

THE DIELECTRIC CONSTANT OF CRYSTALS FROM THE QUANTUM VIEWPOINT

G. M. GANDEL'MAN and V. M. ERMACHENKO

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The study of the integral equation for the inverse dielectric constant operator started by Falk and by Adler^[1,2] is continued. An expression is obtained for $\epsilon(\omega)$ suitable for the direct calculation of the dependence of $\epsilon(\omega)$ on the density of the medium. Under certain assumptions the behaviour of $\epsilon(0)$ during transition to the metallic state is studied, and the singularities in $\epsilon(\omega)$ at the start of the absorption band are clarified. The possibility is shown of calculating the optical anisotropy of cubic crystals in the framework of the approximation.

INTRODUCTION

A number of papers^[1,2] in recent years have considered the problems associated with the quantum treatment of the dielectric constant of crystals. When the correlation corrections to the energy obtained in the Hartree-Fock approximation are considered, an equation naturally arises relating the so-called effective interaction in the medium to the simple Coulomb interaction. Hubbard^[3] has given the most detailed derivation of this equation. Martin and Schwinger^[4] and Falk^[1] established that the dielectric constant of the medium is directly related to this effective interaction. Falk^[1] considered by this means the case of almost free electrons, and attempted to take into account the effect on $\epsilon(\omega)$ of the so-called correction to the local field. The question of the correction to the local field has been treated most fully in the paper by Adler^[2].

In our work we continue the study commenced in^[1,2] of the integral equation for the inverse dielectric constant operator.

The principal aim of our work is to develop a convenient method of calculating the static dielectric constant—the method being suitable for finding the variation of $\epsilon(0)$ with the density of the medium. It should be pointed out at once that in our work, as also in^[1,2], the effect of excitons on the dielectric constant is not considered at all. In particular this fact manifests itself in that absorption in dielectrics starts not at Δ/\hbar , where Δ is the width of the forbidden gap, but earlier, at exciton levels. This fact is important when the variation of the dielectric constant with frequency ω is sought; we consider, however, that taking exciton states into account does not greatly change the value of the static dielectric constant. In further

work we shall attempt to take this effect into account.

In the present work a formula is obtained which allows $\epsilon(0)$ to be calculated if the wave functions and the energy spectrum of the electrons in the crystal are known^[5]; a rigorous upper estimate for $\epsilon(\omega)$ is also obtained in the range of frequencies for which there is no absorption. In particular for $\epsilon(0)$ we have:

$$\epsilon(0) < 1 - D(\mathbf{k}, \mathbf{k}, 0), \quad |\mathbf{k}| \rightarrow 0.$$

Here $D(\mathbf{k}, \mathbf{k}, 0)$ is a simple function of well known quantities (wave functions and energy spectrum). Under certain assumptions an estimate is made of the character of the singularity in $\epsilon(\omega)$ when $\omega \rightarrow \Delta$. Here it is found that $\epsilon(\omega)$ is finite as $\omega \rightarrow \Delta$ but its derivative is discontinuous:

$$\frac{\partial}{\partial \omega} \operatorname{Re} \epsilon(\omega) = \begin{cases} \text{const} / \sqrt{\Delta - \omega}, & \omega = \Delta - \epsilon, \\ \text{const}, & \omega = \Delta + \epsilon; \end{cases}$$

$$\operatorname{Im} \epsilon(\omega) \sim \sqrt{\omega - \Delta}, \quad \omega = \Delta + \epsilon, \quad \epsilon \rightarrow 0.$$

The same estimate shows that under compression $\epsilon(0)$ should increase and at the transition to a metal should jump discontinuously to infinity.

In addition the possibility of calculating the optical anisotropy of cubic crystals within the framework of the approximation is demonstrated in the paper.

1. THE INTEGRAL EQUATION FOR THE INVERSE DIELECTRIC CONSTANT OPERATOR AND THE STUDY OF THE SINGULARITIES OF THIS EQUATION

As already noted in the introduction, when the correlation corrections to the energy calculated in the Hartree-Fock approximation are considered, an equation for the effective Coulomb interaction $F(x, x')$ is obtained:

$$F(x, x') = J(x - x') + \int dydz J(x - y) M(y, z) F(z, x'), \quad (1)$$

where $J(x - y) = e^2 \delta(x_0 - y_0) / |\mathbf{x} - \mathbf{y}|$ is the simple Coulomb interaction, the nucleus is

$$M(y, z) = iS(y, z) S(z, y) - \int dudv J(u - v) S(y, v) S(v, z) S(z, u) S(u, y), \quad (2)$$

and $S(y, z)$ is the electronic Green function in the crystal calculated in the Hartree-Fock approximation. The kernel $M(y, z)$ includes the two diagrams of lowest order in the interaction, simple polarization and exchange, as shown in Fig. 1.

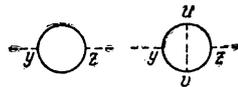


FIG. 1

For a more detailed introduction to this question we refer the reader to Hubbard's paper^[3].

We show the relation between $F(x, x')$ and the dielectric constant. We make certain transformations. We multiply (1) by $M(x', u)$ and integrate with respect to dx' . Using the notation

$$\int F(x, x') M(x', u) dx' = L(x, u),$$

we obtain

$$L(x, u) = \int dx' J(x - x') M(x', u) + \int dydz J(x - y) M(y, z) L(z, u).$$

We introduce the notation $B(x, u) = L(x, u) + \delta(x - u)$; then

$$B(x, u) = \delta(x - u) + \int dydz J(x - y) M(y, z) B(z, u). \quad (3)$$

It is easy to show that the function

$$G(x, x') = \int dt B(x, t) J(t - x') \quad (4)$$

coincides with $F(x, x')$. In fact, substituting in (4) $B(x, t)$ from (3), we obtain

$$G(x, x') = J(x - x') + \int dydz J(x - y) M(y, z) G(z, x'),$$

which agrees with (1).

The significance of the operator $B(x, x')$ is seen in the following example. Let the charge density be $\rho(x')$. Then it creates in the medium a potential

$$\varphi_{eff}(x) = \int dx' F(x, x') \rho(x')$$

$$\begin{aligned} &= \int dt dx' B(x, t) J(t - x') \rho(x') \\ &= \int B(x, t) \varphi(t) dt \\ &(\varphi(t) = \int J(t - x') \rho(x') dx'). \end{aligned}$$

Here $\varphi(t)$ is the potential created by the given charge distribution without taking into account the polarization of the medium. In the homogeneous case when $B(x, t) = B(x - t)$ we obtain for the Fourier transforms of the functions $\varphi_{eff}(x)$ and $B(x - t)$

$$\varphi_{eff}(\mathbf{k}, \omega) = B(\mathbf{k}, \omega) 4\pi k^{-2} \rho(\mathbf{k}, \omega),$$

whence it is obvious that $B(\mathbf{k}, \omega)$ is the inverse dielectric constant operator $\epsilon^{-1}(\mathbf{k}, \omega)$. The reader interested in a more rigorous proof of the identity of $B(\mathbf{k}, \omega)$ and $\epsilon^{-1}(\mathbf{k}, \omega)$ is referred to^[1,4].

Thus, to find the dielectric constant it is necessary to solve equation (3), the study of which we are concerned with.

From expression (2) for $M(y, z)$ it follows that $M(y, z)$ depends on the difference of the times $(y_0 - z_0)$ and satisfies the periodic condition

$$M(\mathbf{y} + \mathbf{R}, \mathbf{z} + \mathbf{R}, y_0 - z_0) = M(\mathbf{y}, \mathbf{z}, y_0 - z_0)$$

(\mathbf{R} are translation vectors of the direct lattice), since

$$\begin{aligned} S(y, z) &= \epsilon(y_0 - z_0) \sum_j^{occ} U_j^*(y) U_j(z) e^{iE_j(y_0 - z_0)} \\ &- \epsilon(z_0 - y_0) \sum_\alpha^{unocc} U_\alpha^*(y) U_\alpha(z) e^{iE_\alpha(y_0 - z_0)}, \end{aligned} \quad (5)$$

where $U_j(y)$ is the solution of the Hartree-Fock equations. The index j labels the quasi-momentum \mathbf{k}_j and the band number n_j . In what follows the italic letters j, i will refer to occupied electronic states, and the Greek letters α, β to unoccupied.

We take the Fourier transform of Eq. (3).

Using the properties of $M(y, z)$, we can consider it to be a function of the difference $\mathbf{y} - \mathbf{z}$ and of one of the variables, for example, y , where it must be periodic in this variable. Then

$$\begin{aligned} M(y, z) &= \sum_{\mathbf{g}} \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{d\omega}{2\pi} M(\mathbf{k}, \mathbf{g}, \omega) \\ &\times \exp[i\mathbf{g}\mathbf{y} - i\mathbf{k}(\mathbf{y} - \mathbf{z}) - i\omega(y_0 - z_0)], \\ B(x, x') &= \sum_{\mathbf{g}} \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{d\omega}{2\pi} B(\mathbf{k}, \mathbf{g}, \omega) \\ &\times \exp[i\mathbf{g}\mathbf{x} - i\mathbf{k}(\mathbf{x} - \mathbf{x}') - i\omega(x_0 - x'_0)], \\ J(x - y) &= \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{d\omega}{2\pi} \frac{4\pi e^2}{k^2} \\ &\times \exp[-i\mathbf{k}(\mathbf{x} - \mathbf{y}) - i\omega(x_0 - y_0)] \end{aligned} \quad (6)$$

(\mathbf{g} is a vector of the reciprocal lattice).

The Fourier transform of (3) becomes

$$B(\mathbf{k}, \mathbf{g}, \omega) = \delta_{\mathbf{g}, 0} + \sum_{\mathbf{m}} \frac{4\pi e^2}{|\mathbf{k} - \mathbf{g}|^2} M(\mathbf{k} - \mathbf{m}, \mathbf{g} - \mathbf{m}, \omega) B(\mathbf{k}, \mathbf{m}, \omega). \quad (7)$$

Using (2) and (5) we obtain

$$M(\mathbf{k}, \mathbf{g}, \omega) = \frac{1}{V} \sum_{j, \beta} H_{j\beta}^*(\mathbf{k} - \mathbf{g}) H_{j\beta}(\mathbf{k}) \left[P \frac{2(E_j - E_\beta)}{(E_j - E_\beta)^2 - \omega^2} - \pi i \delta(E_j - E_\beta + \omega) - \pi i \delta(E_j - E_\beta - \omega) \right]; \quad (8)$$

P stands for the principal value,

$$H_{j\beta}(\mathbf{k}) = \int d\mathbf{r} U_j^*(\mathbf{r}) e^{i\mathbf{k}\mathbf{r}} U_\beta(\mathbf{r}). \quad (9)$$

In this expression for $M(\mathbf{k}, \mathbf{g}, \omega)$ only the term $iS(y, z)S(z, y)$ is taken into account. The following term, which takes into account the effect of the exchange diagram, is of higher order in the interaction, and it will be evaluated at the end of the article.

From (7) and (9) it is obvious that, as $\mathbf{k} \rightarrow \mathbf{g}$, the kernel of (7) has a pole $|\mathbf{k} - \mathbf{g}|^{-1}$. To remove this singularity we introduce the function $B(\mathbf{k}, \mathbf{g}) = \mathbf{k} |\mathbf{k} - \mathbf{g}|^{-1} b(\mathbf{k}, \mathbf{g})$ (for brevity we omit ω). We use the notation

$$\frac{4\pi e^2}{|\mathbf{k} - \mathbf{g}|} \frac{M(\mathbf{k} - \mathbf{m}, \mathbf{g} - \mathbf{m})}{|\mathbf{k} - \mathbf{m}|} = D(\mathbf{k} - \mathbf{m}, \mathbf{k} - \mathbf{g}). \quad (10)$$

It is obvious that $D(\mathbf{k} - \mathbf{m}, \mathbf{k} - \mathbf{g})$ has no singularities as $\mathbf{k} \rightarrow \mathbf{m}$, $\mathbf{k} \rightarrow \mathbf{g}$. From this the equation for $b(\mathbf{k}, \mathbf{g})$ has the form

$$b(\mathbf{k}, \mathbf{g}) = \delta_{\mathbf{g}, 0} + \sum_{\mathbf{m}} D(\mathbf{k} - \mathbf{m}, \mathbf{k} - \mathbf{g}) b(\mathbf{k}, \mathbf{m}). \quad (11)$$

We now establish the relation between the dielectric constant and the function $b(\mathbf{k}, \mathbf{g}, \omega)$. We have

$$\varphi_{eff}(x) = \int B(x, t) \varphi(t) dt.$$

Let $\varphi(x) = \varphi_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{x} - i\omega x_0}$; then

$$\varphi_{eff}(x) = \sum_{\mathbf{m}} B(\mathbf{k}, \mathbf{m}, \omega) \varphi_{\mathbf{k}} e^{i(\mathbf{m}-\mathbf{k})\cdot\mathbf{x} - i\omega x_0}. \quad (12)$$

Here $\varphi_{eff}(x)$ is the microscopic potential which contains rapidly varying terms. Averaging as usual over the region where $\mathbf{k}\mathbf{x}$ changes little, but which is large compared with the dimensions of the unit cell, we obtain

$$\langle \varphi_{eff}(x) \rangle = B(\mathbf{k}, 0, \omega) \varphi_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{x} - i\omega x_0}.$$

Hence we determine $\epsilon(\mathbf{k}, \omega) = B^{-1}(\mathbf{k}, 0, \omega)$ by analogy with the formula

$$\varphi_{eff}(\mathbf{k}, \omega) = \frac{4\pi\rho(\mathbf{k}, \omega)}{k^2\epsilon(\mathbf{k}, \omega)}. \quad (13)$$

We note the fact that the Fourier components $B(\mathbf{k}, \mathbf{g}, \omega) = \epsilon^{-1}(\mathbf{k}, \mathbf{g}, \omega)$ have poles at the points $\mathbf{k} = \mathbf{g}$ because $B(\mathbf{k}, \mathbf{g}, \omega) = \mathbf{k} |\mathbf{k} - \mathbf{g}|^{-1} b(\mathbf{k}, \mathbf{g}, \omega)$ but $b(\mathbf{k}, \mathbf{g}, \omega)$ has no zeroes for $\mathbf{k} = \mathbf{g}$. The condition $\mathbf{k} = \mathbf{g}$ coincides exactly with the well-known Bragg law for the reflection of x rays.

We remark that if $\epsilon(\mathbf{k}, \omega)$ is a tensor, as happens in the general case for a crystal, then $\epsilon(\mathbf{k}, \omega)$ in formula (13) must be replaced by $\hat{\mathbf{k}}\epsilon(\mathbf{k}, \omega)\hat{\mathbf{k}} = k_i^0 \epsilon_{ij}(\mathbf{k}, \omega) k_j^0$ where k_i^0 are the direction cosines of $\hat{\mathbf{k}}$.

Thus, remembering that $B(\mathbf{k}, 0, \omega) = b(\mathbf{k}, 0, \omega)$ we obtain

$$\hat{\mathbf{k}}\epsilon(\mathbf{k}, \omega)\hat{\mathbf{k}} = b^{-1}(\mathbf{k}, 0, \omega). \quad (14)$$

In what follows we limit ourselves to the case of an insulator in that range of frequencies for which there is no absorption, i.e. $\omega < \min(E_\beta - E_j)$, and consider only the frequency dispersion of the dielectric constant

$$\epsilon(\omega) = \lim_{\mathbf{k} \rightarrow 0} \epsilon(\mathbf{k}, \omega). \quad (15)$$

2. SOLUTION OF THE EQUATION FOR $b(\mathbf{k}, \mathbf{g})$

We consider Eq. (11) for $b(\mathbf{k}, \mathbf{g})$. For $b(\mathbf{k}, 0)$ we have

$$b(\mathbf{k}, 0) [1 - D(\mathbf{k}, \mathbf{k})] = 1 + \sum_{\mathbf{m} \neq 0} D(\mathbf{k} - \mathbf{m}, \mathbf{k}) b(\mathbf{k}, \mathbf{m}). \quad (16)$$

For $\mathbf{g} \neq 0$

$$b(\mathbf{k}, \mathbf{g}) = D(\mathbf{k}, \mathbf{k} - \mathbf{g}) b(\mathbf{k}, 0) + \sum_{\mathbf{m} \neq 0} D(\mathbf{k} - \mathbf{m}, \mathbf{k} - \mathbf{g}) b(\mathbf{k}, \mathbf{m}). \quad (17)$$

We divide (16) and (17) by $b(\mathbf{k}, 0)$ and label

$$\alpha(\mathbf{k}, \mathbf{m}) = b(\mathbf{k}, \mathbf{m})/b(\mathbf{k}, 0), \quad \mathbf{m} \neq 0. \quad (18)$$

Then

$$b^{-1}(\mathbf{k}, 0) = 1 - D(\mathbf{k}, \mathbf{k}) - \sum_{\mathbf{m} \neq 0} D(\mathbf{k} - \mathbf{m}, \mathbf{k}) \alpha(\mathbf{k}, \mathbf{m}), \quad (19)$$

$$\alpha(\mathbf{k}, \mathbf{g}) = D(\mathbf{k}, \mathbf{k} - \mathbf{g}) + \sum_{\mathbf{m} \neq 0} D(\mathbf{k} - \mathbf{m}, \mathbf{k} - \mathbf{g}) \alpha(\mathbf{k}, \mathbf{m}). \quad (20)$$

It follows from (14), (15) and (19)

$$\hat{\mathbf{k}}\epsilon(\omega)\hat{\mathbf{k}} = \lim_{\mathbf{k} \rightarrow 0} \left\{ 1 - D(\mathbf{k}, \mathbf{k}, \omega) - \sum_{\mathbf{m} \neq 0} D(\mathbf{k} - \mathbf{m}, \mathbf{k}, \omega) \alpha(\mathbf{k}, \mathbf{m}, \omega) \right\}. \quad (21)$$

The functions $\alpha(\mathbf{k}, m)$ are found from (20). Before we show the way to solve (20), we demonstrate in a general form that $\hat{\kappa}\epsilon(\omega)\hat{\mathbf{k}}$ is always smaller than the quantity $[1 - D(\mathbf{k}, \mathbf{k}, \omega)]$, $\mathbf{k} \rightarrow 0$.

We multiply the complex conjugate of (20) by $\alpha(\mathbf{k}, \mathbf{g})$ and sum with respect to $\mathbf{g} \neq 0$:

$$\sum_{\mathbf{g} \neq 0} |\alpha(\mathbf{k}, \mathbf{g})|^2 = \sum_{\mathbf{g} \neq 0} D^*(\mathbf{k}, \mathbf{k} - \mathbf{g}) \alpha(\mathbf{k}, \mathbf{g}) + \sum_{\mathbf{m}, \mathbf{g} \neq 0} \alpha^*(\mathbf{k}, \mathbf{m}) D(\mathbf{k} - \mathbf{m}, \mathbf{k} - \mathbf{g}) \alpha(\mathbf{k}, \mathbf{g}).$$

In the absence of absorption $D(\mathbf{k} - \mathbf{g}, \mathbf{k}) = D^*(\mathbf{k}, \mathbf{k} - \mathbf{g})$. It is clear, therefore, that

$$\sum_{\mathbf{m} \neq 0} D(\mathbf{k} - \mathbf{m}, \mathbf{k}) \alpha(\mathbf{k}, \mathbf{m}) = \sum_{\mathbf{m} \neq 0} |\alpha(\mathbf{k}, \mathbf{m})|^2 + \frac{4\pi e^2}{V} \sum_{i\beta} \frac{2(E_\beta - E_i)}{[(E_i - E_\beta)^2 - \omega^2]} \left| \sum_{\mathbf{m} \neq 0} \frac{H_{i\beta}(\mathbf{k} - \mathbf{m})}{|\mathbf{k} - \mathbf{m}|} \alpha^*(\mathbf{k}, \mathbf{m}) \right|^2 > 0,$$

because $(E_\beta - E_i) > 0$. Thus $\hat{\kappa}\epsilon(\omega)\hat{\mathbf{k}} < 1 - D(\mathbf{k}, \mathbf{k}, \omega)$, $\mathbf{k} \rightarrow 0$.

We now show how one must find $\alpha(\mathbf{k}, m)$ in the case of a crystal. We expand $\alpha(\mathbf{k}, m)$ in spherical functions, which depend on the angles between m and an arbitrary vector, \mathbf{k} , for example:

$$\alpha(\mathbf{k}, m, \omega) = \sum_{q,\mu} C_{q\mu}(\mathbf{k}, m, \omega) Y_{q\mu}(-m^0), \quad (22)$$

where m^0 are the direction cosines of the direction m . Then we have from (20)

$$\sum_{q,\mu} C_{q\mu}(\mathbf{k}, \mathbf{g}, \omega) Y_{q\mu}(-g^0) = D(\mathbf{k}, \mathbf{k} - \mathbf{g}) + \sum_{\mathbf{m}, q, \mu} D(\mathbf{k} - \mathbf{m}, \mathbf{k} - \mathbf{g}) C_{q\mu}(\mathbf{k}, m, \omega) Y_{q\mu}(-m^0). \quad (23)$$

For a crystal the wave functions can be represented as a sum of spherical harmonics (n_i is the number of the band):

$$U_i(\mathbf{r}) = U_{k_i}^{n_i}(\mathbf{r}) = \sum_{l_i, m_i} A_{l_i, m_i}^{n_i}(\mathbf{k}_i) f_{l_i}^{n_i}[r, E_{n_i}(\mathbf{k}_i)] Y_{l_i, m_i}(r^0).$$

When calculating $H_{i\beta}(\mathbf{k} - \mathbf{g})$ we easily see that $\mathbf{k}_\beta = \mathbf{k}_i - \mathbf{k}$ but since we consider $\mathbf{k} \rightarrow 0$ then $\mathbf{k}_\beta \approx \mathbf{k}_i$ and

$$H_{i\beta}(-\mathbf{g}) = \sum_{l_i, m_i, l_2, m_2} A_{l_i, m_i}^{n_i} \times (\mathbf{k}_i) A_{l_2, m_2}^{n_i}(\mathbf{k}_i) \int dr \cdot r^2 f_{l_i}^{n_i}[r, E_{n_i}(\mathbf{k}_i)] f_{l_2}^{n_i}[r, E_{n_i}(\mathbf{k}_i)] \times \int Y_{l_i, m_i}^*(r^0) Y_{l_2, m_2}(r^0) e^{-igr} d\Omega.$$

It can be shown that

$$\int Y_{l_i, m_i}^*(r^0) Y_{l_2, m_2}(r^0) e^{-igr} d\Omega = \sqrt{4\pi} (-1)^{m_1} \sum_{\rho=|m_2-m_1|}^{\infty} i^\rho [j_\rho(gr) - \delta_{\rho,0}]$$

$$\times B_{l_1, -m_1; l_2, m_2}^{p, m_2-m_1} B_{l_1, 0; l_2, 0}^{p, 0} \times \sqrt{\frac{(2l_1+1)(2l_2+1)}{(2\rho+1)}} Y_{\rho, m_2-m_1}(-g^0),$$

where $|l_1 + l_2 - \rho|$ is an even number, $B_{l_1 m_1; l_2 m_2}^{p, M}$ are Clebsch-Gordan coefficients, and $j_\rho(gr)$ are spherical Bessel functions.

Further

$$\frac{H_{i\beta}(-\mathbf{g})}{g} = \sum_{l_1, m_1, l_2, m_2} \sqrt{4\pi} \times (-1)^{m_1} A_{l_1, m_1}^{n_i}(\mathbf{k}_i) A_{l_2, m_2}^{n_i}(\mathbf{k}_i) \sum_{\rho=|m_2-m_1|}^{\infty} i^\rho B_{l_1, -m_1; l_2, m_2}^{p, m_2-m_1} \times B_{l_1, 0; l_2, 0}^{p, 0} \sqrt{\frac{(2l_1+1)(2l_2+1)}{(2\rho+1)}} \times F_{l_1, l_2, \rho}^{n_i, n_i}(\mathbf{g}, \mathbf{k}_i) Y_{\rho, m_2-m_1}(-g^0), \quad (24)$$

$$F_{l_1, l_2, \rho}^{n_i, n_i}(\mathbf{g}, \mathbf{k}_i) = \int dr \cdot r^2 f_{l_1}^{n_i} \times [r, E_{n_i}(\mathbf{k}_i)] f_{l_2}^{n_i}[r, E_{n_i}(\mathbf{k}_i)] \frac{j_\rho(gr) - \delta_{\rho,0}}{g}. \quad (25)$$

We multiply equation (23) by $Y_{q\mu}^*(-g^0)$ and integrate with respect to $d\Omega_{g^0}$. We obtain

$$C_{q\mu}(\mathbf{k}, \mathbf{g}, \omega) = \int D(\mathbf{k}, \mathbf{k} - \mathbf{g}, \omega) Y_{q\mu}^*(-g^0) d\Omega_{g^0} + \sum_{i,\beta} \frac{8\pi e^2}{V} \frac{E_i - E_\beta}{[(E_i - E_\beta)^2 - \omega^2]} \times h_{q\mu}^{n_i, n_i}(\mathbf{g}, \mathbf{k}_i) \sum_{m, \rho, \nu} C_{\rho\nu}(\mathbf{k}, m, \omega) h_{\rho\nu}^{n_i, n_i}(m, \mathbf{k}_i),$$

$$h_{q\mu}^{n_i, n_i}(\mathbf{g}, \mathbf{k}_i) = \sum_{l_1, m_1} \sqrt{4\pi} (-1)^{m_1} i^q \sqrt{\frac{(2l_1+1)(2l_2+1)}{2q+1}} \times B_{l_1, -m_1; l_2, m_1+\mu}^{q, \mu} \times B_{l_1, 0; l_2, 0}^{q, 0} A_{l_1, m_1}^{n_i}(\mathbf{k}_i) A_{l_2, m_1+\mu}^{n_i}(\mathbf{k}_i) F_{l_1, l_2, q}^{n_i, n_i}(\mathbf{g}, \mathbf{k}_i) \quad (26)$$

($l_1 + l_2 + q$ is even).

Here we have replaced the summation over the directions m_0 by an integration:

$$\int D(\mathbf{k}, \mathbf{k} - \mathbf{g}, \omega) Y_{q\mu}^*(-g^0) d\Omega_{g^0} = \frac{8\pi e^2}{V} \sum_{i\beta} \frac{(E_i - E_\beta)}{[(E_i - E_\beta)^2 - \omega^2]} \frac{H_{i\beta}^*(\mathbf{k})}{k} h_{q\mu}^{n_i, n_i}(\mathbf{g}, \mathbf{k}_i).$$

Thus we have a system of algebraic equations in terms of $C_{q\mu}(\mathbf{k}, \mathbf{g}, \omega)$:

$$C_{q\mu}(\mathbf{k}, \mathbf{g}, \omega) = \frac{8\pi e^2}{V} \sum_{i\beta} \frac{(E_i - E_\beta)}{[(E_i - E_\beta)^2 - \omega^2]} \times h_{q\mu}^{n_i, n_i}(\mathbf{g}, \mathbf{k}_i) \left[\frac{H_{i\beta}^*(\mathbf{k})}{k} + \sum_{m, \rho, \nu} h_{\rho\nu}^{n_i, n_i}(m, \mathbf{k}_i) C_{\rho\nu}(\mathbf{k}, m, \omega) \right]. \quad (27)$$

We note that in the calculation of $k^{-1}H_{i\beta}(\mathbf{k})$ ($k \rightarrow 0$) in (24) only the term with $p = 1$ remains.

The dielectric constant is given in terms of $C_{q\mu}(\mathbf{k}, \mathbf{g}, \omega)$ in the following way:

$$\hat{\mathbf{k}}\epsilon(\omega)\hat{\mathbf{k}} = \lim_{k \rightarrow 0} \left\{ 1 - D(\mathbf{k}, \mathbf{k}, \omega) - \frac{8\pi e^2}{V} \sum_{i\beta} \frac{H_{i\beta}(\mathbf{k})}{k} \right. \\ \left. \times \frac{(E_i - E_\beta)}{(E_i - E_\beta)^2 - \omega^2} \sum_{m p \nu} h_{p\nu}^{n_i n_\beta}(\mathbf{m}, \mathbf{k}_i) C_{p\nu}(\mathbf{k}, \mathbf{m}, \omega) \right\}. \quad (28)$$

Formula (28) is the basic one for the calculation of $\epsilon(\omega)$.

We remark that, although it is clear theoretically that in a cubic crystal $\epsilon_{ik}(\omega) = \epsilon(\omega)\delta_{ik}$, errors in the calculation can make it appear that $\epsilon_{xx}(\omega)$, $\epsilon_{yy}(\omega)$ and $\epsilon_{zz}(\omega)$ differ somewhat from one another. It is therefore necessary in practice to put successively in (28)

$$\mathbf{k} = \begin{pmatrix} k_x \\ 0 \\ 0 \end{pmatrix}, \quad \mathbf{k} = \begin{pmatrix} 0 \\ k_y \\ 0 \end{pmatrix}, \quad \mathbf{k} = \begin{pmatrix} 0 \\ 0 \\ k_z \end{pmatrix}$$

and calculate $\epsilon_{xx}(\omega)$, $\epsilon_{yy}(\omega)$ and $\epsilon_{zz}(\omega)$ as $k \rightarrow 0$. The mean value $\epsilon(\omega) = \frac{1}{3} \text{Sp} \epsilon_{ik}(\omega)$ should be taken for $\epsilon(\omega)$.

It is possible that a good approximation for the solution of the system (26) will be to take into account only certain values of the modulus m — the vector of the reciprocal lattice. Knowing the wave functions and the energy eigen values in the crystal,^[5] we can calculate the functions

$F_{l_1 l_2 p}^{n_i n_\beta}(\mathbf{g}, \mathbf{k}_i)$ and $h_{q\mu}^{n_i n_\beta}(\mathbf{g}, \mathbf{k}_i)$. This procedure can be applied for various values of the density.

Thus the change of $\epsilon(\omega)$ when the crystal is compressed will be found. We note that if $|D(\mathbf{k}, \mathbf{k} - \mathbf{g}, \omega)| < 1$ ($\mathbf{g} \neq 0$) then, solving (20) by an iteration method, we obtain

$$\hat{\mathbf{k}}\epsilon(\omega)\hat{\mathbf{k}} = \lim_{k \rightarrow 0} \left\{ 1 - D(\mathbf{k}, \mathbf{k}, \omega) - \sum_{\mathbf{m} \neq 0} D(\mathbf{k}, \mathbf{k} - \mathbf{m}, \omega) D(\mathbf{k} - \mathbf{m}, \mathbf{k}, \omega) - \dots \right\}. \quad (28')$$

VARIOUS LIMITING CASES FOR $\epsilon(\omega)$

We now consider several particular cases for $\epsilon(\omega)$. In the case of a free electron gas $U_i(\mathbf{x}) = V^{-1/2} e^{i\mathbf{k}\mathbf{x}}$. A direct calculation of $D(\mathbf{k}, \mathbf{g}, \omega)$ shows that only $D(\mathbf{k}, \mathbf{k}, \omega)$ the diagonal expressions, do not vanish. It is therefore obvious from (21) that

$$\epsilon(\omega) = \lim_{k \rightarrow 0} [1 - D(\mathbf{k}, \mathbf{k}, \omega)].$$

Calculation gives

$$\epsilon(\omega) = 1 - 4\pi n e^2 / m \omega^2,$$

where n is the number of electrons per cm^3 ; this expression agrees with the classical one for free electrons.

The other limiting case is that of isolated atoms, in the sense that the wave functions of the system of electrons can be represented by the strong binding method. Here we consider only the case of completely filled bands when the Bloch and Heitler-London methods coincide. Then

$$\psi_{\mathbf{k}_i}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}_i \mathbf{R}} \varphi_i(\mathbf{r} - \mathbf{R}) \quad (29)$$

(N is the number of atoms in the crystal, and $\varphi_i(\mathbf{r})$ are the atomic functions).

Calculating $D(\mathbf{k}, \mathbf{g}, \omega)$ with these wave functions, and using (28') for $\epsilon(\omega)$, we obtain in the dipole approximation for the interaction between the atoms the well known Lorenz-Lorentz formula:

$$\epsilon = 1 + 4\pi n \alpha / (1 - \frac{4}{3} \pi n \alpha), \quad (30)$$

where α is the polarizability of one atom, taking into account the self-polarization correction (see [2]).

We now clarify the qualitative behavior of $\epsilon(\omega)$ close to the absorbing region, i.e., when $\omega \rightarrow \Delta$ ($\Delta = \min(E_\beta - E_i)$ is the energy gap between filled and unfilled states). We limit ourselves to considering only the term $D(\mathbf{k}, \mathbf{k}, \omega)$ in $\epsilon(\omega)$ (see equation (21)), since it can be shown that including the following term does not change the character of the singularity.

By definition

$$D(\mathbf{k}, \mathbf{k}, \omega) = \frac{4\pi e^2}{V} \sum_{i\beta} \frac{|H_{i\beta}(\mathbf{k})|^2}{k^2} \frac{2(E_\beta - E_i)}{[(E_\beta - E_i)^2 - \omega^2]}.$$

The uppermost filled band and the subsequent unfilled band play the principal role in this sum. The dependence $E(\mathbf{k})$ for these bands typical for an insulator is shown in Fig. 2 (k_0 is the limiting momentum of filling). For the calculation we put

$$E_i(\mathbf{k}) = A_i - B_i k^2, \quad E_\beta(\mathbf{k}) = A_\beta + B_\beta k^2,$$

$$k^{-2} |H_{i\beta}(\mathbf{k})|^2 = \text{const} \cdot \delta_{\mathbf{k}_i, \mathbf{k}_\beta}$$

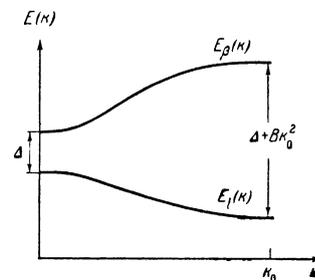


FIG. 2

(const. has the dimensions of cm^2 and is of order $|\langle i | r | \beta \rangle|^2$). The second condition assumes a weak dependence of the wave function on quasi-momentum.

Under these assumptions we obtain

$$-D(\mathbf{k}, \mathbf{k}, \omega) \underset{k \rightarrow 0}{\approx} \begin{cases} \text{const.} \cdot \left[\frac{2k_0}{B} - \frac{\sqrt{\Delta - \omega}}{B^{3/2}} \arctg k_0 \sqrt{\frac{B}{\Delta - \omega}} - \frac{\sqrt{\Delta + \omega}}{B^{3/2}} \arctg k_0 \sqrt{\frac{B}{\Delta + \omega}} \right], & \omega < \Delta \\ \text{const.} \cdot \left[\frac{2k_0}{B} - \frac{1}{2} \frac{\sqrt{\omega - \Delta}}{B^{3/2}} \ln \left| \frac{\sqrt{\omega - \Delta} + k_0 \sqrt{B}}{\omega - \Delta - k_0 \sqrt{B}} \right| - \frac{\sqrt{\Delta + \omega}}{B^{3/2}} \right] \times \\ \times \arctg k_0 \sqrt{\frac{B}{\Delta + \omega}}, & \omega > \Delta. \end{cases}$$

It is not difficult to show that as $\omega \rightarrow \Delta$ this function is finite; however, its derivative has a discontinuity:

$$\frac{\partial}{\partial \omega} (-D(\mathbf{k}, \mathbf{k}, \omega)) \underset{k \rightarrow 0}{\approx} \begin{cases} \frac{C_1}{\sqrt{\Delta - \omega}} & \text{for } \omega = \Delta - \varepsilon, \\ -C_2 & \text{for } \omega = \Delta + \varepsilon. \end{cases}$$

Thus we see that $\epsilon(\omega)$ has a peak (break) at $\omega = \Delta$ (Fig. 3). When the crystal is compressed

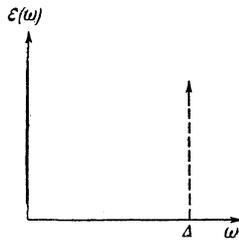


FIG. 3

as $\Delta \rightarrow 0$ this peak will be displaced in the direction of smaller frequencies and will grow in magnitude. When the bands cross and the insulator turns into a metal, intraband transitions provide an important contribution to $\epsilon(\omega)$ because, after crossing, we have two partially filled bands. A similar calculation shows that this changes $\epsilon(\omega)$ by the amount $-cn/\omega^2$ ($c > 0$; n is the number of filled states in the band which were previously empty, or the number of holes in the previously filled band). This contribution changes $\epsilon(\omega)$ smoothly when $\omega \neq 0$, since to start with $n = 0$ and then increases, but for $\omega = 0$ the value of $\epsilon(0)$ becomes infinite, which agrees with the fact that we now have a metal and not an insulator.

We now show that, when an imaginary part of $\epsilon(\omega)$ appears, the character of the singularity of the real part does not change, and we also clarify

$$-D(\mathbf{k}, \mathbf{k}, \omega) \underset{k \rightarrow 0}{\approx} \text{const.} \cdot \int_0^{k_0} dk \cdot k^2 \left[\frac{1}{\Delta - \omega + Bk^2} + \frac{1}{\Delta + \omega + Bk^2} \right],$$

where $\Delta = A_\beta - A_i$ is the energy gap, and $B = B_\beta + B_i$. Evaluating the integral we have*

qualitatively the behavior of $\text{Im } \epsilon(\omega)$ at the start of the absorption band.

We put $D(\mathbf{k}, \mathbf{g}, \omega) = D'(\mathbf{k}, \mathbf{g}, \omega) + iD''(\mathbf{k}, \mathbf{g}, \omega)$ where $D'(\mathbf{k}, \mathbf{g}, \omega)$ is the same as $D(\mathbf{k}, \mathbf{g}, \omega)$ when there is no absorption, and

$$D''(\mathbf{k}, \mathbf{g}, \omega) = \pi \frac{4\pi e^2}{V} \sum_{j, \beta} \frac{H_{j\beta}^*(\mathbf{k})}{k} \frac{H_{j\beta}(\mathbf{g})}{g} \delta(E_j - E_\beta + \omega).$$

Writing the quantities $\alpha(\mathbf{k}, \mathbf{m}, \omega)$ in (21) in a similar way, i.e., $\alpha(\mathbf{k}, \mathbf{m}, \omega) = \alpha'(\mathbf{k}, \mathbf{m}, \omega) + i\alpha''(\mathbf{k}, \mathbf{m}, \omega)$ we see that an additional contribution to the real part $\epsilon'(\omega)$ appears:

$$\sum_{\mathbf{m} \neq 0} D''(\mathbf{k} - \mathbf{m}, \mathbf{k}) \alpha''(\mathbf{k}, \mathbf{m}),$$

and the imaginary part is:

$$\begin{aligned} \epsilon''(\omega) = & -D''(\mathbf{k}, \mathbf{k}, \omega) - \sum_{\mathbf{m} \neq 0} D(\mathbf{k} - \mathbf{m}, \mathbf{k}) \alpha'(\mathbf{k}, \mathbf{m}) \\ & - \sum_{\mathbf{m} \neq 0} D'(\mathbf{k} - \mathbf{m}, \mathbf{k}) \alpha''(\mathbf{k}, \mathbf{m}). \end{aligned}$$

We estimate $D''(\mathbf{k}, \mathbf{k}, \omega)$ as $\omega \rightarrow \Delta$ under the same assumptions:

$$D''(\mathbf{k}, \mathbf{k}, \omega) \underset{k \rightarrow 0}{=} \text{const.} \cdot \int_0^{k_0} \delta(\omega - \Delta - Bk^2) k^2 dk = \begin{cases} 0, & \omega < \Delta, \\ \text{const.} \cdot B^{-3/2} \sqrt{\omega - \Delta}, & \Delta + Bk_0^2 > \omega > \Delta, \\ 0, & \omega > \Delta + Bk_0^2. \end{cases}$$

It is not difficult to see that, since in the first approximation $\alpha''(\mathbf{k}, \mathbf{g}) \approx D''(\mathbf{k}, \mathbf{k} - \mathbf{g})$, the contribution to the real part $\epsilon'(\omega)$ is proportional to $\omega - \Delta$ as $\omega \rightarrow \Delta$, i.e., the singularity in $\epsilon'(\omega)$ noted above is retained.

Estimates made to take into account the contribution of the exchange diagram to $\epsilon(\omega)$ show that

* $\arctg = \tan^{-1}$.

in the first approximation this again leads to a decrease of $\epsilon(\omega)$ relative to the magnitude

$$[1 - D_{k \rightarrow 0}(k, k, \omega)].$$

We note in conclusion that using the results obtained we can easily take into account spatial dispersion of the dielectric constant. Expanding in (21) with respect to ka (a is the lattice constant), and retaining only the terms quadratic in ka (the linear terms disappear due to the cubic symmetry), we see that a certain tensor is added to the scalar quantity $\epsilon(\omega)$; with this is associated the optical anisotropy of cubic crystals.^[6]

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