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II-1. The Phenomenological Interpretation of the Two Phonon Raman Scattering and Infra-Red Absorption Spectra

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Two phonon infra-red absorption spectra and Raman scattering spectra provide information about both the phonon spectra of crystals and the interaction between phonons and electrons in filled valence bands. These optical spectra depend on both the phonon frequencies and eigenvectors and, in principle, one could test lattice dynamical models more fully than by just fitting neutron scattering data. The difficulty is, of course, that we know even less about the electron-phonon interactions and in this paper we discuss various approaches to this problem.

§ 1. Introduction

Two types of intrinsic optical spectra can be observed when light photons interact with a pair of phonons in a crystal: one the infra-red absorption spectra, and the other the two phonon Raman scattering spectra. Since the light wave vectors used in these observations are small compared with the reciprocal lattice vectors the phonons conserve momentum by having equal or equal and opposite wave vectors and thus all phonons in the Brillouin zone can contribute to the resulting spectra. The reasons for studying these spectra, apart from their intrinsic importance, is that they provide information about both the phonon spectrum of the crystal and the electron phonon interaction. One can obtain direct information about phonon dispersion curves by neutron scattering measurements but these provide little or no information about phonon eigenvectors. One can also obtain information about electron-phonon interactions from transport phenomena but these are usually concerned with the interactions between electrons in the conduction band and phonons rather than the interactions between electrons in the filled valence bands and phonons. The infra-red and Ramam spectra depend on the frequencies, occupation numbers and eigenvectors of the phonon states and also on the interactions between phonons and the electrons in the valence band. If all these quantities were known the problem of calculating the spectra would be almost trivial but in practice this information is simply not available and we are forced to use phenomenological theories for both the phonon spectrum and the electron-phonon interactions.

In this paper we shall first outline the usual treatments of these ploblems, then comment on their physical justification and finally discuss some of the results obtained to date.

§ 2. Lattice Dynamics

In treating the dynamics of a crystal with n atoms per unit cell one is dealing with sets of $3n$ equations and it is convenient to use $3n$ component vectors for momentum, P, and displacement, U and $3n \times 3n$ matrices for force constants etc. Using this matrix notation we can write the lattice hamiltonian, H, in the harmonic approximation as:

$$H = \tfrac{1}{2} \sum_{l} \tilde{P}(l) M^{-1} P(l) + \tfrac{1}{2} \sum_{l,l'} \tilde{u}(l)\, \Phi(l,l') u(l') \quad (1)$$

where $\Phi(l,l')$ is the force constant matrix connecting atoms in unit cells l and l', $M = m(k)\, \delta_{s,s'}$; $m(k)$ is the mass of atom type k and s is an index running from 1 to $3n$. It is well known[1] that the lattice dynamical problem reduces to the problem of finding the eigenvalues $\omega^2(q,s)$ and the eigenvectors $\Psi(q,s)$ of the dynamical matrix in reciprocal space $D(q)$, which is given by the expression:

$$D(q) = \sum_{l'} \phi^{+}(q,l)\, M^{-1/2}\, \Phi(l,l')\, M^{-1/2}\, \phi(q,l') \quad (2)$$

where $\phi(q,l) = e^{i\mathbf{q}\cdot\mathbf{r}(l,k)}\delta_{s,s'}$

thus $\Psi^{+}(q,s)\, D(q)\, \Psi(q,s') = \omega^2(q,s)\, \delta_{s,s'}$. (3)

Once this problem is solved we can then write the displacement and momentum of the nuclei in terms of phonon destruction, $a(q,s)$, and creation, $a^*(q,s)$, operators as follows[1)]

$$u(l)=\left(\frac{\hbar}{2N}\right)^{1/2}\sum_{q,s}(\omega(q,s))^{-1/2}M^{-1/2}$$
$$\times[a(q,s)\phi(q,l)\Psi(q,s)+c\cdot c]$$
$$P(l)=-i\left(\frac{\hbar}{2N}\right)^{1/2}\sum_{q,s}(\omega(q,s))^{1/2}M^{1/2}$$
$$\times[a(q,s)\phi(q,l)\Psi(q,s)-c\cdot c]. \tag{4}$$

When these expressions are substituted back into eq. (1) we obtain after some reduction

$$\begin{aligned} H&=\tfrac{1}{2}\sum_{q,s}\hbar\omega(q,s)\,[a^*(q,s)\,a(q,s)+c\cdot c]\\ &=\sum_{q,s}\hbar\omega(q,s)\,[a^*(q,s)\,a(q,s)+\tfrac{1}{2}]\\ &=\sum_{q,s}\hbar\omega(q,s)\,[n(q,s)+\tfrac{1}{2}],\end{aligned} \tag{5}$$

where $n(q,s)$ is the number of phonons occupying state (q,s).

§ 3. Infra-Red Spectra

The two phonon infra-red spectra is treated formally by assuming that the electric dipole moment of a unit cells contains contributions of the form

$$\mathscr{M}=\sum_{l'}\tilde{u}(l)\,C(l,l')\,u(l'), \tag{6}$$

where $C(l,l')$ is a $3\times 3\,n\times 3\,n$ tensor coupling unit cells l and l'. The absorption or emission of radiation polarised in the x-direction is then proportional to $|\mathscr{M}_x|^2$. If we substitute for $u(l)$ in eq. (6) from eq. (4) and exclude terms which do not conserve wave vector or energy with the incident radiation ω, we obtain, after some reduction

$$|\mathscr{M}_x|^2\,\alpha\sum_{q,s,s'}(\omega(q,s)\omega(q,s'))^{-1}\,|C_x(q,s,s')|^2$$
$$\{(n(-q,s)+1)(n(q,s')+1)\,\delta(\omega-\omega(q,s)-\omega(q,s'))$$
$$+(n(-q,s)+1)\,n(-q,s')\,\delta(\omega-\omega(q,s)+\omega(q,s'))$$
$$+n(q,s)(n(q,s')+1)\,\delta(\omega+\omega(q,s)-\omega(q,s'))$$
$$+n(q,s)\,n(-q,s')\,\delta(\omega+\omega(q,s)+\omega(q,s'))\}, \tag{7}$$

where $C_x(q,s,s')=\sum_{l'}\Psi^+(q,s)\,\phi^+(q,l)\,M^{-1/2}\,C_x(l,l')\,M^{-1/2}\,\phi(q,l')\,\Psi(q,s')$. The δ-functions requiring negative ω correspond, of course, to emission and the net absorption is the difference between absorption and emission at the same frequency.

§ 4. Raman Spectra

The two phonon Raman spectra is treated formally by assuming that the polarisability tensor contains a contribution of the form

$$\mathscr{P}=\sum_{l'}\tilde{u}(l)\,\mathscr{P}(l,l')\,u(l'), \tag{8}$$

where $\mathscr{P}(l,l')$ is a $3\times 3\times 3\,n\times 3\,n$ tensor coupling unit cells l and l'. If the incident radiation has a polarisation vector E the induced dipole moment is given by

$$\mathscr{M}=\mathscr{P}E. \tag{9}$$

As before the emission of radiation polarised in the x-direction is proportional to $|\mathscr{M}_x|^2$ and we can, by very similar reduction, write

$$|\mathscr{M}_x|^2\;\alpha\sum_{q,s,s'}(\omega(q,s)\,\omega(q,s'))^{-1}\,|\mathscr{P}_x(q,s,s')|^2$$
$$\times\{(n(-q,s)+1)(n(q,s')+1)\,\delta(\varDelta\omega-\omega(q,s)-\omega(q,s'))$$
$$+(n(-q,s)+1)\,n(-q,s')\delta(\varDelta\omega-\omega(q,s)+\omega(q,s'))$$
$$+n(q,s)(n(q,s')+1)\,\delta(\varDelta\omega+\omega(q,s)-\omega(q,s'))$$
$$+n(q,s)\,n(-q,s')\,\delta(\varDelta\omega+\omega(q,s)+\omega(q,s'))\}, \tag{10}$$

where $\varDelta\omega=$ incident frequency — scattered frequency and $\mathscr{P}_x(q,s,s')$ is given by a similar expression to $C_x(q,s,s')$.

§ 5. Discussion

It has been shown above that the two phonon infra-red and Raman spectra depend on the following: the matrix elements of the electron-phonon interaction in normal coordinate representation, the occupation numbers of the phonon states, and finally the density of two phonon states. The main purpose of studying these spectra is to relate them to the lattice dynamics of the crystal and to attempt to understand the nature of the electron-phonon interaction. This last point is crucial to an understanding of the nature of phonons themselves since phonons are closely coupled vibrations of cores and electrons. We shall illustrate this point as follows. The direct interaction between nuclei in a typical crystal is approximately 10^3 eV but this is largely screened by the tightly bound inner core electrons and the resulting interaction reduced to approximately 10 eV. The typical displacements of these cores in lattice vibrations would then involve energies of 10^{-1} eV, much larger than most phonon energies. Thus it follows that the loosely bound valence electrons play a vital part in lattice vibrations. In other words *in order to account for the energies of phonons it is necessary to include the interaction between cores and valence electrons.*

Fortunately the Born-Oppenheimer approximation shows that a knowledge of the average rather than the instantaneous positions of the electrons is sufficient to determine the interaction with the cores. Butcher and Sennett[2] have developed a general treatment of this problem by use of the variational method. They write the electronic wave functions as $\Psi(r,X,\alpha_i)$ where r and X are electron and neuclear coordinates and α_i are variational parameters. The effective potential function is then

$$\Phi(X,\alpha_i)=\int \Psi^*(r,X,\alpha_i)(H-T_N)\Psi(r,X,\alpha_i)\,dr, \tag{11}$$

where H is the crystal hamiltonian and T_N is the nuclear kinetic energy. The variational principle then requires that

$$\partial\Phi(X,\alpha_i)/\partial\alpha_i=0 \tag{12}$$

for all i and thus the equations of motion for the nuclei become

$$\begin{aligned} -M\ddot{X} &= d\Phi(X,\alpha_i)/dX \\ &= \partial\Phi(X,\alpha_i)/\partial X. \end{aligned} \tag{13}$$

The force constants represented in the above equation can be split into long range Coulomb forces and short range forces described by adjustable parameters. The Coulomb forces are usually expanded in terms of multiple moments of the charge distribution at each lattice site and interactions from moments higher than dipole are thrown into the short range interactions. If we follow this procedure and make the dipole moments depend only on the variational parameters eqs. (12) and (13) can readily be transformed into the shell model equations of motion[2].

The shell model[3] and similar models[4] have been very successful in fitting phonon dispersion curves and is undoubtedly the best interpolation formula currently available. However we would like to make the following comments:

(i) There are no measurements of eigenvectors to test the model against and thus there is some doubt that parameters chosen to fit the eigenvalues may not be giving correct eigenvectors.

(ii) There are alternative ways of describing the electron distribution other than multipole moments which might lead to better results.

(iii) The description of electron distributions in terms of localised real space variables is very artificial since the interaction is not with a dipole localised at a lattice site but with a polarisation wave, *i.e.* a polar exciton. This is evident if one thinks of a phonon as being renormalised through its interactions with the elementary excitations of the static lattice.

We next consider the problem of calculating the additional electric moment or polarisibility of the crystal when phonons are present. These extra contributions can be represented in the lattice hamiltonian as anharmonic terms. Cowley[5] has given a very complete calculation of the two phonon infra-red and Raman spectra based on this approach and this method has many advantages. However, we would like to make the following comments on this.

(i) The use of an anharmonic lattice hamiltonian for predicting infra-red spectra is well founded since the frequencies used are small compared with the band gap but in Raman spectra the frequencies used are seldom small compared with the band gap and the full crystal hamiltonian should be used. For example the lattice hamiltonian could not predict the resonant Raman effect[6].

(ii) When anharmonic terms are added to the lattice hamiltonian one must still make drastic simplifying assumptions to reduce the disposable parameters to manageable numbers.

As a consequence of these considerations we feel that a phenomenological apporoach aimed at evaluating the dipole moment and polarisibility tensors as a function of frequency is better. One would then, with the aid of a lattice dynamical model, evaluate these as functions in real or reciprocal space and thus obtain information about the electron phonon interactions involved.

We have so far only attempted to evaluate the tensors in real space, but this is already a problem of some complexity and the results are only tentative. The difficulty is that the spectra depend on several functions of frequency, in particular the density of two phonon states and the eigenvectors. Fortunately some features arise primarily from one or the other of these functions. It is known that most of these spectra bear some resemblance to the density of two phonon states (e.g. critical points) and this is one of the simplest and most reliable quantities to calculate. Other features such as the absence of overtone contributions in some infra-red spectra arise from general symmetry restrictions on the eigenvectors[7]. Symmetry arguments can be used on the real space representations of the dipole moment and polarisibility tensors to reduce the number of disposable parameters but finally one must make drastic assumptions about these and then see if the computed spectra bears any resemblance to the observed results. The usual method is to assume that all contributions beyond first or second neighbour lattice sites are zero.

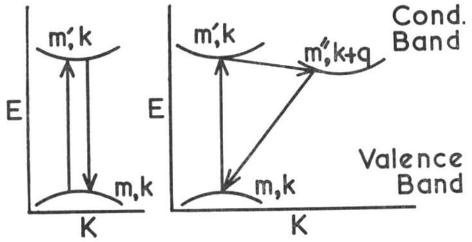
Dolling and Cowley[8] have used this phenomenological approach and the shell model to compute the two phonon infra-red spectrum of silicon and germanium. They use the real space representation of the dipole moment tensor with first and second neighbour contributions only. With only first neighbour contributions the results were wildly wrong and even the best second neighbour models were very disappointing. There could be two reasons for this failure.

(i) The eigenvectors of the shell model they used may be badly wrong in spite of the fact that the eigenvalues are very good.

(ii) The restriction of the real space representation of the dipole moment tensor to first and second neighbour contributions may be a gross oversimplication.

We cannot comment on the first possibility for lack of experimental data but if the failure were largely due to the second possibility then we would suggest that more progress could be made by working directly with the reciprocal space representation of the dipole moment tensor. This alternative approach has been outlined by Hobson and Paige[9] who consider the different possible virtual transitions that contribute to the dipole moment tensor. These are represented diagramatically in Fig. 1.

In Fig. 1 a the electron makes a virtual transition from (m, k) to (m', k), interacts simultaneously with a pair of phonons (s, q) and $(s', -q)$, then returns to (m, k). In Fig. 1 b the electron makes a virtual transition from (m, k) to (m', k), interacts with a phonon (s, q) is scattered to $(m'', k+q)$ then interacts with a second phonon $(s', -q)$ and is scattered back to (m, k). The virtual transition in 1 a has an energy denominator$=(E(m', k)-E(m, k))$ and that in 1 b an energy denominator $(E(m', k)-E(m, k))(E(m'', k+q)-E(m, k))$. The energy denominator of 1 b will give an asymmetry to the dipole moment tensor since it is a minimum at the indirect band gap.



(a) (b)

Fig. 1. Virtual transitions in two phonon infra-red absorption.

We would thus expect the electron-phonon coupling to be greatest when the phonon wave vectors were close to that of the conduction band minimum. For example we would expect that in silicon phonons near the X point would play a more important role than others, while for germanium those near the L point would be dominant and thus we would anticipate that differences between the infra-red spectra of the two would illustrate this*. That this is so can be seen in Fig. 2. Here the combination $TO+LA(L)$ is forbidden by crystal symmetry but $TO+LA(X)$ is allowed. Now for germanium the peak at $TO+LA(X)$ is very weak while that in silicon is relatively much stronger. In this case the effect is accentuated by the fact that the matrix element is increasing in both cases as one moves $L \rightarrow X$. Further if Ge is al-

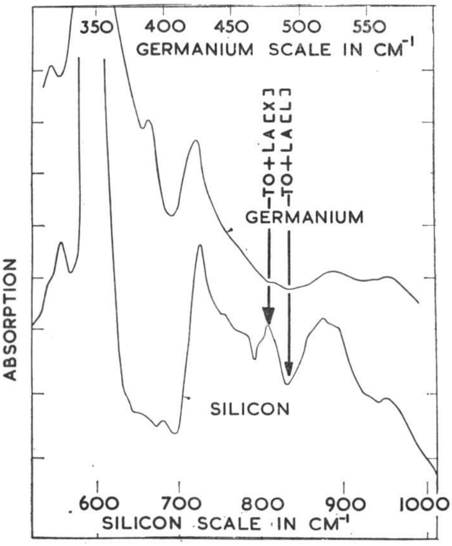


Fig. 2. Comparison of lattice bands in silicon and germanium.

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* This argument assumes, of course, that the eigenvectors and joint density of states are fairly similar.

loyed into silicon the $TO + LA(X)$ peak disappears by the addition of 6% Ge and, of course, the indirect band gap crosses from $X \rightarrow L$ at 12% Ge[10].

The main difficulty in working with real space representations is that as one progressively limits the summation to nearer neighbours, one progressively introduces more restrictions on the form of the tensor than are actually required by crystal symmetry. Dolling and Cowley's work clearly indicates that for the dipole moment tensor the restrictions imposed by taking first neighbour terms only are far too severe. In the case of two phonon Raman spectra of GaP[11] and Na Cl[12] the experimental results indicate an unexpectedly severe restriction namely the very much greater intensity of the Γ_1^+ contribution to others. If we confine our attention to the Γ_1^+ spectrum and, as a first approximation, assume that other contributions are zero we find that even the first neighbour contribution to the polarisibility is not sufficiently restrictive. To obtain the required restriction we must impose further constraints on the parameters. One way of achieving the required selection rule is to assume that the porarisibility tensor is affected only by displacements along the bond joining a pair of neighbours and further, that the principle axes of the tensor are parallel or perpendicular to the bond. When this is done the tensor has the form

$$\alpha(\boldsymbol{i}\boldsymbol{i}+\boldsymbol{j}\boldsymbol{j}+\boldsymbol{k}\boldsymbol{k})\boldsymbol{r}\boldsymbol{r}+\beta\,\boldsymbol{r}\boldsymbol{r}\boldsymbol{r}\boldsymbol{r}$$

where $\boldsymbol{i}, \boldsymbol{j}$ and $\boldsymbol{k}$ are unit vectors along the coordinate axes and $\boldsymbol{r}$ is a unit vector along the bond.

We hope to present results of calculation of the Raman spectrum based on this assumption.

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DISCUSSION

Cardona, M.: How justified are you in saying that the main contribution to electron-phonon interaction comes from direct and indirect lowest gaps when the density of states is so much larger at higher critical points of the saddle-point type (~100 times) so as to overcome energy denominator effects ?

Johnson, F. A.: The energy denominators are squared in the final expression so this enhances the importance of low energy indirect transitions but strictly one must include all possible indirect band gaps. It may turn out in a detailed calculation that indirect gaps other than the lowest may be important.

Smith, S. D.: The suggestion was made that considering the electron-phonon interaction responsible for 2-phonon absorption in terms of virtual valence-conduction transitions specific points in the zone could be distinguished. If so, a material like InSb with a small direct gap might give observable effects in a magnetic field. Are there any criteria to indicate the conditions for observation of such effects ?

Johnson, F. A.: There are no hard criteria. Hobson and Paige (Proc. Phys. Soc. (London), **88** (1966) 437) have observed changes in the infrared lattice bands of Si due to strain which appear to come primarily from changes in the conduction band.