Polarons in Anisotropic Energy Bands*†

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The polaron weak-coupling approximation has been applied to the problem of an electron on a spheroidal energy surface interacting with longitudinal optical phonons. The binding energy and effective masses are calculated. For $SrTiO_3$, where the observed masses are $m_l*m_0 = 6.0$ and $m_t*/m_0 = 1.5$, the calculated bare masses are 4.7 and 0.96, respectively, and the binding energy is 0.26 eV. It is also shown how the polaron properties may be calculated when the band edge is of the degenerate type.

I. INTRODUCTION

THE experimental study of electronic transport effects in semiconducting crystals of an ionic nature, such as $SrTiO_3$,[1,2] $BaTiO_3$,[3] $KTaO_3$,[4] and TiO_2,[5] brings attention to the relevance of polaron theory to the interpretation of the observations in terms of band structure. The interaction of an electron with long-wavelength optical modes of vibration of a crystal has been the object of considerable theoretical study, and has been reviewed by Fröhlich,[6] Schultz,[7] and Allcock.[8] To the author's knowledge, the only consideration of band-structure effects in all treatments has been through the inclusion of a constant isotropic bare effective mass. Thus the question is raised as to the effect of polaron coupling on the nature of the observed bands.

In this report the results are given for the case of an electron on a spheroidal energy surface, in interaction with the longitudinal optical modes. The anisotropic mass will be treated exactly within the weak-coupling approximation. Application will be made to the case of $SrTiO_3$, which is believed to have a many-valley conduction band.[1,9] Finally, it will be shown how the polaron may be treated in weak coupling in the case of degenerate bands, in the framework of the effective-mass approximation.[10,11]

II. SPHEROIDAL ENERGY SURFACES

The polaron Hamiltonian in reduced units (as established by Fröhlich[6]), modified for a spheroidal energy

surface, is given by

$$\mathcal{H} = -\left(\frac{m_0}{m_t}\right)\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) - \left(\frac{m_0}{m_l}\right)\frac{\partial^2}{\partial z^2} + \sum_q b_q^\dagger b_q$$
$$+ i\left(\frac{4\pi\alpha}{S}\right)^{1/2}\sum_q \frac{1}{q}(b_q^\dagger e^{-i\mathbf{q}\cdot\mathbf{r}} - b_q e^{i\mathbf{q}\cdot\mathbf{r}}), \quad (1)$$

with

$$\alpha = \frac{1}{2}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right)\frac{e^2}{\hbar\omega}\left(\frac{2m_0\omega}{\hbar}\right)^{1/2}. \quad (2)$$

Here α is the dimensionless coupling constant dependent on the high- and low-frequency dielectric constants ϵ_∞ and ϵ_0, respectively. In Eqs. (1) and (2), x, y, z are the electron coordinates, m_0 the free-electron mass, m_l and m_t the longitudinal and transverse bare masses, and $b_q^\dagger$ and b_q the annihilation and creation operators for phonon of wave vector $\mathbf{q}$, which is in units of $(2m_0\omega/\hbar)^{1/2}$. S is a normalization volume. Energies are in units of $\hbar\omega$, the phonon energy. (Phonon dispersion is neglected for the long-wavelength case considered.) Other symbols have the usual meaning as in Fröhlich's review.[6]

In the weak-coupling approximation the energy is given to second order by the standard perturbation formulas[6]:

$$E(k) = \frac{m_0}{m_t}(k_x^2 + k_y^2) + \frac{m_0}{m_l}k_z^2 - \frac{4\pi\alpha}{S}\sum_q \frac{1}{q^2}$$
$$\times\left[1 + \frac{m_0}{m_l}(q_z^2 - 2q_z k_z) + \frac{m_0}{m_t}(q_x^2 + q_y^2 - 2q_x k_x \right.$$
$$\left. - 2q_y k_y)\right]^{-1}. \quad (3)$$

On expanding to second order in $\mathbf{k}$, we obtain the binding energy and corrections to the kinetic energy. The results are found to be

$$E_b = -\alpha(m_l/m_0)^{1/2}[1/(K-1)]^{1/2}$$
$$\times \sin^{-1}[(K-1)/K]^{1/2}, \quad (4a)$$

$$\Delta E_z = -\frac{1}{2}\alpha(m_0/m_l)^{1/2}k_z^2[1/(K-1) - (1/(K-1)^{3/2})$$
$$\times \sin^{-1}((K-1)/K)^{1/2}], \quad (4b)$$

$$\Delta E_x = -\frac{1}{4}\alpha(m_0/m_l)^{1/2}K^2 k_x^2\{1/K - [1/(K-1)]$$
$$+ [1/(K-1)^{3/2}] \sin^{-1}[(K-1)/K]^{1/2}\}. \quad (4c)$$

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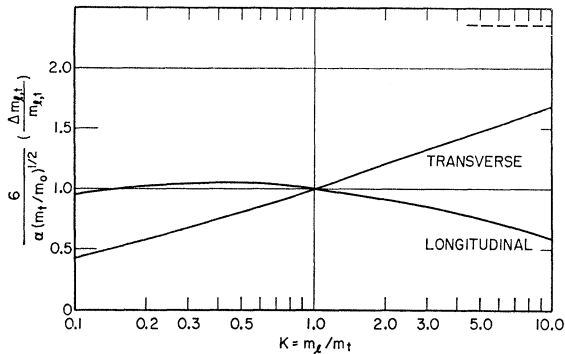[11] C. Kittel and A. H. Mitchell, Phys. Rev. 96, 1488 (1954).

FIG. 1. Fractional change in effective mass due to polaron coupling. Here m_l and m_t are bare masses, longitudinal and transverse, respectively. α is the coupling constant. The polaron mass is given by $m_{l,t}{}^* = m_{l,t} + \Delta m_{l,t}$.

Here E_b is the binding energy, ΔE_z and ΔE_x are the changes of kinetic energy, and $K = m_l/m_t$. ΔE_y is of the same form as ΔE_x, by symmetry. Equations (4) are specifically written for $K > 1$. For $0 < K < 1$ they are also valid and may be put into usable form by application of the identity $\sin^{-1}ix = i\sinh^{-1}x$. These energy changes may be put into the form of effective-mass changes. This has been done and the results plotted in Fig. 1. The binding energy is shown in Fig. 2, as a function of the bare-mass ratio.

III. APPLICATION TO STRONTIUM TITANATE

In $SrTiO_3$ the conduction-band edge is composed of six prolate half-spheroids believed to be centered at the edges of the Brillouin zone in the $\langle 100 \rangle$ direction. The observed masses are $m_l{}^* = 6.0\ m_0$ and $m_t{}^* = 1.5\ m_0$, with $K = 4.0$. These results are derived from analysis of the magnetic susceptibility[12] and the heat capacity[13] of the carriers, and magnetoresistance.[1,2] It is believed that these should be considered to be polaron masses. From the analysis of the preceding section we may
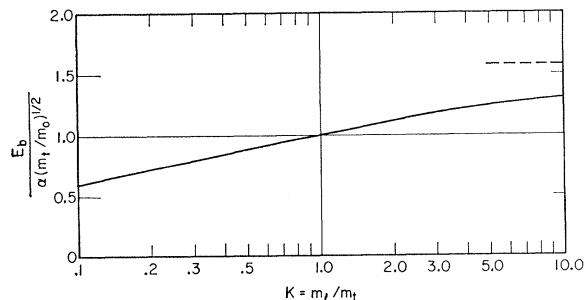

FIG. 2. Polaron binding energy, in units of the LO phonon quantum $\hbar\omega_0$, versus bare-mass anisotropy. m_l and m_t are bare masses, m_0 is the free-electron mass, and α is the coupling constant.

determine the binding energy and bare masses. It should be possible to obtain the bare masses by a Faraday-effect experiment.[14]

$SrTiO_3$ has three active LO modes. The coupling constants have been estimated by Eagles.[15,16] The results for bare masses are quoted in Table I. The observed masses, the calculated bare masses, and the binding energy are shown. The assumption has been made that the separate modes contribute additively to the polaron effects. The magnitude of the binding energy, 0.26 eV, is rather large, in fact comparable to the bandwidth in the longitudinal direction. The mass changes are also significant. The use of the weak-coupling approximation at values of α slightly above 2 is somewhat questionable, but the results may be expected to give a significant estimate of the values of the polaron effects.[17] For the isotropic case, $m^*/m = 1 + \frac{1}{6}\alpha$ for intermediate coupling, while $m^*/m = 1/(1 - \frac{1}{6}\alpha)$ for weak coupling. Thus for the isotropic case, at $\alpha = 1.8$, we find that the weak-coupling effective

TABLE I. Experimental data and calculated results for $SrTiO_3$.

	$\hbar\omega$ (eV)	α
ω_1	0.022	0.01
ω_2	0.058	0.50
ω_3	0.099	1.83
Observed masses	Calculated bare Bloch masses	
$m_l{}^* = 6.0\ m_0$	$m_l = 4.7\ m_0$	
$m_t{}^* = 1.5\ m_0$	$m_t = 0.96\ m_0$	
$K = 4.0$	$K = 4.9$	
	Binding energy	
	$E_b = 0.26$ eV	

mass differs from the more exact intermediate-coupling result by less than 10%.

It is clear that polaron effects will begin to be reduced when electron concentrations become high enough to produce a screening radius as short as the polaron radius in the absence of screening. We estimate the screening radius by the Thomas-Fermi value $(1/r_s)^2 = 6\pi n e^2/\epsilon_F$, where ϵ_F is the Fermi energy. The polaron radius is approximately $r_p = (\hbar/m^*\omega_0)^{1/2}$. Using the density-of-states mass $(5m_0)$ for an estimate, with a concentration $n \approx 10^{18}$ cm^{-3}, we obtain $r_s \approx 1.5 \times 10^{-8}$ cm. We estimate the polaron radius with the highest mode frequency and obtain 1.4×10^{-8} cm. Including the other modes would make it somewhat smaller. Thus there will be some diminution of the polaron effects at the typical concentration of 10^{18} cm^{-3}. A quantitative study of polarons in degenerate semiconductors including the effects of screening and the

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exclusion principle in scattering has been made by Mahan and Duke.[18]

IV. POLARONS IN DEGENERATE BANDS

One might ask what further influences the polaron interaction might have on the band structure. From the spherical symmetry of the Fröhlich interaction, we see that there will be no reduction of symmetry at any point in the Brillouin zone. Hence there will be no splitting of degeneracy, but only changes in the curvatures of the bands. We now show how the weak-coupling polaron energy may be calculated in the effective-mass approximation near a point of degeneracy.

We now will show how the polaron interaction can be treated in this framework and information obtained without the necessity of first solving for the unperturbed eigenvalues and eigenvectors for all $\mathbf{k}$. The Fröhlich Hamiltonian for the polaron problem, in the effective-mass approximation, becomes

$$H_{ij} = H_{ij}{}^0(-i\nabla) + \sum_v b_v{}^\dagger b_v \delta_{ij}$$
$$+ i\left(\frac{4\pi\alpha}{S}\right)^{1/2} \sum_q \frac{1}{q}(b_q{}^\dagger e^{-i\mathbf{q}\cdot\mathbf{r}} - b_q e^{i\mathbf{q}\cdot\mathbf{r}})\delta_{ij}. \quad (6)$$

To first order in α, the eigenvalues are determined by the following secular equation[21]:

$$\det\left| H(\mathbf{k})_{ij} + \frac{4\pi\alpha}{S}\sum_q \frac{1}{q^2} \times \left[\frac{1}{E\mathbf{1} - \mathbf{H}^0(\mathbf{k}+\mathbf{q}) - \mathbf{1}}\right]_{ij} - E\delta_{ij} \right| = 0. \quad (7)$$

It is understood that the term in square brackets represents the inverse of the matrix in the denominator. In principle this could be solved for E by successive approximation. However, to find E to order αk^2, we expand the denominator, and letting

$$\mathbf{H}^0(\mathbf{k}+\mathbf{q}) = \mathbf{H}^0(\mathbf{k}) + \mathbf{H}^0(\mathbf{q}) + \mathbf{B}(\mathbf{k},\mathbf{q}), \quad (8)$$

As an example we consider the case of a degenerate band edge at $k=0$ in a crystal of cubic symmetry. In this case the energy, to order k^2, is obtained by finding the eigenvalues of the matrix[19]

$$H_{ij}{}^0(\mathbf{k}) = D_{ij}{}^{\alpha\beta}k_\alpha k_\beta, \quad (5)$$

where the constant matrix $\mathbf{D}$ is symmetric in α and β, the components of $\mathbf{k}$, and the indices i and j refer to the degenerate basis states for $k=0$. The eigenvectors of $\mathbf{H}^0$ determine the "right linear combinations" of zero-order wave functions for a given direction of $\mathbf{k}$. For the case of degenerate bands, as from p states in a cubic crystal, H_0 takes the form[20]

$$\begin{bmatrix} Lk_x{}^2 + M(k_y{}^2+k_z{}^2) & Nk_xk_y & Nk_xk_z \\ Nk_xk_y & Lk_y{}^2 + M(k_x{}^2+k_z{}^2) & Nk_yk_z \\ Nk_xk_z & Nk_yk_z & Lk_z{}^2 + M(k_x{}^2+k_y{}^2) \end{bmatrix}.$$

where

$$B(\mathbf{k},\mathbf{q})_{ij} = D_{ij}{}^{\alpha\beta}(q_\alpha k_\beta + q_\beta k_\alpha), \quad (9)$$

we obtain

$$\det\left| H^0(\mathbf{k})_{ij} - \frac{4\pi\alpha}{S}\sum_q \frac{1}{q^2}\left[\frac{1}{H^0(q)+1}\right]_{ij} \right.$$
$$- \frac{4\pi\alpha}{S}\sum_q \frac{1}{q^2}\left[\frac{1}{\mathbf{H}^0(q)+1}\mathbf{B}(\mathbf{kq})\frac{1}{\mathbf{H}^0(q)+1}\right.$$
$$\left. \times \mathbf{B}(k,q)\frac{1}{\mathbf{H}^0(q)+1}\right]_{ij} - E\delta_{ij} \left| = 0. \quad (10)\right.$$

In Eq. (10) above, there are no terms linear in $\mathbf{B}$ as these vanish when the sums on q are performed. The binding energy is obtained from the second term only, which has only diagonal elements. The inverse matrices needed are sufficiently complicated as to require numerical computation for individual cases. For non-degenerate bands this result reproduces that of the earlier part of this paper.

An interesting possible occurrence would be the situation of a degenerate conduction-band minimum at $k=0$, with one band of infinite mass, i.e., $L=0$ in Shockley's case.[20] Then the polaron coupling could turn the curvature of the heavy band downward causing the minimum to be displaced away from $k=0$. Though there is no evidence for this being the case in strontium titanate, it is worth noting that the energy shifts due to polaron effects are of the same order of magnitude as the observed bandwidths, and such an occurrence might be possible.

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