Electron Tunneling and Schottky Ionization from Excited F Centers in an Electric Field

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It is known that an applied electric field can ionize an excited F center. Assuming a simple Coulomb field the probability of this process is calculated for tunneling and for Schottky ionization. The results compare satisfactorily with experiment and they lead to the possibility of an evaluation of the separation between the excited state of an F center and the conduction band adjusted to the excited state.

IT has been shown experimentally by Lüty[1] that excited F centers can be ionized by applied electric fields. The strong temperature dependence of this field ionization points to the presence of a Schottky effect down to about 10 or 20°K. At lower temperatures a tunneling effect has to be assumed to interpret the experimental data. In both cases it is the electron in the $2p$ state of the F center which reaches the conduction band, thus destroying the center. These phenomena are of importance for the understanding of the formation of F centers because the first step in the capture of an electron by a vacancy occurs in the formation of the excited state of an F center.[1] Thus, strong enough electric fields due to neighboring interstitial ions, vacancies, charged dislocations, and other defects will prevent F centers from being formed.

An excited F-center electron subjected to an external electric field has three alternatives. It can return to the ground state by radiative transfer with a probability per second $1/\tau_r$, it can thermally escape to the conduction band with a probability per second $1/\tau_t$, or finally, the applied electric field may cause the electron to tunnel to the conduction band with a probability per second $1/\tau_\epsilon$. The reciprocal lifetime of the excited state is, consequently,

$$1/\tau=1/\tau_r+1/\tau_\epsilon+1/\tau_t\,, \tag{1}$$

where both τ_ϵ and τ_t depend on the applied field, but only τ_t depends on temperature. In the absence of an external field Swank and Brown[2] have experimentally determined for KCl τ_r and

$$1/\tau_t=(1/\tau_0)\exp(-E_0/kT)\,, \tag{2}$$

obtaining $\tau_r=0.6\times10^{-6}$ sec, $\tau_0=2.5\times10^{-13}$ sec, and $E_0=0.142$–0.162 eV with an average value of 0.150 eV.

This paper will discuss τ_ϵ and τ_t as a function of the applied electric field and temperature. Atomic units will be used throughout this paper except where other units are specifically given.

TUNNELING

The problem of electron tunneling from F centers is physically similar to the problem of the ionization of an atom in an external electric field, discussed among others by Landau and Lifshitz,[3] and by Bethe and Salpeter.[4] Schrödinger's equation for an electron in a Coulomb field and in an external electric field ϵ is separated in parabolic coordinates. It can be shown[4] that the probability current for the electron leaving the atom is given by the expression

$$\frac{1}{\tau_\epsilon}=\frac{\exp\left[-2\int_{\eta_0}^{\eta_f}(|\phi(\eta)|)^{1/2}d\eta\right]}{4\int_{\eta_i}^{\eta_0}(|\phi(\eta)|)^{-1/2}d\eta}\,, \tag{3}$$

$$\phi(\eta)=-\tfrac{1}{2}E+\beta_1/\eta d-[(m^2-1)/4\eta^2]+\tfrac{1}{4}\epsilon\eta\,,$$

where $\eta=r-z$ is a parabolic coordinate, d is the effective dielectric constant, and E is the (positive) magnitude of the binding energy. The quantities β_1 and m are connected with the parabolic quantum numbers, and will be taken to be $\frac{1}{2}$ and 1, respectively. The quantities η_i and η_0 delineate the classically permitted interior region for the electron, while η_f marks the beginning of the classically permitted exterior region. Thus

$$\begin{gathered}\phi(\eta)=-\tfrac{1}{2}E+(2\eta d)^{-1}+\tfrac{1}{4}\epsilon\eta\,,\\ \phi(\eta_i)=\phi(\eta_0)=\phi(\eta_f)=0\,.\end{gathered} \tag{4}$$

When the electric field strength ϵ is equal to $\epsilon_{c1}=E^2d/2$, the roots η_0 and η_f are equal. There is then no classically forbidden region and no tunneling is necessary to ionize the atom. If one defines $\kappa\equiv\eta_0/\eta_f$,

[1] F. Lüty, Z. Physik **153**, 247 (1958); *Halbleiterprobleme* (Friedrick Vieweg und Sohn, Braunschweig, 1960), Vol. VI, p. 276; and (private communication).

[2] R. K. Swank and F. C. Brown, Phys. Rev. Letters **8**, 10 (1962); Phys. Rev. **130**, 34 (1963).

[3] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics, Non-Relativistic Theory* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1958), pp. 257–258.

[4] H. Bethe and E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York, 1957), Sec. 54.

then the following relationships can be easily obtained:

$$\frac{\epsilon}{\epsilon_{c1}}=\frac{4\kappa}{(1+\kappa)^2},\quad \eta_f=\frac{2E/\epsilon}{1+\kappa},\quad\text{and}\quad \eta_0=\frac{1+\kappa}{Ed}.$$

The exponential part of Eq. (3) can be then written in the form

$$\exp\left[-\eta_f\left(\frac{2E}{1+\kappa}\right)^{1/2}\int_\kappa^1(1-x)^{1/2}\left(1-\frac{\kappa}{x}\right)^{1/2}dx\right]=10^{-F(\kappa)d^{-1}E^{-\frac{1}{2}}},\quad(5)$$

where

$$F(\kappa)=0.409\kappa^{-1}(1+\kappa)^{1/2}[(1+\kappa)\mathbf{E}(1-\kappa)-2\kappa\mathbf{K}(1-\kappa)],\quad(6)$$

with $\mathbf{E}(k^2)$ and $\mathbf{K}(k^2)$ indicating complete elliptic integrals.[5] The function $F(\kappa)$ is plotted in Fig. 1.

The denominator of Eq. (3) is an integral over the interior of the F center. A rough estimate of the denominator can be made by assuming a square well potential with a radius around 5.3 a.u., and with a depth equal to the Madelung constant divided by 5.3, or about 0.33 a.u. If the total electron energy is roughly -0.01 a.u., the kinetic energy of the electron is around 0.32 a.u. The denominator is then approximately 40.

Remembering that the atomic unit of frequency is 4.13×10^{16} per sec, the reciprocal lifetime for tunneling becomes

$$1/\tau_\epsilon=10^{15-F(\kappa)E^{-\frac{1}{2}}d^{-1}}\text{ per second.}\quad(7)$$

In this formula the energy gap E is, strictly speaking, the energy difference between the excited state of the F center with the lattice adjusted accordingly and the bottom of the conduction band with the same lattice configuration. The "thermal" value E_0 found by Swank and Brown is, on the other hand, the energy difference between the excited state of the F center with the lattice adjusted accordingly, and the conduction band with the lattice relaxed around the empty vacancy. The difference between these two values of E is hard to estimate, but one would expect the "thermal" E_0 to be lower than the "tunneling" E. Consequently, Swank and Brown's value 0.150 will be used for thermally activated processes, while $E\geqslant E_0$ will be used for tunneling phenomena.

TABLE I. Effect of parameters τ_ϵ, d, and E on ϵ.

τ (sec)	E (eV)	d	10^5 V/cm
10^{-5}	0.159	2.13	0.88
10^{-6}	0.159	2.13	0.94
10^{-7}	0.159	2.13	0.98
10^{-8}	0.159	2.13	1.05
10^{-6}	0.109	2.13	0.69
10^{-6}	0.190	2.13	1.28
10^{-6}	0.272	2.13	2.4
10^{-6}	0.544	2.13	7.7
10^{-6}	0.159	1	0.59
10^{-6}	0.159	2	0.90
10^{-6}	0.159	3	1.1

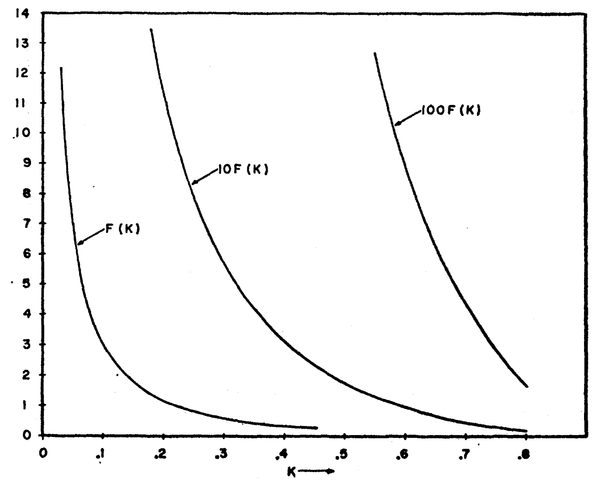

FIG. 1. Plot of function $F(\kappa)$, where κ is the ratio of the interior classical turning piont η_0 to the exterior turning point η_f.

In order for tunneling to have an observable effect, ϵ must be sufficiently large so that τ_ϵ is smaller than τ_r and τ_t. The former, as pointed out above, is around 10^{-6} sec, the latter can be made arbitrarily long by lowering temperature. Figure 2 shows the necessary connection between the field ϵ and the energy E to give τ_ϵ equal to 10^{-5} and 10^{-9} sec. Table I shows the dependence of ϵ upon τ_ϵ, d, and E for KCl. The nonvarying parameters in each case are the best guesses for KCl. Typical values of η_0 and η_f are around 100 and 500 a.u. Table II gives the dependence of τ_ϵ upon ϵ for KCl. These results are in good agreement with Lüty's experimental data in which a field of the order of 10^5 V cm^{-1}

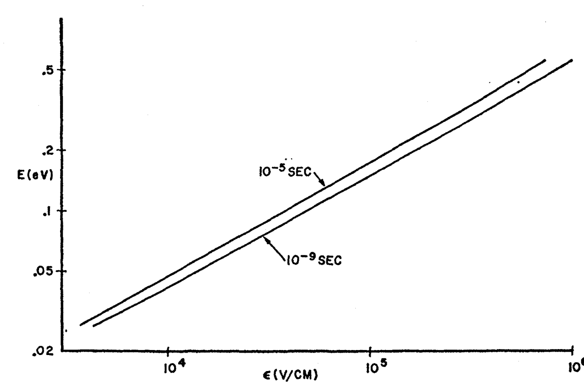

FIG. 2. Electric field ϵ (in V/cm) that is necessary to ionize an electron with a binding energy $-E$ (in eV) with τ_ϵ equal to 10^{-5} and 10^{-9} sec. The dielectric constant d is taken to be 2.13.

[5] We follow the notation of E. Jahnke and F. Emde, *Tables of Functions* (Dover Publications, Inc., New York, 1945).

TABLE II. The relationship between τ_ϵ and ϵ for KCl with the assumptions $d=2.13$, and $E=0.159$ eV.

10^6 V/cm	τ_ϵ (sec)
0.6	1.3×10^5
0.7	2.2
0.8	4.5×10^{-4}
0.9	4.3×10^{-6}
1.0	1.0×10^{-7}
1.1	2.4×10^{-9}
1.2	8.1×10^{-11}
1.3	8.4×10^{-12}
1.4	1.2×10^{-12}

produced considerable reduction of the previously excited F centers. A quantitative comparison of the dependence of τ_ϵ on ϵ with experiment requires a knowledge of the excitation probability of an F center by the incident F light.

Formula (7) and Fig. 2 show the rapid dependence of the tunneling probability on the only approximately known energy E. Actually, a careful measurement of the absolute rate of tunneling and of its dependence on the field would permit accurate determination of E, and a comparison with the "thermal" value E_0 would indicate the role of lattice relaxation on the relevant energy level.

SCHOTTKY IONIZATION

The applied field ϵ lowers the original barrier over which the electron has to be thermally excited in order to reach the conduction band. The corresponding lifetime is given by

$$1/\tau_t=(1/\tau_0)\exp(-\Delta E/kT), \tag{8}$$

where $\Delta E=E_0-E_m$ and $E_m^2=2\epsilon d^{-1}$. It is clear that at low enough temperatures and sufficiently high fields this effect will be suppressed and temperature-independent tunneling will take over. It is interesting to calculate at what temperature this crossover of the two phenomena will take place. Using the results of the previous section and Eq. (8), one obtains for $\epsilon=10^6$ V/cm and $E_0=0.150$ eV the temperatures 24, 30, and 45°K for $E=0.170$, 0.160, and 0.150 eV, respectively. If the lower limit 0.142 eV of the observed values of E_0 is assumed, then the same procedure gives 18, 23, and 30°K for the three values of E. These temperatures are only slightly higher than those reported by Lüty. It follows that the lower value for E_0 and $E>E_0$ improves the agreement with experiment. This gives another possibility of evaluating this quantity and comparing it with E_0.

It should be pointed out that the calculations here described were based on an ideal crystal with no charged defects. Actually, as shown by Redfield,[6] most nonmetals are pervaded by high fields, 10^4 V/cm being a typical average. It is thus clear that external fields lower than this value will have little effect on existing F centers. This is in accord with Lüty's experiments. Furthermore, the temperature at which tunneling gives way to Schottky ionization will be also affected by these internal fields. The main effect will be to spread this transition over a considerable range of temperatures below and above the value of an ideal crystal.

Another consequence of the existence of internal fields is the conclusion that F centers produced by irradiation at, say, 4°K may begin to bleach under F light in the range of temperatures calculated above. The observed temperature would permit these fields to be evaluated as a function of lattice perfection. It will be essential to separate this effect from the recombination of vacancies and interstitials which seems to occur in the same range of temperatures.

[6] D. Redfield, Phys. Rev. **130**, 914 (1963).