# DETAILED STUDY OF THE ELECTRON-PHONON INTERACTION IN ALKALI HALIDES\* PART I

THE TRANSPORT OF ELECTRONS WITH ENERGIES BETWEEN . 25 AND 7.5 eV

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#### ABSTRACT

The interaction between conduction electrons with energies from .25 to 7.5 eV and longitudinal optical phonons in alkali halides is studied in detail by time dependent perturbation theory. Expressions for the rate and angular distribution of scattering are obtained. The electron transport problem is then solved with the exact quantum mechanical scattering results by a direct simulation Monte Carlo method. Probabilities of escape and average energy losses for electrons generated isotropically at a certain depth in the material, with a given initial energy, are computed for CsI, KCl, NaF, and LiF. A simple theory shows the effective mass and temperature dependence. The effect of including scattering to angles other than forward is quite apparent in the results.

## I. INTRODUCTION

The interaction between electrons and the optical modes of the lattice vibrations has long been recognized to be the predominant interaction controlling the transport of low energy (a few eV) electrons in pure ionic crystals. In 1937, Fröhlich<sup>1</sup> was able to compute the high field breakdown of ionic crystals, with reasonable agreement with experimental results, by considering the collisions between free conduction electrons and the longitudinal optical mode lattice vibrations. In 1939, the same author<sup>2</sup> improved on his previous work by showing that it is possible to solve the same problem without having to compute the reduced masses and vibration frequencies of the lattice. Instead, experimentally determined dielectric constants and infrared absorption frequencies can be used, and these may easily be determined even for crystals which are not fully ionic in character. Dekker<sup>3, 4</sup> has developed a simplified one-dimensional random walk model, based on the electron-phonon interaction theory of Fröhlich, which predicts the temperature dependence of the secondary emission coefficient  $\delta$  for ionic crystals, and in particular for MgO. For two temperatures  $T_1$  and  $T_2$ , the ratio of the yields is

$$\frac{\delta_1}{\delta_2} = \left[ (2n_{T2} + 1) / (2n_{T1} + 1) \right]^{1/2}$$
(1)

where

$$n_{Ti} = 1 / \left[ \exp \left( \hbar \omega / kT_{i} \right) - 1 \right]$$
(2)

is the average number of phonons in one mode at temperature  $T_i$ , and  $\omega$  is the angular frequency of the longitudinal optical vibrations of the lattice. The agreement with experiment has been further investigated by Stuchinskii<sup>5</sup> at temperatures ranging from 100<sup>°</sup>K to 600<sup>°</sup>K and found to be quite good for MgO,

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although the experimental temperature dependence was slightly stronger than the one predicted by Dekker. Khokley and van Vliet have continued to investigate the escape mechanism of secondary electrons in polar crystals in the absence of an electric field, <sup>6</sup> and with field enhancement, <sup>7</sup> by setting up a Boltzmann transport equation based on(the following simplifying assumptions:

- 1. The spatial dependence of the internal secondary electron distribution is one dimensional.
- 2. The secondary electrons can be characterized by a single isotropic effective mass m\*, with energy  $\mathcal{E} = \hbar^2 k^2 / 2m^*$  measured with respect to the bottom of the conduction band.
- 3. The electrons interact with lattice vibrations (longitudinal optical modes) which cause only forward scattering for  $\mathcal{E} \gg \hbar \omega$  (the phonon energy).

It is the purpose of this paper to examine more carefully the third of these assumptions and to show that a detailed calculation of the transport of lowenergy electrons (secondary or photo-excited) requires a more complete characterization of the electron-phonon scattering than the one used by Khokley and van Vliet. After obtaining expressions for the rate and angle of scattering from time dependent perturbation theory, the transport problem is solved by a Monte Carlo method. Numerical results for the escape probabilities and energy losses of electrons generated internally are obtained for CsI, KCl, NaF, and LiF, selected to span the range of alkali-halide compounds from highest to lowest atomic number. Particularly detailed results are presented for CsI to illustrate the main points of this paper. Only the case with no applied external field has been considered.

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## **II.** THE ELECTRON PHONON INTERACTION

Fröhlich first calculated the scattering rate for electrons interacting with the optical modes of an ionic lattice by time-dependent perturbation theory.<sup>1, 2</sup> In that approach the adiabatic principle is used: the electronic states are largely independent of the lattice vibrational states; the unperturbed wavefunctions are products of the lattice and electronic wavefunctions; and the perturbing Hamiltonian operates on the product wavefunctions. The transition rates are proportional to the square of the matrix elements of the perturbing Hamiltonian. This paper uses perturbation theory to calculate the electron-phonon interaction for electrons with energies characteristic of secondary- and photo-emission; i.e., from the first fundamental absorption in the alkali-halides (5.5 to 11 eV) down to an energy about 10 times the phonon energy (0.1 to 1 eV). The validity of such an approach is borne out both by the good quantitative results obtained by Fröhlich, and by the theoretical expectation that in this energy range the electron-lattice coupling will be much weaker than for electrons near the bottom of the conduction band in which case perturbation theory is, of course, not applicable. (See the articles by H. Fröhlich and D. Pines in Ref. 8.)

The unperturbed electronic wavefunctions have been taken to be plane waves

$$|\mathbf{k}\rangle = (1/V^{1/2}) \exp(i\underline{k} \cdot \underline{\mathbf{r}})$$
 (3)

with energy  $E_{\underline{k}} = \hbar^2 k^2 / 2m^*$  where  $m^*$  is the effective mass of the electron. The unperturbed wavefunctions for the lattice vibrations corresponding to a given mode and branch are represented by  $|q\rangle$  obeying a Hamiltonian

$$H = \frac{1}{2} \sum_{q} \frac{\hbar \omega_{q}}{2} \left( a_{q}^{*} a_{q}^{*} + a_{q}^{*} a_{q}^{*} \right)$$
(4)

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in which  $\underline{q}$  is a vector in wavenumber space within the Brillouin zone. The phonon creation and annihilation operators are represented by  $a^*$  and a, respectively. By considering the lattice to be a continuum with a polarization field due to the relative displacement of the ions in the longitudinal optical vibrational modes, Ziman<sup>9</sup> and Fröhlich<sup>10</sup> obtain an interaction Hamiltonian

$$H_{inter} = 4\pi i \left(\frac{e^2\hbar}{2\gamma\omega V}\right)^{1/2} \sum_{\mathbf{q}} \frac{1}{\mathbf{q}} \left(a_{\mathbf{q}}^* e^{-i\mathbf{q}\cdot\mathbf{r}} - a_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}}\right), \quad \mathbf{q} \neq 0$$
(5)

where  $\gamma$  is a constant containing the part of the dielectric constant which is due to lattice polarization, and is defined by

$$\frac{1}{\gamma} = \frac{\omega^2}{4\pi} \left( \frac{1}{\epsilon_{\infty}} - \frac{1}{\epsilon} \right) \quad . \tag{6}$$

In this expression  $\epsilon$  is the static dielectric constant,  $\epsilon_{\infty}$  is the square of refractive index, and  $\omega$  is the vibrational frequency of the longitudinal optical modes of the lattice. This frequency  $\omega$  is approximately related to the observable residual ray or reststrahl absorption frequency  $\omega_r$  by<sup>11</sup>

$$\boldsymbol{\omega} = \left(\frac{\epsilon}{\epsilon_{\infty}}\right)^{1/2} \quad \boldsymbol{\omega}_{\mathbf{r}} \qquad \boldsymbol{\cdot} \tag{7}$$

The assumption of a single value of  $\omega$  for all  $\underline{q}$  (flat longitudinal optical branch) is made throughout. The limitation of  $q \neq 0$  is discussed by Fröhlich.<sup>10</sup> The  $\underline{q} = 0$  term corresponds to a dc polarization which cannot exist by the requirement of charge neutrality.

The matrix element for the transition of one electron in state  $\underline{k}$  to  $\underline{k}$ ' with the loss of one phonon of wavenumber  $\underline{q}$  is

$$\mathbf{M}^{-}(\underline{\mathbf{k}},\underline{\mathbf{k}}') = 4\pi \mathbf{i} \left(\frac{\mathbf{e}^{2}}{2\gamma\omega V}\right)^{1/2} \frac{1}{\mathbf{q}} \sqrt{\mathbf{n}}_{\underline{\mathbf{q}}} \quad \text{for} \quad \underline{\mathbf{k}}' = \underline{\mathbf{k}} + \underline{\mathbf{q}} \quad . \tag{8}$$

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Similarly, for transitions with the gain of one phonon,

$$M^{+}(\underline{k},\underline{k}') = -4\pi i \left(\frac{e^{2}\hbar}{2\gamma\omega V}\right)^{1/2} \frac{1}{q} \sqrt{n_{\underline{q}}+1} \quad \text{for} \quad \underline{k} = \underline{k}' + \underline{q} \quad . \tag{9}$$

For the problem under study,  $n_q$  is a constant depending only on the material and temperature. The vector notation at the subscript will be dropped.

### **III.** RATE AND ANGLE OF SCATTERING

The transition rate for electrons from a state  $|\underline{k}\rangle$  to a state  $|\underline{k}'\rangle$  is given by the standard result of perturbation theory

$$W_{\underline{k}\underline{k}'} = \frac{1}{\hbar^2} \left| M_{\underline{k}\underline{k}'} \right|^2 \frac{\partial}{\partial t} \frac{\sin^2 \beta_t}{\beta^2}$$
(10)

where

$$\boldsymbol{\beta} = \frac{1}{2\hbar} \left[ \boldsymbol{\mathcal{E}}_{\underline{k}'} - \left( \boldsymbol{\mathcal{E}}_{\underline{k}} + \hbar \boldsymbol{\omega} \right) \right]$$
(11)

for the case in which electrons gain energy (phonon annihilation).

For this case, the rate will be

$$W_{\underline{k}\underline{k}'} = \frac{1}{\hbar} \frac{(4\pi)^2 e^2}{2\gamma\omega V} \quad \frac{1}{q^2} n_q \frac{\partial}{\partial t} \frac{\sin^2\beta_t}{\beta^2}$$
(12)

The total scattering rate from a state k to all the other available states k' can be found by summing over all k', but it is more convenient to do the sum as an integral over q with the angular relationships as defined in Fig. 1a.

$$W_{\underline{k}}^{-} = \int_{q=q_{\min}}^{q_{\max}} \int_{\phi=0}^{2\pi} \int_{\theta^{*}=0}^{\pi} \frac{1}{\hbar} \frac{(4\pi)^{2} e^{2}}{2\gamma \omega V} - \frac{1}{q^{2}} n_{q} \frac{\partial}{\partial t} \frac{\sin^{2}\beta t}{\beta^{2}} \frac{V}{8\pi^{3}} q^{2} dq \sin\theta^{*} d\theta^{*} d\phi$$

$$(13)$$

In terms of q, k and  $\theta^*$ ,

$$\beta = \frac{\lambda}{4m^*} \quad q^2 - \frac{h}{2m^*} \quad kq \cos \theta^* - \frac{\omega}{2} \quad . \tag{14}$$

The integration over  $\theta$  \* can than be converted to an integral over  $\beta$  which, when carried out, results in the conservation of energy requirement ( $\beta = 0$ ), leaving

$$W_{k}^{-} = \int_{q_{\min}}^{q_{\max}} \frac{4\pi e^{2}m^{*}n_{q}}{\hbar^{2}\gamma\omega} \frac{1}{k} \frac{1}{q} dq \qquad (15)$$

To find the total transition rate, the integral is carried out over all possible q, with the limits of integration set by the conservation of energy to insure the existence of a  $\theta^*$  which satisfies  $\beta = 0$  (Ziman, <sup>9</sup> Sect. 10.5).

From Eq. (14), setting  $\beta = 0$ , solving for q, and allowing cos  $\theta^*$  to range from -1 to 1, we obtain the minimum and maximum positive values of q possible

$$k\left[\left(1+\frac{\hbar\omega}{\mathcal{E}_{\underline{k}}}\right)^{1/2}-1\right] < q < k\left[\left(1+\frac{\hbar\omega}{\mathcal{E}_{\underline{k}}}\right)^{1/2}+1\right]$$
(16)

Integrating Eq. (15) over these limits we obtain

$$W_{\underline{k}}^{-} = \frac{4\pi e^{2} m^{*} n_{q}}{\hbar^{2} \gamma \omega} \quad \frac{1}{k} \ln \left\{ \frac{\left(1 + \frac{\hbar \omega}{\mathcal{E}_{\underline{k}}}\right)^{1/2} + 1}{\left(1 + \frac{\hbar \omega}{\mathcal{E}_{\underline{k}}}\right)^{1/2} - 1} \right\} \quad \left( \begin{array}{c} \text{Phonon} \\ \text{Annihilation} \end{array} \right)$$
(17)

For transitions between electronic states  $|\underline{k}\rangle$  and  $|\underline{k'}\rangle$  with the creation of one phonon of wavevector  $\underline{q}$ , Fig. 1b shows the angular relationships of interest. For this case

$$\beta = \frac{\chi}{4m^*} q^2 - \frac{\chi}{2m^*} kq \cos \theta^* + \frac{\omega}{2}$$
(18)

$$W_{k}^{+} = \int_{q_{\min}}^{q_{\max}} \frac{4\pi e^{2}m^{*}(n_{q}+1)}{\pi^{2}\gamma\omega} \frac{1}{k} \frac{1}{q} dq \qquad (19)$$

The limits of integration are somewhat different:

$$k\left[1 - \left(1 - \frac{\hbar\omega}{\mathcal{E}_{k}}\right)^{1/2}\right] < q < k\left[1 + \left(1 - \frac{\hbar\omega}{\mathcal{E}_{k}}\right)^{1/2}\right]$$
(20)

leading to a total scattering rate

$$W_{\underline{k}}^{\dagger} = \frac{4\pi e^{2} m^{*} (n_{\underline{q}} + 1)}{\underline{\Lambda}^{2} \gamma \omega} \quad \frac{1}{k} \ln \left\{ \frac{1 + \left(1 - \frac{\hbar \omega}{\underline{\mathcal{E}}_{\underline{k}}}\right)^{1/2}}{1 - \left(1 - \frac{\hbar \omega}{\underline{\mathcal{E}}_{\underline{k}}}\right)^{1/2}} \right\} \quad \left( \begin{array}{c} \text{Phonon} \\ \text{Creation} \end{array} \right) \quad . \tag{21}$$

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Figure 2 shows a plot of  $W_{k}^{-}$  and  $W_{k}^{+}$  computed for CsI and KCl, using values  $\epsilon, \epsilon_{\infty}$  and  $\omega_{r}$  published by Bak.<sup>12</sup> The wavelength of the longitudinal waves,  $\lambda$ , is obtained from the reststrahl frequency,  $\omega_{r}$ , by use of Eq. (7).

The logarithmic terms in Eqs. (17) and (21) are practically identical to each other for a given  $\mathcal{E}$ , with increasing magnitude from  $\mathcal{E} = .25$  eV to  $\mathcal{E} = 6$  eV by approximately a factor of 2.

The mean-free path between collisions

$$\langle \lambda \rangle = \frac{(2\mathcal{E}/m^*)^{1/2}}{W_{\underline{k}} + W_{\underline{k}}^{\dagger}}$$
(22)

has been plotted in Fig. 3 as a function of electron energy for several alkali halides.

One characteristic of the results for  $\langle \lambda \rangle$  which becomes apparent at the lower electron energies, is that the mean-free path is comparable to the lattice constant. The effect is most severe for low atomic number materials such as NaF and LiF. The applicability of the theory under discussion, based on a macroscopic polarization field and on plane wave electron states, seems quite questionable under such circumstances. The results presented in this paper should therefore be interpreted with caution at the lower energy end.

The angular distribution of the scattering can be obtained readily from the integrands of Eqs. (15) and (19). For the case of phonon annihilation,

$$\frac{4\pi e^2 m^* n_q}{\hbar^2 \gamma \omega} \frac{1}{k} \frac{1}{q} dq$$
(23)

is the rate of scattering into a ring of area  $2\pi {\rm k'}^2 \sin\theta \, {\rm d}\theta$ , with the relationships

$$q^{2} = k^{2} + k'^{2} - 2kk' \cos \theta$$

$$qdq = kk' \sin \theta \ d\theta \ .$$
(24)

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Substituting Eq. (24) into (23) shows that the probability of scattering into a ring between  $\theta$  and  $\theta + d\theta$  is proportional to

$$\frac{k' \sin \theta \, d\theta}{k^2 + k'^2 - 2kk' \cos \theta} \tag{25}$$

where

$$k'^2 = k^2 \pm \frac{2m^*\omega}{\hbar} \tag{26}$$

The plus sign in Eq. (26) corresponds to the case of phonon annihilation, the minus sign to phonon creation. A graph of the function corresponding to expressions (25) and (26), normalized to unit area, as shown in Fig. 4a for CsI. Figure 4b shows a similar calculation for LiF. Arrows indicate the angles  $\overline{\theta}$  at which the probability of an electron being scattered to  $\theta < \overline{\theta}$  is 0.5. Although it is clear that the scattering is predominantly forward, there is significant wide angle scattering which, coupled with multiple scattering in thick films, renders the assumption of only forward scattering (Khokley and van Vliet<sup>6, 7</sup>) inappropriate for this study. In particular such an assumption would offer no explanation for the quantum yields above 0.5 observed in photoemission experiments with alkali halides.<sup>13</sup>

## IV. MONTE CARLO SOLUTION

A Boltzmann transport equation based on the scattering characteristic described above has been developed, but is not susceptible of solution either analytically or by numerical integration. The problem is ideally suited to solution by a Monte Carlo method of direct simulation, which consists in computing the path of a particle from its generation with a particular initial position, direction, and energy until its "death" by absorption or escape to a different

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medium. Given a mean-free time between collisions t, the probability that a particle be scattered during any interval of time  $\Delta t$  of its life is approximately  $\Delta t/t$ , for  $\Delta t \ll t$ .

For an electron which at some time has an energy  $\mathcal{E}$ , Eqs. (17) and (21) determine the mean-free times  $t^-(\mathcal{E})$  and  $t^+(\mathcal{E})$ , between collisions. Choosing an interval  $\Delta t \ll t^-$  or  $t^+$ , the probability that the electron suffers a collision in that interval of time is  $(\Delta t/t^-) + (\Delta t/t^+)$ . Let  $\xi$ 's be numbers from a set of uniformly distributed random numbers between 0 and 1. For every interval of time  $\Delta t$  of the life of the electron, we draw one random number. If  $0 \leq \xi < \Delta t/t^-$ , the electron suffers a collision with the annihilation of one phonon. If  $\Delta t/t^- \leq \xi < (\Delta t/t^-) + (\Delta t/t^+)$ , the electron suffers a collision with phonon creation. If  $(\Delta t/t^-) + (\Delta t/t^+) \leq \xi < 1$ , there is no collision and the electron follows with the same energy and direction for a time  $\Delta t$ .

Whenever there is a collision, the electron is assumed to emerge instantaneously with a new energy  $\boldsymbol{\mathcal{E}} \pm \delta$ , depending on the type of collision. The change in  $\theta$  with respect to the old direction is computed by properly weighting random numbers so that their distribution becomes the one given by Eqs. (25) and (26). This is done by inversion of the distribution.<sup>14</sup> Let  $\theta'$  be the random angle with distribution given by Eq. (25), while  $\boldsymbol{\xi}$  is uniformly distributed between 0 and 1. After obtaining a random number  $\boldsymbol{\xi}$ , we require

$$\frac{\int_{0}^{\theta'} \frac{\varepsilon^{1/2} \sin \theta \, d\theta}{\varepsilon + \varepsilon^{1} - 2(\varepsilon \varepsilon^{1})^{1/2} \cos \theta}}{\int_{0}^{\pi} \frac{\varepsilon^{1/2} \sin \theta \, d\theta}{\varepsilon + \varepsilon^{1} - 2(\varepsilon \varepsilon^{1})^{1/2} \cos \theta}} = \xi$$
(27)

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$$\xi \log \frac{\boldsymbol{\mathcal{E}} + \boldsymbol{\mathcal{E}}' + 2(\boldsymbol{\mathcal{E}}\boldsymbol{\mathcal{E}}')^{1/2}}{\boldsymbol{\mathcal{E}} + \boldsymbol{\mathcal{E}}' - 2(\boldsymbol{\mathcal{E}}\boldsymbol{\mathcal{E}}')^{1/2}} = \log \frac{\boldsymbol{\mathcal{E}} + \boldsymbol{\mathcal{E}}' - 2(\boldsymbol{\mathcal{E}}\boldsymbol{\mathcal{E}}')^{1/2} \cos \theta'}{\boldsymbol{\mathcal{E}} + \boldsymbol{\mathcal{E}}' - 2(\boldsymbol{\mathcal{E}}\boldsymbol{\mathcal{E}}')^{1/2}}$$
(28)

Solving for  $\cos \theta'$ , we obtain

$$\cos \theta' = \frac{\boldsymbol{\mathcal{E}} + \boldsymbol{\mathcal{E}}}{2(\boldsymbol{\mathcal{E}}\boldsymbol{\mathcal{E}}')^{1/2}} (1 - B^{\boldsymbol{\mathcal{E}}}) + B^{\boldsymbol{\mathcal{E}}}$$
(29)

where

$$B = \frac{\mathcal{E} + \mathcal{E}' + 2(\mathcal{E}\mathcal{E}')^{1/2}}{\mathcal{E} + \mathcal{E}' - 2(\mathcal{E}\mathcal{E}')^{1/2}} \quad . \tag{30}$$

The computations for  $\cos \theta$ ' are carried out in double precision on the IBM 360/75 computer; otherwise the short computer "word" results in high scatter-ing angles never being reached.

The change in  $\phi$  with respect to the old direction is computed by sampling a distribution function which is uniform between 0 and  $2\pi$ .

A laboratory set of coordinates is defined with the z direction perpendicular to the crystal exit surface, and an appropriate coordinate transformation is used at each collision point to keep track of the z coordinate and momentum  $p_z$  of the particle.

In order to determine the number of Monte Carlo trajectories required to establish the result with a desired certainty, the following method described by Cashwell and Everett<sup>17</sup> has been used. Let "p" be the <u>true</u> probability that electrons generated with certain characteristics will escape from a crystal. After carrying out N trials, it is found that M electrons escaped. Then, the ratio of the number of sequences of N trials resulting in a ratio M/N satisfying

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or

the inequality

$$\left|\frac{M}{N} - p\right| < \epsilon \tag{31}$$

to the totality of all possible sequences of N trials is, approximately,

$$f(t) = \operatorname{erf} \left( t / \sqrt{2} \right) \tag{32}$$

where

$$\mathbf{t} = \epsilon \left( N/p \left( 1 - p \right) \right)^{1/2} \tag{33}$$

and

erf (x) = 
$$\frac{2}{\sqrt{\pi}} \int_{0}^{x} e^{-x^{2}} dx$$
 (34)

Enough electron trajectories have been computed so that escape probabilities could be determined with a value of  $\epsilon$  in the inequality (31) of .03, with 95% certainty. Depending on material and initial characteristics of the electrons, this varied from 200 to 800 trajectories.

The next question to be considered is the behavior of an electron reaching the surface of the crystal. The customary approach is that of assuming a potential barrier at the surface which acts on the normal component of velocity. This is considerably more reasonable for the treatment of electron emission from single crystals than for the case of evaporated films consisting of many small randomly oriented crystals, for which a simpler form of barrier seems justifiable. From UV absorption, photoemission and/or photoconduction in alkali halide films, one can obtain reasonably good information about the location of the bottom of the conduction band for a number of materials. From photoemission data, one can obtain the approximate location of the vacuum level, although the disturbances associated with excitons make accurate determinations difficult.

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A survey of the relevant literature on the subject  $^{13, 15, 16}$  indicates that the electron affinity of alkali halides is quite small. For those materials which have been better studied (KF, NaCl, KCl, CsCl, CsI) values of electron affinity given are between -.1 and +.1 eV.

For the purposes of these calculations, a value for the surface barrier  $\epsilon_{\min} = 0.1 \text{ eV}$  will be assumed for all four selected materials. If the energy of any electron during its trajectory falls below  $\epsilon_{\min}$ , it will be considered absorbed, and will not contribute to secondary emission. It will become apparent that the results do not strongly depend on  $\epsilon_{\min}$ , for any reasonable choice thereof.

#### IV. RESULTS OF COMPUTATIONS

Computations for escape probabilities and energy losses have been carried out for electrons moving in films of thickness equal to 250 Å. As shown in Fig.5, a metallic substrate is assumed to exist at x = 0 acting as a sink for electrons, and the exit surface is located at x = 250 Å. Electrons are assumed generated with initial angle  $\theta$  with respect to the forward direction.

For these computations, the film is divided into a 3-dimensional mesh with 5 initial locations of the generated electrons: x = 25, 75, 125, 175, and 225 Å; 8 initial energies between  $\mathcal{E}_0 = .25$  and  $\mathcal{E}_0 = 7.5 \text{ eV}$ , and 7 initial angles:  $\theta = 0$ , 30, 60, 90, 120, 150, and 180°. This results in 280 calculations, each with several hundred trajectories. With the IBM 360/75 computer, the amount of computer time required is approximately 1 hour per material investigated, using a Fortran H code, Optimization 2. The choice of 250 Å for film thickness was dictated as a necessary compromise between computation time and accuracy of results, as discussed in Sect. IV a., below.

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## a. Results for Cesium Iodide, $m^*/m = 1$ , $T = 300^{\circ}K$

Figure 6, a through g, shows the probabilities of escape  $P(\mathcal{E}_0, x, \theta)$  through the forward exit surface of electrons generated with an energy  $\mathcal{E}_0$ , at a position x, with a direction  $\theta$  with respect to the forward direction. The range of errors shown is for 95% certainty in each computation, as discussed above. The effect of scattering other than forward is very marked, particularly at the lower energies where the probability of escape for electrons generated at  $\theta > 90^\circ$  is very substantial.

When the electrons are generated isotropically, the escape probability averaged over all angles can be obtained from

1

$$P(\mathcal{E}_0, x) = \frac{1}{2} \int_0^{\pi} P(\mathcal{E}_0, x, \theta) \sin \theta \, d\theta$$
(35)

Having divided  $\theta$  into six sections of 30<sup>°</sup> each, the above integral can be evaluated approximately by a summation. The results are shown in Fig. 7; the estimated statistical errors are approximately  $\pm .035$ .

The escape probability for .25 eV electrons has an exponential character. When plotted versus x on a semilogarithmic plot, the result is a straight line corresponding to a characteristic exponential escape length  $L_s \simeq 62$  Å, except for small x (near the substrate), where the escape probability is smaller than that given by the exponential. This reflects the fact that the substrate constitutes a sink for electrons arriving at x = 0 with negative components of velocity. If there were more alkali halide material for x < 0, such electrons would have a chance of being scattered into the forward direction and of contributing to secondary emission. For electrons of energy 0.5 eV and higher, the escape probabilities are best fitted by straight lines in the linear plot of Fig. 7, which result is attributed again to the presence of the sink for electrons

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at x = 0. The effect becomes important when the thickness of the film is comparable to the exponential length characteristic of a semi-infinite medium. For example, for  $\mathcal{E}_0 = .5 \text{ eV}$ , the exponential length,  $L_s$ , obtained from the results of the calculation for a 250 Å film by fitting to the two points of largest x is  $L_s \approx 220$  Å. This value of characteristic escape length  $L_s$  coincides quite well with the results of computations carried out for 500 Å films. Equally good agreements are obtained at higher energies.

Neglecting the effects of the sink for electrons at the substrate, i.e. for film thickness considerably more than 250 Å, one can define escape probabilities of the form

$$P(\mathcal{E}_0, x) = P_0(\mathcal{E}_0) \exp\left[-(\tau - x)/L_s(\mathcal{E}_0)\right]$$
(36)

where  $\tau$  is the thickness of the film. Table 1 gives values of  $P_0(\mathcal{E}_0)$  and  $L_s$  so computed for CsI and for the three other materials selected.

The energy distribution of emitted electrons has a very characteristic shape. Figure 8 shows  $P(\mathcal{E}_i; \mathcal{E} = 1 \text{ eV}, \theta = 0, x)$ , the probability that one electron with initial energy of 1 eV, generated in the forward direction from a source at x will emerge with energy  $\mathcal{E}_i$ . The analysis of energies has been carried out in channels with a width of .05 eV. The approximate error in each channel is  $\pm$ .03 to .05 for 95% certainty. Normalization of Fig. 8 is to the actual probability of escape. In general,  $P(\mathcal{E}_i)$  becomes less peaked when the initial angle  $\theta$  departs from zero and when the energy is made lower because of an increased number of collisions.

A quantity of interest in studies of electron emission is the mean energy loss of those electrons which do escape the film. Figure 9a shows the mean energy loss in CsI for electrons of initial energy  $\mathcal{E}_0$  generated isotropically at a position x within the film. Two details must be pointed out regarding the

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results: (1) The channel width for the analysis of energy is .05 eV. Therefore, if most of the electrons fall in the channel adjacent to the one corresponding to the initial energy (e.g., for  $\mathcal{E}_0 = 4.5 \text{ eV}$ ), the mean energy loss will be 1/2channel by design of the computer program. Thus, when the losses are low and the energy distribution becomes narrow, the mean energy loss converges to .025 eV instead of going towards zero. (2) When the initial energy  $\mathcal{E}_0$  is low, the electrons which are able to escape from the film can only have lost a small amount of energy, because of the proximity between  $\mathcal{E}_0$  and  $\mathcal{E}_{\min}$ , the threshold energy for absorption. Thus the curve of energy loss for  $\mathcal{E}_0 = .25 \text{ eV}$ appears below the one for  $\mathcal{E}_0 = .5 \text{ eV}$  in Fig. 9a. In the case of CsI, the choice of  $\mathcal{E}_{\min}$  affects only the results for  $\mathcal{E}_0 = .25$  in any significant way. The standard deviation of the energy spectrum, giving a measure of the spread of energies is shown in Fig. 9b.

The correlation between the energy and angle for electrons escaping from the film can be studied approximately by defining a correlation coefficient  $\chi$ as

$$X = \frac{\sum_{i} \left( \mathcal{E}_{i} - \overline{\mathcal{E}} \right) \left( \theta_{i} - \overline{\theta} \right) P\left( \mathcal{E}_{i}, \theta_{i} \right)}{\sigma_{\mathcal{E}} \sigma_{\theta}}$$
(37)

where the summation is over all outgoing electrons;  $P(\mathcal{E}_i, \theta_i)$  is a normalized probability that electrons which started isotropically from a given "x" and energy will reach the surface in a channel corresponding to  $(\mathcal{E}_i, \theta_i)$ . The means  $\overline{\mathcal{E}}$  and  $\overline{\theta}$ , and the standard deviations  $\sigma_{\mathcal{E}}$  and  $\sigma_{\theta}$  have the customary definitions. When calculated in this way, X only has a definite physical meaning when the distributions are Gaussian. This is not the case here, but  $P(\mathcal{E}_i)$  and  $P(\theta_i)$  are well behaved and roughly symmetrical. Therefore Xshould be a useful measure of correlation.

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For 250 Å films of CsI and NaF, electron generation at a few selected initial energies and positions has been analyzed. The largest correlation  $(X\sim0.1)$  occurs for low energy electrons generated far from the exit surface. The effect of scattering to directions other than purely forward has the effect of randomizing the electron distribution, destroying the definite energy-angular relationship obtained by Khokley and van Vliet.<sup>6</sup>

## b. Results for KCl, NaF, and LiF, $m^*/m = 1$ , $T = 300^{\circ}K$

Table 1 gives the values of  $P_0(\mathcal{E}_0)$  and  $L_s$  for the escape of electrons generated isotropically in KCl, NaF, LiF, and CsI.

Progressing from alkali halides with high Z towards those with low Z, the phonon energy increases and  $n_q$  decreases. Since the rate of collisions with electron energy gain is proportional to  $n_q$  and the rate with energy loss is proportional to  $n_q + 1$ , collisions with energy loss are most predominant for the lighter ions. Also, the energy loss per collision increases for the lighter ions. These qualitative considerations predict a decreasing value of  $L_s$ , for a given initial energy, in going from CsI to LiF, as is reflected in the results of the table. The randomizing effect due to non-forward collisions becomes very strong for the lighter ions, particularly at low  $\mathcal{E}_0$ , as is seen by comparing  $P_0$  ( $\mathcal{E}_0$ ) for a given initial energy, for the different materials.

Figures 10, 11, and 12 show mean energy loss and standard deviation for electrons generated isotropically at position x, with energy  $\mathcal{E}_0$  in KCl, NaF, and LiF films, respectively. Although the mean energy losses were of the order of 0.1 eV in a 250 Å film of CsI, they become of the order of 1 eV for NaF, and even larger for LiF. The distribution of energies broadens as the losses increase.

## V. DEPENDENCE ON EFFECTIVE MASS AND TEMPERATURE

Equations (15) and (19) indicate that, for a given energy  $\mathcal{E} = \pi^2 k^2 / 2m^*$ , the scattering rate is proportional to  $(m^*)^{1/2}$ . The velocity is proportional to  $(m^*)^{-1/2}$ , so it follows that the mean-free path is proportional to  $(m^*)^{-1}$ . For a film with thickness large compared to the characteristic escape length of the electrons under study, the effect on the escape probabilities and energy losses can easily be seen. Consider the following Monte Carlo experiment: Take one electron generated in some particular direction at a depth "d" from the exit surface. Take a sequence of random numbers prescribing a trajectory for the electron ending with its escape into the vacuum, for  $m^* = m$ . Next consider the same sequence of random numbers for the same initial conditions but with  $m^*/m = \alpha_m$ . As the experiment progresses, the length of each straight section in the trajectory will be the original length divided by  $\alpha_{\rm m}$ . At the end of the sequence the electron will have travelled  $1/\alpha_{\rm m}$  of its way to the exit surface, or  $d/\alpha_m$  towards the vacuum. It follows that its probability of escape and exit energy would be the same as if the electron had  $m^* = m$  but had been generated at a depth  $\alpha_m d$ .

The mean-free path is proportional to  $1/(2n_q + 1)$ , and the temperature dependence enters through  $n_q$ , as given in Eq. (2). Analogously to the m\* case above, this leads to a length-modifying factor:

$$\alpha_{\tau} = \left(2n_{q}(T) + 1\right) / \left(2n_{q}(300^{\circ}K) + 1\right)$$
 (38)

In general, the dependence of the escape probability on  $\alpha$  is given by Eq. (36) with a modified escape length,  $L_s/\alpha$ 

$$P(\boldsymbol{\mathcal{E}}_{0}, \mathbf{x}) = P_{0}(\boldsymbol{\mathcal{E}}_{0}) \exp\left(-(\boldsymbol{\tau}-\mathbf{x}) \alpha/L_{s}(\boldsymbol{\mathcal{E}}_{0})\right)$$
(39)

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The results of the Monte Carlo calculations presented above give an accurate account of the electron transport phenomenon due to the electron-phonon interaction, as computed from perturbation theory. Qualitatively, the results seem quite plausible. The companion paper provides a quantitative experimental verification by the study of transmission secondary emission from thin films of alkali halides.

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TABLE 1

$T = 300^{\circ} K, m^*/m = 1$							
CsI, $\hbar\omega_{long.} = .0105 \text{ eV}$ , $n_q = 1.987$ NaF, $\hbar\omega_{long.} = .0513 \text{ eV}$ , $n_q = .159$							
KCl, $\hbar \omega_{\text{long.}} =$	.026 eV, n <sub>q</sub>	=.557	LiF, $\hbar\omega_{\text{long.}} = .0822 \text{ eV}, n_{q} = .0435$				
CsI			<u>KCl</u>				
$\mathcal{E}_0^{(eV)}$	$P_0(\mathcal{E}_0)$	L <sub>S</sub> (Å)	$\mathcal{E}_0^{(eV)}$	$P_0(\mathcal{E}_0)$	L <sub>s</sub> (Å)		
.25	. 9	62	.25	≈1.0	<10Å		
.5	.83	220	. 5	. 9	29		
1.0	.81	260	1.0	.8	121		
1.75	. 76	295	1.75	.8	240		
2.5	. 71	375	2.5	. 76	280		
3.5	. 68	395	3.5	.71	330		
4.5	. 63	540	4.5	.69	360		
5.5	. 62	650	5.5	. 68	370		
NaF		_	LiF		2		
$\mathcal{E}_0^{(eV)}$	$P_0(\mathcal{E}_0)$	L <sub>S</sub> (Å)	$\mathcal{E}_0^{(eV)}$	$P_0(\mathcal{E}_0)$	L <sub>S</sub> (Å)		
.5	≃1	<12Å					
1.0	. 98	22	1	≈1	< 12Å		
1.75	.8	77	1.75	. 9	29		
2.5	. 78	130	2.5	.86	57		
3.5	. 77	240	3.5	. 75	128		
4.5	. 76	265	4.5	.75	185		
5.5	. 77	290	5.5	.76	240		
6.5	. 77	330	6.5	. 75	270		
7.5	. 7	380	7.5	.76	285		

Values of  $P_0(\mathcal{E}_0)$  and  $L_s$  for CsI, KCl, NaF and LiF as a function of initial energy  $\mathcal{E}_0$  for electrons generated isotropically.

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Fig. 1

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Fig. 4a



Fig. 4b



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Fig. 5



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Fig. 7



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Fig. 9









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Fig. 11



Fig. 12