cdot\boldsymbol{\delta})(\boldsymbol{E}'\cdot\boldsymbol{\delta})(G_{0l}-G_{\delta l})\cdot\boldsymbol{\delta} \tag{10}$$

where the reference site is labelled 0, and the $\boldsymbol{\delta}$ are unit vectors joining the site l with its neighbours. In the Bethe lattice the summation over all sites can be performed in outgoing shells, taking care of the tetrahedral vector relations between the $\boldsymbol{\delta}$. After much algebraic manipulation the Raman cross section can be put in terms of $\langle G\rangle$:

$$R(\omega) = -\frac{\omega}{\pi}\,\mathrm{Im}\left[\langle G\rangle\left\{1-\frac{4}{3}\left[\frac{\kappa_\parallel}{(1-\kappa_\parallel)}+\frac{2}{3}\left(\frac{\kappa_\perp}{(1-\kappa_\perp)}+\frac{2\eta\kappa_\perp}{(1-\eta\kappa_\perp)}\right)\right]\right\}^{-1}\right] \tag{11}$$

where κ is a transfer matrix and $\eta = \cos(3\varphi)$ is an average of the dihedral second-neighbour contribution, arising from the uncertainty on the relative direction of next-neighbour bonds in the effective medium. If the angle between bonds is taken as $\varphi - \pi/3$, then

$$\eta = \begin{cases} 1 & \text{staggered case} \quad \varphi = 0 \\ 0 & \text{random case} \quad \varphi = \pi/6 \\ -1 & \text{eclipsed case} \quad \varphi = \pi/3. \end{cases}$$

This quantity can be used as a parameter to consider the disorder introduced in the lattice by the defects; the absence of dihedral angle disorder in the crystal corresponds to $\eta = 1$. The transfer matrices are given by (Barrio and Elliott 1982)

$$\kappa_\parallel = 1 - \alpha_{\mathrm{eff}}/\alpha \tag{12a}$$

$$\kappa_\perp = 1 - \beta_{\mathrm{eff}}/\beta. \tag{12b}$$

The effective force constants α_{eff} and β_{eff} are defined by

$$G = I\cdot[M\omega^2 - \tfrac{4}{3}(\alpha_{\mathrm{eff}} + 2\beta_{\mathrm{eff}})]^{-1} \tag{13}$$

and considering that the Green function at a Ge site in the effective medium is written as

$$\langle G_G\rangle = I\cdot[M\omega^2 - \gamma - \tfrac{4}{3}(\sigma_\parallel + 2\sigma_\perp)]^{-1}. \tag{14}$$

The symmetry implies that

$$\alpha_{\mathrm{eff}} = \sigma_\parallel + (P_{GG} + P_{GV})\alpha + (P_{GP1} + P_{GP2})\alpha' \tag{15a}$$

$$\beta_{\mathrm{eff}} = \sigma_\perp + (P_{GG} + P_{GV})\beta + (P_{GP1} + P_{GP2})\beta'. \tag{15b}$$

3. Results

Figure 1 shows the calculated DOS of germanium for several concentrations of vacancies (x_1 and x_2 equal zero). We observe that when increasing the number of vacancies the states in the acoustic region of the band mode gain weight at the expense of the optical region. This effect is in agreement with the fact that light impurities, as a vacancy is an

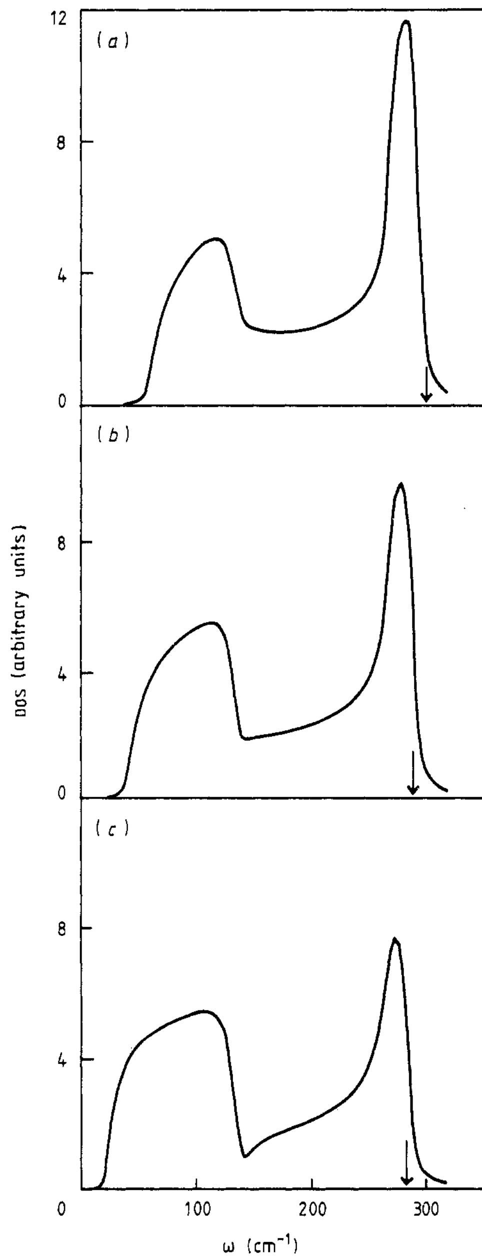

Figure 1. Calculated density of states for (*a*) pure Ge, (*b*) Ge with a concentration of vacancies x_v = 0.1 and (*c*) with $x_v = 0.2$. The position of the Raman band mode is shown by an arrow in each case.

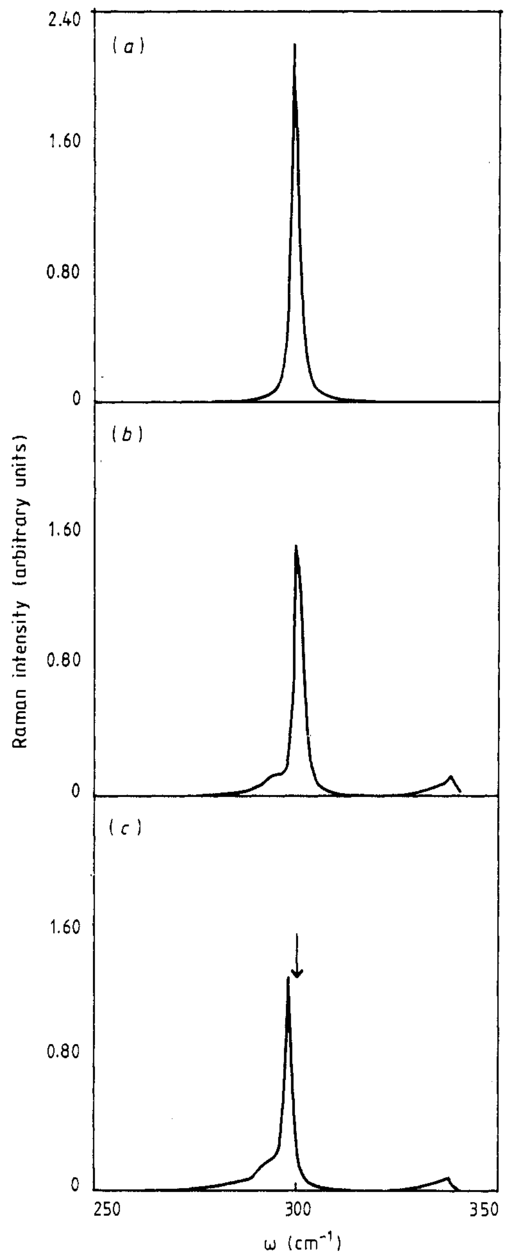

Figure 2. Calculated Raman response of (*a*) a sample of pure Ge, (*b*) a sample with a concentration of trigonal inactive P impurities of x_1 = 0.024, a concentration of tetrahedral active P impurities of $x_2 = 0.0024$ and a concentration of vacancies $x_v = 0$, and (*c*) with x_1 and x_2 the same as (*b*) but with $x_v = 0.025$.

extreme case, produce more modes at lower frequencies in the bands, as reported for the amorphous Si–hydrogen alloy (Barrio *et al* 1983).

In the case of a perfect diamond lattice, equation (12) gives a delta function for the Raman response at the upper edge of the band. The Raman peak position is shown in figure 1 with arrows. It should be noticed that there is a shifting of the Raman peak with the introduction of vacancies. This fact is important, since it is thought that electrically inactive trigonal impurities in the semiconductor introduce vacancies associated with them (see CTSC). In order to examine more carefully the results let us concentrate in reproducing the conditions of sample 5 in CTSC.

The result of equation (12) for the first-order Raman spectrum of pure crystalline Ge ($\eta = 1$) is a single δ function at the upper edge of the spectrum and it is shown in figure 2(*a*). The peak position is fixed at $\omega = 300\ \mathrm{cm^{-1}}$ with a FWHM of about $2\ \mathrm{cm^{-1}}$, according to the experimental results (Menendez and Cardona 1984). The effect of disorder could be examined by varying the parameter η. When η is less than 1 (being zero for totally random dihedral angles), all the modes in the band become active, although the high-frequency modes have more weight, relative to the DOS. This effect would only modify the width of the Raman signal and would be ignored from now on.

The calculations for ultraheavily P-doped Ge (sample 5 in CTSC) with $x_1 = 0.0246$ and $x_2 = 0.00248$ are shown in figures 2(*b*), where we have put $x_v = 0.0$. We note that the P-LVM is at $338.5\ \mathrm{cm^{-1}}$, whereas the Ge mode is located at $300\ \mathrm{cm^{-1}}$. A small shoulder in the low-frequency side of the peak appears as a consequence of defect-activated Raman modes. In the experiments there is indeed a slight asymmetry of this signal, as is seen in figure 1 of Contreras *et al* (1983). Since the position of the Raman mode in the band is not modified by the sole introduction of impurities, one has to conclude that the mass-defect-activated Raman modes should not be the reason for the observed shifting.

The results of figure 1 suggest that the effect of vacancies in the peak position is important. One way of estimating the vacancy concentration in this sample is based on a model to explain the electrical inactivity of impurities by a compensation of donor impurities by neighbouring vacancies. Therefore, x_v must be of the same order of x_1.

Figure 2(*c*) shows the results including vacancies with $x_v = 0.025$; the spectrum has almost the same shape as for $x_v = 0$, but with a small shift of the band mode to lower frequency by about $2\ \mathrm{cm^{-1}}$, which is in perfect agreement to the observed softening. In the figure there is an arrow marking the position of the peak in the pure case.

In this calculation no relaxation of the lattice around the vacancy has been considered. That is, the sp^3 hybridisation is supposed to be conserved in the sites with one dangling bond and three back bonds in the tetrahedral geometry. In reality, molecular calculations around a vacancy (Barrio *et al* 1989) have shown that the atoms relax outwards, adopting a more planar symmetry of the back bonds, approaching a more sp^2-like condition, which softens the force constants. Therefore a change of the force constants due to the inclusion of vacancies is expected, although this effect should be small, according to the experimental observations.

In order to justify this statement, we performed a calculation changing the force constants of the bonds associated with a Ge atom with three bonds. The equations (5) and (7*c*), which give R_{GV} and γ, were modified for this case by considering α_v and β_v in the three bonded sites.

In CTSC they found a decrease of the lattice constant with increasing impurity concentration. This lattice parameter change is somehow related to the force constants through Grüneissen's relation. If one considers the optical branch in the Γ point of Ge, the change in the force constants is estimated to be about 1.5%. This number is in

agreement with a parabolic fitting of the total energy obtained as a function of position in *ab initio* calculations performed in a cluster containing a vacancy (Barrio *et al* 1989). The calculation of equation (12) with an exaggerated softening of the force constants of 2.5% did not change the position of the peak by more than 0.5 cm^{-1}.

4. Conclusions

We have presented a theory to calculate not only the DOS but also the Raman spectrum of a semiconductor with various defects, as vacancies and high concentration of impurities.

In order to compare the results of the theory with real systems it is essential to model the Raman response, and then very subtle effects, detected with this very sensitive experimental technique, become apparent in the theory.

We have concentrated on the behaviour of the band mode in the Raman spectrum of ultraheavily doped Ge with P. The small softening of the mode is explained by the introduction of vacancies associated with the presence of electrically inactive impurities. It was corroborated that, at the concentrations used in real samples, the force constant changes introduced at the defect sites is not detectable. The agreement between theory and experiment allows us to have a good insight into the microscopic composition of the system.

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