

Excitonic insulator as a ferroelectric material

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It is shown that an excitonic dielectric with a resolved dipole transition is a ferroelectric material.

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The purpose of this paper is to focus attention on the fact that an excitonic dielectric with an allowed dipole transition is polarized. The known mechanisms for ferroelectricity are in some way associated with a lattice; however, here we have a new, purely electronic mechanism: polarization occurs as a result of transition to the excitonic dielectric state caused by an attraction between electrons and holes.

The effective Hamiltonian of an excitonic dielectric with an allowed dipole transition in a two-band approximation has the form¹

$$H = \begin{pmatrix} \xi & \Delta \\ \Delta^* & -\xi \end{pmatrix}, \quad \Delta = \Delta_0 + \mathbf{p}\mathbf{v}_{12}. \quad (1)$$

Here $\xi = \frac{p^2}{2m} - \mu$ (m , the effective mass, is assumed to be the same for an electron and a hole and μ characterizes the degree of overlapping of the bands; $\mu > 0$ for a semimetal), \mathbf{v}_{12} is a matrix element of the operator $-i\nabla/m_0$ which was calculated by using Bloch's functions corresponding to the extrema of the analyzed bands, and Δ_0 is the order parameter ($\Delta_0 = \text{const}$ in the BCS-type model). The Δ_0 phase differs from the \mathbf{v}_{12} phase by $\pm \pi/2$; if we assume that \mathbf{v}_{12} is a purely imaginary vector, $\mathbf{v}_{12} = i\mathbf{v}_0$, then Δ_0 will be real. The Hamiltonian (1) is independent of the spin indices—a singlet pairing is assumed.

The eigenfunction of the Hamiltonian (1) is a (u/v) column; specifically, we have for u and v

$$u \begin{matrix} * \\ v \end{matrix} = \pm \frac{\Delta}{2E}, \quad E = \sqrt{\xi^2 + |\Delta|^2}; \quad (2)$$

where the upper sign refers to the upper (empty for $T = 0$) band of an excitonic dielectric with an energy E and the lower sign refers to the lower (filled) band with an energy $-E$.

To calculate the polarization, we must explicitly assume that the eigenfunctions are the Bloch's functions in the coordinate representation

$$\psi = u \psi_1 + v \psi_2, \quad \psi_n \approx U_{n0} e^{i \mathbf{p} \cdot \mathbf{r}} \quad (n = 1, 2) \quad (3)$$

(modulations of the U_n Bloch's functions can be approximately taken in the extrema of the bands). The ψ and ψ_n functions are assumed to be normalized in the volume V . The v_{12} value mentioned above is

$$v_{12} = \int d^3 r U_{10}^* \left(\frac{-i \nabla}{m_0} \right) U_{20}. \quad (4)$$

We shall discuss the properties of the U_{no} functions briefly. Let us assume that the crystal has a preferred axis and that the symmetry plane is perpendicular to this axis. In this case the U_{no} eigenfunctions can be classified according to the parity of reflection in the plane, and v_{12} is nonvanishing for the states of different parity, which is predicted for U_{10} and U_{20} . There is no polarization for a system with such properties, but it appears as a result of a transition to the excitonic dielectric state. We shall calculate this value.

We must determine the average coordinate from the states (3):

$$\begin{aligned} \langle \mathbf{r} \rangle &= |u|^2 \mathbf{r}_{11} + |v|^2 \mathbf{r}_{22} + u^* v \mathbf{r}_{12} + u v^* \mathbf{r}_{21}, \\ \mathbf{r}_{nm} &= \int d^3 r U_{n0}^* \mathbf{r} U_{m0}. \end{aligned} \quad (5)$$

The first two terms on the right-hand side of Eq. (5) are the diverging expressions whose divergence can be partially eliminated if the contribution of the positive compensating nuclear charge corresponding to one electron is taken into account. Thus, we obtain an expression for the dipole moment (for one particle) of a certain symmetric crystal such as an NaCl crystal that is pulled along one of the cube's edges; the dipole moment of such a crystal is equal to zero. Thus, the contribution of the first two terms on the right-hand side of Eq. (5) must also be assumed equal to zero, i.e.,

$$\langle \mathbf{r} \rangle = u^* v \mathbf{r}_{12} + u v^* \mathbf{r}_{21} \quad (6)$$

(the conclusion that the contribution of the \mathbf{r}_{nn} terms is zero is independent of the

simplification $U_{np} \rightarrow U_{no}$; in general, we would have to consider the pairs of states that change into each other as a result of reflection in a plane). The matrix element r_{12} is related to v_{12} by the well-known relation:

$$i(E_1 - E_2)r_{12} = v_{12}, \quad E_1 - E_2 = 2\mu. \quad (7)$$

Substituting expressions (2) and (7) in Eq. (6), we obtain

$$\langle r \rangle = \mp \frac{i}{4\mu E} (\Delta^* v_{12} - \text{c.c.}) \quad (8)$$

Finally, summing over all the states with a quasi-particle distribution function, we obtain the polarization produced at an arbitrary temperature

$$\mathcal{P} = \frac{ie}{4\mu} \frac{1}{V} \sum_p \frac{\text{th} \frac{E}{2T}}{E} (\Delta^* v_{12} - \text{c.c.}) = - \frac{e\Delta_0(T)}{g\mu} v_0 \quad (9)$$

where the equation for the order parameter has been taken into account:

$$1 = \frac{g}{V} \sum_p \frac{\text{th} \frac{E}{2T}}{2E}.$$

Thus, a preferred direction—a dipole moment—appears in the system, whereas there is only the preferred axis above the transition point. Since the v_{10} vector changes its direction when one of the U_{no} functions changes its sign, it has no physical meaning in itself. The direction of the dipole moment can be either parallel to v_0 or antiparallel to it, depending on the sign of Δ_0 . Such arbitrariness in the direction of \mathcal{P} is common in ferroelectric crystals. In this case, however, the direction of \mathcal{P} is determined by the sign of the order parameter, rather than by the sublattice shift which does not occur in the examined model if the v_0 vector has been selected.

Equation (9) gives the polarization for a single spin projection. If both projections are taken into account, then this result will either double or will become zero, depending on the signs of the two order parameters. This degeneracy can be removed, for example, by a dipole interaction (which, as is known, can by itself produce a ferroelectric transition), so that the result (9) will double.

In conclusion, we note that there is no polarization in the effective-mass approximation, a fact that can be verified by calculating the energy of the system in an electric field using the results obtained by us.²

¹B. A. Volkov, Yu. V. Kopaev, and V. V. Tugushev, Pis'ma Zh. Eksp. Teor. Fiz. **27**, 615 (1978) [JETP Lett. **27**, 582 (1978)].

²É. G. Batyev and V. A. Borisuyuk, Zh. Eksp. Teor. Fiz. **79**, 12 (1980) [Sov. Phys. JETP **52**, No. 1 (1980) (in press)].

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