Quantum-mechanical expression for microscopic dielectric tensor in incommensurate phases

O.S.Kushnir, L.O.Lokot

Ivan Franko L'viv National University, 8 Kyryl and Mefodiy Str., 79005 L'viv, Ukraine

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Abstract

Quantum-mechanical calculations for the dielectric permittivity tensor in incommensurately modulated ionic-type insulators are carried out. The microscopic Fourier components of the tensor are obtained. The role of different reciprocal lattice vectors in the optical response of crystal is clarified.

Key words: insulator, dielectric permittivity tensor, incommensurate phase

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Introduction

Last decade an increasing number of studies has appeared in the literature, devoted to crystal optical properties of the insulators with incommensurate (IC) phases, in particular concerned with the problem of optical activity in those materials (see, e.g., [1-3]). From the fundamental point of view, optical anisotropy of crystals is related to the dielectric permittivity tensor in the optical frequency range. Some features of this tensor in the IC insulators have been discussed earlier, including symmetry relations, a transition from a microscopic to a macroscopic level, and a role of Fourier components of the dielectric tensor associated with the long-wavelength reciprocal lattice vectors [1, 2]. To our knowledge, there has been the only work [4] where the microscopic theory of optical properties of the IC crystals is developed, although in a dipole approximation which disregards completely spatial dispersion effects.

In this brief note we present the preliminary results on the derivation for the microscopic dielectric tensor in the IC phases and elucidate the contribution of nonzero reciprocal lattice vectors to the optical response of the crystal.

Calculations

Let us restrict ourselves to considering a displacive structural transformation in ionic-type insulator. The IC structure can be modeled as a distortion over the basic structure of a high-temperature parent phase. It is described by the displacement vector field which determines the modulated positions of the (point-like) ions (see [5]):

$$\boldsymbol{R}_{\boldsymbol{n}} = \boldsymbol{r}_{\boldsymbol{n}\alpha} + \boldsymbol{f}_{\alpha} \sin m\varphi, \qquad (1)$$

where $\boldsymbol{r}_{\boldsymbol{n}\alpha} = \boldsymbol{n} + \mathrm{r}_{\alpha}^{u}$, $\boldsymbol{n}$'s are the translation vectors for the underlying lattice, u labels the ions of different kind in a unit cell, and the last term accounts for the effect of the IC modulation ($\boldsymbol{f}_{\alpha}$ being the amplitude of the modulation, $\varphi = \varphi_{\alpha} + \boldsymbol{q}\boldsymbol{r}_{\boldsymbol{n}\alpha}$, $\boldsymbol{q}$ the modulation wave vector and m an integer). Note, that in A_2BX_4-type crystals $\boldsymbol{q} = \gamma \boldsymbol{b}_3$, where $\boldsymbol{b}_3$ is one of the basic reciprocal lattice vectors and γ an irrational number [1].

Let the electromagnetic wave (the frequency ω and the wavevector $\boldsymbol{k}$) be incident upon the crystal which consists of particles with the masses m_α and charges e_α, including the ions and the embedded electrons. Quantum-mechanical derivation of the dielectric tensor lies in calculating the expectation value of the current induced by the electric field of electromagnetic wave [6]. To determine the response of crystal on the external perturbation imposed by the wave, we have also used the density matrix technique [7] which combines both quantum-mechanical and statistical averaging.

In the linear approximation the expectation value for the current operator $\boldsymbol{J}$ in the system with the interaction Hamiltonian $\boldsymbol{H}_{\text{int}}$ is defined by (see [7]):

$$< \mathbf{J} > = \mathrm{Tr}\left(\rho^{(0)}\mathbf{J}\right) + \sum_{l',l} \frac{f(\varepsilon_{l'}) - f(\varepsilon_l)}{\varepsilon_{l'} - \varepsilon_l - \hbar\omega} < l', m \left|\mathbf{H}_{\text{int}}\right| l, m, \mathbf{k} > < l, m, \mathbf{k} \left|\mathbf{J}\right| l', m >, \quad (2)$$

where $\rho^{(0)}_{l'l} = f(\in_l)\delta_{l'l}$ is the matrix element of the density operator $\hat{\rho}$ in zero approximation, $f(\in_l)$ the Fermi distribution functions, $\delta_{l'l}$ the Kroneker delta, and $\in_l$ the energies corresponding to one-particle eigenstates l. In equation (2), $|l,m>$ and $|l,m,\boldsymbol{k}>$ denote, respectively, the wave functions of the particles in the unperturbed states and the states perturbed by the field

$$\left|l, m\right\rangle = (1/V)\sum_{\boldsymbol{n}} \exp(i\boldsymbol{q}_l \boldsymbol{R}_{\boldsymbol{n}\alpha})\hat{\boldsymbol{a}}^+_{\boldsymbol{n}}\left|0\right\rangle,$$

with V the crystal volume, $\hat{\boldsymbol{a}}^+_{\boldsymbol{n}}$ the operator for the creation of particles, the wavevector $\boldsymbol{q}_l$ defining the quasi-momentum associated with the state l, and $|0>$ the wave function of a free space). Accounting on single-photon processes only, we write the interaction Hamiltonian as:

$$\hat{\boldsymbol{H}}_{\text{int}} = -\sum_\alpha \frac{e_\alpha}{2m_\alpha c}\left[\hat{\boldsymbol{p}}^\alpha \hat{\boldsymbol{A}}(\boldsymbol{R}_{\boldsymbol{n}\alpha}, t) + \hat{\boldsymbol{A}}(\boldsymbol{R}_{\boldsymbol{n}\alpha}, t)\hat{\boldsymbol{p}}^\alpha\right], \quad (3)$$

where the α summation extends over all particles, $\boldsymbol{A}$ is the normalized vector field potential operator (see [7]) and $\hat{\mathbf{p}}^\alpha = -i\hbar\partial/\partial\mathbf{R}_{\mathbf{n}\alpha}$ the momentum operator.

It is convenient to expand the function $\exp(ix\sin\varphi)$ (see, e.g., (1) and (3)) in a Fourier series, where the expansion coefficients would be the Bessel functions $J_\mu(x)$. On performing calculations, one can arrive at the expression for the average current density. Further consideration of the selection rules for the matrix elements in (2) leads to the conclusion that the only Fourier components of the induced current in the IC crystal are those which correspond to the wavevectors $\boldsymbol{k}' = \boldsymbol{k} + \boldsymbol{h}$, where $\boldsymbol{h} = n_i\boldsymbol{b}_i + m_0\boldsymbol{q}$ are the generalized reciprocal lattice vectors, with the summation over the repeated indices understood, n_i integer microscopic indices (see [1]) and $m_0 = \mu m$. Then on the basis of the well-known relations for the current density and electric field vectors and the complex conductivity tensor, we finally obtain the Fourier components of the dielectric permittivity tensor (cf. with [6]):

$$\varepsilon_{ij}^{n_i,m}(\omega, \mathbf{k}, \varphi) = \delta_{ij}\left(1 - \frac{4\pi}{\omega^2 V}\sum_{\alpha,\mu,l'} \frac{e_\alpha^2}{m_\alpha} J_\mu\left((\mathbf{k} - \mathbf{k}')\mathbf{f}_\alpha\right) f(\varepsilon_{l'}) M_{l'l'}\delta_{\mathbf{k}-\mathbf{k}'}\right) -$$

$$-\frac{4\pi}{\omega^2 V}\sum_{\alpha,\beta,\mu,\nu,l',l} \frac{e_\alpha e_\beta}{4m_\alpha m_\beta} \frac{f(\varepsilon_{l'}) - f(\varepsilon_l)}{\varepsilon_{l'} - \varepsilon_l - \hbar\omega} J_\nu(\mathbf{k}\mathbf{f}_\alpha) J_\mu(\mathbf{k}'\mathbf{f}_\beta) N_{l'l} P_{ll'}, \quad (4)$$

where

$$M_{l'l'} = \left\langle l', m \left| e^{i(\boldsymbol{h}\boldsymbol{r}_{\boldsymbol{n}\alpha} + m_0\varphi_\alpha)} \right| l', m \right\rangle,$$

$$N_{l'l} = \left\langle l', m \left| \hat{p}_i^\alpha e^{-i(\boldsymbol{k}\boldsymbol{r}_{\boldsymbol{n}\alpha} + \nu m\varphi)} \right| l, m, \boldsymbol{k} \right\rangle,$$

$$P_{ll'} = \left\langle l, m, \boldsymbol{k} \left| \hat{p}_j^\beta e^{i(\boldsymbol{k}'\boldsymbol{r}_{\boldsymbol{n}\beta} + m_0\varphi_\beta)} \right| l', m \right\rangle, \quad (5)$$

and φ can be interpreted as the phase of the IC wave.

Discussion

Formula (4) represents a generalization of the tensor [6] and may be reduced to the latter when taking properly the limit of a classical non-modulated crystal. Let's notice that the expression (4) disregards any phonon motions, whereas the calculation of the matrix elements $M_{l'l'}$, $N_{l'l}$ and $P_{ll'}$ appearing in the r.h.s. of (4) is not attempted here. Nevertheless, a useful analysis of structure of the dielectric tensor is already possible.

In the commensurate crystal optics it is sufficient to retain in (4) the only Fourier component with $\boldsymbol{h} = 0$. In the case of the IC A_2BX_4-type crystals, the most important are the reciprocal lattice vectors $\boldsymbol{h} = (0,0,n_3,m_0)$ whose index combination n_3/m_0 is close to $-\gamma$ (see above). We call these vectors as the "ultralong-wavelength" ones, since the increase in the indices according to $\lim_{s\to\infty}(n_3/m_0)_s = -\gamma$ gives a rise to decreasing their length, contrary to the situation known for ordinary crystals. The disputable problem of the contribution of the "ultralong-wavelength" vectors to optical response, which have been neglected without proper reasoning by the authors [1], becomes now easy to solve. As seen from (5), $\varepsilon_{ij}^{n_i,m}$ decreases proportional to m^{-p} for large m, where $(p-1)$ is a number of continuous derivatives of the wave function. That is why the restriction to the lowest-index vectors $\boldsymbol{h}$ adopted in [1,2] is indeed correct. This also agrees well with the results of morphological studies for the importance of IC-satellite crystal faces and the data of the X-ray-diffraction experiments (see [1,3,8]).

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