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# A quasi-ion approach to lattice dynamics and electron–phonon interaction with applications

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**Abstract.** A model for the density response function recently proposed and applied to the lattice dynamics of Si is now used to calculate the phonon frequencies in Ge and GaAs. Furthermore as an alternative method to the linear response theory, the quasi-ion approach has been developed using Si as an example, and is now extended to Ge and GaAs. Finally, this approach is also used to calculate the electronic contribution to phonon dynamics in terms of quasi-ion potentials. An application is presented for Si and compared to the previous investigations within the rigid-ion approximation.

## 1. Introduction

The microscopic theory of lattice dynamics and electron–phonon interaction deals quantitatively with the response of the electronic charge distribution to the motion of the ions. Over the last few years progress has been achieved mainly following two different routes: (i) the density response or dielectric approach to lattice dynamics, proposed by Pick *et al* (1970) and by Sham (1969); (ii) the density functional theory of Hohenberg and Kohn (1964) and Kohn and Sham (1965), which has led to the frozen-phonon approach. In this method (Wendel and Martin 1979, Kunc and Martin 1981, Yin and Cohen 1982) the lattice dynamical properties are calculated from the total ground state of the solid as a function of the atomic positions by comparing the energies and density distributions of the solid with the atoms in different displacement patterns. In this way the energy corresponding to high-symmetry phonon modes can be calculated to all orders in the perturbation.

In contrast to the frozen-phonon method, the density response approach imposes no restrictions to the symmetry of the distortion. If the density response function  $D$  or the inverse dielectric function  $\epsilon^{-1}$  has been calculated, the electronic response of the crystal to any perturbation is known in linear order. In the following we focus our interest on the density response approach in connection with the quasi-ion description.

In § 2 the formal theory of lattice dynamics is briefly reviewed and a renormalised expression for the density response function is given. Section 3 deals with the application of the renormalised density description to the lattice dynamics of covalent materials. The model response function previously proposed has already been used to calculate

the phonon dispersion in Si (Falter *et al* 1984c) and is now applied to Ge and GaAs. Section 4 then gives a review of the quasi-ion description of crystals (Falter *et al* 1984a, b, 1985a, b, c, d). This method has led to models of bonding in solids as well as of lattice dynamics. The recent calculations of the phonon dispersion of Si within the quasi-ion model is extended to investigations of the phonon dispersion of Ge and GaAs. Finally, in § 5 the quasi-ion approach is used to express the electron–phonon interaction in terms of quasi-ion (-atom) potentials. By this procedure it has become possible to include approximately the information about the charge density redistributions which accompany the displacements of the ions into the electron–phonon interaction. An application is presented for Si and compared to previous investigations within the rigid-ion approximation.

## 2. Formal theory of lattice dynamics and the renormalised density response function

We shall not review the derivation of the theory as originally worked out by Pick *et al* (1970) and Sham (1969). Instead we start from a formulation already proposed by Brenig (1954, 1955) and Leibfried (1955). Their derivation is based on the Hellmann–Feynman theorem, which provides the following expression for the electronic contribution to the force in  $i$ -direction exerted on an ion located at  $\mathbf{R}^A = \mathbf{R}^a + \mathbf{R}^\alpha$  in short  $\mathbf{A} = \mathbf{a} + \alpha$  in the crystal.  $\mathbf{a}$  and  $\alpha$  denote the cell and the non-primitive basis indices of the crystal structure. Accordingly we have

$$E F_i^A = \frac{\partial E[\dots A' \dots]}{\partial A_i} = \langle \psi | \frac{\partial H}{\partial A_i} | \psi \rangle. \quad (1)$$

$H$  is the Hamiltonian of the electrons in the field of the fixed ions (adiabatic approximation) and  $\psi$  the corresponding many-electron ground-state function depending on the electronic coordinates  $\mathbf{r}_1 \dots \mathbf{r}_n$  as well as on the coordinates  $\{\dots A' \dots\}$  of the ions as parameters. From equation (1) we obtain the expression

$$E F_i^A = \int d\nu \rho(\mathbf{r}; [\dots A' \dots]) \frac{\partial}{\partial A_i} V_\alpha(\mathbf{r} - \mathbf{A}) \quad (2)$$

because  $H$  contains the coordinates of the ions only through their potential energy:

$$V = \sum_{i=1}^n V(\mathbf{r}_i) \quad V(\mathbf{r}) = \sum_A V_\alpha(\mathbf{r} - \mathbf{A}) \equiv \sum_A V^A(\mathbf{r}). \quad (3)$$

$\rho$  is the electronic density depending on the coordinates of the ions as parameters. Differentiating equation (2) with respect to a second ionic coordinate ( $\mathbf{B} j$ ) yields for the electronic part of the harmonic force constants

$$E \varphi_{ij}^{AB} = \int d\nu \left( \frac{\partial}{\partial A_i} \rho(\mathbf{r}) \right) \frac{\partial}{\partial B_j} V_\beta(\mathbf{r} - \mathbf{B}) + \delta_{AB} \int d\nu \rho(\mathbf{r}) \frac{\partial^2}{\partial A_i \partial B_j} V_\beta(\mathbf{r} - \mathbf{B}) \quad (4)$$

which can also be written (using translational invariance) as

$$E \varphi_{ij}^{AB} = \int d\nu \left( \frac{\partial}{\partial A_i} \rho(\mathbf{r}) \right) \frac{\partial}{\partial B_j} V_\beta(\mathbf{r} - \mathbf{B}) + \delta_{AB} \sum_{A'} \int d\nu \left( \frac{\partial}{\partial A'_i} \rho(\mathbf{r}) \right) \frac{\partial}{\partial B_j} V_\beta V_\beta(\mathbf{r} - \mathbf{B}). \quad (5)$$

The correspondence to linear response theory is easily accomplished by noting that in case of small ionic displacements (harmonic theory) the change of the electronic density can be expressed by the density response function  $D$

$$\frac{\partial}{\partial A_i} \rho(\mathbf{r}) \equiv P_i^A(\mathbf{r}) = \int dV' D(\mathbf{r}, \mathbf{r}') \frac{\partial}{\partial A_i} V_\alpha(\mathbf{r}' - \mathbf{A}). \quad (6)$$

The vector field  $P^A(\mathbf{r})$  has the meaning of the charge density variation caused by a unit displacement of ion  $A$  and plays a central role in the definition of quasi-ions in § 4. The phonon frequencies  $\omega_\sigma(\mathbf{q})$  and the corresponding normal modes of vibrations  $e^\alpha(\mathbf{q}\sigma)$  are determined by diagonalisation of the dynamical matrix  $t(\mathbf{q})$ , which is the Fourier transform of the force constants.  $\mathbf{q}$  is a wave-vector of the first Brillouin zone and  $\sigma$  numbers the normal modes for a definite  $\mathbf{q}$ -vector. The microscopic expression for  $t(\mathbf{q})$  follows from equations (4–6) if the corresponding direct ion–ion contribution to the force constants is also taken into account. Thus we obtain

$$t_{ij}^{\alpha\beta}(\mathbf{q}) = (M_\alpha M_\beta)^{-1/2} (\Lambda_{ij}^{\alpha\beta}(\mathbf{q}) - \delta_{\alpha\beta} \sum_\gamma \Lambda_{ij}^{\alpha\gamma}(\mathbf{0})) \quad (7)$$

with

$$\Lambda_{ij}^{\alpha\beta}(\mathbf{q}) = {}^I\Lambda_{ij}^{\alpha\beta}(\mathbf{q}) + {}^E\Lambda_{ij}^{\alpha\beta}(\mathbf{q}). \quad (8)$$

$M_\alpha$  is the mass of the ion of type  $\alpha$  in a cell  $\mathbf{a}$ . The direct ion–ion term  ${}^I\Lambda$  is treated following Ewald's method, resulting in ( $\mathbf{B} = \mathbf{b} + \beta$ )

$$\begin{aligned} {}^I\Lambda_{ij}^{\alpha\beta}(\mathbf{q}) &= \frac{1}{V_z} \sum_{\mathbf{G}} (\mathbf{q} + \mathbf{G})_i (\mathbf{q} + \mathbf{G})_j \exp\{i[\mathbf{G} \cdot (\mathbf{R}^\alpha - \mathbf{R}^\beta)]\} V_{\alpha\beta}^I(\mathbf{q} + \mathbf{G}) \\ &= Z_\alpha Z_\beta \left[ \sum_b - \left( \frac{\partial^2}{\partial R_i \partial R_j} \frac{\text{erfc}(R\sqrt{\eta})}{R} \right)_{R=|\mathbf{A}-\mathbf{B}|} \exp\{i[\mathbf{q} \cdot (\mathbf{A} - \mathbf{B})]\} \right. \\ &\quad \left. + \frac{4\pi}{V_z} \sum_{\mathbf{G}} (\mathbf{q} + \mathbf{G})_i (\mathbf{q} + \mathbf{G})_j \exp\{i[\mathbf{G} \cdot (\mathbf{R}^\alpha - \mathbf{R}^\beta)]\} \right. \\ &\quad \left. \times \frac{\exp(-|\mathbf{q} + \mathbf{G}|^2/4\eta)}{|\mathbf{q} + \mathbf{G}|^2} \right] \quad (9) \end{aligned}$$

$$V_{\alpha\beta}^I(\mathbf{q} + \mathbf{G}) = \frac{4\pi Z_\alpha Z_\beta}{|\mathbf{q} + \mathbf{G}|^2}. \quad (10)$$

$V_z$  is the volume of the elementary unit cell,  $Z_\alpha$  is the ionic charge,  $\mathbf{G}$  is a reciprocal-lattice vector and  $\eta$  is the convergence-parameter of the Ewald procedure. The electronic contribution to the dynamical matrix  ${}^E\Lambda$  is described by the (static) density response function  $D$  and the bare-ion pseudopotential  $V^A(\mathbf{r})$  or its form factor  $V^\alpha(\mathbf{q} + \mathbf{G})$  by the relations

$${}^E\Lambda_{ij}^{\alpha\beta}(\mathbf{q}) = -\frac{1}{V_z} \sum_{\mathbf{G}, \mathbf{G}'} V_{|i}^{\alpha*}(\mathbf{q} + \mathbf{G}) D(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}') V_{|j}^{\beta}(\mathbf{q} + \mathbf{G}') \quad (11)$$

with

$$V_{|j}^{\beta}(\mathbf{q} + \mathbf{G}) = -i(\mathbf{q} + \mathbf{G})_j V^\beta(\mathbf{q} + \mathbf{G}) \exp[-i(\mathbf{G} \cdot \mathbf{R}^\beta)]. \quad (12)$$

The formulation given above presents a formal solution of harmonic lattice dynamics. An actual solution requires a detailed investigation of  $D$  which involves complicated quantum mechanical many-electron problems. In most cases definite calculations of the density response function start with the polarisability function  $\pi$  and the (inverse) dielectric function  $\varepsilon^{-1}$  using the relations (with the sign of  $\pi$  according to the definition in equation (15))

$$D = \pi\varepsilon^{-1} \equiv \pi(1 + \bar{v}\pi)^{-1} \quad (13)$$

where we have introduced the effective electron-electron interaction

$$\bar{v} = v - v_{xc}. \quad (14)$$

$v$  is the direct Coulomb interaction and  $v_{xc}$  the exchange-correlation contribution. In order to visualise how the microscopic elements of the electronic structure and also the different problems enter the response formulation we give the self-consistent field expression for the polarisability for a crystal in Bloch basis, see e.g. Sham (1974)

$$\begin{aligned} \pi(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}') = & -2 \sum_{\substack{n, n' \\ k}} \frac{f_n(\mathbf{k} + \mathbf{q}) - f_{n'}(\mathbf{k})}{\varepsilon_n(\mathbf{k} + \mathbf{q}) - \varepsilon_{n'}(\mathbf{k})} \langle n' \mathbf{k} | \exp[-i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r}] | n \mathbf{k} + \mathbf{q} \rangle \\ & \times \langle n \mathbf{k} + \mathbf{q} | \exp[i(\mathbf{q} + \mathbf{G}') \cdot \mathbf{r}] | n' \mathbf{k} \rangle. \end{aligned} \quad (15)$$

From this equation we see that the microscopic elements like the particle statistics expressed by the Fermi factors  $f_n(\mathbf{k})$ , the band structure  $\varepsilon_n(\mathbf{k})$ , and the wavefunction  $|n\mathbf{k}\rangle$  enter the expression for the polarisability. Two problems arise. We get a summation problem concerning the higher excited states ( $n, n'$ ) which is rather slowly convergent (Van Camp *et al* 1983), and also an inversion problem for  $\varepsilon$  with respect to the reciprocal lattice vectors ( $\mathbf{G}, \mathbf{G}'$ ). In § 3 we comment on a model which tries to overcome these problems at least approximately within the renormalised density response description. According to this method (Falter and Selmke 1980, 1981) the density response function is subdivided into the response of a suitable reference system ( $\bar{D}$ ) and a complementary part where all the interactions are renormalised by the dielectric function of the reference system. This allows for a renormalised perturbation theory of the lattice dynamical properties of a solid. Such a transformation is achieved by choosing an arbitrary but suitable reference system characterised by a polarisability  $\bar{\pi}$  and defining the remaining part  $\Delta$ , by

$$\pi = \bar{\pi} + \Delta \quad (16)$$

$\Delta$  contains all the polarisation processes not considered in the reference system. Such a decomposition yields the following renormalisation transformation for the density response

$$D[\bar{v}, \pi] = \pi\varepsilon^{-1} = \pi(1 + \bar{v}\pi)^{-1} \rightarrow \bar{D} + (\bar{\varepsilon}^{-1})\dagger D_r \bar{\varepsilon}^{-1} \quad (17)$$

with

$$D_r[\bar{v}, \Delta] = \Delta\varepsilon_r^{-1} = \Delta(1 + \bar{v}\Delta)^{-1} \quad \bar{v} = \bar{\varepsilon}^{-1}\bar{v} \quad (18)$$

$$\bar{D} = \bar{\pi}\bar{\varepsilon}^{-1} = \bar{\pi}(1 + \bar{v}\bar{\pi})^{-1} \quad (19)$$

and

$$\varepsilon^{-1}[\bar{v}, \pi] \rightarrow \varepsilon_r^{-1}\bar{\varepsilon}^{-1}. \quad (20)$$

Equations (16–20) reveal the effect of the renormalisation on the density response function: the ‘change of scale’ induced by the decomposition of the polarisability in equation (16) allows for a partition of the density response function  $D$  in equation (17). The latter is expressed by the sum of the response of the reference system  $\bar{D}$  and a remaining term, which contains only renormalised quantities. Inserting now equation (17) into equation (11) results in a corresponding decomposition of  ${}^E\Lambda$  and the dynamical matrix  $t$  into ionic ( ${}^I\Lambda$ ), ‘reference’ ( ${}^E\bar{\Lambda}$ ), and renormalised ( ${}^E\Lambda'$ ) contributions, i.e.

$$\Lambda_{ij}^{\alpha\beta}(\mathbf{q}) = {}^I\Lambda_{ij}^{\alpha\beta}(\mathbf{q}) + {}^E\bar{\Lambda}_{ij}^{\alpha\beta}(\mathbf{q}) + {}^E\Lambda_{ij}^{\prime\alpha\beta}(\mathbf{q}). \quad (21)$$

The detailed form of the particular terms is given by Falter *et al* (1984c).

### 3. A renormalised density response model with application to Si, Ge and GaAs

First we give a short review of the renormalised density response model as proposed by Falter *et al* (1984c) for an approximate description of the dielectric properties in semiconductors and being applied to the calculation of the phonon dispersion of Si. In the renormalised density response description discussed above the polarisability  $\pi$  is decomposed according to equation (16) by separating the polarisation processes within an effective gap approximation into contributions from the lower and higher excited states. Then, the inversion problem is solved in the subspace of the lower excitations ( $\bar{\pi}$ ) while the effect of the higher excited states, which are contained in  $\Delta$ , is treated in perturbation theory using a closure approximation. In this way the inversion and the cut-off problem are handled in the same approximation. It should be noted that the procedure differs from the type of calculations by Van Camp *et al* (1979a, b) where the energy denominators appearing in the polarisability function are put to a constant value equal to the Phillips gap for *all* type of states and closure is used to sum over all the intermediate states. The decomposition of  $\pi$  in our model is given in Fourier space representation by

$$\pi(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}') = \bar{\pi}(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}') + \Delta(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}') \quad (22)$$

with

$$\bar{\pi}(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}') = \frac{4}{V_z \Delta E_l} \sum_{\sigma} f_{\mathbf{q}+\mathbf{G}}^{\sigma*} f_{\mathbf{q}+\mathbf{G}'}^{\sigma} \quad (23)$$

and

$$\Delta(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}') = {}^s\Delta(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}') + {}^n\Delta(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}'), \quad (24)$$

where  ${}^s\Delta$  and  ${}^n\Delta$  represent the separable and non-separable part of  $\Delta$ , respectively:

$${}^s\Delta(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}') = -\frac{4}{V_z \Delta E_h} \sum_{\tau} d_{\mathbf{q}+\mathbf{G}}^{\tau*} d_{\mathbf{q}+\mathbf{G}'}^{\tau} \quad (25)$$

$${}^n\Delta(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}') = \frac{4}{V_z \Delta E_h} \sum_{\mu \in V} d_{\mathbf{G}'-\mathbf{G}}^{\sigma\mu\sigma\mu} = \frac{4}{\Delta E_h} \rho(\mathbf{G} - \mathbf{G}'). \quad (26)$$

( $\rho$ : valence charge density.) In deriving these formulae the projection operators appearing in the effective gap approximation have been expressed in a localised representation.

For the Fourier transformed overlap density  $f^\sigma$ ,  $d^\tau$  between the localised basis functions  $\langle r|\mathbf{a}\mu\rangle$  belonging to valence states (V) and conduction states (C), respectively, this leads to

$$f_{\mathbf{q}+\mathbf{G}}^\sigma \equiv f_{\mathbf{q}+\mathbf{G}}^{\mathbf{a}'\mu'} = \int d v \langle \mathbf{a}'\mu' | r \rangle \exp[i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r}] \langle r|\mathbf{a}\mu\rangle \quad (27)$$

( $\mu \in$  valence states,  $\mu' \in$  lower conduction states.)

$$d_{\mathbf{q}+\mathbf{G}}^\tau \equiv d_{\mathbf{q}+\mathbf{G}}^{\mathbf{a}'\mu'} = \int d v \langle \mathbf{a}'\mu' | r \rangle \exp[i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r}] \langle r|\mathbf{a}\mu\rangle. \quad (28)$$

( $\mu \in$  valence states,  $\mu' \in$  lower conduction *and* valence states.) Now the corresponding density response function of the reference system  $\bar{D}$ , which is defined by  $\bar{\pi}$ , follows as

$$\bar{D}(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}') = \frac{4}{V_z \Delta E_l} \sum_{\sigma\sigma'} f_{\mathbf{q}+\mathbf{G}}^\sigma (1 + B(\mathbf{q}))_{\sigma\sigma'}^{-1} f_{\mathbf{q}+\mathbf{G}'}^{\sigma'} \quad (29)$$

with

$$B(\mathbf{q})_{\sigma\sigma'} = \frac{4}{V_z \Delta E_l} \sum_{\mathbf{G}, \mathbf{G}'} f_{\mathbf{q}+\mathbf{G}}^\sigma \bar{v}(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}') f_{\mathbf{q}+\mathbf{G}'}^{\sigma'}. \quad (30)$$

With the help of equations (17, 18) and the equations (1–9) the contributions  ${}^E\bar{\Lambda}$ ,  ${}^E\Lambda^\tau$  to the dynamical matrix can be calculated. Up to linear order in  $\Delta$  we obtain

$${}^E\bar{\Lambda}_{ij}^{\alpha\beta}(\mathbf{q}) = -\frac{1}{V_z} \sum_{\sigma\sigma'} T_{\alpha i}^{\sigma'}(\mathbf{q}) (1 + B(\mathbf{q}))_{\sigma\sigma'}^{-1} T_{\beta j}^{\sigma}(\mathbf{q}) \quad (31)$$

$$T_{\alpha i}^{\sigma}(\mathbf{q}) = \left( \frac{4}{V_z \Delta E_l} \right)^{1/2} \sum_{\mathbf{G}} f_{\mathbf{q}+\mathbf{G}}^\sigma V_{|i}^\alpha(\mathbf{q} + \mathbf{G}) \quad (32)$$

and

$${}^E\Lambda_{ij}^{\tau\alpha\beta}(\mathbf{q}) \equiv {}^E\Lambda_{ij}^{s\alpha\beta}(\mathbf{q}) + {}^E\Lambda_{ij}^{n\alpha\beta}(\mathbf{q}) \quad (33)$$

with

$$\begin{aligned} {}^E\Lambda_{ij}^{s\alpha\beta}(\mathbf{q}) &= -\frac{1}{V_z} \sum_{\mathbf{G}, \mathbf{G}'} \bar{V}_{|i}^{\alpha'}(\mathbf{q} + \mathbf{G})^s \Delta(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}') \bar{V}_{|j}^{\beta}(\mathbf{q} + \mathbf{G}') \\ &= \frac{\Delta E_l}{\Delta E_h} \frac{1}{V_z} \sum_{\tau} \bar{T}_{\alpha i}^{\tau'}(\mathbf{q}) \bar{T}_{\beta j}^{\tau}(\mathbf{q}) \end{aligned} \quad (34)$$

$$\begin{aligned} {}^E\Lambda_{ij}^{n\alpha\beta}(\mathbf{q}) &= -\frac{1}{V_z} \sum_{\mathbf{G}, \mathbf{G}'} \bar{V}_{|i}^{\alpha'}(\mathbf{q} + \mathbf{G})^n \Delta(\mathbf{G} - \mathbf{G}') \bar{V}_{|j}^{\beta}(\mathbf{q} + \mathbf{G}') \\ &= -\frac{\Delta E_l}{\Delta E_h} \frac{4}{\Delta E_l} \sum_{\mathbf{G}, \mathbf{G}'} \bar{V}_{|i}^{\alpha'}(\mathbf{q} + \mathbf{G}) \rho(\mathbf{G} - \mathbf{G}') \bar{V}_{|j}^{\beta}(\mathbf{q} + \mathbf{G}'). \end{aligned} \quad (35)$$

In equations (34, 35) the following definitions have been used

$$\begin{aligned} \bar{V}_{|i}^{\alpha}(\mathbf{q} + \mathbf{G}) &= V_{|i}^{\alpha}(\mathbf{q} + \mathbf{G}) - \left( \frac{4}{V_z \Delta E_l} \right)^{1/2} \sum_{\mathbf{G}'} \bar{v}(\mathbf{q} + \mathbf{G}', \mathbf{q} + \mathbf{G}') \\ &\quad \times \sum_{\sigma\sigma'} f_{\mathbf{q}+\mathbf{G}'}^\sigma (1 + B(\mathbf{q}))_{\sigma\sigma'}^{-1} T_{\alpha i}^{\sigma'}(\mathbf{q}) \end{aligned} \quad (36)$$

and

$$\bar{T}_{\alpha i}^{\tau}(\mathbf{q}) = \left( \frac{4}{V_z \Delta E_1} \right)^{1/2} \sum_{\mathbf{G}} d_{\mathbf{q}+\mathbf{G}}^{\tau} \bar{V}_i^{\alpha}(\mathbf{q} + \mathbf{G}). \quad (37)$$

Finally, because the double-gap approximation as used by the above equations overestimates the influence of the highest excited states we modify the polarisability by approximately taking into account the increase of the energy for these states. Instead of assuming a constant value for  $\Delta E_h$  we choose a lower limit  $\Delta E_h > \Delta E_1$ , where  $\Delta E_1$  is determined from the lower maximum of the optical spectrum and apply an effective-mass approximation for the diagonal elements of  $\pi$  in the limit  $|\mathbf{G}| \rightarrow \infty$

$$\Delta E_h \rightarrow \Delta E_h + |\mathbf{q} + \mathbf{G}|^2 / 2m^*.$$

For the non-diagonal elements in  $\Delta$  we assume  $\Delta E_h$  to have the form of a product

$$\begin{aligned} \Delta E_h &\rightarrow \Delta E_h (1 + A|\mathbf{q} + \mathbf{G}|^2)^{1/2} (1 + A|\mathbf{q} + \mathbf{G}'|^2)^{1/2} \\ A &= (2m^* \Delta E_h)^{-1} \end{aligned}$$

for  $m^*$  we take the free-electron mass which is correct for  $|\mathbf{G}| \rightarrow \infty$ . For the localised wavefunctions  $\langle r|\mathbf{a}\mu\rangle$  entering the overlap densities  $f^{\sigma}$  and  $d^{\tau}$  we assume bonding and anti-bonding functions centred in the bond directions. These functions are constructed from a set of *ansatz* functions which are expanded in terms of gaussians for computational reasons. The *ansatz* functions are then orthonormalised in a way that the function on a given bond and its six back bonds are orthogonal (Selmke *et al* (1984)). The bonding functions correspond to the four valence bands and the anti-bonding functions represent the four lowest conduction bands. The additional input quantities for the model are the ionic pseudopotential  $V_{\alpha}$  and the exchange-correlation contribution  $v_{xc}$  of the effective electron interaction  $\bar{v}$ . For the pseudopotential we use a soft-core potential of Appelbaum–Hamann type and for  $v_{xc}$  an approximately screened Coulomb potential which takes approximately into account the semiconducting *gap* in the screening of the Coulomb interaction. For the details concerning the determination of the wavefunctions, the potentials and of the exchange-correlation contributions we refer to Falter *et al* (1984a) where this model was applied for the calculation of the density response function and the phonon dispersion of Si. In particular the influence of the higher excited states, the larger reciprocal lattice vectors, determining the dimension of the dielectric matrix in reciprocal space, and of the exchange-correlation contributions  $v_{xc}$  was investigated. The main results are summarised as follows:

(i) In order to obtain convergence for the phonon frequencies a sufficient number of reciprocal lattice vectors has to be summed. The actual number depends on the kind of pseudopotential used. If higher excitations are taken into account in the calculations of  $D$ , 331 reciprocal lattice vectors have to be considered. Neglecting higher excitations, 169 are sufficient. The reason for this lies in the fact that the contribution  $\Delta$  and in particular  ${}^n\Delta$  decreases only very slowly with increasing  $|\mathbf{G}|$ . For this reason direct inversion in reciprocal space is very difficult.

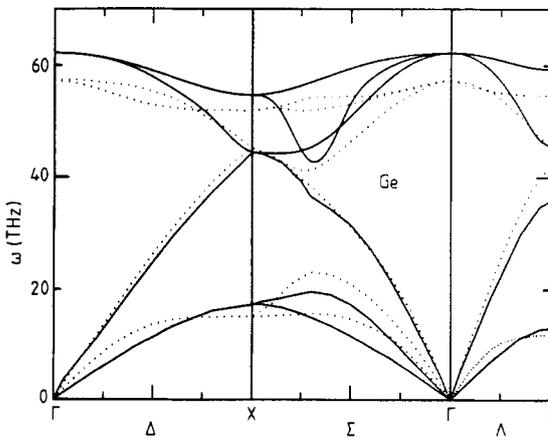
(ii) Neglecting higher excitations leads to optical phonon frequencies being far too high. This is true in RPA as well as in the calculation including approximately exchange correlation contributions in  $\bar{v}$ . A reason for this behaviour can be found in the fact that ignoring the polarisation processes of the higher excited states leads to an insufficient amount of screening charge in the case of these phonon modes. The stronger distortions

of the local environment in these modes correspond to more important contributions to the charge redistribution from high excitations. Neglecting those leads to an insufficient (short-ranged) screening.

(iii) For the transverse acoustic modes, both effects, neglecting higher excited states as well as exchange correlation leads to imaginary phonon frequencies.

We conclude from these investigations that a reliable model for the density response and phonon dispersion in covalent crystals should include a sufficient number of reciprocal lattice vectors, higher excited states and exchange-correlation corrections.

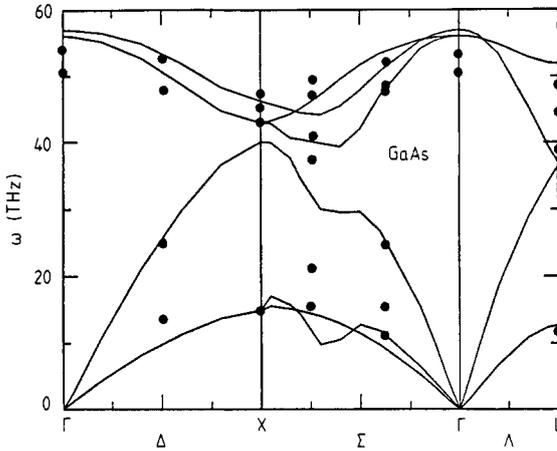
In our calculations of the phonon dispersion of Ge and GaAs we have used the same type of *ansatz* functions, pseudopotentials and exchange-correlations as for Si; the model construction is completely analogous to that given previously (Falter *et al* 1984c). The parameters involved in the *ansatz* functions are obtained by adjusting them to give a reasonable first approximation of the valence charge densities of Ge and GaAs.  $\Delta E_1$  is determined from the lower maxima of the corresponding optical spectra and  $\Delta E_h/\Delta E_1$  is obtained by fitting it to the macroscopic dielectric constant  $\epsilon_\infty$ . Finally the parameters of the Appelbaum–Hamann-type pseudopotentials are chosen from a fit of the phonon dispersion at  $0.4(2\pi/a)$  in the  $\Delta$ -direction and at the X-point. For internal consistency this procedure should then be checked by recalculating the charge density  $\rho$  from the obtained model density response function  $D$  and the corresponding pseudopotential  $V_\alpha$ . This can be achieved by using equations (38–40), which also play a central role for the construction of the quasi-ion model discussed in § 4. Such an investigation has been performed earlier by Falter *et al* (1985a) in case of Si. It was found (figure 2 of Falter *et al* 1985c) that the result for  $\rho$  determined in this way agrees rather well with band-structure calculations (Chelikowsky and Cohen 1976, Wang and Klein 1982). A similar quality for  $\rho$  is now obtained within the model construction as described above for Ge and GaAs. As an example we have displayed the result for the valence charge density of GaAs when calculated with the help of equations (38–40) in figure 8(a). As in Si and



**Figure 1.** Phonon dispersion of Ge along the main symmetry directions  $\Delta$ ,  $\Sigma$  and  $\Lambda$  (full curves) as calculated from the model-density response function within the renormalised density response approach. The dotted curves represent the spline fitted experimental results.

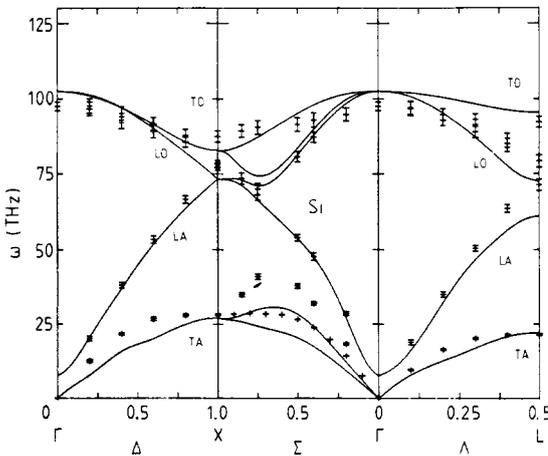
Ge the agreement with band-structure calculations (Walter and Cohen 1971, Chelikowsky and Cohen 1976, Wang and Klein 1982) is satisfactory.

The actual calculations have been performed with 331 reciprocal lattice vectors and take into account higher excited states and exchange correlation. The results for the phonon dispersion is shown for the main symmetry directions in figure 1 for Ge and figure 2 for GaAs. For a comparison the earlier calculations for Si have also been



**Figure 2.** Phonon dispersion of GaAs along  $\Delta$ ,  $\Sigma$  and  $\Lambda$  (full curves as calculated within the renormalised density response model). The full circles represent the experimental data.

reproduced in figure 3. Our calculations for Si, Ge and GaAs show that for most of the phonon frequencies we obtain satisfactory results. The difficulty concerning the LA mode for  $q \rightarrow 0$ , i.e. the violation of the acoustic sum rule (ASR), which is also inherent in other



**Figure 3.** Phonon dispersion of Si as reproduced from our earlier calculations (Falter *et al* 1984c).

microscopic calculations using the dielectric response approach (see e.g. Resta *et al* 1981), is largest for Si and improves considerably for Ge and GaAs. The other critical  $q$ -space region in our calculations in Si was the region around the  $K$  point ( $0.75(2\pi/a)$ ) in the  $\Sigma$  direction. Here the deviation of the calculated frequencies is still relatively large. This is particularly true for GaAs. In spite of this shortcoming at special  $q$ -points the overall agreement with the experimental data is sufficient, especially if one considers the simple treatment of the electronic energy bands in our model by a modified gap approximation and the restricted range of overlap of the wavefunctions. A possible improvement of the phonon dispersion could be expected essentially from three different sources: the inclusion of the band structure of the lower conduction bands, an extension of the overlap region of the wavefunctions and finally by including the next-order term of the renormalised series expansion in " $\bar{v}\Delta$ ".

#### 4. A quasi-ion description for lattice dynamics with application to Si, Ge, GaAs

The calculations of the phonon dispersion reported so far are based on a modelling of the density response function. In this section we shall discuss an alternative approach, the quasi-ion model, which is derived within linear response theory from a unique decomposition of the valence charge density  $\rho$  into contributions of the individual ions.

Recently, we have given such a decomposition of the total valence charge density  $\rho(\mathbf{r})$  of a crystal into parts (partial densities  $\rho_\alpha(\mathbf{r})$ ) which are uniquely assigned to the different sublattices or ion species  $\alpha$ , respectively (Falter *et al* 1984a, 1985a, d), i.e.

$$\rho(\mathbf{r}) = \sum_A \rho_\alpha(\mathbf{r} - \mathbf{A}) \equiv \sum_A \rho^A(\mathbf{r}). \quad (38)$$

The decomposition of the valence charge density is obtained from the acoustic sum rule (Keating 1968, 1969, Pick *et al* 1970, Sham 1969) of the charge density. In Fourier space we obtain for these partial densities

$$\rho_\alpha(\mathbf{q} + \mathbf{G}) = -\frac{1}{4\pi} \sum_j v_{ij}^*(\mathbf{q} + \mathbf{G}) \sum_{\mathbf{G}'} D(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}') V_{ij}^\alpha(\mathbf{q} + \mathbf{G}') \quad (39)$$

and the decomposition can be expressed as

$$\rho(\mathbf{G}) = \lim_{q \rightarrow 0} \sum_\alpha \rho_\alpha(\mathbf{q} + \mathbf{G}). \quad (39a)$$

The bare Coulomb potential is

$$v_{ij}(\mathbf{q}) = -iq_j 4\pi/q^2. \quad (40)$$

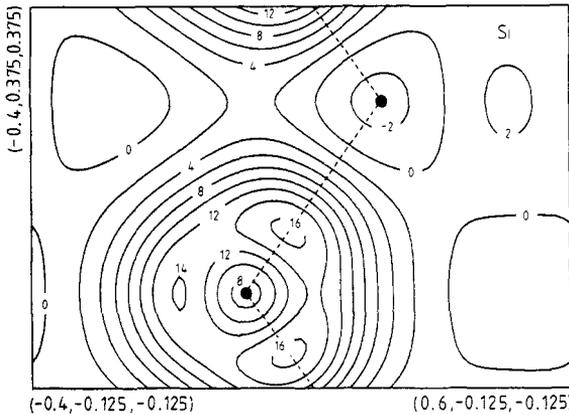
These relations are related to the invariance of the system under rigid translations of the potential and provide a condition between the charge density and the two-particle response function. More general sum rules relating the  $N$ -particle density response function with the  $(N + 1)$ -particle response function can be obtained from invariance under rigid translations and rotations of the system. This is analogous to the Ward identities in quantum field theory as a consequence of gauge invariance of the lagrangian under consideration. Physically the decomposition as provided by equations (38–40) expresses the fact that the *static* density of a crystal can be calculated from the partial densities which are determined by *displacing* the ions.

The ion cores located at  $\mathbf{R}^\alpha$  together with the corresponding distributions of electronic charge  $\rho_\alpha$  define the quasi-ions in a crystal. The introduction of these charge densities

as composite entities building up the crystal can be considered as a generalisation of Ziman's neutral pseudo-atoms in simple metals (Ziman 1964, 1972). This idea has been formally generalised in the work of Ball (1975) leading to a separation of the charge density which would be equivalent to determining  $\rho_\alpha$  from the ASR. Recently, Pickett (1986) has carried out a calculation for the pseudo-atom charge density in Si using the method of Ball. His result is similar to our calculation for the partial charge density for Si according to equation (39) which is reproduced in figure 4 (Falter *et al* 1984a). The most remarkable features shown by  $\rho_\alpha$  are:

(i) It is highly anisotropic with maxima at about  $\frac{1}{3}$  of the bond length reflecting the tetrahedral symmetry of the local environment.

(ii) The enhancement of the density response in the bond directions leads to a very effective (anisotropic) screening of the ionic potential at short distances. On the other hand this overscreening gives rise to space regions surrounding the neighbouring ions where the electrons are pushed away resulting in negative minima. For a detailed discussion of the bonding mechanism in covalent crystals in terms of quasi-ion densities we refer to Falter *et al* (1984a, b, 1985a, b).



**Figure 4.** Partial density  $\rho_1(\mathbf{r})$  in the  $(0\bar{1}1)$  plane for one sublattice of Si. Bonds lying in the plotted plane are indicated by broken lines, atoms are indicated by full circles.  $\rho_1$  is in units of electrons per cell. The coordinates are in units of  $a$  (lattice constant).

For lattice dynamical applications the quasi-ion picture can be used to achieve a decomposition of the displacement induced changes of the valence electron density described by the vector field  $\mathbf{P}^A(\mathbf{r})$  from equation (6) into two parts (Falter *et al* 1985d)

$$\mathbf{P}^A(\mathbf{r}) = \nabla \rho^A(\mathbf{r}) + \nabla \times \mathbf{W}^A(\mathbf{r}) \quad (41)$$

with

$$\begin{aligned} \rho^A(\mathbf{r}) &= -\frac{1}{4\pi} \int dV' \nabla v(\mathbf{r} - \mathbf{r}') \cdot \mathbf{P}^A(\mathbf{r}') \\ &= -\frac{1}{4\pi} \int dV' dV'' \sum_j v_j(\mathbf{r} - \mathbf{r}') D(\mathbf{r}', \mathbf{r}'') \frac{\partial}{\partial A_j} V_\alpha(\mathbf{r}'' - \mathbf{A}) \end{aligned} \quad (42)$$

$$\mathbf{W}^A(\mathbf{r}) = \frac{1}{4\pi} \int dV' \nabla \times (v(\mathbf{r} - \mathbf{r}') \mathbf{P}^A(\mathbf{r}')). \quad (43)$$

The fields  $\rho^A(\mathbf{r})$  and  $W^A(\mathbf{r})$  are not independent from each other and are controlled by certain invariance requirements like the ASR. In the decomposition according to equation (41) the gradient term represents the density distribution (the 'quasi-ion') which follows rigidly the motion of the ions, while the remaining term is due to the distortion during the motion. The relative importance of the two contributions on the charge density redistributions induced by certain phonon modes and on the phonon dispersion itself has been investigated in Falter *et al* (1985d) for Si. The numerical results for Si indicate that a model description of lattice dynamics of covalent crystals in terms of rigidly displaced partial densities yields an adequate approximation for most of the phonon frequencies.

In the approximation of rigid partial densities, i.e. neglecting the distortions in equation (41) and equations (4–6), the dynamical matrix gets simplified drastically compared to the full expression from equations (7–12). The electronic contribution to  $\Lambda$  is (in a short notation)

$$E\Lambda_{ij}^{\alpha\beta}(\mathbf{q}) = \frac{1}{2V_z} (V_{|i}^{\alpha\dagger} \bar{P}_{|j}^{\beta} + \bar{P}_{|i}^{\alpha\dagger} jV_{|j}^{\beta}) \quad (44)$$

with

$$\bar{P}_{|j}^{\beta}(\mathbf{q} + \mathbf{G}) = -i(\mathbf{q} + \mathbf{G})_j \rho_{\beta}(\mathbf{q} + \mathbf{G}) \exp[-i(\mathbf{G} \cdot \mathbf{R}^{\beta})] \quad (45)$$

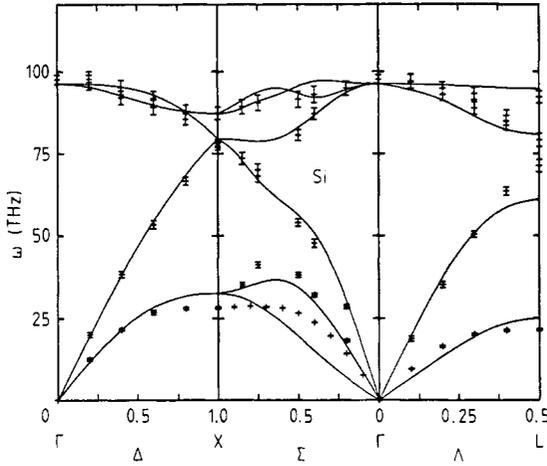
and

$$\rho_{\beta}(\mathbf{q} + \mathbf{G}) = \int dV \rho_{\beta}(\mathbf{r}) \exp[-i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r}]. \quad (46)$$

This approximate formulation of the theory reduces the expense of calculations to a large extent, though being strictly based on the quantum mechanical response theory. The ion and its screening cloud of electrons represented by the partial density  $\rho_{\alpha}$  can be treated as the basis for calculating phonon frequencies, charge density redistributions, and the electron–phonon interaction (see Falter *et al* 1985d). So it is very appealing to propose model calculations based directly on the microscopically well determined partial densities.

We have constructed a model (Falter *et al* 1985c, d) for the partial density of Si by expanding  $\rho_{\alpha}(\mathbf{r})$  in terms of a set of spherical gaussians, while requiring also that the total density  $\rho(\mathbf{r})$  is described as well as possible by the superposition of these model partial densities. Using these partial densities together with the Appelbaum–Hamann potential (Appelbaum and Hamann 1973) we obtain the phonon dispersion for Si as reconstructed in figure 5 using equations (44–46). These curves show good agreement with the experimental data with some deviations for the TA branches which could be expected from our calculations (Falter *et al* 1985d) where the additional flattening was shown to arise from the distortion contributions of the density response. Because the anisotropic shape of  $\rho_{\alpha}$  introduces a certain violation of rotational invariance for the force constants if distortions are neglected these deviations of the phonon frequencies (being largest at the zone boundary in diamond structure) are a measure for the importance of satisfying rotational invariance.

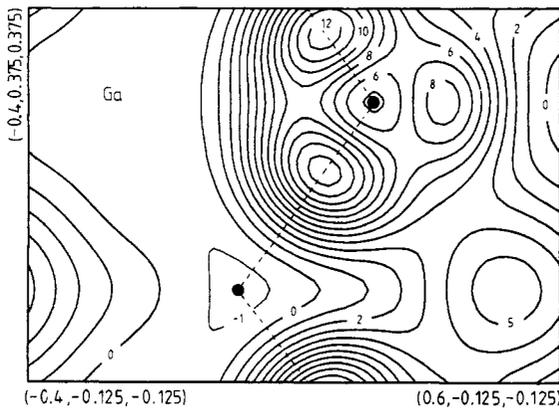
In the case of Ge and GaAs we use an analogous model description for  $\rho_{\alpha}(\mathbf{r})$  in terms of spherical gaussians requiring also that the total density  $\rho(\mathbf{r})$  is described as well as possible by the superposition of these model partial densities. As in the direct density response model described in § 3 the ionic pseudopotentials we assumed to be of Appelbaum–Hamann type. Such a model construction appears to be useful, because we know



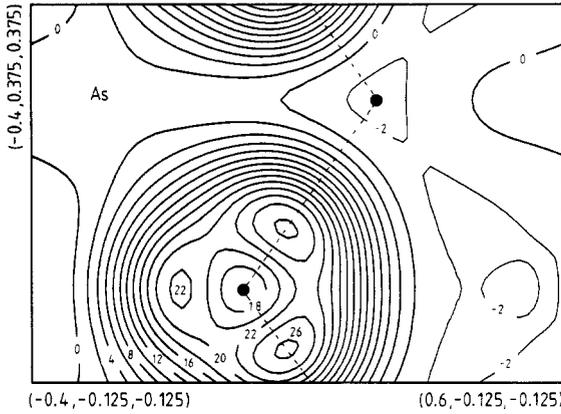
**Figure 5.** Phonon dispersion for Si along  $\Delta$ ,  $\Sigma$  and  $\Lambda$  as calculated with the rigid partial-density model via equations (44–46).  $\bar{\omega}$  represents experimental phonon frequencies.

from the Hohenberg–Kohn theory (1964) that the charge density  $\rho$  plays a central role in the determination of the cohesive and dynamical properties of the lattice. For the actual representation of the model density for Ge we have used a simple set of three gaussians centred on an ion and another three functions centred along each of the four bond directions. The result is very similar to that in the case of Si and therefore not given here. In the case of GaAs an additional function is placed along the directions to the second neighbours and another one on the back-bond axis of the nearest neighbours.

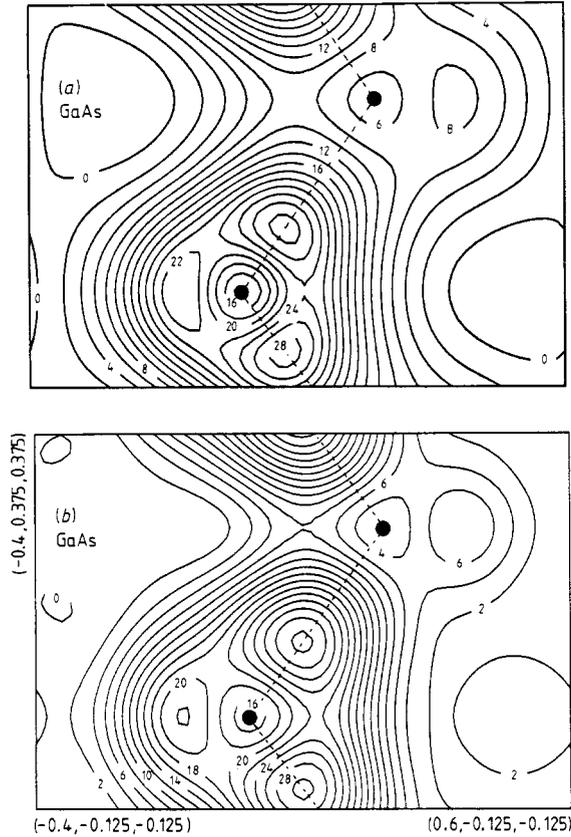
The results of our calculations within the rigid partial density model for Ge and GaAs are shown in figures 6–10. The results for the partial densities of Ga and As in GaAs are displayed in figures 6 and 7 respectively. Both distributions exhibit the qualitative features already discussed in connection with the partial density of Si. In the case of Ga, however, the bond maxima show an outward relaxation towards the As-ion and a less



**Figure 6.** Partial density  $\rho_{\text{Ga}}(r)$  in the  $(0\bar{1}1)$  plane of GaAs. Description of units, coordinates, bonds and ions as in figure 4.



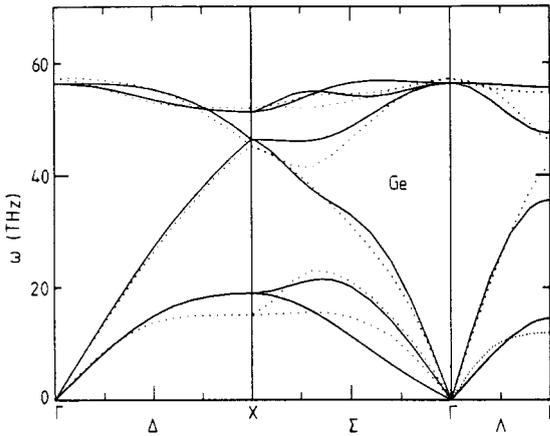
**Figure 7.** Partial density  $\rho_{As}(r)$  in the  $(0\bar{1}1)$  plane of GaAs. Description of units, coordinates, bonds and ions as in figure 4.



**Figure 8.** (a) Valence charge density  $\rho$  of GaAs in the  $(0\bar{1}1)$  plane as calculated from equations (38–40). Bonds lying in the plane are indicated by broken lines, ions are marked by full circles (As, lower left; Ga, upper right).  $\rho$  is in units of electrons per cell. (b) Valence charge density  $\rho(r)$  of GaAs in the  $(0\bar{1}1)$  plane as obtained by superposing the partial densities from figures 6 and 7.

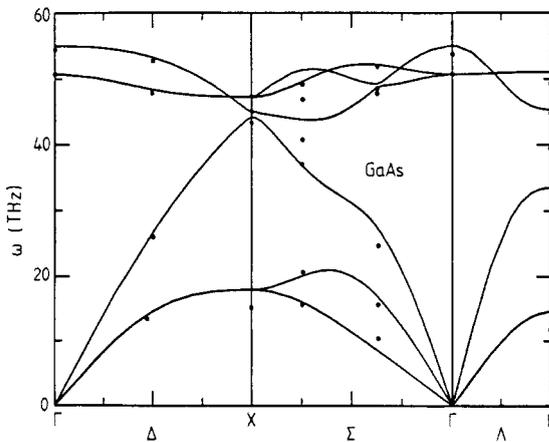
deep negative minimum region at the neighbouring ions. This could be expected for physical reasons because the ionic potential is less attractive. The partial density of As, on the other hand, is higher as well as more localised in the bonds which derives from the fact that the As potential is more attractive than the Ga potentials in the environment. Moreover, the bond maxima show an inward relaxation towards the As ion opposite to the relaxation in Ga. Altogether we observe a contraction of charge at the anion site. Figure 8(b) is then the valence charge density of GaAs as obtained by superposing the partial density of the Ga ion with the partial density of the As ion.

Our results for the phonon dispersion curves of Ge and GaAs within the quasi-ion



**Figure 9.** Phonon dispersion for Ge (full curves) as calculated from the rigid partial density model. Experimental data are represented by a spline fit (dotted curves).

model are given in figures 9 and 10 for the main symmetry directions  $\Delta$ ,  $\Sigma$  and  $\Lambda$ . The calculations are of similar quality as our earlier results for Si in figure 5. In particular the deviations at the X-point should also be due to distortions as it is the case in Si. For ionic



**Figure 10.** Phonon dispersion of GaAs within the partial density model. The calculations are compatible with the partial densities from figures 6, 7. Experimental data are given by dots.

crystals of zincblende structure like GaAs the symmetrisation used in equation (44) leads to a violation of effective charge neutrality and as a consequence the ASR and the LO-TO split for the frequencies at the  $\Gamma$ -point are not correctly reproduced. The condition for satisfying the ASR within the rigid partial density model is obtained to be

$$Z_{\alpha}\rho_{\beta}(\mathbf{q} \rightarrow 0) = Z_{\beta}\rho_{\alpha}(\mathbf{q} \rightarrow 0)$$

which is obviously violated when inversion symmetry is broken as is the case for GaAs. The violation of this equation is also a measure for violation of the ASR. Furthermore in order to obtain the correct LO-TO split at the  $\Gamma$ -point the following charge correction has to be included in  ${}^E\Lambda$  in the limit  $\mathbf{q} \rightarrow 0$ :

$${}^E\Lambda_{ij}^{\alpha\beta}(\mathbf{q} \rightarrow 0) = -\frac{4\pi q_i q_j}{V_z q^2} [\frac{1}{2}(Z_{\alpha}Z_{\beta}^L + Z_{\alpha}^L Z_{\beta}) - Z_{\alpha}^L \epsilon_{\alpha} Z_{\beta}^L]$$

where  $Z_{\alpha,\beta}^L$  is the longitudinal (Callen) charge (see Falter *et al* 1985a). With this correction term the ASR is satisfied, too.

Summarising we can say that the rigid partial density model evolving from the microscopic response theory seems to be a very promising basis for future calculations. Improvements can be expected by extending the present model to also include distortion contributions yielding an improved description in particular for the TA modes. Such extensions are currently being investigated and a few remarks can be made here. In the case of non-spherical partial densities this approximation is equivalent to introducing general anisotropic two-body forces which reduce to central forces for spherical densities. On the other hand proper three-body (and higher many-body) forces can be introduced into the quasi-ion description by coupling the charge density variation induced by displacing an ion  $A$  to the positions of the neighbouring ions maintaining rotational invariance.

A simple model being now investigated includes as a special type of distortions rotations of the (non-spherical) partial densities of the neighbouring atoms ( $N(A)$ ); it leads to the following contribution to the distortion part of the vector field  $\mathbf{P}^A$ :

$$\mathbf{P}_{\text{tot}}^A(\mathbf{r}) = \sum_{B \in N(A)} \Phi(|\mathbf{A} - \mathbf{B}|) \left( \frac{(\mathbf{A} - \mathbf{B})}{|\mathbf{A} - \mathbf{B}|^2} \times [(\mathbf{r} - \mathbf{B}) \times \nabla \rho^B(\mathbf{r})] \right).$$

Here the parameters of rotation  $\Phi$  can be chosen in order to guarantee rotational invariance.

Such an extension of the rigid partial density model points in a similar direction as a discussion recently given by Kane (1985), where it is noted that the usual interpretation of the bond bending interaction used in empirical models is in a sense misleading since it implies that the bond remains straight and the angle between bonds changes. A better picture seems to be a set of rigid tetrahedrally oriented hybrids on each atom which are free to rotate relative to each other. Unfortunately, such a model is difficult to realise and so it was abandoned by Kane.

## 5. Application of the quasi-ion description to the electron-phonon interaction

The basic quantity to be calculated in the electron-phonon interaction problem is the change of the total self-consistent crystal potential  $\tilde{V}_i^A(\mathbf{r})$  felt by an electron at space point  $\mathbf{r}$  in the case of a unit displacement of ion  $A$  in the  $i$ -direction. For small enough ionic displacements, we can use for the calculation of  $\tilde{V}_i^A(\mathbf{r})$  linear response theory.

Accordingly we have (Pickett 1979, Falter *et al* 1985d)

$$\tilde{V}_i^A(\mathbf{r}) = \int dV' \varepsilon^{-1}(\mathbf{r}, \mathbf{r}') \frac{\partial}{\partial A_i} V_\alpha(\mathbf{r}' - \mathbf{A}) \quad (47)$$

or in compact notation

$$\tilde{V}_i^A = \varepsilon^{-1} V_i^A = (1 - \bar{v}D) V_i^A = V_i^A - \bar{v}P_i^A. \quad (48)$$

Equation (48) shows that the vector field  $P^A$  and its decomposition into rigid and distortion parts from equation (41) is likewise of great importance for the calculation of the electron–phonon interaction as in microscopic lattice dynamics.

Almost all approximations for  $\tilde{V}_i^A$  are versions of the rigid-ion approximation which assumes that the  $\tilde{V}_i^A$  are derivatives of some atomic potentials  $v_\alpha(\mathbf{r} - \mathbf{A})$  which sum up to give the ‘band-structure potential’

$$V(\mathbf{r}) = \sum_A v_\alpha(\mathbf{r} - \mathbf{A}). \quad (49)$$

Following this procedure no contributions of the distortion parts of the field  $P^A$  are taken into account and the rigid part remains completely arbitrary. Furthermore no information on the charge density redistributions induced by the displacements of the ions is contained in the potentials. A typical modelling of the rigid part is for example provided by the rigid muffin-tin approximation (Gaspari and Gyorffy 1972, Evans *et al* 1973).

The arbitrariness in the procedure to divide the potential into atom-like contributions is overcome in the work of Pickett (1979) in a way that is mathematically similar to the approach of Ball (1975). Pickett has shown that the total crystal potential can be uniquely divided into atom-like potentials which move rigidly with the ions. Additional non-rigid contributions to the potentials are due to the distortions.

Our method of decomposing the valence charge density  $\rho$  with the help of the ASR into partial densities  $\rho_\alpha$  is equivalent to the method of Ball and Pickett. Consequently it is also possible to express the potentials of the quasi-atoms (or quasi-ions in ionic compounds) in terms of the  $\rho_\alpha$ . The rigid partial density approximation of  $\tilde{V}_i^A$  from equations (47, 48) means, when expressed in Fourier space representation, that the full expression

$$\sum_{G'} \varepsilon^{-1}(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}') V_{ij}^\alpha(\mathbf{q} + \mathbf{G}') \quad (50)$$

should be approximated by

$$V_{ij}^{\text{EP}\alpha}(\mathbf{q} + \mathbf{G}) = +i(\mathbf{q} + \mathbf{G})_i V_\alpha^{\text{EP}}(\mathbf{q} + \mathbf{G}) \quad (51)$$

where the effective electron–phonon potential  $V_\alpha^{\text{EP}}(\mathbf{q} + \mathbf{G})$  is defined in terms of the partial densities by

$$V_\alpha^{\text{EP}}(\mathbf{q} + \mathbf{G}) = V^\alpha(\mathbf{q} + \mathbf{G}) + \bar{v}(\mathbf{q} + \mathbf{G}) \rho_\alpha(\mathbf{q} + \mathbf{G}). \quad (52)$$

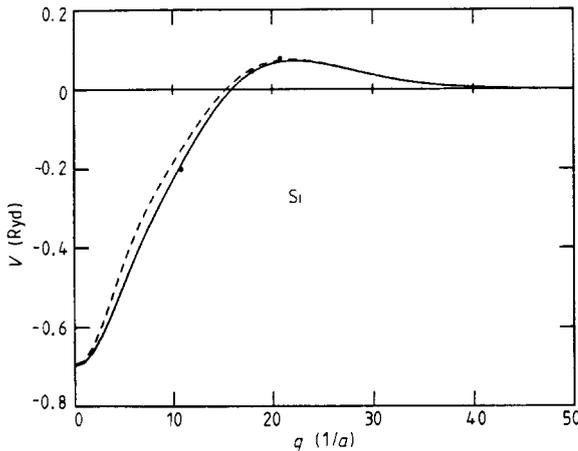
In equations (51, 52) we have assumed a diagonal approximation for the effective electron–electron interaction  $\bar{v}$  which means a diagonal approximation for exchange correlation. We note, that in case of a non-diagonal exchange-correlation contribution  $v_{\text{xc}}$  to  $\bar{v}$  the form-factor for the crystal potential has to be determined from a more general expression, i.e.

$$V^\alpha(\mathbf{q} + \mathbf{G}) + v(\mathbf{q} + \mathbf{G}) \rho_\alpha(\mathbf{q} + \mathbf{G}) + \frac{1}{4\pi} \sum_j v_j^*(\mathbf{q} + \mathbf{G}) \sum_{G', G''} v_{\text{xc}}(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}'') \times D(\mathbf{q} + \mathbf{G}'', \mathbf{q} + \mathbf{G}') V_{ij}^\alpha(\mathbf{q} + \mathbf{G}'). \quad (53)$$

This form reduces to equation (52) for a diagonal  $v_{xc}$ .

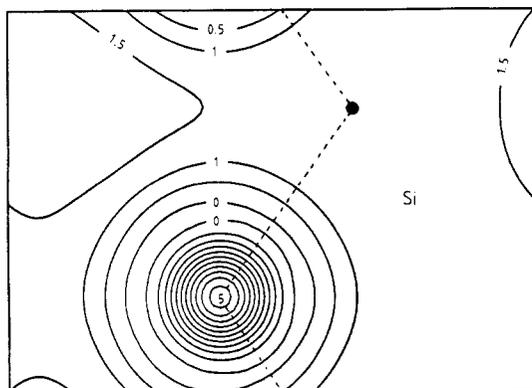
In the work of Allen and Cardona (1981, 1983) on the temperature dependence of the energy bands in Si and Ge the contribution deriving from the renormalisation of the band energies by electron–phonon interactions is calculated by taking for the expression from equation (50) a rigid pseudo-ion model where (50) is replaced by  $i(\mathbf{q} + \mathbf{G})_i V(\mathbf{q} + \mathbf{G})$ . The numerical values for the (screened) form factor  $V(\mathbf{G})$  of the pseudopotential are taken from band theory (Cohen and Bergstresser 1966). In this approach the ambiguity in the pseudopotential components  $V(\mathbf{q} + \mathbf{G})$  for  $\mathbf{q} \neq 0$  is still present because in reciprocal space an infinite variety of curves  $V(\mathbf{q})$  can be drawn which pass through the known values  $V(\mathbf{G})$  when  $\mathbf{q} = \mathbf{G}$ . Allen and Cardona (1983) assume for the pseudopotential of Si to pass through the Cohen–Bergstresser (1966) empirical values of  $V(\mathbf{G})$  for  $\mathbf{G} \neq 0$ . For the extrapolation of  $V(\mathbf{q})$  for  $\mathbf{q} \rightarrow 0$  two choices have been considered. One uses  $V(0) = -\frac{2}{3}\epsilon_F$ ,  $\epsilon_F$ : Fermi energy (Allen and Cardona 1981, 1983; for a similar choice see also Glembocki and Pollak (1982)). The other, proposed by Bednarek and Rössler (1982), assumes a very different extrapolation taking  $V(\mathbf{q} \rightarrow 0) = 0$ .

Our calculation for the electron–phonon potential  $V^{EP}(\mathbf{q})$  for Si from equation (52) is displayed in figure 11 for the  $\Delta$  and  $\Sigma$  directions and should be compared with the form-factor interpolations as listed by Allen and Cardona (1983). For comparison we have also included the Cohen–Bergstresser (1966) values as dots. Our potential uses the same partial density and bare ion potential as has been used in the calculation of the phonon dispersion displayed in figure 5 and therefore includes a good deal of information on the charge density redistributions of the electronic system when the ions are displaced. The expression for  $v_{xc}$  was taken from Falter *et al* (1984c, equation (52)).



**Figure 11.** Effective electron–phonon potential  $V_{\alpha}^{EP}(\mathbf{q})$  for Si according to equation (52) for  $\mathbf{q}$  along  $\Delta$  (full curve) and  $\Sigma$  (broken curve). The Cohen–Bergstresser values (1966) are indicated by dots.

We observe some anisotropy in  $V^{EP}(\mathbf{q})$  for different  $\mathbf{q}$ -directions. The  $\mathbf{q} \rightarrow 0$  limit of our potential is a bit larger than the extrapolation of about  $-0.84$  Ryd by Glembocki and Pollak (1982). In figure 12 we have shown a contour-line plot of the direct space



**Figure 12.** Contour plot of the Fourier transformed effective electron-phonon potential for  $q \rightarrow 0$  of one sublattice of Si in the  $(0 \bar{1} 1)$  plane. Units are in  $(e^2/4\pi\epsilon_0 a)(1/V_z)$ . Bonds in the plane are indicated by broken lines.

representation of this quasi-ion potential in the  $(0, -1, 1)$  plane. As a characteristic feature we observe a spherical shape of the potential in the neighbourhood of the ion and a ring-shaped minimum at a distance of about  $\frac{1}{3}$  of the bond length which is just the distance at which the bond maxima of the partial densities are located. On the other hand, the potential as well as the partial density are fairly flat in the interstitial region. Moreover, in these most open parts of the structure the potential is repulsive and non-spherical.

From the present status of our investigations, we think that the analysis of the phonon dispersion as presented in § 4 and of the electron-phonon interaction according to § 5, eventually with an improved representation of the partial densities and an inclusion of distortions, will provide a useful area of study for future work.

### Acknowledgments

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