

Microscopic optical fields and mixing coefficients of x-ray and optical frequencies in solids

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Abstract. Simple approximation schemes are developed to calculate induced optical fields and local field corrections to the linear optical dielectric function in metals like aluminium and in insulators like germanium. In these calculations, the unperturbed electronic states in Ge are described within the framework of the bonding orbital approach, whereas the nearly-free-electron approximation is used for Al. As expected, explicit numerical calculations show that the contribution to secondary longitudinal induced fields is more appreciable in Ge. The second order susceptibility describing the non-linear mixing of an optical frequency with an x-ray frequency, which depends upon the magnitude of the microscopic induced optical charge density, is also calculated for these solids. For most relevant wavevectors of secondary optical fields, it is found to be of the order of 10^{-12} esu in Ge and 10^{-14} esu in Al.

Keywords. Microscopic fields; local field corrections; bilinear susceptibility; germanium; aluminium.

1. Introduction

The study of the microscopic linear dielectric response function $\epsilon(\mathbf{r}, \mathbf{r}', t - t')$ of electrons in a solid is important for understanding various physical processes in the medium (Agranovich and Ginzburg 1966). For example, it allows us to compute the local field corrections to the macroscopic dielectric function (Adler 1962, Wiser 1963). It has also been shown recently (Freund and Levine 1970, Eisenberger and McCall 1971, Woo and Jha 1972) that in order to calculate the amount of nonlinear mixing of x-ray and optical frequencies, it is crucial to know the relevant components of the optical microscopic dielectric function having rapid spatial variations. When a light wave with wavevector \mathbf{q} is incident on a crystal it induces optical polarization fields varying with wavevectors \mathbf{q} and $\mathbf{q} + \mathbf{G}$, where \mathbf{G} is any reciprocal lattice vector of the crystal. These induced microscopic polarizations $\mathbf{P}(\mathbf{q})$ and $\mathbf{P}(\mathbf{q} + \mathbf{G})$, for different non-zero \mathbf{G} , give rise to fields $\mathbf{E}(\mathbf{q})$ and $\mathbf{E}(\mathbf{q} + \mathbf{G})$ in the medium, which are called the primary and secondary fields respectively. The total field $\mathbf{E}(\mathbf{r})$ in the medium, which contains both transverse and longitudinal components, and which must be a self-consistent solution of the appropriate Maxwell's equations, is the so-called microscopic field. The slowly varying macroscopic electric field is nothing but the spatial average of this microscopic field, over any unit cell in the crystal. If, however, one averages the microscopic field over the region occupied by the electrons, the contribution to the average being greater from those parts of the unit cell which contain more

easily polarizable electrons, one obtains the well-known local or the effective macroscopic field.

The induced microscopic charge density in the solid, oscillating with the incident optical frequency, is proportional to the divergence of the induced optical microscopic field in the medium. Unless the crystal is birefringent and anisotropic the divergence of the electric field, varying with the optical wavevector q , is zero. However, the secondary fields varying with wavevectors $q + G$, $G \neq 0$ have, in general, longitudinal components with non-vanishing divergence. Since the non-linear mixing of a wave at the x-ray frequency with the wave at the optical frequency is proportional (*see* Woo and Jha 1972) to the field amplitude at the x-ray frequency and the induced optical charge density, it is the rapidly varying secondary field which is responsible for the mixing.

Adler (1962) and Wiser (1963) have proposed a general theory for the calculation of microscopic dielectric function for the Bloch electrons in a solid, including the estimation of the local field corrections. Van Vechten and Martin (1972) and Sinha *et al* (1971) have used this theory for the local field calculation in diamond and silicon, respectively. In section 2 of this paper we use this approach to derive expressions for the self-consistent microscopic fields and the local field correction to the macroscopic dielectric function. The microscopic field in Al is calculated in section 3, using the nearly-free-electron approximation for the electronic motion in the conduction band. In this case, it is found that the secondary induced fields are small compared to the primary field, justifying the usual neglect of local field corrections in metals. Taking Ge as a representative example of IV-IV semiconductors, the microscopic field is calculated for such solids in section 4, using the molecular orbital approach (Coulson *et al* 1962) for the valence and conduction band states. The secondary fields and the local field correction to the linear dielectric function are no longer negligible in this case. In section 5, we determine for both Al and Ge the second order nonlinear susceptibility which describes the mixing of x-ray and optical waves. As expected, the mixing effect is much more dominant in the case of Ge as compared to Al. We discuss our results in section 6.

2. Microscopic fields and local field corrections

The induced linear polarization $P(\mathbf{r}, t)$ is related to the self-consistent microscopic electric field $E(\mathbf{r}, t)$ by the general relation

$$P(\mathbf{r}, t) = \int dt' \int d^3r' \chi(\mathbf{r}, \mathbf{r}', t - t') \cdot E(\mathbf{r}', t') \quad (2.1)$$

which defines the generalised microscopic susceptibility tensor χ . In terms of the Fourier components

$$\chi(\mathbf{Q}, \mathbf{Q}', \omega) = \frac{1}{V^2} \int \int d^3r d^3r' \exp(-i\mathbf{Q} \cdot \mathbf{r} + i\mathbf{Q}' \cdot \mathbf{r}') \chi(\mathbf{r}, \mathbf{r}', \omega) \quad (2.2)$$

one has

$$P(\mathbf{Q}, \omega) = \sum_{\mathbf{Q}'} \chi(\mathbf{Q}, \mathbf{Q}', \omega) \cdot E(\mathbf{Q}', \omega) \quad (2.3)$$

For a spatially homogeneous system, note that χ is a function of $\mathbf{r} - \mathbf{r}'$ alone, which implies that in this case \mathbf{Q}' has to be equal to \mathbf{Q} in the above summation. In

such a case, one usually denotes $\chi(\mathbf{Q}, \mathbf{Q}, \omega)$ simply by $\chi(\mathbf{Q}, \omega)$. For a periodic crystal on the other hand, \mathbf{Q}' can differ from \mathbf{Q} by any reciprocal lattice vector \mathbf{G} of the crystal, including, of course, $\mathbf{G} = 0$. Thus for a crystalline solid, we have

$$\mathbf{P}(\mathbf{q} + \mathbf{G}, \omega) = \sum_{\mathbf{G}'} \chi(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}', \omega) \cdot \mathbf{E}(\mathbf{q} + \mathbf{G}', \omega) \quad (2.4)$$

where \mathbf{q} lies in the first Brillouin zone.

Let us now assume that the incident optical field (primary field) has a fixed wave-vector \mathbf{q} in the medium. The displacement vector, $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}$, is

$$\mathbf{D}(\mathbf{q} + \mathbf{G}, \omega) = \sum_{\mathbf{G}'} \epsilon(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}', \omega) \cdot \mathbf{E}(\mathbf{q} + \mathbf{G}', \omega) \quad (2.5)$$

where the generalised microscopic dielectric function is given by

$$\epsilon(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}', \omega) = \delta_{\mathbf{G}, \mathbf{G}'} + 4\pi\chi(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}', \omega) \quad (2.6)$$

Since $\nabla \cdot \mathbf{D} = 0$, one thus finds

$$\begin{aligned} (\mathbf{q} + \mathbf{G}) \cdot \epsilon(\mathbf{q} + \mathbf{G}, \mathbf{q}, \omega) \cdot \mathbf{E}(\mathbf{q}, \omega) \\ = -(\mathbf{q} + \mathbf{G}) \cdot \sum_{\mathbf{G}' \neq 0} \epsilon(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}', \omega) \cdot \mathbf{E}(\mathbf{q} + \mathbf{G}', \omega) \end{aligned} \quad (2.7)$$

This is an infinite set of homogeneous tensorial equations for obtaining $\mathbf{E}(\mathbf{q} + \mathbf{G}, \omega)$ for each \mathbf{G} . Since the optical frequency ω enters only as a parameter in these equations, in what follows we will suppress the explicit frequency dependence in our equations.

In the special case of a cubic crystal, ϵ is a diagonal tensor. The relation $\epsilon_{jj} E_j = E_j^{\text{ext}}$ in this case, where E_j is a vector and ϵ_{jj} is a matrix in the reciprocal lattice vector space, leads to a simple expression for the secondary field in terms of the primary field:

$$\mathbf{E}_j(\mathbf{q} + \mathbf{G}) = \frac{\epsilon_{jj}^{-1}(\mathbf{q} + \mathbf{G}, \mathbf{q}) \mathbf{E}_j(\mathbf{q})}{\epsilon_{jj}^{-1}(\mathbf{q}, \mathbf{q})} \quad (2.8)$$

For the 'local' macroscopic dielectric function defined by $\mathbf{D}(\mathbf{q}) = \epsilon^{\text{loc}}(\mathbf{q}, \mathbf{q}) \cdot \mathbf{E}(\mathbf{q})$, eqs (2.5) and (2.8) lead to the expression

$$\epsilon_{jj}^{\text{loc}}(\mathbf{q}, \mathbf{q}) = \epsilon_{jj}(\mathbf{q}, \mathbf{q}) + \sum_{\mathbf{G} \neq 0} \frac{\epsilon_{jj}(\mathbf{q}, \mathbf{q} + \mathbf{G}) \epsilon_{jj}^{-1}(\mathbf{q} + \mathbf{G}, \mathbf{q})}{\epsilon_{jj}^{-1}(\mathbf{q}, \mathbf{q})} \quad (2.9)$$

For the general non-cubic case, one can get a simple expression for the secondary fields only if these are assumed to be much smaller than the primary field at the wavevector \mathbf{q} . We may then use a perturbation approach in which, to the first approximation, the off-diagonal elements ($\mathbf{G} \neq \mathbf{G}'$) of $\epsilon(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}')$ may be neglected on the right hand side of eq (2.7). In this approximation, one has

$$(\mathbf{q} + \mathbf{G}) \cdot \epsilon(\mathbf{q} + \mathbf{G}, \mathbf{q}) \cdot \mathbf{E}(\mathbf{q}) \approx -(\mathbf{q} + \mathbf{G}) \cdot \epsilon(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}) \cdot \mathbf{E}(\mathbf{q} + \mathbf{G}) \quad (2.10)$$

for determining the self-consistent field \mathbf{E} . The tensorial nature of this equation is still difficult to handle. However, for $\mathbf{G} \neq 0$, using Maxwell's equation

$$(\omega^2/c^2) \mathbf{D}(\mathbf{q} + \mathbf{G}) - (\mathbf{q} + \mathbf{G})^2 \mathbf{E}(\mathbf{q} + \mathbf{G}) + (\mathbf{q} + \mathbf{G})(\mathbf{q} + \mathbf{G}) \cdot \mathbf{E}(\mathbf{q} + \mathbf{G}) = 0, \quad \mathbf{G} \neq 0$$

one can show that the component of the secondary field $E(\mathbf{q} + \mathbf{G})$ transverse to $(\mathbf{q} + \mathbf{G})$ is of the order of $(\omega^2/c^2)/(\mathbf{q} + \mathbf{G})^2$ times the corresponding longitudinal component, and at optical frequencies it may be neglected in the first approximation. Retaining only the longitudinal components of the secondary fields ($\mathbf{G} \neq 0$) in eq (2.9), one, therefore, finds

$$(\mathbf{q} + \mathbf{G}) \cdot \mathbf{E}(\mathbf{q} + \mathbf{G}) \approx - \frac{(\mathbf{q} + \mathbf{G}) \cdot \epsilon(\mathbf{q} + \mathbf{G}, \mathbf{q}) \cdot \mathbf{E}(\mathbf{q})}{(\hat{\mathbf{q}} + \hat{\mathbf{G}}) \cdot \epsilon(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}) \cdot (\hat{\mathbf{q}} + \hat{\mathbf{G}})} \quad (2.12)$$

for the secondary fields in terms of the primary field. Under the same approximation the local macroscopic dielectric function is

$$\epsilon^{\text{loc}}(\mathbf{q}, \mathbf{q}, \omega) \approx \epsilon(\mathbf{q}, \mathbf{q}, \omega) - \sum_{\mathbf{G} \neq 0} \frac{\epsilon(\mathbf{q}, \mathbf{q} + \mathbf{G}, \omega) \cdot (\hat{\mathbf{q}} + \hat{\mathbf{G}}) (\hat{\mathbf{q}} + \hat{\mathbf{G}}) \cdot \epsilon(\mathbf{q} + \mathbf{G}, \mathbf{q}, \omega)}{(\hat{\mathbf{q}} + \hat{\mathbf{G}}) \cdot \epsilon(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}, \omega) \cdot (\hat{\mathbf{q}} + \hat{\mathbf{G}})} \quad (2.13)$$

3. Microscopic dielectric function in aluminium

A general expression for the microscopic linear susceptibility tensor or the microscopic dielectric function may be obtained by using the usual linear response theory, where one calculates (see Jha and Warke 1968) the induced polarizations in a medium by the self-consistent electric field $\mathbf{E}(\mathbf{r}, t)$. For the electrons moving in a single-particle periodic potential $V(\mathbf{r})$ in a crystal, one has

$$\begin{aligned} \epsilon_{ij}(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}', \omega) &= \delta_{ij} \delta_{\mathbf{G}, \mathbf{G}'} - (4\pi e^2/m\omega^2 V) \sum_{\alpha} f_{\alpha} [\langle \alpha | \exp i(\mathbf{G}' - \mathbf{G}) \cdot \mathbf{r} | \alpha \rangle \delta_{ij} + \\ &+ \frac{1}{m} \sum_{\alpha' \neq \alpha} \left\{ \frac{\langle \alpha | \exp \{-i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r}\} \{p - \frac{1}{2} \hbar(\mathbf{q} + \mathbf{G})\}_i | \alpha' \rangle \times \langle \alpha' | \exp \{i(\mathbf{q} + \mathbf{G}') \cdot \mathbf{r}\} \{p + \frac{1}{2} \hbar(\mathbf{q} + \mathbf{G}')\}_j | \alpha \rangle}{E_{\alpha} - E_{\alpha'} + \hbar\omega + i\delta} - (\alpha \leftrightarrow \alpha') \right\} \end{aligned} \quad (3.1)$$

where $|\alpha\rangle$ and E_{α} are the eigenstates and eigenvalues of the single-particle electronic Hamiltonian, and f_{α} is the Fermi function at energy E_{α} .

In the nearly-free-electron approximation for the conduction band in Al, we expand the periodic potential $V(\mathbf{r})$ as

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V(\mathbf{G}) \exp(i\mathbf{G} \cdot \mathbf{r}), \quad V(\mathbf{G}) = V^*(-\mathbf{G}) \quad (3.2)$$

and treat $V(\mathbf{G})/(\hbar^2 G^2/2m)$, $\mathbf{G} \neq 0$, as a small expansion parameter in the problem. In what follows, we calculate different components of ϵ only to the lowest non-vanishing order in this parameter. For non-resonant optical frequencies, we further assume that $\hbar\omega/(\hbar^2 G^2/2m)$ is also much less than 1. In the long wavelength limit for the incident optical wave ($\mathbf{q} \rightarrow 0$), and with the neglect of contributions of all bands other than the conduction band, we then find

$$\epsilon_{ij}(0, 0) = \delta_{ij} - \frac{4\pi n e^2}{m\omega^2} \left(1 - \sum_{\mathbf{G} \neq 0} \frac{3}{2} \frac{k_F^2}{(4k_F^2 - G^2)} \frac{|V(\mathbf{G})|^2}{E_F^2} \frac{G_i G_j}{G^2} I(\mathbf{G}) \right) \quad (3.3)$$

$$\epsilon_{Gj}(G, 0) = \frac{q_{FT}^2 I(G)}{(4k_F^2 - G^2)} \frac{V(G)}{(\hbar^2 G^2/2m)} \frac{G_j}{G} \quad (3.4)$$

$$\epsilon_{iG}(0, G) = \frac{q_{FT}^2 I(G)}{(4k_F^2 - G^2)} \frac{V^*(G)}{(\hbar^2 G^2/2m)} \frac{G_i}{G} \quad (3.5)$$

$$\epsilon_{GG}(G, G) = 1 + \frac{q_{FT}^2 I(G)}{2G^2} \quad (3.6)$$

where

$$I(G) = 1 + \frac{(4k_F^2 - G^2)}{4k_F G} \ln \left| \frac{2k_F + G}{2k_F - G} \right| \quad (3.7)$$

and where k_F is the Fermi wavevector, E_F is the Fermi energy, q_{FT} is the Thomas-Fermi wavevector and n is the electron density of the conduction band. Note that we have introduced the convention under which $\hat{G} \cdot \epsilon \cdot \hat{e}_j$ is written simply as ϵ_{Gj} . For several values of the reciprocal lattice vector G , we tabulate the values of these microscopic dielectric functions for Al in table 1. In the same table, we also give the ratio of the longitudinal components of secondary fields with respect to the field at the incident wavevector q , in the limit $q \rightarrow 0$. For this purpose the numerical values for the unscreened periodic potential in Al are taken from the paper by Bennet, Maraduddin and Swanson (1972). The screened $V(G)$ of this paper is obtained by dividing the corresponding unscreened Fourier components of the potential by our $\epsilon_{GG}(G, G)$. In this calculation, n is taken to be equal to $1.76 \times 10^{23} \text{ cm.}^{-3}$ and the lattice constant $a = 4.04 \text{ \AA}$. It has to be noted that the secondary fields are quite small in this case, and decrease rapidly with increasing G , so that both expression (2.8) and (2.12) give almost identical results.

Table 1. Microscopic dielectric function in case of Al, and the ratio of the induced longitudinal secondary field in it to the primary fields in the x-direction

$G = \frac{2\pi}{a} (n_1 n_2 n_3)$	$G/2k_F$	$V(G)$ (eV)	$\epsilon_{GG}(G, G)$	$\epsilon_{Gx}(G, 0)$ (10^{-3})	$\epsilon_{xG}(0, G)$ (10^{-3})	$\frac{\hat{G} \cdot E(G)}{\hat{X} \cdot E(0)}$ (10^{-3})
111, 1 $\bar{1}\bar{1}$, 11 $\bar{1}$, 1 $\bar{1}$ 1	0.78	0.136	1.44	-3.7	-3.7	-2.6
$\bar{1}\bar{1}\bar{1}$, $\bar{1}\bar{1}$ 1, $\bar{1}\bar{1}$ 1, $\bar{1}$ 1 $\bar{1}$	0.78	0.136	1.44	3.7	3.7	2.6
200	0.89	0.686	1.28	-43.2	-43.2	-33.6
$\bar{2}00$	0.89	0.686	1.28	43.2	43.2	33.6
220, 202, 2 $\bar{2}0$, 20 $\bar{2}$	1.27	0.691	1.06	2.0	2.0	1.9
$\bar{2}\bar{2}0$, $\bar{2}0\bar{2}$, $\bar{2}20$, $\bar{2}02$	1.27	0.691	1.06	-2.0	-2.0	-1.9
222, 2 $\bar{2}\bar{2}$, 2 $\bar{2}$ 2, 2 $\bar{2}$ 2	1.55	0.129	1.03	0.05	0.05	0.05
$\bar{2}\bar{2}\bar{2}$, $\bar{2}22$, $\bar{2}\bar{2}2$, $\bar{2}2\bar{2}$	1.55	0.129	1.03	-0.05	-0.05	-0.05
400	1.79	0.145	1.01	0.03	0.03	0.03
$\bar{4}00$	1.79	0.145	1.01	-0.03	-0.03	-0.03

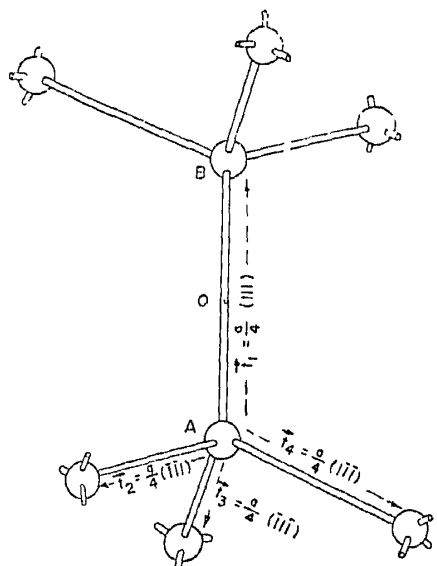


Figure 1. Tetrahedral bonds for Ge, pointing in $\{111\}$ directions. About the centre of any of the bonds, there is a complete inversion symmetry.

Using eq (2.13) and table 1, we can calculate the local field correction $\epsilon^{loc}(q, q, \omega) - \epsilon(q, q, \omega)$ to the dielectric function, since higher values of G contribute insignificantly to this correction. For Al we thus find this correction to ϵ_{xx} to be of the order of -3.0×10^{-3} only.

4. Microscopic dielectric function in germanium

In order to calculate the electronic dielectric tensor in insulators, one needs very accurate band structures, at least for the valence and conduction bands, over the whole Brillouin zone. However, since in the non-resonant region, only the average properties of the electrons over the Brillouin zone are involved, one may use the well-known bonding orbital approach for this calculation. In particular, as discussed by Coulson *et al* (1962), the eight valence electrons per unit cell of Ge can be considered to form four equivalent tetrahedral covalent bonds, which are localized between adjacent atoms in the crystallographic $\{111\}$ directions (figure 1). The four bonding sp^3 orbitals centered on these adjacent atoms form the valence band states, whereas, the four antibonding combination of these sp^3 orbitals give the conduction band states. Thus, *e.g.*, the unperturbed wavefunctions $\psi_{t_1}^V$ and $\psi_{t_1}^C$ for the bond in the direction t_1 , corresponding to the valence band and the conduction band, respectively, are

$$\psi_{t_1}^V = \frac{1}{\sqrt{2}} (\phi_{t_1}^A + \phi_{t_1}^B) \quad (4.1)$$

$$\psi_{t_1}^C = \frac{1}{\sqrt{2}} (-\phi_{t_1}^A + \phi_{t_1}^B) \quad (4.2)$$

$$\phi_{t_1}^A = \frac{1}{2} (\phi_{ns} + \sqrt{3}\phi_{np_{t_1}}) \quad (4.3)$$

$$\phi_{t_1}^B = \frac{1}{2} (\phi_{ns} - \sqrt{3}\phi_{np_{t_1}}) \quad (4.4)$$

where $\phi_{ns}^{A,B}$ and $\phi_{np_{t_1}}^{A,B}$ are s- and p-type hydrogen like normalized atomic wave functions centered on the atoms A and B.

In the case of localized electrons, the general expression (3.1) for the components $(\hat{q} + \hat{G}) \cdot \epsilon(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}') \cdot (\hat{q} + \hat{G}')$ of the microscopic dielectric tensor may be rewritten in the form

$$\epsilon_{\mathbf{q}+\mathbf{G}, \mathbf{q}+\mathbf{G}'}(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}', \omega) = \delta_{\mathbf{G}, \mathbf{G}'} + (4\pi e^2 / |\mathbf{q} + \mathbf{G}| |\mathbf{q} + \mathbf{G}'| \mathcal{V}) \times \sum_{\alpha\alpha'} f_{\alpha} \left[\frac{\langle \alpha' | \exp i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r} | \alpha \rangle \langle \alpha | \exp i(\mathbf{q} + \mathbf{G}') \cdot \mathbf{r} | \alpha \rangle}{E_{\alpha'} - E_{\alpha} + \hbar\omega} - (\alpha \leftrightarrow \alpha') \right] \quad (4.5)$$

by using the identity

$$\frac{(\hbar/m) \mathbf{Q} \cdot \langle \alpha | \exp(i\mathbf{Q} \cdot \mathbf{r}) (p + \hbar\mathbf{Q}/2) | \alpha' \rangle}{\alpha \neq \alpha'} = (E_{\alpha} - E_{\alpha'}) \langle \alpha | \exp i\mathbf{Q} \cdot \mathbf{r} | \alpha' \rangle, \quad (4.6)$$

Thus in this formalism, in the long wavelength limit ($\mathbf{q} \rightarrow 0$), and in the non-resonant region ($\omega \rightarrow 0$), we obtain

$$\epsilon_{\mathbf{G}\mathbf{G}}(\mathbf{G}, \mathbf{G}) = 1 + (8\pi e^2 N / G^2 E_g) \sum_t |\langle \psi_t^c | \exp(-i\mathbf{G} \cdot \mathbf{r}) | \psi_t^v \rangle|^2 \quad (4.7)$$

$$\epsilon_{\mathbf{G}\mathbf{j}}(\mathbf{G}, 0) = i(8\pi e^2 N / G E_g) \sum_t \langle \psi_t^v | \exp(-i\mathbf{G} \cdot \mathbf{r}) | \psi_t^c \rangle \langle \psi_t^c | r_j | \psi_t^v \rangle \quad (4.8)$$

$$\epsilon_{i\mathbf{G}}(0, \mathbf{G}) = -i(8\pi e^2 N / G E_g) \sum_t \langle \psi_t^v | r_i | \psi_t^c \rangle \langle \psi_t^c | \exp i\mathbf{G} \cdot \mathbf{r} | \psi_t^v \rangle \quad (4.9)$$

$$\epsilon_{ij}(0, 0) = \delta_{ij} + (8\pi e^2 N / E_g) \sum_t \langle \psi_t^v | r_i | \psi_t^c \rangle \langle \psi_t^c | r_j | \psi_t^v \rangle \quad (4.10)$$

where N is number of Ge atoms per unit volume and E_g is the energy gap between the antibonding and bonding states. Summations over t in eqs (4.7) to (4.10) imply simply summations over all the four bonds.

Note that because of the symmetry, for X, Y, Z along the rectangular crystallographic axis, eq (4.10) leads to

$$\epsilon_{XY}(0, 0) = \epsilon_{YX}(0, 0) = \epsilon_{ZX}(0, 0) = \epsilon_{XZ}(0, 0) = \epsilon_{YZ}(0, 0) = \epsilon_{ZY}(0, 0) = 0 \quad (4.11)$$

$$\epsilon_{XX}(0, 0) = \epsilon_{YY}(0, 0) = \epsilon_{ZZ}(0, 0) = 1 + (32\pi e^2 N / E_g) |\langle x \rangle_{vo}|^2 \quad (4.12)$$

$$\langle x \rangle_{vo} = \langle \psi_t^v | x | \psi_t^c \rangle \quad (4.13)$$

Assuming that the bonding and the antibonding states by themselves saturate the wellknown Thomas-Kuhn f -sum rule, we obtain another relation

$$(2m/\hbar^2) E_g |\langle x \rangle_{vo}|^2 = 1. \quad (4.14)$$

If we argue now that the value of the microscopic dielectric function $\epsilon_{XX}(0, 0)$ is somehow known, e.g., for Ge we take $\epsilon_{XX}(0, 0)$ to be 17.0 eqs (4.12) and (4.13) determine E_g in terms of the dipole matrix element $\langle x \rangle_{vo}$ in two different ways. Any consistent parametrization of the sp^3 orbitals to calculate $\langle x \rangle_{vo}$ from eqs (4.13) and (4.1) to (4.4), therefore, must make these two values of E_g to be the same. For Ge, we use hydrogen like wavefunctions with the principle quantum number $n = 4$, and treat the common effective Z -value for both s - and p -orbitals as a parameter. For consistency of eqs (4.12) and (4.14) for Ge, we then obtain

$$Z_{eff} = 12.4 \quad (4.15)$$

$$\langle x \rangle_{vo} = 0.992 \text{ \AA} \quad (4.16)$$

Table 2. Microscopic dielectric function in case of Ge, and the ratio of the induced longitudinal secondary field in it to the primary field in the x-direction

$G = \frac{2\pi}{a} (n_1 n_2 n_3)$	$\epsilon_{GG}(G, G)$	$\epsilon_{GX}(G, 0)$	$\epsilon_{XG}(0, G)$	$\hat{G} \cdot \hat{E}(G) / \hat{X} \cdot \hat{E}(0)$
111, $\bar{1}\bar{1}\bar{1}$, $\bar{1}\bar{1}1$, $1\bar{1}\bar{1}$	1.81	-0.38	-0.38	-0.21
$\bar{1}\bar{1}\bar{1}$, $1\bar{1}\bar{1}$, $1\bar{1}1$, $1\bar{1}\bar{1}$	1.81	0.38	0.38	0.21
220, 202, $\bar{2}\bar{2}0$, $\bar{2}\bar{2}2$	1.01	-0.19	-0.19	-0.19
$\bar{2}\bar{2}0$, $20\bar{2}$, $2\bar{2}0$, $02\bar{2}$	1.01	0.19	0.19	0.19
222, $2\bar{2}\bar{2}$, $2\bar{2}2$, $2\bar{2}\bar{2}$	1.01	-0.15	-0.15	-0.15
$\bar{2}\bar{2}\bar{2}$, $\bar{2}22$, $\bar{2}\bar{2}2$, $\bar{2}\bar{2}\bar{2}$	1.01	0.15	0.15	0.15
400	1.00	-0.06	-0.06	-0.06
$\bar{4}00$	1.00	0.06	0.06	0.06

$$E_g = 3.9 \text{ eV.} \quad (4.17)$$

The value of Z_{eff} so obtained is not very much different from the values given by Burns (1964), and the magnitude of the average gap E_g is also close to that given by Phillips (1969) for Ge.

Now, it is straightforward to calculate the relevant component of the microscopic dielectric function and the secondary fields. Although more exact expression (2.8) for the secondary fields gives a slightly different result from that obtained by using the expression (2.12), we have used the latter for simplicity. These results are given in table 2. It should be emphasized that the secondary fields are no longer negligible in this case. The local field correction $\epsilon_{XX}^{loc}(q, q, \omega) - \epsilon_{XX}(q, q, \omega)$ turns out to be of the order of -1.2 . Thus the figure for the optical dielectric function for Ge, including the local field correction is 15.8 in our calculation.

5. Mixing coefficients of x-ray and optical waves

The efficiency for mixing of x-ray and optical waves in a medium depends upon the induced microscopic charge density at the optical frequency. The effective coupling Hamiltonian for a light wave of (positive or negative) frequency ω and an x-ray of (positive or negative) frequency ω_R , in terms of the corresponding bilinear current density $J_{AA}(r, \omega + \omega_R)$ are given by (Woo and Jha 1972):

$$\mathcal{H}_{eff} = \frac{1}{i(\omega + \omega_R)c} \int d^3r J_{AA}(r, \omega + \omega_R) \cdot E(-\omega - \omega_R) \quad (5.1)$$

$$\begin{aligned} J_{AA}(r, \omega + \omega_R) &= -i(\omega + \omega_R) P^{NL}(r, \omega + \omega_R) \\ &= -i(e/4\pi m\omega_R) E(r, \omega_R) \nabla \cdot E(r, \omega) \end{aligned} \quad (5.2)$$

Since $\nabla \cdot E(r, \omega)$ is non-zero, in general, only for the secondary fields, for non-birefringent crystals we have to consider only these fields. The longitudinal components of $E(q + G, \omega)$, $G \neq 0$ in a cubic crystal, may be related back to the

Table 3. Non-linear susceptibility tensor for mixing of x-ray and optical frequencies.

$$\chi_{xxx}^{NL} = \chi_{yyx}^{NL} = \chi_{zzx}^{NL}; \quad \chi_{xxy}^{NL} = \chi_{yyx}^{NL} = \chi_{zzy}^{NL}; \quad \chi_{xxz}^{NL} = \chi_{yyz}^{NL} = \chi_{zzz}^{NL}$$

Al				Ge			
G	$-i\chi_{xxx}^{NL}$ (10^{-14} esu)	$-i\chi_{xxy}^{NL}$ (10^{-14} esu)	$-i\chi_{xxz}^{NL}$ (10^{-14} esu)	G	$-i\chi_{xxx}^{NL}$ (10^{-12} esu)	$-i\chi_{xxy}^{NL}$ (10^{-12} esu)	$-i\chi_{xxz}^{NL}$ (10^{-12} esu)
(111)	1.3	1.3	1.3	(111)	0.75	0.75	0.75
(200)	19.6	0	0	(220)	1.11	1.11	0
(220)	-1.6	1.6	0	(222)	1.07	1.07	1.07
(222)	-0.05	0.05	0.05				
(400)	-0.04	0	0	(400)	0.50	0	0

primary optical field $E(\mathbf{q}, \omega)$ by using eq. (2.8). Assuming the incident x-ray wave to vary with wave vector \mathbf{q}_R , eqs (5.1), (5.2) and (2.8) then lead to

$$P^{NL}(\mathbf{q} + \mathbf{q}_R + \mathbf{G}, \omega + \omega_R) = \chi^{NL}(\mathbf{q} + \mathbf{q}_R + \mathbf{G}, \mathbf{q}_R, \mathbf{q}, \omega + \omega_R): E(\mathbf{q}_R, \omega_R) E(\mathbf{q}, \omega), \quad G \neq 0 \quad (5.3)$$

where the bilinear susceptibility describing the mixing of x-ray and optical waves is

$$\chi_{\mu\nu\delta}^{NL}(\mathbf{q} + \mathbf{q}_R + \mathbf{G}, \mathbf{q}_R, \mathbf{q}, \omega_R + \omega) = \frac{ie\delta_{\mu\nu}}{4\pi m\omega_R(\omega_R + \omega)} \times \frac{(\mathbf{q} + \mathbf{G}) \cdot \hat{\mathbf{e}}_\delta \epsilon_{\delta\delta}^{-1}(\mathbf{q} + \mathbf{G}, \mathbf{q}, \omega)_2}{\epsilon_{\delta\delta}^{-1}(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}, \omega)}, \quad G \neq 0 \quad (5.4)$$

In the long wavelength limit for the optical wave, \mathbf{q} in the right hand side of the above equation can be neglected everywhere. For lowest values of G , we calculate $\chi_{\mu\mu\delta}^{NL}$ for Al and Ge, with the x-ray frequency $\omega_R = 1.5 \times 10^{18} \text{ sec}^{-1}$ ($\approx 1 \text{ keV}$ x-ray) and the optical frequency $\omega \ll \omega_R$. The results are given in table 3. Note that in Ge, χ^{NL} is of the order of 10^{-12} in esu. This may be significant enough to ensure the experimental observation of this mixing.

6. Conclusions

The detailed calculations in this paper of microscopic optical fields in solids show that the secondary fields and the local field corrections are unimportant in metals like Al, whereas these are appreciable in insulators like Ge. This confirms the usual ideas that in dense systems, more tightly bound electrons give larger local field corrections to the dielectric function. For the same reason, the non-linear mixing coefficient for x-ray and optical waves is much smaller in Al than in Ge. For systems much more tightly bound than Ge, the mixing coefficient may be still higher. As pointed out by Eisenberger and McCall (1971) who have also used the wave function approach to calculate the secondary fields in solid hydrogen, our actual numerical values for Ge may not be very accurate. Our calculation for Al can be criticised on the grounds that we should have used the bare crystal potential instead of the pseudo-potential to describe the electronic state. In the

optical region, we feel this should not lead to serious errors, since in that case core excitations would not play a dominant role (see Van Vechten and Martin 1972).

References

- Adler S L 1962 *Phys. Rev.* **126** 413
Agranovich V M and Ginzburg V L 1966 *Spatial dispersion in crystal optics and the theory of excitons* (Interscience Publishers: New York)
Bonnet B I, Maradudin A A and Swanson L R 1972 *Ann. Phys.* **71**, 357
Burns G 1964 *J. Chem. Phys.* **41** 1521
Coulson C, Redei L and Stocker D 1962 *Proc. Roy. Soc. London A* **270** 357
Eisenberger P M and McCall S L 1971 *Phys. Rev.* **A3** 1145
Freund I and Levine B F 1970 *Phys. Rev. Lett.* **25** 1241
Jha S S and Warke C S 1968 *Nuovo Cimento* **53B** 120
Phillips J C 1969 *Covalent bonding in crystals, molecules and polymers* (The University of Chicago Press)
Pine A S 1965 *Phys. Rev.* **A139** 901
Sinha S K, Gupta R P and Price D L 1971 *Phys. Rev. Lett.* **26** 1324
Van Vechten J A and Martin R M 1972 *Phys. Rev. Lett.* **28** 446
Wiser N 1963 *Phys. Rev.* **129** 62
Woo J W F and Jha S S 1972 *Phys. Rev.* **B6** 4081