

# POLAR MODES OF LATTICE VIBRATION AND POLARON COUPLING CONSTANTS IN RUTILE (TiO<sub>2</sub>)

D. M. EAGLES

National Bureau of Standards, Washington, D.C.†

(Received 27 December 1963; in revised form 20 April 1964)

**Abstract**—Published experimental infrared reflection data are analysed to obtain information about the long wavelength polar modes of lattice vibration in rutile (TiO<sub>2</sub>). The continuum polarization model of electron-phonon interactions is extended to apply to crystals with several types of longitudinal polar phonons, and the results are used to discuss polaron theory in rutile.

## 1. INTRODUCTION

RUTILE is a tetragonal crystal with six atoms per unit cell and several types of polar modes of lattice vibration. Since the electronic properties of ionic crystals can be greatly affected by the interaction of electrons with longitudinal polar phonons, a preliminary step required for almost any theory of electronic processes in such crystals is a quantitative evaluation of the strength of this type of interaction. In this paper we consider the coupling between electrons and long wavelength polar phonons in rutile in some detail. Some of the results should be of use in discussing other substances with large numbers of ions in a unit cell.

In section 2 we make use of the data of SPITZER *et al.*<sup>(1)</sup> (to be referred to as SMKH) from infrared reflection measurements, together with the classical theory of KUROSAWA<sup>(2)</sup> (to be referred to as K), to obtain the frequencies of the various long wavelength longitudinal polar modes and the amount of polarization associated with each transverse and longitudinal mode. In section 3 a discussion of the results is given. In section 4 electron-phonon interactions in crystals with many types of polar modes are considered within the framework of a continuum polarization model, and polaron coupling constants in rutile are estimated. The results are used to give a brief discussion of other polaron properties in this material.

## 2. ANALYSIS OF POLAR LATTICE VIBRATIONS

The method of analysis is described below, and the results are summarized in Tables 1 and 2.

### 2.1 $P \perp c$

The polar modes of zero wave-vector with the polarization  $P$  perpendicular to the  $c$  axis in rutile belong<sup>(3,4)</sup> to the symmetry class  $E_u$ . Choosing axes as indicated in Fig. 1, the modes with  $P \parallel Ox$  can be built up from the three basic motions illustrated. The long wavelength polar transverse and longitudinal modes with polarization  $P \parallel Ox$  also have displacements within one cell constructed from the same three basis functions. Let us introduce six-component vectors  $x_{t\mu}$  and  $x_{\ell\mu}$  ( $\mu = 1-3$ ) to denote the displacements within one cell associated with these three types of transverse and longitudinal modes, and use the normalization condition

$$\sum_{i=1}^6 M_i x_{\beta\mu i}^2 = A(\beta = t \text{ or } \ell, \mu = 1 \text{ to } 3), \quad (1)$$

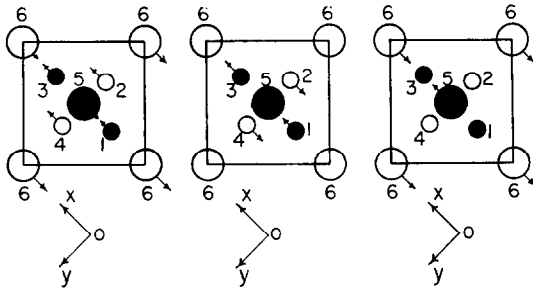
where  $M_i$  is the mass of the ions of the  $i$ th sublattice,  $x_{\beta\mu i}$  represents the displacement of the ions of the  $i$ th sublattice in the  $x$  direction, and  $A$  is a constant.

We introduce an effective charge  $e_{ix}^*$  associated with the  $i$ th sublattice for transverse modes with  $P \parallel Ox$  as in (K-2.1) by writing

$$P = N \sum_i e_{ix}^* x_i, \quad (2)$$

\* Present address: Post Office Research Station, London, N.W.2, England.

for general sublattice displacements  $x_i$  in a specimen in which there is no depolarization field. Here  $P$  and  $N$  are the magnitude of the polarization and the number of unit cells per unit volume, respectively.



$$\begin{array}{lll} x_1 = x_2 = x_3 = x_4 & x_1 = x_3 = -x_2 = -x_4 & x_1 = x_2 = x_3 = x_4 = 0 \\ x_5 = x_6 & x_5 = x_6 = 0 & x_5 = -x_6 \end{array}$$

$$2M_1 x_1 + M_5 x_5 = 0$$

FIG. 1. Basis motions for long wavelength polar modes with  $P \perp c$  in rutile (symmetry  $E_u$ ). The figure shows a cross-section of a unit cell perpendicular to the  $c$  axis. Small circles denote oxygen atoms and large circles titanium atoms. Shaded atoms lie at a height  $c/2$  above the basal plane. The arrows indicate the directions of motion.  $M_1$  and  $M_5$  are the masses of oxygen and titanium ions, respectively.

Let us write the angular frequencies of the long wavelength transverse and longitudinal modes with  $P \parallel Ox$  as  $\omega_{\beta\mu}$  ( $\beta = t$  or  $\ell$ ,  $\mu = 1-3$ ), and define polarizations  $p_{\beta\mu}$  associated with the modes by

$$p_{\beta\mu}^2 \equiv [(\sum_i e_{ix}^* x_{\beta\mu i})^2 / A] \quad (\beta = t \text{ or } \ell, \mu = 1-3). \quad (3)$$

The quantities  $p_{t\mu}^2$  for the transverse modes may be found with the help of equation (K-2.15), which in the notation to be used here becomes

$$\epsilon_a(\omega) = \epsilon_{\infty a} + 4\pi N \sum_{\mu} [p_{t\mu}^2 / (\omega_{t\mu}^2 - \omega^2)], \quad (4)$$

where  $\epsilon_{\infty a}$  and  $\epsilon_a(\omega)$  are the dielectric constants for fields perpendicular to the  $c$  axis at high frequencies and frequency  $\omega$ , respectively. Using the values obtained by SMK by Kramers-Kronig analysis of infrared reflection data for the frequencies and absorption strengths  $4\pi\rho_{\mu}$  associated

with the transverse modes ( $4\pi\rho_{\mu}$  is the contribution of the mode  $t_{\mu}$  to the static dielectric constant and is thus related to  $p_{t\mu}^2$  by  $4\pi\rho_{\mu} = 4\pi N p_{t\mu}^2 / \omega_{t\mu}^2$ ), we deduce the values of  $p_{t\mu}^2$ . Hence, using (K-2.17), which may be written as

$$(4\pi N / \epsilon_{\infty a}) [\sum_{\mu} p_{t\mu}^2 / (\omega_{t\mu}^2 - \omega^2)] = -1, \quad (5)$$

we obtain a cubic equation for the squares of the longitudinal mode frequencies, which we solve numerically.

Next we expand the longitudinal mode displacements in terms of those for the transverse modes, i.e. we write

$$x_{\ell\mu'} = \sum_{\mu} b_{\mu'\mu} x_{t\mu}. \quad (6)$$

Making use of the equation before (K-2.17), which we write as

$$b_{\mu'\mu} = - \frac{4\pi N}{\epsilon_{\infty a} (\omega_{t\mu}^2 - \omega_{\ell\mu'}^2)} p_{t\mu} p_{\ell\mu'}, \quad (7)$$

and remembering that

$$\sum_{\mu} b_{\mu'\mu}^2 = 1, \quad (8)$$

we obtain the quantities  $p_{\ell\mu'}$  and  $b_{\mu'\mu}$ .

The results up to this point are given in Tables 1 and 2.

## 2.2. $P \parallel c$

There is only one possible type of motion for long wavelength polar modes with  $P$  parallel to the  $c$  axis.<sup>(3,4)</sup> It has symmetry  $A_{2u}$  as illustrated in Fig. 2. The frequency  $\omega_t$  of the transverse mode of this type is deduced from (SMKH-12), which we write as

$$1 - \epsilon_{\infty c} = 4\pi\rho / [1 - (\omega_m / \omega_t)^2], \quad (9)$$

where  $\epsilon_{\infty c}$  is the high frequency dielectric constant for fields parallel to the  $c$  axis,  $4\pi\rho$  is the absorption strength of the mode, and  $\omega_m$  is the frequency of the reflection minimum on the short wavelength side of the reflection band. Equation (9) is valid under neglect of some damping terms. We insert SMK's values of  $\rho$  and  $\omega_m$  into this equation, but take the dielectric constant  $\epsilon_{\infty c}$  from the refractive index measurements of DE VORE<sup>(5)</sup> instead

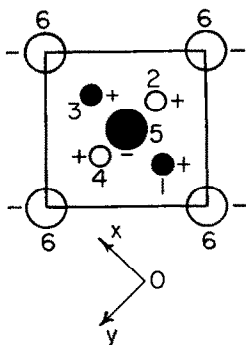
Table 1. Information about long wavelength polar modes of lattice vibration in rutile\*

(A) $P \perp c$				
Mode label ( $\beta\mu$ )	Frequency $\omega_{\beta\mu}/2\pi$ (cm <sup>-1</sup> )	Absorption strength of transverse modes <sup>(1)</sup> $4\pi\rho_{\mu}$	$p_{\beta\mu}^2/[\sum_{\mu}(p_{\beta\mu}^2)]$ (equation (3))	$\sum_{\mu} p_{\beta\mu}^2$ ((e.s.u.) <sup>2</sup> /g)
$t_1$	183	81.5	0.805	$6.0 \times 10^5$
$t_2$	388	1.08	0.048	
$t_3$	500	2.0	0.147	
$\ell_1$	373	—	0.007	$6.0 \times 10^5$
$\ell_2$	458	—	0.024	
$\ell_3$	806	—	0.969	

(B) $P \parallel c$		
Mode label	Frequency (cm <sup>-1</sup> )	$p_c^2$ (equation (10)) ((e.s.u.) <sup>2</sup> /g)
$t$	167	$8.0 \times 10^5$
$\ell$	811	

\* The value for the high frequency dielectric constant for  $P \perp c$  was taken as<sup>(1)</sup>  $\epsilon_{\infty a} = 6.0$  and the high frequency and static constants used for  $P \parallel c$  were<sup>(5)</sup>  $\epsilon_{\infty c} = 7.2$  and<sup>(6)</sup>  $\epsilon_{sc} = 170$ . We took<sup>(7)</sup>  $N = 1.60 \times 10^{22}$  cm<sup>-3</sup>.



$$Z_1 = Z_2 = Z_3 = Z_4$$

$$Z_5 = Z_6$$

$$2M_1 Z_1 + M_5 Z_5 = 0$$

FIG. 2. Polar modes with  $P \parallel c$  in rutile (symmetry  $A_{2u}$ ). The figure shows a cross-section of the unit cell perpendicular to the  $c$ -axis. Small circles denote oxygen atoms and large circles titanium atoms. Shaded atoms lie at a height ( $c/2$ ) above the basal plane. The plus and minus signs denote motion in the plus and minus  $x$  directions.

of using the value quoted by SMK. The longitudinal frequency  $\omega_l$  is deduced from the relation  $\omega_l = (\epsilon_{sc}/\epsilon_{\infty c})^{1/2} \omega_t$ , where  $\epsilon_{sc}$  is the static dielectric constant for  $P \parallel c$ . This relation follows from (K-2.22), since there is only one type of long wavelength polar mode with polarization in the  $c$ -direction. As for  $P \perp c$ , from the experimental absorption strength we may calculate the quantity  $p_c^2$  defined by

$$p_c^2 \equiv (\sum_i e_{iz}^* z_i)^2 / A, \quad (10)$$

where  $e_{iz}^*$  is the effective charge of the  $i$ th sublattice associated with transverse modes with displacements in the  $z$  direction, and  $A$  is a normalization factor as in equation (1). The results for  $\omega_t$ ,  $\omega_l$  and  $p_c$  are recorded in the lower half of Table 1.

### 3. DISCUSSION

The most striking result of the mode analysis is that although 80 per cent of the polarization for transverse modes with  $P \perp c$  is contained in the lowest frequency transverse mode, 97 per cent of

Table 2. Squares of expansion coefficients ( $b_{\mu}^2$ ) of longitudinal mode vectors in terms of transverse mode vectors (see equation (6))

$b_{11}^2 = 0.15$	$b_{12}^2 = 0.82$	$b_{13}^2 = 0.03$
$b_{21}^2 = 0.20$	$b_{22}^2 = 0.10$	$b_{23}^2 = 0.70$
$b_{31}^2 = 0.66$	$b_{32}^2 = 0.06$	$b_{33}^2 = 0.28$

the polarization for longitudinal modes lies in the highest frequency longitudinal mode. This result illustrates a general tendency for modes with large polarization to have low transverse and high longitudinal frequencies.

In order to find the amount of our three basis functions of Fig. 1 occurring in the displacement vectors  $\mathbf{x}_{\beta\mu}$  of the polar modes, and to obtain information about the other modes, we should have to introduce a force constant model.<sup>(3,4,8)</sup>

To obtain our results the assumption is made that the classical type of theory used by KUROSAWA<sup>(2)</sup> is valid. However, we should note that SMKX cannot fit their reflectivity results in rutile particularly well by the use of the simple classical theory. Thus it is possible that our deduced mode data would have to be modified somewhat if an interpretation of the results were made on the basis of a more refined theory, although some recent work of BARKER and HOPFIELD<sup>(9)</sup> on a classical theory involving coupled oscillators makes one expect that any changes involved will be rather small.

#### 4. POLARONS IN RUTILE

We conclude by making use of our results to write down the form of the electro-phonon interaction in a continuum polarization model for longitudinal modes with wave-vectors parallel or perpendicular to the symmetry axes. We then make some comments on the types of polaron theories applicable to electrons and holes in rutile.

##### 4.1 Coupling constants

In the continuum polarization model<sup>(10)</sup> the electron-phonon interaction  $H^{e-p}$  satisfies

$$H^{e-p} = - \int \mathbf{D} \cdot \mathbf{P} \, d\tau, \quad (11)$$

where  $\mathbf{D}$  is the electric displacement vector at  $\mathbf{r}$

due to an electron at  $\mathbf{r}_e$ ,  $\mathbf{P}$  is the polarization per unit volume associated with the lattice vibrations, and the integration is over all space. Expanding the longitudinal part  $\mathbf{P}_l$  of  $\mathbf{P}$  in a Fourier series

$$\mathbf{P}_l = \sum_{\mathbf{w}} \mathbf{P}_{l\mathbf{w}} \exp(i\mathbf{w} \cdot \mathbf{r}), \quad (12)$$

we see that

$$H^{e-p} = 4\pi ie \sum_{\mathbf{w}} (\mathbf{P}_{l\mathbf{w}} \cdot \hat{\mathbf{w}}/\mathbf{w}) \exp(i\mathbf{w} \cdot \mathbf{r}_e), \quad (13)$$

where  $\hat{\mathbf{w}}$  is a unit vector in the direction of  $\mathbf{w}$ .

For small wave-vectors  $\mathbf{w} \perp c$  in rutile we may use the results of section 2 to write

$$\mathbf{P}_{l\mathbf{w}} = \sum_{\mu=1}^3 \mathbf{P}_{l\mu\mathbf{w}}, \quad (14)$$

where  $\mathbf{P}_{l\mu\mathbf{w}}$  is the polarization associated with each of our three polar modes. For  $\mathbf{w} \parallel c$  it is convenient to introduce two non-polar modes of symmetry  $B_{2u}$  in MATOSSI's notation.<sup>(4)</sup> For these modes  $z_1 = -z_2 = z_3 = -z_4$ , and  $z_5 = -z_6$ , using the numbering of the atoms of Figs. 1 and 2. Equation (14) may then be used for  $\mathbf{w} \parallel c$  as well, with  $\mathbf{P}_{l1\mathbf{w}} = \mathbf{P}_{l2\mathbf{w}} = 0$ . We will use the suffix  $\mu = 3$  to refer to the only polar mode in this case.

We write the displacements associated with the long wavelength longitudinal modes of wave-vector  $\mathbf{w}$  as  $(NV)^{-1/2} q_{\ell\mu\mathbf{w}} \mathbf{r}_{\ell\mu\mathbf{w}}$ , where  $q_{\ell\mu\mathbf{w}}$  is a normal co-ordinate,  $\mathbf{r}_{\ell\mu\mathbf{w}}$  is an eighteen-dimensional vector consisting of the displacements of the six sublattices subject to a normalization condition of the type of equation (1),  $V$  is the volume of the crystal, and as before,  $N$  is the number of cells per unit volume. Choosing  $\mathbf{r}_{\ell\mu\mathbf{w}}$  for  $\mathbf{w} \perp c$  or  $\mathbf{w} \parallel c$  such that the vector polarization associated with  $\mathbf{r}_{\ell\mu\mathbf{w}}$  lies in the positive axial directions, we find that

$$\mathbf{P}_{l\mu\mathbf{w}} \cdot \hat{\mathbf{w}} = \pm (N/V)^{1/2} q_{\ell\mu\mathbf{w}} p_{\ell\mu\gamma} \epsilon_{\infty\gamma}^{-1} A^{1/2}, \quad (\gamma = a \text{ or } c) \quad (15)$$

where the positive or negative signs are taken according to whether  $\mathbf{w}$  lies along the positive or negative axial directions, and  $p_{\ell\mu a}$  and  $p_{\ell\mu c}$  are defined as are  $p_{\ell\mu}$  and  $p_c$  in equations (3) and (10), respectively. We can show that, with suitable choice of phases, the  $q$ 's introduced above are related to creation and annihilation operators  $b^\dagger$  and  $b$  for the modes by

$$q_{\ell\mu w} = (\hbar/2A\omega_{\ell\mu w})^{1/2}(b_{\ell\mu, -w}^\dagger + b_{\ell\mu w}), \quad (16)$$

where  $\omega_{\ell\mu w}$  is the angular frequency of the  $\ell\mu$ th mode.

The long wavelength longitudinal mode frequencies are the same as those for the zero wave-vector vibrations in a direction normal to the plane of a disk-shaped specimen.<sup>(11)</sup> Let us consider a disk such that this normal lies along one of our principal symmetry axes,  $\gamma$  ( $\gamma = a$  or  $c$ ). We write the polarization arising in such a specimen in response to a uniform static field  $\mathbf{D}$  in the direction of this normal as

$$\mathbf{P} = \left(\sum_{\mu} \mathbf{P}_{\mu\gamma}\right) + \mathbf{P}_{\infty}, \quad (17)$$

where  $\mathbf{P}_{\mu\gamma}$  is the polarization associated with the  $\mu$ th polar mode with polarization in the  $\gamma$ -direction, and  $\mathbf{P}_{\infty}$  is the purely electronic polarization. By comparing the response to static and high frequency fields, we see that

$$4\pi\left(\sum_{\mu} \mathbf{P}_{\mu\gamma}\right) = [(1/\epsilon_{\infty\gamma}) - (1/\epsilon_{s\gamma})]\mathbf{D}. \quad (18)$$

Next, using an equation like (15) for the zero wave-vector vibrations in the  $\gamma$ -direction, we can show that the lattice potential energy  $W_{\ell\gamma}$  associated with the polarization  $\mathbf{P}$  satisfies

$$W_{\ell\gamma} = \sum_{\mu} \frac{1}{2} V B_{\mu\gamma} P_{\mu\gamma}^2, \quad (19)$$

where the summation is over the polar modes,  $V$  is the volume of our specimen, and

$$B_{\mu\gamma} = (1/N)(\omega_{\ell\mu\gamma}\epsilon_{\infty\gamma}/p_{\ell\mu\gamma})^2. \quad (20)$$

Here we have written the frequency of the  $\mu$ th zero wave-vector normal mode for vibrations in the direction  $\gamma$  normal to the disk as  $\omega_{\ell\mu\gamma}$ . The interaction energy  $W_i$  between the field and the polarization satisfies  $W_i = [-(\mathbf{D} \cdot \mathbf{P})V]$ , and so,

minimizing the sum of  $W_i$  and  $W_{\ell\gamma}$  of (19) with respect to  $\mathbf{P}_{\mu\gamma}$ , we find that in equilibrium

$$\mathbf{P}_{\mu\gamma} = \mathbf{D}/B_{\mu\gamma}. \quad (21)$$

Hence, substituting from (21) and (20) into (18), we find that

$$\frac{p_{\ell\mu\gamma}}{\omega_{\ell\mu\gamma}} = f_{\mu\gamma} \left[ \left( \frac{1}{4\pi N} \right) \left( \frac{\epsilon_{\infty\gamma}}{\epsilon_{s\gamma}} \right) (\epsilon_{s\gamma} - \epsilon_{\infty\gamma}) \right]^{1/2}, \quad (22)$$

where

$$f_{\mu\gamma}^2 = (p_{\ell\mu\gamma}^2/\omega_{\ell\mu\gamma}^2) / \sum_{\mu=1}^3 (p_{\ell\mu\gamma}^2/\omega_{\ell\mu\gamma}^2). \quad (23)$$

For rutile, using the results of section 2,  $f_{\mu a}$  may be found by putting  $p_{\ell\mu a}^2 \equiv p_{\ell\mu}^2$  and  $\omega_{\ell\mu a}^2 \equiv \omega_{\ell\mu}^2$ , where  $p_{\ell\mu}$  and  $\omega_{\ell\mu}$  are given in Table 1, while for modes with  $\mathbf{P} \parallel c$  we have  $f_{\mu c}^2 = \delta_{\mu,3}$ , since, for  $\mathbf{w} \parallel c$ ,  $\mu = 1$  and  $\mu = 2$  refer to non-polar modes.

Remembering that for small wave-vectors  $\mathbf{w}$  in the  $\gamma$  direction  $\omega_{\ell\mu w} = \omega_{\ell\mu\gamma}$ , and writing

$$H^{e-p} = \sum_{\lambda, \mathbf{w}} V_{\lambda, \mathbf{w}} (b_{\lambda, -\mathbf{w}} + b_{\lambda, \mathbf{w}}) \exp(i\mathbf{w} \cdot \mathbf{r}_e), \quad (24)$$

where  $\lambda$  is a label denoting the mode branch, from (13), (15), (16) and (22), we find, for long wavelength longitudinal modes with  $\mathbf{w} \perp c$  or  $\mathbf{w} \parallel c$ , that

$$V_{\ell\mu w} = \pm \frac{ie}{w} f_{\mu\gamma} \left[ 2\pi \left( \frac{1}{\epsilon_{\infty\gamma}} - \frac{1}{\epsilon_{s\gamma}} \right) \hbar \omega_{\ell\mu w} / V \right]^{1/2}, \quad (25)$$

where, as in equation (15), the positive or negative signs are taken according to whether  $\mathbf{w}$  lies along the positive or negative axial directions.

If we imagine that as the direction of  $\mathbf{w}$  moves away from the axes the longitudinal modes remain longitudinal and that the electron-phonon interaction and frequencies interpolate smoothly between the limiting values given above, then it is plausible to suppose that some polaron properties may be obtained by the use of an isotropic interaction with  $V_{\ell\mu w}$  replaced by  $V_{\ell\mu|\mathbf{w}|}$  defined by

$$\frac{|V_{\ell\mu|\mathbf{w}|}|^2}{\hbar \bar{\omega}_{\ell\mu|\mathbf{w}|}} = \frac{2\pi e^2}{w^2 V} \left\langle f_{\mu\gamma}^2 \left( \frac{1}{\epsilon_{\infty\gamma}} - \frac{1}{\epsilon_{s\gamma}} \right) \right\rangle_{av}, \quad (26)$$

where  $\bar{\omega}_{\ell\mu|\mathbf{w}|}$  is some average frequency (the average being weighted in favor of the directions for which the modes are most polar), and  $\langle \rangle_{av}$  denotes a simple average over the three axial directions. Comparing with the usual expression<sup>(10)</sup> for

$He-p$  in an isotropic crystal with a single longitudinal mode frequency, we may define effective coupling constants  $\alpha_\mu$  for our three branches by

$$\alpha_\mu = \frac{1}{2} \frac{e^2}{r_\mu \hbar \omega_\mu} \left\langle f_{\mu\gamma}^2 \left( \frac{1}{\epsilon_{\infty\gamma}} - \frac{1}{\epsilon_{s\gamma}} \right) \right\rangle_{av}, \quad (27)$$

where

$$\omega_\mu = \lim_{|w| \rightarrow 0} \bar{\omega}_{\ell\mu|w|}, \quad (28)$$

and  $r_\mu$  is a length defined by

$$r_\mu = (\hbar/2m\omega_\mu)^{1/2}, \quad (29)$$

where  $m$  is the rigid-lattice electron effective mass (to be referred to as the bare mass).

Taking  $\omega_\mu$  for  $\mu = 1, 2$  equal to the long wavelength frequencies for  $w \perp c$  (those for  $w \parallel c$  are not known, but we wish to weight the frequencies in favor of the most polar modes), and  $\omega_3$  as an average over directions of the highest longitudinal mode frequencies (since these frequencies for different directions are practically identical, it does not matter what sort of average we take), we have calculated the values in rutile of  $f_{\mu\gamma}$ ,  $r_\mu(m/m_e)^{1/2}$  and  $\alpha_\mu(m_e/m)^{1/2}$ , making use of Table 1 and equations (23), (29) and (27). The results are given in Table 3. We notice that, as would be expected, the largest coupling constant is associated with the most polar mode.

#### 4.2. Self energies and effective masses

When there is only one branch of the phonon spectrum, fairly good results for the self energies and effective masses of slow polarons at low temperatures may be obtained for coupling constants up to about three by using a variational method to

determine the low energy states of the system of electron and phonons, with trial wave-functions of a type such that any number of phonons may mix in with the bare electron states, but in such a way that the probability amplitudes for the presence of different phonons are not correlated.<sup>(10,12)</sup>

If we assume that a similar method is valid for our case for a total coupling constant of less than three, then we can show (e.g. by slightly modifying the calculations described in section 4.2 of reference (10)) that the polaron binding energy  $E_p$  and effective mass  $m^*$  satisfy

$$E_p = \sum_\mu \alpha_\mu \hbar \omega_\mu, \quad (30)$$

and

$$m^*/m = 1 + \frac{1}{6} \sum_\mu \alpha_\mu. \quad (31)$$

For rutile the condition

$$\left( \sum_\mu \alpha_\mu \right) < 3$$

requires bare masses of less than  $2.9 m_e$ .

For bare masses larger than this value we could try assuming that all the interaction is with our highest frequency mode and use FEYNMAN's theory,<sup>(13)</sup> modified by introducing a cut-off in phonon wave-vectors.<sup>(12)</sup> However, at  $m = 3 m_e$  we see from Table 3 that the characteristic length  $r_3$  for the highest frequency modes is only  $3.7 \times 10^{-8}$  cm, and so it is probable that the assumption (occurring in all the theories mentioned in SCHULTZ's article<sup>(12)</sup>) that the total effect of the periodic potential of the rigid lattice is to give an electron a bare mass different from the free

Table 3. Parameters occurring in polaron theory for rutile\*

Branch label ( $\mu$ )	$\hbar\omega_\mu$ (eV)	$\gamma = a$	$f_{\mu\gamma}^2$ $\gamma = c$	$r_\mu(m/m_e)^{1/2}$ (cm)	$\alpha_\mu(m_e/m)^{1/2}$
1	0.046	0.029	0	$9.1 \times 10^{-8}$	0.05
2	0.057	0.069	0	$8.2 \times 10^{-8}$	0.11
3	0.100	0.902	1	$6.2 \times 10^{-8}$	1.61

\* Values for  $p_{\ell\mu}$ ,  $\omega_{\ell\mu}$ ,  $\epsilon_{sc}$ ,  $\epsilon_{\infty c}$ ,  $\epsilon_{\infty a}$  were taken as shown in and below Table 1. In addition we used<sup>(6)</sup>  $\epsilon_{sa} = 86$ .

electron mass, will not be good when the weak coupling method breaks down.

An upper limit to polaron binding energies is given by the small polaron<sup>(14,15)</sup> binding energy for zero overlap integral between electron wavefunctions on different sites. In our notation this binding energy  $E_b$  satisfies

$$E_b \simeq \sum_{\mu, w} \left\{ \frac{|V_{\ell \mu w}|^2}{\hbar \omega_{\ell \mu w}} \right\}. \quad (32)$$

Using our simplified expression (26) for the interaction, and replacing the Brillouin zone by a sphere, we find from equations (23), (26) and (32) that

$$E_b \simeq \left\langle \frac{1}{\epsilon_{\infty \gamma}} - \frac{1}{\epsilon_{s \gamma}} \right\rangle_{av} (e^2 w_0 / \pi), \quad (33)$$

where  $w_0$  satisfies

$$(4/3)\pi(w_0/2\pi)^3 = N. \quad (34)$$

For rutile, equations (33) and (34) give  $E_b \simeq 0.7$  eV.

The overall width of the valence bands in rutile as determined by X-ray emission data on the  $K$ -series of titanium<sup>(16)</sup> is about 4 eV. Hence effective masses for some or all of these bands probably lie near to  $m_e$ , and for such bands a weak coupling type of theory should apply.

Band structure calculations<sup>(17)</sup> indicate that the overall width of the titanium  $d$ -electron conduction bands in rutile is about 2–3 eV, hence the bare effective mass  $m$  for some of the conduction bands should also lie near  $m_e$ . However, the lowest conduction bands in these calculations have masses which are very large in at least one direction. Further, combined Hall effect and thermoelectric power data analysed on a one band model indicate<sup>(18)</sup> that the density of states mass  $m_d$  for the lowest conduction band satisfied  $m_d \sim 20 m_e$ , and a preliminary analysis assuming two conduction bands separated by a few hundredths of an electron volt<sup>(19)</sup> suggests that the density of states mass for the lower of these two bands is somewhat larger than the above value. From SCHULTZ's article<sup>(12)</sup> we see that for a coupling constant  $\alpha = 5$ , which will be obtained in rutile with a bare mass  $m$  of about  $8 m_e$  in our approximations, Feynman's theory without a cut-off predicts that

the polaron mass  $m^*$  satisfies  $m^*/m = 3.89$ , i.e. for rutile it predicts that if the bare mass satisfies  $m \simeq 8 m_e$ , then the polaron mass  $m^*$  would be given by  $m^* \simeq 31 m_e$ . Use of a cut-off in wave-vector would reduce this value somewhat. However, the characteristic length  $r_3$  for a bare mass of  $8 m_e$  is  $2.2 \text{ \AA}$ , which is only just over a nearest-neighbor distance. Hence to predict the observed masses a polaron theory which takes into account the atomic nature of the lattice explicitly will have to be used, perhaps something resembling small polaron theory.

#### 4.3. Mobility

Polaron mobility calculations are very difficult even in the case where there is only one branch of the phonon spectrum.<sup>(12)</sup> Nevertheless, judging from a simple resonance picture of the scattering,<sup>(12,20)</sup> at temperatures well below the optical phonon temperatures but sufficiently high for optical phonon scattering to be dominant, provided that masses are isotropic, then one expects that the temperature dependence of the mobility  $\mu$  may be obtained from a formula  $\mu = (e\tau/m^*)$ , with a relaxation time  $\tau$  which satisfies

$$1/\tau = \sum_{\mu} (1/\tau_{\mu}),$$

where the  $\tau_{\mu}$ 's are the relaxation times associated with the individual branches of the phonon spectrum. If the polaron mass is independent of temperature, this results in a temperature dependence for  $\mu$  of the form

$$[1/\mu(T)] \propto \sum_{\mu} \alpha_{\mu} \omega_{\mu} \bar{n}_{\mu}, \quad (35)$$

where  $\bar{n}_{\mu}$  is the thermal occupation number for phonons of frequency  $\omega_{\mu}$ .

If the electron masses are anisotropic but finite, then on a resonance picture the temperature dependence of the part of the mobility due to scattering by optical phonons should still be given by (35) at sufficiently low temperatures. However, if the mass is much larger in one direction than in the other two, a thermal polaron wave-vector in the heavy mass direction can easily become greater than the resonance wave-vector in the low mass direction, and then scattering of polarons producing appreciable changes of momentum in the high mass direction should be dominated by phonons.

with wave-vectors in the same direction (Fig. 3). Hence in an anisotropic crystal we could get a different temperature dependence of the mobility for different directions. There appears to be some evidence that this is the case in rutile.<sup>(19)</sup>

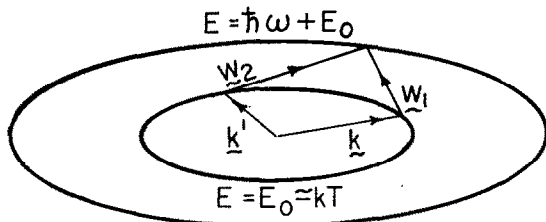


FIG. 3. Resonance scattering with anisotropic masses. The figure represents scattering of a thermal polaron of wave-vector  $k$  and energy  $E_0$  to a state  $k'$  of the same energy via an intermediate state on the resonance energy surface  $E = E_0 + \hbar\omega$ , where  $\omega$  is a phonon frequency. In order that there should be an appreciable change of polaron momentum in the heavy mass direction, it is necessary that one or both of the absorbed and emitted phonon wave-vectors  $w_1$  and  $w_2$  should lie approximately in the heavy mass direction.

#### 4.4 Optical absorption

A tentative interpretation of the main band-to-band absorption edge at room temperature in rutile can be made by using the theory of reference (15), and assuming that the absorption is due to transitions from a wide valence band, with negligible electron-phonon coupling, to a small-polaron conduction band. If phonons of just one energy  $\hbar\omega$  are important in the electron-phonon coupling, and the simplifications are made of taking delta-function and step-function densities of states for the conduction and valence bands, respectively, then the theory predicts absorption at low temperatures of the form

$$K(\Omega) \propto (1/n\Omega) \sum_{p=0}^{p_1} (D^p/p!). \quad (36)$$

Here  $K$  is the absorption coefficient,  $\Omega$  is the photon energy,  $n$  is the refractive index,  $p_1$  is the largest integer less than  $(\Omega - E_G)$ , where  $E_G$  is the energy gap, and  $D$  is a parameter related to the small polaron binding energy  $E_b$  for zero band-width by

$$E_b \simeq D\hbar\omega. \quad (37)$$

For rutile we took the phonon energy  $\hbar\omega$  to be 0.1 eV, and adjusted  $D$ ,  $E_G$ , and the magnitude of the absorption to give a fair fit to the experimental

data published by a number of authors.<sup>(21,22)</sup> The results are shown in Fig. 4. The refractive indices used in the "theoretical" curve in the figure were taken from the results of MOCH *et al.*<sup>(22)</sup> on 542 Å films. In drawing the theoretical curve we assumed that some mechanism smooths out the artificial steps given by equation (36).

The energy gap obtained by this curve fitting is 3.0 eV and the parameter  $D$  satisfies  $D = 10$ . If the continuum polarization model is used for the electron-phonon interaction, then, using equations (33) and (37), one calculates  $D \simeq 7$ .

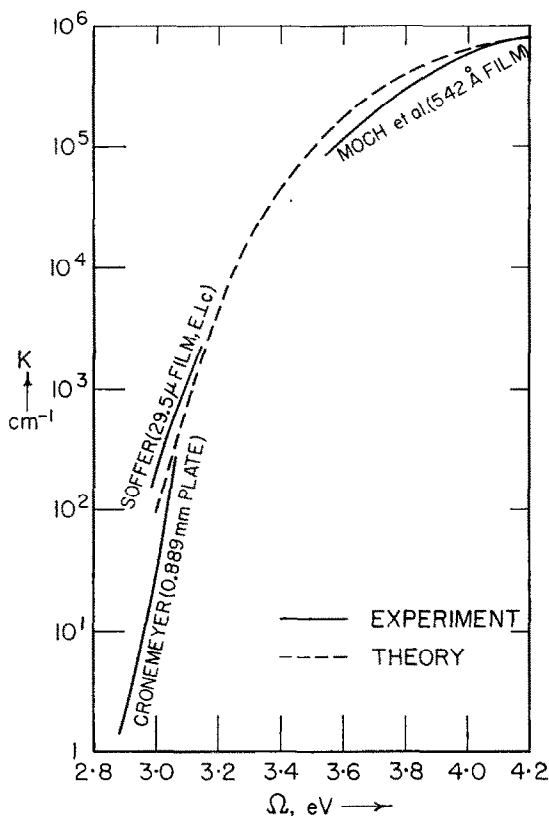


FIG. 4. Plot of absorption coefficient  $K$  vs. photon energy  $\Omega$  in rutile at 295°K. The experimental data<sup>(21,22)</sup> were obtained from the work of the authors named in the figure. The curve marked Soffer was estimated approximately by the present author from SOFFER's published optical density data and reflection losses. The "theoretical" curve is a smoothed-out version of that given by equation (36) of the text, with  $D = 10$  and  $E_G = 3.0$  eV. The refractive index as a function of energy was taken from the results of MOCH *et al.*<sup>(22)</sup> on thin films.



As the data fitted do not cover the entire range of energy concerned, and also three adjustable parameters have been used, it would not be surprising if other interpretations of the results can be given. In particular, we cannot rule out the possibility that the low energy part of the curve may be due to exciton absorption with the exciton excitation energy  $E_e$  equal to about 3.0 eV. If this were the case, then the energy gap would be larger than the above value by an amount equal to the exciton binding energy.

### 5. CONCLUSION

From the discussions of the previous subsections we conclude that, although for some of the valence and conduction bands in rutile a weak coupling type of polaron theory should be used, with three types of phonons and coupling constants given in Table 3, a theory for polarons with masses which may be anisotropic and very large in at least one direction should be developed for the lowest conduction band. **We expect that some properties similar to those of small polarons will occur in such a theory.**

*Acknowledgements*—I am grateful to J. H. BECKER, R. D. DESLATTES, W. R. HOSLER, A. J. LEYENDECKER, A. H. KAHN and W. R. THURBER for providing information about work which has not been published at present. I should also like to thank J. H. BECKER, H. P. R. FREDERIKSE, A. H. KAHN and R. F. WALLIS for some comments on the manuscript.

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