Polarons in Anisotropic Energy Bands*†

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ABSTRACT

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 $m_\ell^*/m_o = 6.0$ and $m_t^*/m_o = 1.5$, 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.

Keywords: Effective mass, energy bands, ionic crystals, polarons, semiconductors, strontium titanate.

1.

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.[9,1] 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.

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

$$\mathcal{H} = - (m_o/m_t) \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) - (m_o/m_\ell) \frac{\partial^2}{\partial z^2} + \sum_q b_q^+ b_q \qquad (1)$$

$$+ i \left(\frac{4\pi\alpha}{S}\right)^{1/2} \sum_q \frac{1}{q} (b_q^+ e^{-i\underset{\sim}{q}\cdot\underset{\sim}{r}} - b_q e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}}),$$

with $\quad \alpha = \frac{1}{2} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_o}\right) \frac{e^2}{\hbar\omega} \left(\frac{2 m_o \omega}{\hbar}\right)^{1/2}.$ $\qquad (2)$

Here α is the dimensionless coupling constant dependent on the high and low frequency dielectric constants ϵ_∞ and ϵ_o, respectively. In Eqs. (1) and (2), x, y, z are the electron coordinates, m_o the free electron mass, m_ℓ and m_t the longitudinal and transverse bare masses, b_q^+ and b_q the annihilation and creation operators for phonon of wave vector $\underset{\sim}{q}$. 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:

$$E(k) = \frac{m_o}{m_t} (k_x^2 + k_y^2) + \frac{m_o}{m_\ell} k_z^2 - \frac{4\pi\alpha}{S} \sum_q \frac{1}{q^2} \left[1 + \frac{m_o}{m_\ell} (q_z^2 - 2q_z k_z)\right.$$

$$\left. + \frac{m_o}{m_t} (q_x^2 + q_y^2 - 2q_x k_x - 2q_y k_y)\right]^{-1}. \qquad (3)$$

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

$$E_b = -\alpha \, (m_\ell/m_o)^{1/2} \, (1/\sqrt{K-1}) \, \sin^{-1}\sqrt{(K-1)/K} \qquad (4a)$$

$$\Delta E_z = -(\alpha/2) \, (m_o/m_\ell)^{1/2} \, k_z^2 \, [1/(K-1) - (1/(K-1)^{3/2})\sin^{-1}\sqrt{(K-1)/K}\,] \quad (4b)$$

$$\Delta E_x = -(\alpha/4) \, (m_o/m_\ell)^{1/2} \, K^2 \, k_x^2 \left\{ 1/K - [1/(K-1)] + [1/(K-1)^{3/2}] \right. \qquad (4c)$$

$$\left. \sin^{-1}\sqrt{(K-1)/K} \right\}.$$

Here E_b is the binding energy; ΔE_z and ΔE_x are the changes of kinetic

energy. ΔE_y is of the same form as ΔE_x, by symmetry. 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 <100> direction. The masses observed are $m_\ell^* = 6.0 \, m_o$ and $m_t^* = 1.5 \, m_o$, 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 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 L.O. 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,

4.

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 band width 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,[17] but the results may be expected to give a significant estimate of the values of the polaron effects.

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 $(1/r_s)^2 = 6\pi ne^2/\epsilon_F$, where ϵ_F is the Fermi energy. The polaron radius is approximately $r_p = (\hbar/m^*\omega_o)^{1/2}$. Using the density of state mass ($5 m_o$) 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}.

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.

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[18]

$$H^0_{ij}(k) = D_{ij}{}^{\alpha\beta} k_\alpha k_\beta, \tag{5}$$

where the constant matrix $\underset{\sim}{D}$ is symmetric in α and β, the components of $\underset{\sim}{k}$, and the indices i and j refer to the degenerate basis states for k = 0. The eigenvectors of $\underset{\sim}{H}^0$ determine the "right linear combinations" of zero order wave functions for a given direction of $\underset{\sim}{k}$. For the case of degenerate bands, as from p-states in a cubic crystal, H_0 takes the form[19]:

$$
\begin{bmatrix}
L k_x^2 + M(k_y^2 + k_z^2) & N k_x k_y & N k_x k_z \\
N k_x k_y & L k_y^2 + M(k_x^2 + k_z^2) & N k_y k_z \\
N k_x k_z & N k_y k_z & L k_z^2 + M(k_x^2 + k_y^2)
\end{bmatrix}
$$

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 $\underset{\sim}{k}$. The Fröhlich Hamiltonian for the polaron problem, in the effective mass approximation, becomes

$$H_{ij} = H^0_{ij}(-i\underset{\sim}{\nabla}) + \Sigma\, b^+_v b_v\, \delta_{ij}$$

$$\tag{6}$$

$$+ i \left(\frac{4\pi\alpha}{s}\right)^{1/2} \Sigma\, \frac{1}{q}\, (b^+_q e^{-iq\cdot\underset{\sim}{r}} - b_q e^{iq\cdot\underset{\sim}{r}})\, \delta_{ij}.$$

To first order in α, the eigenvalues are determined by the following

6.

secular equation[20]

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

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

$$H^o(k+q) = H^o(k) + H^o(q) + B(k,q),\tag{8}$$

where

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

we obtain

$$\det \left| H^o(k)_{ij} - \frac{4\pi\alpha}{S} \sum_q \frac{1}{q^2} \left[\frac{1}{H^o(q) + 1} \right]_{ij} \right.$$

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

In Eq. (10) above, there are no terms linear in 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. XXXXXXXXXX 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.[19]) 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 band widths,
and such an occurrence might be possible.

Table I. Experimental data and calculated results

for $SrTiO_3$.

	$\hbar\omega$	α	Observed
ω_1	.022 eV	.01	$m_\ell^* = 6.0\, m_o$
ω_2	.058	.50	$m_t^* = 1.5\, m_o$
ω_3	.099	1.83	$K = 4.0$

Calculated

Bare Bloch Masses

$$m_\ell = 4.7\, m_o$$

$$m_t = 0.96\, m_o$$

$$K = 4.9$$

Binding Energy

$$E_b = 0.26\ eV$$

References

[1] H. P. R. Frederikse, W. R. Hosler, and W. R. Thurber, Phys. Rev. 143, 648 (1966).

[2] H. P. R. Frederikse, W. R. Hosler, W. R. Thurber, J. Babiskin, and P. G. Siebenmann, Phys. Rev. 158, 775 (1967).

[3] C. N. Berglund and W. S. Baer, Phys. Rev. 157, 358 (1967).

[4] S. H. Wemple, Phys. Rev. 137, A1575 (1965).

[5] J. H. Becker and W. R. Hosler, Phys. Rev. 137, A1872 (1965).

[6] H. Fröhlich, Advances in Physics 3, 325 (1954).

[7] T. D. Schultz, Tech. Rept. No. 9, Solid State and Molecular Physics Group, M. I. T., Cambridge, Mass. (1956).

[8] G. R. Allcock, Advances in Physics 5, 412 (1956).

[9] A. H. Kahn and A. J. Leyendecker, Phys. Rev. 135, A1321 (1964).

[10] J. M. Luttinger and W. Kohn, Phys. Rev. 78, 173 (1950).

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

[12] H. P. R. Frederikse and G. A. Candela, Phys. Rev. 147, 583 (1966).

[13] E. Ambler, J. H. Colwell, W. R. Hosler, and J. E. Schooley, Phys. Rev. 148, 280 (1966).

[14] J. W. Hodby, private communication.

[15] D. M. Eagles, J. Phys. Chem. Solids 25, 1243 (1964).

[16] D. M. Eagles, J. Phys. Chem. Solids 26, 672 (1965).

[17] G. Whitfield and R. Puff, Phys. Rev. 139, A338 (1965).

[18] W. Kohn, Solid State Phys. 5, 297 (1957).

[19] W. Shockley, Phys. Rev. 78, 173 (1950).

[20] This secular equation may be derived by projection of the Schrödinger equation onto the subspace spanned by the set of degenerate Bloch states at k = 0. See, e.g., A. Messiah, Quantum Mechanics, Vol. II (North Holland Publishing Co., Amsterdam, 1962), pp. 994 et seq.

Figure Captions

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 $m_{\ell,t}^* = m_{\ell,t} + \Delta m_{1,t}$.

Fig. 2. Polaron binding energy, in units of the LO phonon quantum $\hbar\omega_o$,
vs. bare mass anisotropy. m_{ℓ} and m_t are bare masses, m_o the
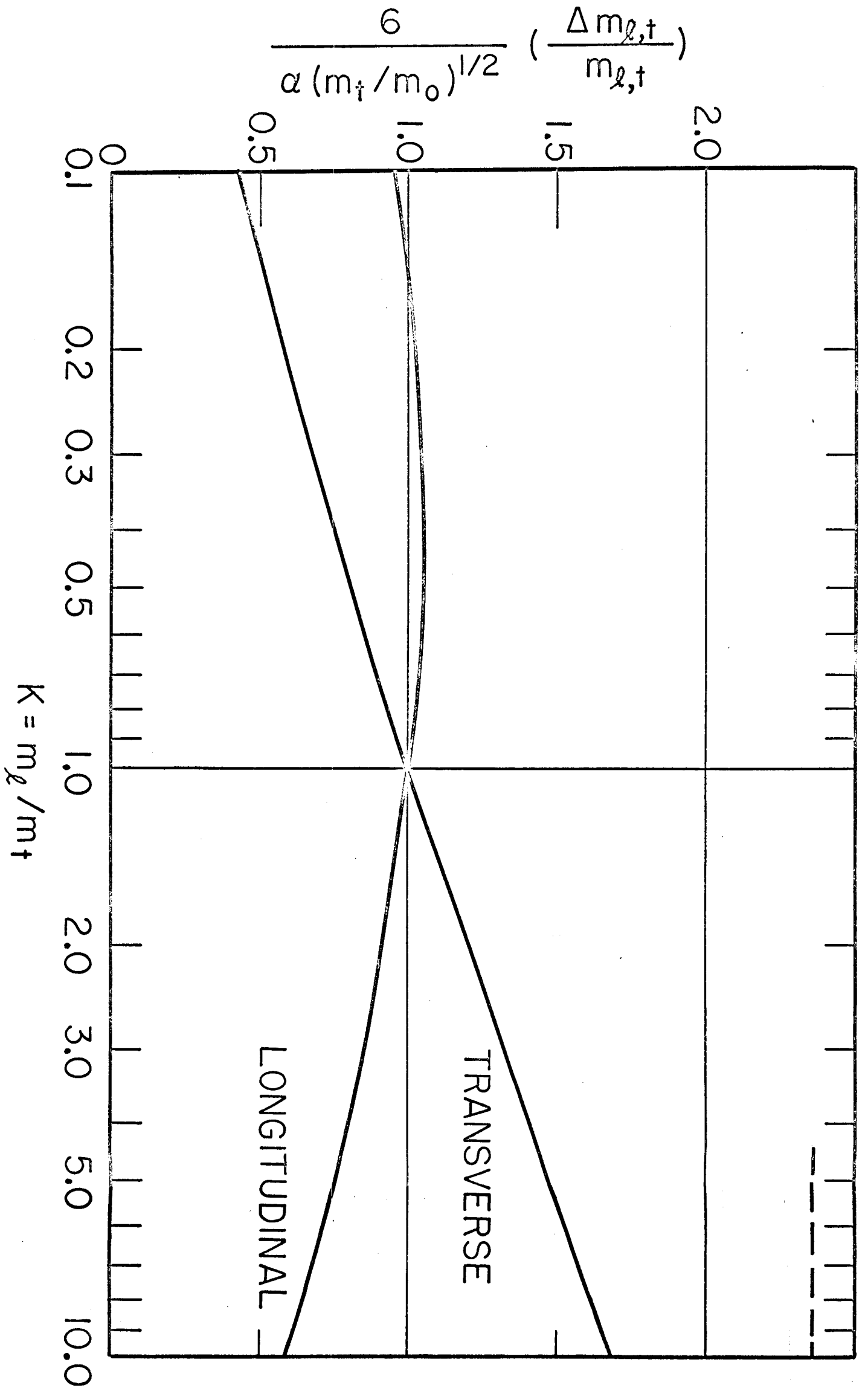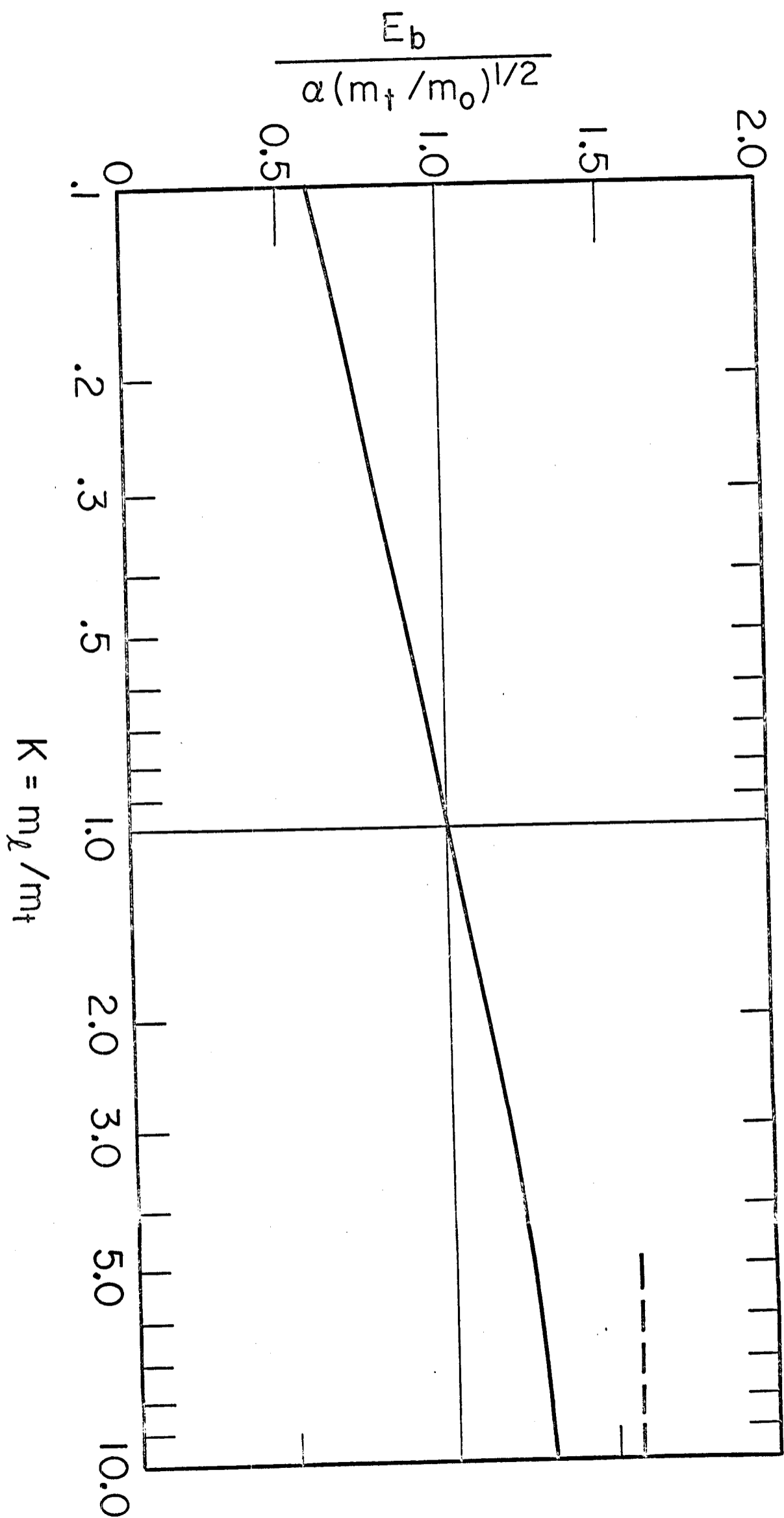free electron mass, and α the coupling constant.

Fig. 1

$$\frac{E_b}{\alpha (m_t / m_o)^{1/2}}$$

$K = m_\ell / m_t$

Fig. 2