

calculation of Friedmann and Kimel⁹ was able to yield the same results as the detailed calculation of Ref. 3 to such a good degree of accuracy. We shall give a more complete discussion of the successes of the model of Ref. 9 elsewhere.¹⁰

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COMMENTS AND ADDENDA

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Thermally Stimulated Exoelectron Emission

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The recently described phenomenological theories of thermally stimulated luminescence and conductivity are extended to thermally stimulated exoelectron emission. This latter process can have a marked effect on the magnitude of the former processes when one considers thin films or specimens with a high surface-to-volume ratio.

The mechanism of exoelectron emission, known also as the Kramer effect, is presently not clearly understood. In dielectric materials and oxide layers on metal surfaces, exoelectron emission appears to be closely related to the presence of electron traps in a thin surface layer. Comprehensive reviews of the present experimental facts and theories about exoelectron emission have been given recently by Bohun¹ and Scharmann and co-workers.²

It is obvious, from these sources, that exoelectron emission has been correlated with certain other thermally and optically stimulated phenomena. In

some of the alkali halides,¹ for example, thermally stimulated exoelectron emission (TSEE) exhibits a temperature dependence closely related to that of thermally stimulated luminescence (TSL) and conductivity (TSC). In some specimens,¹ there is a further correlation of these effects with optically stimulated exoelectron emission and thermally bleached optical absorption. All these effects should be studied in the same material to gain insight into the complex mechanism of trapping phenomena.

Recently, the exact solutions of the kinetic equa-

tions governing TSC and TSL have been published.³ (Reference 3 is hereafter referred to as KLB.) The purpose of the present paper is to show that exact solutions can also be obtained for TSEE. Further, by including a surface-vacuum interface in the model of KLB, we obtain the correlated solutions of TSC, TSL, and TSEE, and show that under certain conditions the shapes of TSC and TSL glow curves are highly dependent on the magnitude of the TSEE process.

The energy-level scheme in Fig. 1 constitutes the model for our discussion. As shown, the thin surface layer emitting electrons is taken to have bulk properties. In Fig. 1, J_i and J_0 denote the current densities into and out of the surface, respectively. Simply stated, the present problem is to describe the net current density $J_x \equiv J_0 - J_i$ as a function of temperature for all physically realistic combinations of the trapping parameters characterizing the solid. In the notation of KLB and with a heating rate of unity, the kinetic equations for this model are given by

$$\dot{n} + \dot{n}_c = -\gamma n_c(n + n_c + M + N_x) - \dot{N}_x, \quad (1)$$

$$\dot{n} = \beta n_c(N - n) - \beta N_c n e^{-E/kT}, \quad (2)$$

$$\dot{N}_x = J_x/\delta, \quad (3)$$

where δ is the surface layer thickness and is of the same order of magnitude as the mean free path of a conduction electron, and

$$N_x \equiv \int_{T_0}^T \dot{N}_x dT$$

is the number of electrons/cm³ that have been emitted from the surface at a temperature T . In order to solve Eqs. (1)–(3), it is necessary to have J_x as a function of temperature and carrier concentration. This one can obtain as follows.

Consider the electrons to be in a box with the

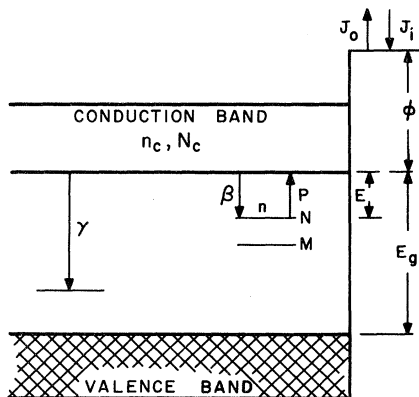


FIG. 1. Energy-level diagram forming the model analyzed in this paper.

solid-vacuum interface as one wall. When the velocity distribution is Maxwellian, one readily obtains the following expression⁴ for the emitted current density:

$$J_0 = n_c \left(\frac{kT}{2\pi m} \right)^{1/2} e^{-\phi/kT}, \quad (4)$$

where m is the effective mass of a conduction electron and ϕ the effective work function or electron affinity. Generally, however, the mechanism of electron return is unknown in such detail. Consequently, we assume that $J_i = fJ_0$, where $0 \leq f \leq 1$, so that the net current density is given by

$$J_x = (1 - f) J_0. \quad (5)$$

Only the idealized cases $f = 1$ and $f = 0$ are considered here. In the former case, the model represents an electrically neutral thin surface. Ignoring electrode effects, there is no TSEE in this case since each emitted electron is immediately replaced by an electron from the surrounding vacuum during the emission process. In the latter case, however, the sample charges up during the emission process. Ignoring the effect of charge buildup on the emission process yields $TSEE \propto J_x = J_0$. One would expect that TSEE experiments on thin films yield results somewhere between these two extremes.

The set of Eqs. (1)–(5) are readily solved by standard numerical techniques³; however, they also reduce to the set considered by KLB whenever $n + n_c + M \gg N_x + \dot{N}_x/\gamma n_c$. Consequently, whenever this inequality is satisfied, one can obtain the solution for TSEE ($\propto J_x$) from the solutions of n_c given by KLB, multiplied by the appropriate factor in Eq. (4). For any such case, the shape of TSL [$\propto n_c(n + n_c + M + N_x)$] or the shape of TSC ($\propto n_c$) is not affected by the TSEE process. When the inequality is not satisfied, it is necessary to solve the set (1)–(5). Figure 2 illustrates numerical solutions of Eqs. (1)–(5) for a given set of trapping parameters, for the two cases $f = 0$ and $f = 1$. Of immediate consequence is the marked effect on the shapes of TSC and TSL due to a TSEE process. The rapid falloff after the maximum of both TSC and TSL is predicted by the work of KLB in view of the fact that the term $(N_x + \dot{N}_x/\gamma n_c)$ is equivalent to considering M (in the work of KLB) as an increasing monotonic function of temperature. In KLB, all large M cases show the marked falloff.

In general, TSL (and TSC) will consist of a surface contribution TSL_s and a volume contribution TSL_v . The measured $TSL = \sum TSL_s + \sum TSL_v$, with the sums over all surface and volume elements. Strictly speaking, then, the marked effect of the TSEE process will only be seen in films of thickness $\approx \delta$ or in solids where the volume contribution to TSL (and TSC) is negligible. And, of course, if TSL and TSC are basically volume effects, one

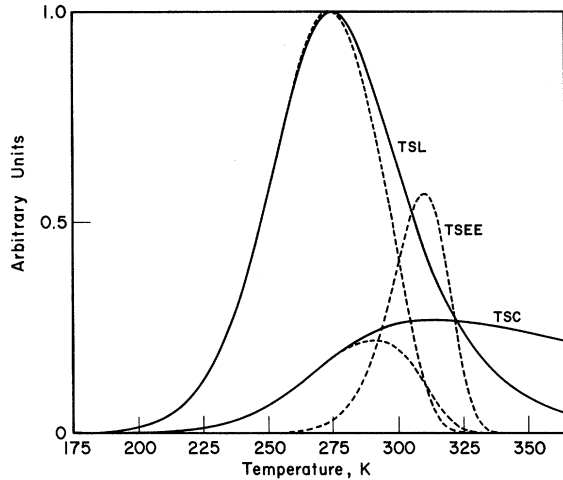


FIG. 2. TSL, TSC, and TSEE solutions of the kinetic equations (1)–(5) with $f=1$ (solid lines) and $f=0$ (dashed lines), for the following set of trapping parameters: $\beta=\gamma=10^{-14}$ cm³/K; $N_c=10^{19}$ (states)/cm³; $M=0$; $N=10^{15}$ cm⁻³; $\delta=5\times 10^{-7}$ cm; $\phi=2E=8000$ K; and $m=m_0$. And initial conditions: $T_0=100$ K; $n_c(T_0)=N$.

should expect no correlations with TSEE.

Figure 2 also illustrates that under the above conditions TSC, TSL, and TSEE are correlated phenomena. Application of the "initial-rise" method⁵

to the leading edge of the TSEE curve yields the sum of the energies E and ϕ . Further, it follows quite generally from Eqs. (1)–(5) that the TSEE maximum always is preceded by the maxima of TSL and TSC, provided the electron affinity is positive. The TSC maximum will be after the TSEE maximum only if ϕ is negative.

The number of emitted electrons N_x reaches a value of $\approx 0.2\times 10^{15}$ electrons/cm³ at 360 K for the case shown in Fig. 2. In a TSEE experiment this number will be reduced by $\sim 10^6$ because of the small emitting volume. 10^8 – 10^9 electrons/cm³ is of the right order of magnitude for such experiments.⁶

Optically stimulated emission and thermally bleached optical absorption can be treated in a similar manner. Time-dependent solutions of Eqs. (1)–(5) are readily obtained given the proper form of the escape probability P (taken here as $\beta N_c \times e^{-E/kT}$). Exact solutions of a similar set already exist.^{7,8} It is expected that mixed optical and thermal processes will present no serious numerical problems, although a full analysis of the extent of possible correlations is left to the individual researcher in the field of thermally and optically stimulated processes.

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This solution of J_0 can be obtained by multiplying the full line curve of n_c (Fig. 2) by the appropriate factor in Eq. (4), which is $\sim 0.4 \times 10^6 e^{-\phi/kT}$. But, because of the almost constant concentration of n_c ($\sim 10^{12}$ cm⁻³) after the maximum is reached, one finds that J_0 is an ever increasing exponential function whose magnitude is too large to explain satisfactorily. Any simple surface-state mechanism of TSEE will certainly have to contain a proposed electron-return mechanism.

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