THE EFFECT OF A STRONG ELECTRIC FIELD ON THE OPTICAL PROPERTIES OF INSULATING CRYSTALS

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The absorption coefficient is calculated for a crystal placed in a uniform electric field, for frequencies at which the crystal does not normally absorb in the absence of a field. It is shown that there is a shift in the red absorption limit toward the longer wavelengths, by an amount which may reach hundreds of angstroms for reasonable field strengths.

IT is known that a uniform electric field greatly alters the electron states in a crystal. Strictly speaking, there is no stationary state at all under these conditions. Instead of the Bloch functions $\psi_j(\mathbf{p}, \mathbf{r})$ for the electrons, we have functions of the form

$$\psi_j(\mathbf{p}_0, \mathbf{r}, t)$$
$$= \exp\left\{-\frac{i}{\hbar}\int_0^t \varepsilon_j(\mathbf{p}_0 - e\,\mathbf{E}\,x)\,dx\right\}\psi_j(\mathbf{p}_0 - e\,\mathbf{E}\,t, \mathbf{r}). \quad (1)$$

even in the zero-order approximation. Here $\epsilon_j(\mathbf{p})$ are functions which define the dependence of electron energy on the quasi-momentum in the j-th band; $\mathbf{E}$ is the electric field strength.

These functions satisfy the time-dependent Schrödinger equation for the model under consideration (an electron in a periodic field plus a uniform electric field), accurately up to the exponentially small terms corresponding to the "leakage" of electrons from one band to another under the influence of the field, and describe a uniform acceleration of the electron which is in the state $\psi_j(\mathbf{p}_0, \mathbf{r})$ at the instant t = 0.

In what follows we shall express corrections to the wave function for the system which arise from interaction with light, using an expansion in terms of the functions (1). We could have used for this purpose any other system of functions satisfying the above-mentioned Schrödinger equation, so long as this system is complete and orthogonal at all instants of time (since we shall be considering only those expansion coefficients that change with time). However, the system (1), in addition to its physically descriptive nature, has the further advantage that it is obviously complete and orthogonal. As a matter of fact, although each of the functions varies continuously with time, at every instant the system as a whole is identical with the complete system of Bloch functions for the crystal. The particular choice of functions in which to carry out the expansion is quite immaterial to the final result, since the number of quanta absorbed (or, the number of photoelectrons, which is the same thing) depends on the total sum of the squares of the moduli of the coefficients in the expansion, and therefore does not depend on the choice of the base functions.

The probability that a quantum with frequency ω and polarization vector $\mathbf{e}$ will be absorbed by an electron in the state $\psi_v(\mathbf{p}_0, \mathbf{r}, t)$ is

$$w(\mathbf{p}_0, \omega, t)$$
$$= \left(\frac{e}{m}\right)^2 \frac{2\pi\hbar}{\omega}\left|\int_0^t dt \int d\tau\psi_c^*(\mathbf{p}_0, \mathbf{r}, t)\,e^{-i\omega t}\mathbf{e}\nabla\psi_v(\mathbf{p}_0, \mathbf{r}, t)\right|^2, \quad (2)$$

where the indices v and c refer to the valence and conduction bands respectively; e and m are the charge and mass of electron.

In the general case, in the absence of an electric field, the integrand varies harmonically with time; this implies that the energy must remain constant. The total probability of absorption of a photon $\hbar\omega$ per unit time per unit volume is then given by the expression

$$W(\omega) = \int \frac{dw(\mathbf{p}, \omega, t)}{dt}\frac{d^3p}{(2\pi\hbar)^3} \quad (3)$$
$$= \left(\frac{e}{m}\right)^2\frac{2\pi\hbar}{\omega}\int|e\mathbf{M}_{vc}(\mathbf{p})|^2\,\delta\{\varepsilon_c(\mathbf{p}) - \varepsilon_v(\mathbf{p}) - \hbar\omega\}\frac{d^3p}{(2\pi\hbar)^3},$$

$$\mathbf{M}_{vc}(\mathbf{p}) = \int \psi_c^*(\mathbf{p}, \mathbf{r})\nabla\psi_v(\mathbf{p}, \mathbf{r})\,d\tau, \quad (4)$$

from which it can be seen, in particular, that quanta with frequencies less than $\omega_0 = \epsilon_0/\hbar$, where $\epsilon_0 = \min\{\epsilon_c(\mathbf{p}) - \epsilon_v(\mathbf{p})\}$, are not absorbed at all. To be specific, we shall assume that the transition (4) is not forbidden by symmetry considerations, i.e., $\mathbf{M}_{vc}(\mathbf{p}_m) \neq 0$, where $\mathbf{p}_m$ is the value of the quasi-momentum corresponding to the absolute minimum in the function $\epsilon_c(\mathbf{p}) - \epsilon_v(\mathbf{p})$. This

case corresponds to the steepest absorption edge, and is therefore particularly suitable for observations. In fact, near this edge the expression (3) can be put into an explicit form by noting that in this region the function $\epsilon_c(\mathbf{p}) - \epsilon_v(\mathbf{p})$ can be written as

$$\epsilon_c(\mathbf{p}) - \epsilon_v(\mathbf{p}) = \epsilon_0 + \sum_{i,k}(p_i - p_{im})(p_k - p_{km})/2m_{ik}. \quad (5)$$

Then

$$W(\omega) = \frac{1}{\pi}\frac{e^2}{\hbar c}\frac{c}{\omega}\left[\frac{m_1 m_2 m_3}{m^3}\frac{2(\hbar\omega - \epsilon_0)}{m}\right]^{1/2}|\mathbf{eM}_{vc}(\mathbf{p}_m)|^2, \quad (6)$$

where m_i^{-1} is the principal value of the tensor m_{ik}^{-1}.

The absorption coefficient is thus seen to vary as $(\omega - \omega_0)^{-1/2}$. In the particular case $\mathbf{M}_{vc}(\mathbf{p}_m) = 0$, the coefficient increases much more slowly,[2] as $(\omega - \omega_0)^{3/2}$.

In the presence of an electric field, expression (2) no longer contains delta functions, and therefore the probability of absorbing a quantum of frequency less than ω_0 is not zero. The probability of photon absorption in this case must be calculated in a different manner. We shall first carry out this derivation under the simplifying assumption that the field is directed along one of the axes of a simple cubic lattice with period d. Then because $\epsilon_j(\mathbf{p})$ and $\psi_j(\mathbf{p}, \mathbf{r})$ are periodic functions of the quasi-momentum, the electron undergoes a periodic motion within the j-th band, with the period $T = 2\pi\hbar/eEd$. In this case it is natural to take the absorption probability for one period of this oscillation, $w(\mathbf{p}_0, \omega, 2\pi\hbar/eEd)$, as the characteristic absorption. In order to calculate this quantity, we transform (2) into the new variables of integration $p_x = p_{0x} - eEt$ (the X axis is assumed to be in the field direction) and note that the factor

$$\exp\left\{\frac{i}{e\hbar E}\int[\epsilon_c(\mathbf{p}) - \epsilon_v(\mathbf{p}) - \hbar\omega]\,dp_x\right\}$$

occurring in the integrand has a saddle point $p_x = q(p_y, p_z)$ in the complex p_x plane, determined by the conditions

$$\epsilon_c(q, p_y, p_z) - \epsilon_v(q, p_y, p_z) - \hbar\omega = 0.$$

Making use of this circumstance, we obtain

$$w\left(\mathbf{p}_0, \omega, \frac{2\pi\hbar}{eEd}\right) = \left(\frac{e}{m}\right)^2\frac{2\pi\hbar}{\omega}\frac{2\pi\hbar}{eE}|\mathbf{eM}_{vc}(q, p_{0y}, p_{0z})|^2$$

$$\times\left|\frac{\partial|\epsilon_c(\mathbf{p}) - \epsilon_v(\mathbf{p})|}{\partial p_x}\right|_{p_x=q}^{-1}$$

$$\times\left|\exp\left\{\frac{i}{e\hbar E}\int^{p_x=q}[\epsilon_c(\mathbf{p}') - \epsilon_v(\mathbf{p}') - \hbar\omega]\,dp_x'\right\}\right|^2. \quad (7)$$

Multiplying this expression by the number of oscillations of the electron per unit time, $eEd/2\pi\hbar$,

and integrating over all $\mathbf{p}_0$, we obtain the absorption probability for a photon of frequency ω per unit volume per unit time. Electrons with this same p_{0y} and p_{0z}, but different p_{0x}, will be found to carry out exactly the same motions, but with a shift in time. Hence integration over p_x is equivalent to a simple multiplication by $1/d$, the number of states with a given p_{0y} and p_{0z}. Using the expansion (5), and bearing in mind that, for the almost trivial case under consideration, $m_{ik}^{-1} = m^{*-1}\delta_{ik}$, we arrive at the following final result (for frequencies $\omega < \omega_0$):

$$W(\omega) = \frac{e^2}{\hbar c}\frac{c}{\omega}\left(\frac{m^*}{m}\right)^2\sqrt{2\frac{\epsilon_0 - \hbar\omega}{m^*}}\frac{(e\hbar E)^2}{m^*(\epsilon_0 - \hbar\omega)^3}|\mathbf{eM}_{vc}(\mathbf{p}_m)|^2$$

$$\times\exp\left\{-\frac{4\sqrt{2m^*}}{3e\hbar E}(\epsilon_0 - \hbar\omega)^{3/2}\right\}. \quad (8)$$

It is not difficult to repeat all the steps outlined above for more general cases as well — lattices with any symmetry and with arbitrary field directions, in which the electron motion, generally speaking, is aperiodic (see, for instance, Keldysh[3]). The number of photons absorbed per unit volume in unit time is then given by the following expression (under the condition $\omega < \omega_0$)

$$W(\omega) = \frac{e^2}{\hbar c}\frac{c}{\omega}\sqrt{\frac{m_1 m_2 m_3}{m^3}\frac{2(\epsilon_0 - \hbar\omega)}{m}}\frac{(e\hbar E)^2}{m_{\parallel}(\epsilon_0 - \hbar\omega)^3}|\mathbf{eM}_{vc}(\mathbf{p}_m)|^2$$

$$\times\exp\left\{-\frac{4\sqrt{2m_{\parallel}}}{3e\hbar E}(\epsilon_0 - \hbar\omega)^{3/2}\right\},$$

$$m_{\parallel}^{-1} = \sum_i\cos^2\gamma_i/m_i, \quad (9)$$

where m_i^{-1} are the diagonal terms of the tensor m_{ik}^{-1}, and γ_i are the angles between the field and the principal axes of the tensor m_{ik}^{-1}. This formula applies when $\sqrt{m_{\parallel}}(\epsilon_0 - \hbar\omega)^{3/2}/e\hbar E \gtrsim 1$. For $\omega > \omega_0$ and $\sqrt{m_{\parallel}}(\hbar\omega - \epsilon_0)^{3/2}/e\hbar E \gtrsim 1$, formula (6) is still valid.

Comparison of these two expressions shows that in an electric field $\mathbf{E}$ there is a fundamental change in the frequency dependence of the absorption coefficient near the threshold, which can be integrated between known limits to give a shift of the absorption edge toward the red by a distance of the order of

$$\Delta\omega_E = \frac{1}{\hbar}\left[(eE)^2\frac{\hbar^2}{m_{\parallel}}\right]^{1/3} = \frac{1}{\hbar}\left[(eEd)^2\frac{\hbar^2}{m_{\parallel}d^2}\right]^{1/3}. \quad (10)$$

For crystals whose absorption edge is in the visible region of the spectrum, in electric fields E of the order of 10^5 v/cm, this shift amounts to hundreds of angstroms, if we assume that $m_{\parallel} \sim m = 10^{-27}$ g. However, it is very seldom that either an electron or a hole will have an effective mass much less than m, which would lead to an

increased $\Delta\omega_E$, since $m_\parallel$ is the resultant effective mass of the electrons and holes, and is therefore determined by the smallest of these masses. Thus the most favorable case for observing this effect is one in which the effective mass is small and the forbidden zone is not too wide (of the order of $1-2$ ev), so that the relative value of the shift $\Delta\omega_E/\omega_0$ is not too small. The origin of this effect is analogous to the self-ionization which causes widening in the lines of atomic spectra. This case was considered by Lanczos, in whose work[4] it is shown that spectral lines which are separated from the series limit by a frequency $\Delta\omega$ widen and merge into a comlex spectrum when the applied field satisfies the condition $\Delta\dot\omega_E \sim \Delta\omega$. The basic qualitative difference between the two cases is that in crystals this shift has nothing at all to do with the existence of any discrete lines corresponding to bound states of electrons or holes, much less to any broadening of such lines. Furthermore, the cases most suitable for the observation of the effect are those

in which such states are completely absent, i.e., when the field E is so strong that $\hbar\Delta\omega_E$ is greater than the binding energy, and consequently bound states are practically non-existent. Under the opposite conditions,[5] the picture is similar to the one put forward by Lanczos.

Obviously there will be an analogous shift of the lower threshold which corresponds to absorption with the formation of phonons.

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DEPENDENCE OF THE HYPERFINE STRUCTURE OF F CENTERS ON THE ORIENTATION OF A CRYSTAL IN AN EXTERNAL MAGNETIC FIELD

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Submitted to JETP editor November 10, 1957

J. Exptl. Theoret. Phys. (U.S.S.R.) **34**, 1142-1147 (May, 1958)

The spin Hamiltonian for the interaction between an F-center electron and the angular momenta of the first and second coordinational spheres surrounding the nuclei have been obtained by using the continual and orbital models of F centers in KCl-type lattices. The dependence of the frequency of spin-nuclear transitions on the orientation of the crystal in an external static magnetic field is considered. Comparison of theory with experiment leads to a satisfactory agreement between the angular dependences and (to order of magnitude) of the spin-Hamiltonian coefficient. The square of the F-center wave function in the potassium and chlorine sites of the lattice have been determined by comparison with experiment.

1. The spin-electron resonance of F center in an ionic crystal was considered in Refs. 1 to 3. The most general form of the spin Hamiltonian was obtained in Ref. 4 for the interaction between the localized electron in the crystal and the momenta of the surrounding nuclei. The same reference gives also the spin Hamiltonian of the F center with allowance for the interaction between the electron of the F center and the nuclei of the first coordinational sphere. It was emphasized in Refs. 2 to 4 that the spin Hamiltonian has an anisotropy which, as indicated, should cause the parameters of the