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A Theory on Cathode Luminescence

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A tentative explanation is given of experiments concerning the dependence of the brightness of a luminescent material on the voltage of electron bombardment. A model is assumed in which surface effects prevail over luminescence in using radiation energy. The possibility of a quantitative theoretical treatment is largely due to symmetry properties in the diffusion of scattered electrons in a solid body.

1. INTRODUCTION

T. B. BROWN[1] performed accurate measurements of the amount of light emitted by a luminescent material known as "artificial willemite" (Zn_2SiO_4+about $\frac{1}{2}$ percent MnO_2 activator) when bombarded by cathode rays of 200 to 1300 volts.[2] Measurements were made varying both voltage and current density. Luminescent energy was emitted within a band at about 5500A. The important feature of the experimental result is expressed by the formula:

$$W=5.10^{-6}V^2+0.17. \qquad (1)$$

W is the luminescent energy per impinging electron measured in electron volts, V is the voltage of the impinging electrons. This formula is valid for small currents and represents a very good approximation of the experimental results between 200 and 800 volts; above 800 volts W becomes slightly larger than indicated in (1). We shall call *efficiency* the fraction of the electronic energy converted into light, that is W/V. The efficiency is small: at 200 volts its value is 0.002; that is, one obtains an average of 2/10 of a light quantum per electron. If the slight correction arising from the term 0.17 is neglected, *the efficiency increases proportionally with the energy.* The term 0.17 will be neglected in the general lines of the explanation; its meaning will appear only in the final discussion. It is very striking to find a steady variation of efficiency following a simple formula, since the phenomenon itself is quite complex and since the elementary processes involving slow electrons are not known to follow any simple quantitative law.

Further information may be obtained from experimental results quoted by N. Riehl.[3] This information concerns production of luminescence by α-particles in ZnS+activator Cu which takes place with very high efficiency (order of magnitude 80 percent). The mechanism of the phenomenon is not supposed to be very different in the two cases studied by Brown and Riehl. Assuming that each atom of Cu can only emit one or two quanta under the influence of the same α-particle, Riehl calculates the number of Cu atoms which are needed to convert into light the energy of a single α-particle. From this number he calculates, then, that an α-particle is able to excite Cu atoms at a distance of 4×10^{-5} cm from its path.

It is striking to find a large difference in the order of magnitude of the efficiency of α-rays and cathode rays whose velocities are nearly the same. (Because of general arguments of the theory of the stopping power, the density of production of excited atoms cannot be very different if the velocities are nearly equal.)

2. GENERAL LINES OF EXPLANATION

We shall call Δ the effective range of diffusion of the energy transferred by charged particles to

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[1] T. B. Brown, J. Opt. Soc. Am. **27**, 186 (1937).

[2] An independent research by W. H. Nottingham (J. App. Phys. **8**, 762 (1937)) confirmed Brown's results and was extended to a wider interval of voltage, in which, however, the quantitative relations are not so impressive as in Brown's interval.

[3] N. Riehl, Ann. d. Physik **29**, 636 (1937).

[4] The information given by α-particle experiments precludes any explanation of Brown's small efficiency which would rely on the crowding of excitations along the path and on the fact that crowding decreases with increasing energy. Ultraviolet rays also produce luminescence with very high efficiency (about 50 percent); however, no strong argument may be derived from this since the mechanism of luminescence may conceivably be quite different in the case of ultraviolet rays.

a luminescent crystal. Thus Δ is the maximum distance at which charged particles are able to excite luminescent atoms. It is reasonable to assume that Δ is of the same order of magnitude for α-particles and slow electrons and not very far from the value 4×10^{-5} cm calculated by Riehl.

The energies of α-particles and slow electrons having the same velocities are quite different. Alpha-particles are not strongly scattered and penetrate very deeply ($\sim 3\times 10^{-3}$ cm) into a crystal before being stopped; slow electrons are strongly scattered and readily stopped before penetrating deeply: One may guess that the penetration of 200-volt electrons is about 10^{-7} cm. Hence the penetration of cathode rays into the crystal is much smaller than Δ, whereas it is much larger in the case of α-particles. Therefore the diffusion of energy takes place in the case of α-particles far away from the surface, whereas its very origin lies near the surface in the case of electrons.

Parasitic processes, as production of heat or emission of secondary electrons, may prevent the diffusing energy from reaching luminescent atoms. *We shall assume that parasitic processes are much stronger on the surface* than in the interior of the crystal. This explains that the efficiency of slow electrons is very small and that it increases with increasing energy and penetration of the electrons. Our assumption cannot be proved, since sufficient knowledge of the excited states of crystals is not available, but it may be easily made plausible. As a general rule, the coupling between electronic and nuclear motion in solid matter is very effective in transforming excitation energy into heat; special symmetry and periodicity relations may reduce the intensity of this process strongly, but irregularities of symmetry or periodicity will conversely destroy any metastability. The surface of a crystal constitutes a very important irregularity, not only as a discontinuity, but also because the surface itself may not be smooth.

We shall first make the particular assumption that energy reaching the surface by diffusion is very likely to be lost for the luminescence process. The actual probability of loss on the surface will be deduced as an experimental result.

In §3 we shall consider the diffusion of energy. Excitation energy may be transferred from an atom to the neighboring ones in the lattice; wandering excitations may be treated as diffusing particles, called *excitons*.[5] Excitons are scattered (elastically or inelastically) by any irregularity in the lattice: thermal motion, foreign atoms and so on. The energy of the excitons is absorbed in one or several steps. We shall assume that the efficiency of an exciton is proportional to its probability of diffusing to a distance Δ without having previously reached the surface. Elementary considerations of diffusion theory show then, that *the efficiency is proportional to the distance of the origin of the excitons from the surface* and that the proportionality coefficient is about $1/\Delta$. Hence one obtains *agreement with the experimental efficiency* 10^{-3} for 200 volts, taking as reasonable figures $\Delta\sim 10^{-4}$ cm and the distance of the origin of the excitons from the surface $\sim 10^{-7}$ cm.

One will then investigate (§4) how the "average depth" of production of excitons depends upon the initial energy of the electrons. It is helpful to apply symmetry considerations to the process of multiple scattering and diffusion of the electrons. The "average depth" may be expressed in terms of simpler physical quantities: free path of scattering and stopping power of electrons, and "effective albedo"[6] of the material for impinging electrons.

Free path of scattering and stopping power will require some particular discussion, since the approximations generally used are rather inaccurate within our range of energies. Knowledge of the "effective albedo" would require a detailed solution of the diffusion problem, but one may show that its influence on the results is very small. One will finally show that the average depth of production of excitons is nearly proportional to the electronic energy (§5). The final formula may be fitted quite well to Brown's experimental results (§6).

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[5] The properties of excitons may vary within a wide range, since they are very sensitive to quantitative relations of the particular crystal lattice (reference may be made to a paper by J. Frank and E. Teller, J. Chem. Phys. **6**, 861 (1938)).

[6] Following the analogy with neutron diffusion, we indicate as "effective albedo" a physical quantity concerning that fraction of the impinging electrons, which emerges again from the surface after diffusion.

3. Exciton Diffusion and Surface Absorption

To determine the efficiency η of an exciton of energy ϵ produced at a small distance x from the surface, we assume first that the exciton is lost if it reaches the surface. We conclude from α-particle experiments that the efficiency is practically unity if the surface losses are avoided. The efficiency η is then equal to the probability $p(x)$, that the exciton does not reach the surface and we want to calculate this function under the assumption: $p(x) \ll 1$. A second exciton produced at a depth $2x$ has the probability $p(x)$ of never coming within a distance x from the surface; if, however, it does come within such a distance—the probability for this is $(1-p(x))$—it still has the same probability $p(x)$ of escaping as the exciton considered first. Hence we find a total probability: $p(2x) = p(x) + (1-p(x))p(x) \sim 2p(x)$, neglecting $p(x)^2$, and we deduce, that $\eta = p(x)$ is proportional to the depth:

$$\eta \sim kx \quad \text{if} \quad kx \ll 1. \tag{2}$$

Moreover, since $\eta \sim 1$ for $x \sim \Delta$, we have:

$$k \sim 1/\Delta, \quad \eta \sim x/\Delta, \quad \text{if} \quad x \ll \Delta. \qquad (3)^{7}$$

Calling w the average amount of energy radiated as luminescent light, one has:

$$w = \eta\epsilon \sim x\epsilon/\Delta. \tag{4}$$

We shall now take into account two factors neglected heretofore. First the probability of an exciton's reaching the surface and being reflected by it without absorption is the product of the probability of its reaching the surface, and the reflection coefficient r (which is still supposed to be small). This product is nearly equal to r, since the first factor is $(1-x/\Delta) \sim 1$ within the limits of our approximation. Second, we have so far considered the free path of diffusion l as infinitely small as compared with x (according to the usual assumption of diffusion theory). If $l \neq 0$, but still $l \ll x$, one has to add to (3) a constant of the order of l/Δ. Then, putting C as:

$$C = l/\Delta + r \tag{5'}$$

one has:

$$\eta \sim x/\Delta + C; \quad w \sim x\epsilon/\Delta + C\epsilon. \tag{5}$$

The generalization to the actual production of many excitons by the electrons is carried out by introducing the amount of energy $\epsilon(x)dx$ lost by the electrons between the depths x and $x+dx$. Hence (5) goes over to:

$$W = \frac{\int_0^\infty x\epsilon(x)dx}{\Delta} + C\int_0^\infty \epsilon(x)dx, \tag{6}$$

which is the theoretical expression to be compared with (1). The physical meaning of $\int_0^\infty x\epsilon(x)dx$ is evidently: the *excitation energy times the average depth* at which the excitation takes place.

4. Symmetry Properties of Electron Diffusion

Electrons entering a solid body undergo multiple scattering, which goes over into diffusion and may eventually lead to the re-emission of the electrons. This phenomenon is rather complicated by the parallel action of diffusion and energy losses; slowing down changes the probability of scattering, as the diffusion goes on. The following qualitative considerations of simple diffusion phenomena will be helpful for the calculation of $\int_0^\infty x\epsilon(x)dx$.

We shall consider the diffusion of particles with unit mean lifetime produced at a rate of N per second (their total number is then N). The particles diffuse in a three-dimensional space without boundaries and are produced along the plane $x=a$. Call $n(x)dx$ the number of such particles between the planes x and $x+dx$; we want to discuss the average value of the x coordinate of the particles, that is, $(1/N)\int_{-\infty}^{\infty} xn(x)dx$. The symmetry of the system requires $n(a+\delta) = n(a-\delta)$, and hence:

$$\int_{-\infty}^{\infty} xn(x)dx = aN. \tag{7}$$

We shall now distinguish as particles of "class 1" those particles which have already crossed the plane $x=b$ $(b<a)$ at least once; all

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[7] The formula without the condition $x/\Delta \ll 1$ is of the type:

$$\eta \sim 1 - e^{-x/\Delta}.$$

the remaining particles shall be called of "class 2," so that: $n(x)=n_1(x)+n_2(x)$. The particles of class 1 (N_1 in number) are distributed as particles produced along the plane $x=b$; hence:

$$\int_{-\infty}^{\infty} xn_1(x)dx=bN_1. \tag{7'}$$

Since no particle of class 2 is found to the left of $x=b$, we have:

$$aN=\int_{-\infty}^{\infty} xn(x)dx=\int_{-\infty}^{\infty} xn_1(x)dx + \int_{-\infty}^{\infty} xn_2(x)dx=bN_1+\int_{b}^{\infty} xn_2(x)dx. \tag{8}$$

We consider now particles which are produced at $x=a$ and which are lost if they reach the surface $x=0$. Their distribution is represented by $n(x)=n_2(x)$, if one takes $b=0$; then (8) becomes:

$$\int_{0}^{\infty} xn(x)dx=aN. \tag{9}$$

The integral on the left side of (9) is *independent of the number of surviving particles* $\int_0^\infty n(x)dx$: the more particles flow out through the surface $x=0$, the farther the survivals diffuse in the interior towards $x=\infty$.[8]

If one takes into account that the value of the free path λ of the particles is not negligible one cannot consider the particles of class 1 as if they were produced at $x=b$ because they are all directed towards $x=-\infty$ when they cross this plane. The coherence of their directions is lost at the end of their free path; we have then to substitute in (7′):

$$b\rightarrow b-\lambda\langle|\cos\theta|\rangle_{\text{Av}}, \tag{10}$$

where θ is the angle between the directions of the particles at $x=b$ and the x axis, and where $\langle|\cos\theta|\rangle_{\text{Av}}$ is the average of the absolute value of $\cos\theta$. The same method may be applied to the case of a nonisotropic source of particles, for instance directed towards $x=\infty$, substituting:

$$a\rightarrow a+\lambda\langle|\cos\theta|\rangle_{\text{Av}}. \tag{10'}$$

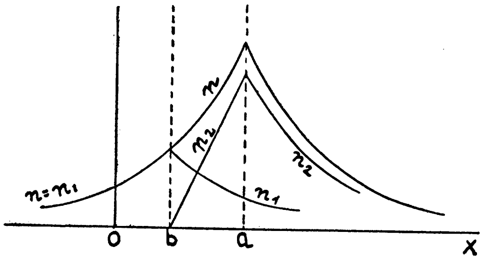

FIG. 1. $n(x)$: Plot of the approximate distribution of particles originating along the plane $x=a$. $n_1(x)$: Plot of the approximate distribution of particles having already crossed the plane $x=b$. $n_2(x)$: Plot of the approximate distribution of particles which have not yet crossed the plane $x=b$.

We consider now the diffusion within a body extending from $x=0$ to $x=\infty$; particles enter the boundary surface $x=0$ and are lost, if they flow out again through it. In this case we have to introduce the substitutions (10) and (10′) into (8) and then to put $a=b=0$. Calling J the current of particles, we have then:

$$\int_0^\infty xn(x)dx=J_{\text{in}}\lambda_{\text{in}}\langle|\cos\theta_{\text{in}}|\rangle_{\text{Av}} + J_{\text{out}}\lambda_{\text{out}}\langle|\cos\theta_{\text{out}}|\rangle_{\text{Av}}. \tag{11}$$

The *average depth* of the particles is thus determined by the flow of particles through the boundary and by their free path, independently of the actual details of the diffusion problem.

The problem of finding $\int_0^\infty x\epsilon(x)dx$ for electrons scattered in a solid body is still more complex. One may consider electrons having been slowed down as classified according to their energy; slowing down shifts electrons from one class to the next one. One finds that symmetry considerations still apply to each class so that a final result analogous to (11) may be found. Anisotropy of scattering has also to be taken into account; this must be done here—as in many other problems—by dividing the actual mean free path by $1-\langle\cos\vartheta\rangle_{\text{Av}}$ ($\vartheta=$deflection).

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[8] The mathematical treatment of the same problem is this: Call $q(x)$ the distribution of production of the particles, τ their mean lifetime, D the diffusion coefficient of the particles. $n(\infty)=0$ with its derivatives is the general boundary condition; $n(0)=0$ is the effect of the absorption at $x=0$. Then:

$$D\frac{d^2n}{dx^2}-\frac{1}{\tau}n(x)+q(x)=0$$

$$\int_0^\infty xn(x)dx=\int_0^\infty x\tau\left[D\frac{d^2n}{dx^2}+q(x)\right]dx$$

$$=D\tau\left[x\frac{dn}{dx}-n\right]_0^\infty+\tau\int_0^\infty xq(x)dx=\tau\int_0^\infty xq(x)dx.$$

We shall now go over to quantitative calculations. We introduce a system of polar coordinates θ, ϕ, having x as polar axis, and call $F(x, s, \theta)$ the current of electrons of residual "true" range s [9] at a depth x with direction θ, per unit residual range, per unit solid angle. We call ϑ the angle between the directions (θ, ϕ) and (θ', ϕ'), $\sigma(\vartheta)d\Omega'$ the differential cross section for elastic scattering from (θ, ϕ) into (θ', ϕ') within the solid angle $d\Omega'$ and N the number of scattering atoms per cc. $F(x, s, \theta)$ is a solution of the equation:

$$\cos\theta\frac{\partial F}{\partial x}=\frac{\partial F}{\partial s}-NF(x, s, \theta)\int_{4\pi}\sigma(\vartheta)d\Omega' +N\int_{4\pi}F(x, s, \theta')\,\sigma(\vartheta)d\Omega'. \quad (12)^{10}$$

Putting:

$$\int_{4\pi}\cos^n\theta\, F(x, s, \theta)d\Omega=F_n(x, s)$$

and taking into account the properties of the spherical harmonics, one has:

$$\frac{\partial F_2}{\partial x}=\frac{\partial F_1}{\partial s}-F_1N\int_{4\pi}\sigma(\vartheta)(1-\cos\vartheta)d\Omega' =\frac{\partial F_1}{\partial s}-F_1\frac{1}{\lambda}, \quad (13)^{11}$$

where:

$$1/\lambda=N\textstyle\int_{4\pi}\sigma(\vartheta)(1-\cos\vartheta)d\Omega',$$

and hence:

$$F_1(x, s)=\int_{\infty}^{s}ds'\frac{\partial F_2(x, s')}{\partial x}\exp\left[-\int_{s}^{s'}\frac{ds''}{\lambda}\right]. \quad (14)$$

$F_1(x, s)$ represents the positive current of particles with residual range s across the plane x. $\int_0^\infty E(s)F_1(x, s)ds$ is the total stream of kinetic energy across it towards $x=\infty$ where $E(s)$ is the energy corresponding to the residual range s. Hence the negative gradient of $\int_0^\infty E(s)F_1(x, s)ds$ represents the density of energy loss of the electrons;

$$\epsilon(x)=-\int_0^\infty E(s)\frac{\partial F_1}{\partial x}ds.$$

Integrating by parts, using (13), changing the order of integrations and using the condition $F=0$ for $x=\infty$, we obtain the final formula:

$$\int_0^\infty x\epsilon(x)dx=\int_0^\infty dsF_2(0, s)\mathcal{E}(s), \qquad \mathcal{E}(s)=\int_0^s ds'E(s')\exp\left[-\int_{s'}^{s}\frac{ds''}{\lambda}\right]. \quad (15)$$

This formula closely corresponds to (11), since $F_2(0, s)$ may be represented as:

$$J_{\text{in}}\langle|\cos\theta_{\text{in}}|\rangle_{\text{Av}}+J_{\text{out}}\langle|\cos\theta_{\text{out}}|\rangle_{\text{Av}}.$$

$\mathcal{E}(s)$ replaces λ; its dimensions are: energy loss of electrons times depth of their penetration. The dependence of $\mathcal{E}(s)$ on the elements determining the penetration, scattering cross section and stopping power dE/ds, appears more clearly in the asymptotic formulae:

$$\mathcal{E}(s)\sim E(s)\lambda(s), \quad \text{if} \quad \lambda(s)\ll s, \quad (16)$$

$$\mathcal{E}(s)\sim E(s_{\text{av}})s, \quad \text{if} \quad \lambda(s)\gg s. \quad (17)$$

A better approximation than (16) is:

$$\mathcal{E}(s)=E(s)\lambda(s)\left(1-\frac{d\lambda}{ds}-\frac{1}{E}\cdot\frac{dE}{ds}+\cdots\right). \quad (16')$$

For the second integral in (6) one has, obviously:

$$\int_0^\infty \epsilon(x)dx=\int_0^\infty dsE(s)F_1(0, s). \quad (18)$$

5. DISCUSSION

We have now to collect the evidence available at present concerning the dependence of the quantity (15) on the initial energy of the

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[9] "True" range is the range measured along the actual path. We consider s as a suitable measurement of the energy of the electrons.

[10] See for an analogous equation: W. Bothe, Zeits. f. Physik **54**, 161 (1929).

[11] Expansion in spherical harmonics may be considered as a general method of attack to the integral-differential equation (12) and transforms it into a chain of differential equations;

$$\frac{l}{2l+1}\frac{\partial F^{(l-1)}}{\partial x}+\frac{l+1}{2l+1}\frac{\partial F^{(l+1)}}{\partial x}=\frac{\partial F^{(l)}}{\partial s}-\frac{1}{\lambda_l}F^{(l)};$$

$$F^{(l)}=\int_{4\pi}F(x, s, \theta)P_l(\cos\theta)d\Omega,$$

$$\frac{1}{\lambda_l}=N(\sigma_0-\sigma_l)=N\int_{4\pi}\sigma(\vartheta)[1-P_l(\cos\vartheta)]d\Omega'.$$

electrons. Equation (15) is given as a function of the free path $\lambda(E)=\lambda(s)$, of the stopping power dE/ds (appearing as $E(s)$) and of $F_2(0, s)$. The quantity $F_2(0, s)$ is an integral over θ and consists of the contributions of the impinging electrons ($\theta \leqslant \pi/2$), which is known, and of the outgoing ones ($\theta \geqslant \pi/2$). The unknown features of the diffusion[12] affect only the integration for $\theta \geqslant \pi/2$.

The contribution to (15) arising from the incoming electrons is proportional to the square of their voltage V^2 if any one of the following conditions is fulfilled:

(a) if $\lambda(s) \ll s$ and $\lambda(E) \sim$ const. E, on account of (16);

(b) if $\lambda(s) \gg s$ and $dE/ds \sim$ const., on account of (17);

(c) if both $\lambda(E) \sim$ const. E and $dE/ds \sim$ const., whatever the average of λ and s may be, since then, putting $\lambda=\alpha E$, $s=\beta E$:

$$\mathcal{E}(s)=\frac{\alpha\beta}{2\alpha+\beta}E^2=\frac{\beta}{2\alpha+\beta}E\lambda=\frac{\alpha}{2\alpha+\beta}Es. \quad (19)$$

The contribution of incoming electrons is sufficient to determine the dependence of (15) on V completely;

(A) if the contribution of the outgoing electrons is negligible;

(B) if the contribution of the outgoing electrons is proportional to the contribution of the incoming ones and the proportionality factor is independent of the energy.

Fulfillment of one among the conditions (a), (b), (c) and of (A) or (B) is sufficient to show that (15) is proportional to V^2. Proportionality of the second term of (6), that is of (18), to V is also a consequence of fulfillment of (A) or (B).

We shall next discuss how (A) and (B) are connected with (a), (b) and (c). Condition (b) leads automatically to (A), since then practically no electron is scattered back. Condition (a) involves an approximation opposite to that of (b); however, (a) is consistent with (A), if the relative energy loss along a free path is not negligible. In this case every free path is shorter than the former one; thus an electron is prevented in most cases from reaching the surface of the crystal soon after its first penetration with a large residual energy. (A) is then fulfilled, since the contribution of outgoing electrons to (15) depends strongly upon their energy (possibly upon its square, according to (a)).[13] Condition (B) is fulfilled if:

(B′) $\sigma(\vartheta)$, as a function of energy, is inversely proportional to s[14] and the relation between energy and range has the form $E=as^b$ where a and b are constants. The proof of this is obtained through a similarity transformation of (11) showing that, if (B′) is fulfilled, a change of initial energy affects the solution F of the diffusion equation only as a change of units of x and s. Condition (c) together with the additional assumption that the dependence of the angular distribution of scattering on the energy may be neglected, is sufficient to fulfill (B′), so that (B) follows then as a consequence. The additional condition is required, since proportionality of λ to s is less stringent than the condition $\sigma(\vartheta) =$ const.$/s$.

Going over to discussion of the quantitative relations involved in (a), (b), (c), we have first to evaluate by a wave-mechanical calculation the effect of shielding on scattering of slow electrons. The scattering cross section in a central field is:

$$\sigma(\vartheta)=\frac{h^2}{32\pi^2 mE}\left|\sum_{l=0}^{\infty}(2l+1)P_l(\cos\vartheta)(e^{2i\delta_l}-1)\right|^2. \quad (20)$$

(m = electron mass, E = electron energy, δ_l = phase shifts of the wave functions determined by field and energy).

$$\frac{1}{\lambda}=N\int_{4\pi}\sigma(\vartheta)(1-\cos\vartheta)d\Omega' =\frac{Nh^2}{2\pi mE}\sum_l l\sin^2(\delta_l-\delta_{l-1}). \quad (21)$$

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[12] The determination of the outgoing part of $F(0, s, \theta)$ is analogous, but more complex, to that of the "albedo" of neutrons impinging on a paraffin block.

[13] This picture is also supported by the experimental evidence, that all but a small fraction of the electronic energy is absorbed in a solid body. See the results discussed by W. Bothe (*Handbuch der Physik*, Vol. XXII/2, 1 (1933)), particularly those of B. F. J. Schonland (*ibid.*, p. 44); very soft re-emitted electrons are not taken into account in these experiments. Secondary electrons emitted by the surface are considered in our theory as "lost excitons."

[14] This condition is fulfilled for instance (neglecting logarithmic factors) in the case of high energy electrons, for which Rutherford scattering is inversely proportional to E^2, while the range is directly proportional to it.

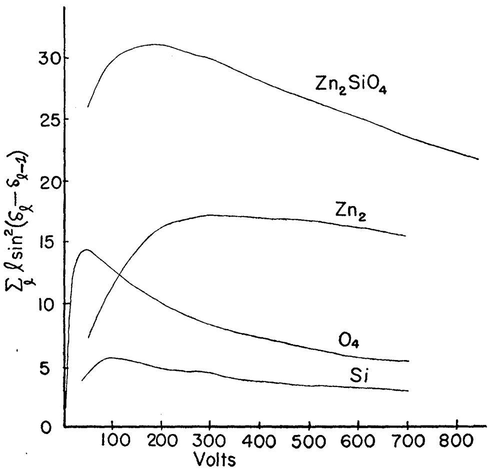

FIG. 2. The effective average cross section for elastic scattering of electrons: $\bar{\sigma} = \int_{4\pi} \sigma(\vartheta)(1-\cos\vartheta)d\Omega$ is given by the square of the wave-length of electrons times $\Sigma_l l \sin^2(\delta_l - \delta_{l-1})$ divided by π. (From calculations based on Thomas-Fermi model.)

Constant δ_l's (and therefore constant λ/E) are the consequence of a potential field $1/r^2$ for all distances from the nucleus. The δ_l for a Thomas-Fermi field have been calculated by Henneberg.[15] For high energy electrons all δ_l's are very small and decrease with increasing energy; therefore the terms $\sin^2(\delta_l - \delta_{l-1})$ also decrease with increasing energy. One finds λ to be proportional to E^2. At $E=0$ all δ_l's are multiples of π and λ tends to a finite value. In the intermediate region (which is the interesting one)

$$\sum_l l \sin^2(\delta_l - \delta_{l-1})$$

—that is E/λ—goes through a *flat maximum.* Inasmuch as this function may be considered as a constant in the neighborhood of its maximum, one finds the relation $\lambda \sim \text{const.}\, E$.[16] Because of the characteristic features of a Thomas-Fermi field, only the waves corresponding to the low values of l [17] are strongly distorted, giving rise to large values of their δ_l; hence the first terms $\sin^2(\delta_l - \delta_{l-1})$ are of the order of 1 and the sum converges rapidly after a certain value of l, which is characteristic for the atomic number, but does not depend upon the energy of the scattered electron.

Figure 2 represents the values of:

$$2\Big[\sum_l l \sin^2(\delta_l - \delta_{l-1})\Big]_{\text{Zn}} + \Big[\sum_l l \sin^2(\delta_l - \delta_{l-1})\Big]_{\text{Si}} + 4\Big[\sum_l l \sin^2(\delta_l - \delta_{l-1})\Big]_{\text{O}}$$

and of its single terms as functions of the energy, deduced from Henneberg's results by graphical methods. Some approximations in these or analogous calculations could hardly be avoided. The result is fairly constant, since it varies only by 28 percent within the range of $E=200$ to 800 volts; as a consequence, λ increases in this interval by a factor ~ 5.6 as compared to 4 in the case of a $1/r^2$ field and 16 in the case of a $1/r$ field. Variations of E/λ are chiefly due to the large amount of oxygen contained in the material, since the typical $1/r^2$ region corresponds for oxygen to energies lower than 200 volts. Henneberg's calculation neglects the effects of electronic exchange and of polarization of the internal electronic shells. Polarization is not expected to influence our result; electronic exchange might be effective in improving the constancy of λ/E appreciably. Both effects are difficult to take into account quantitatively.

Through discussion of the stopping power as a function of energy, we wish to justify two fundamental qualitative assumptions and two subsidiary ones: (1) the range s is definitely larger than λ (this is also known from experiments) and hence (a) is nearly fulfilled; (2) the relative energy loss along a free path $[\sim(\lambda/E) \times (dE/ds)]$ is of the order of $\frac{1}{6}$, hence (A) may be fulfilled together with (a); (3) the stopping power is fairly constant over our range of energies, therefore (c) as well as (a) is nearly fulfilled; (4) the ratio of the free path to the "true" range and the relative energy loss along a free path are fairly constant over a wide range of energies, thus also (B) is not very far from being fulfilled and one feels—though indirectly—encouraged to use formula (19).

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[15] W. Henneberg, Zeits. f. Physik **83**, 553 (1933).

[16] The Thomas-Fermi potential field is: $Ze^2/r \cdot \varphi(r/\mu) = Ze^2/r^2 \cdot r\varphi(r/\mu)$; the function $x\varphi(x)$ has a very flat maximum and varies slightly if one changes the distance from the nucleus within a factor 10. Further evidence on the inverse linear dependence of scattering from the energy is obtained by plotting Lenard's experimental data of apparent absorption coefficients, as given by W. Bothe (*Handbuch der Physik*, Vol. XXII/2 (1933), p. 41).

[17] These values correspond essentially to the possible values of l for atomic electrons (see for instance: E. Fermi, Zeits. f. Physik **48**, 73 (1928)).

One can hardly evaluate the stopping power in our range of energies, since every theory assumes that the particle to be stopped is much faster than atomic electrons, while this condition is not fulfilled in our case. Considering, however, that we need only qualitative results, we shall tentatively use Bloch's formula[18] in the form:

$$\frac{dE}{ds}=0.385N\frac{h^2}{m}\frac{E_0}{E}\log\frac{E}{E_0};\qquad E_0=\frac{6.04}{2\pi}\left(\frac{2}{e}\right)^{\frac{1}{2}}Z\cdot 13.54\sim 11.2Z\text{ volts.}\tag{22}$$

This formula relies on Thomas-Fermi model and might be not too inaccurate for slow electrons, since it has been applied successfully to α-particles having a velocity equal to that of 900-volt electrons. Comparison with experiments is difficult in this region; experiments on ionizing action in gases are available[19] and show a more irregular dependence on energy than (22) does.

The zero point of (22) at $E=E_0$ is obviously incorrect but a rapid improvement in accuracy may be expected for increasing energy. For $E/E_0 \gg 1$ the variation of the log factor is negligible and one has the well-known result $s\sim\text{const. }E^2$. A maximum occurs at $E=E_0e\sim 30Z$ volts, which is very flat. Hence dE/ds is nearly constant over a wide region (point (3) above). This last fact is also due to the different position of the maxima for different elements. Figure 3 represents the stopping power of Zn_2SiO_4 and of its single components. The result is certainly very inaccurate below 600 volts since E_0 is $\sim$336 volts for Zn; the stopping power should probably be larger in this region than is indicated in the figure.

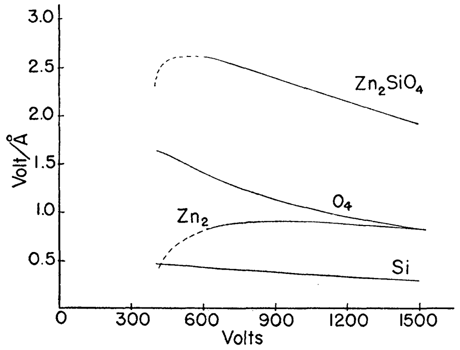

FIG. 3. Stopping power of willemite, calculated from Bloch's formula, assuming density 4. The contributions of the single elements are also indicated.

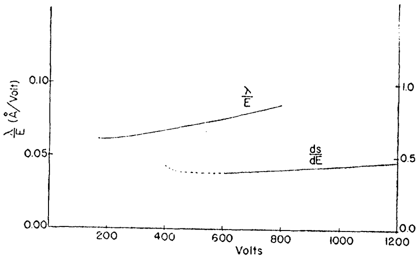

FIG. 4. Correspondence between the "true" residual range of electrons and their energy and between "effective" free path and energy. The ratio $(\lambda/E)/(ds/dE)$ roughly represents the fraction of electronic energy lost along a free path.

The quantities λ/E and ds/dE, which are directly comparable, and, if constant, should be equal to the parameters α and β of (19), are plotted in absolute units in Fig. 4. Points (1), (2), and (4) are verified by inspection of this figure. The asymptotic behavior of both λ/E and ds/dE for large energies ($1/r$ field) is proportional to the energy and their ratio is then $4Z_{\text{Av}}/(Z^2)_{\text{Av}}=1/5.3$; this result gives further evidence for (4).

Figure 4 shows that λ/E may be fairly well represented by a straight line between 200 and 800 volts; then:

$$\lambda\sim 5.5\times 10^{-10}(1+7.3\times 10^{-4}E)E\text{ cm},\tag{23}$$

where E is expressed in volts.

The results (1), (2), (3), (4), indicated above allow us to use any one of the formulae:

$$\mathcal{E}(s)\sim E(s)\lambda(s)\left(1-\frac{d\lambda}{ds}-\frac{1}{E}\frac{dE}{ds}+\cdots\right),\tag{16'}$$

$$\mathcal{E}(s)\sim\frac{\beta}{2\alpha+\beta}E(s)\lambda(s).\tag{19}$$

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[18] F. Bloch, Zeits. f. Physik **81**, 363 (1933). It might be questionable, which way one should take into account the effects arising from the largest energy transfers to atomic electrons. Formula (22) contains elements from Bloch's formula and from a formula by H. A. Bethe (*Handbuch der Physik*, Vol. XXIV/1 (1933), p. 521 (56.10)). This is because the characteristic of Bloch's formula concerns large values of the impact parameter, while the factor $(e/2)^{\frac{1}{2}}$ concerns close impacts. Anyway, a change of this factor would probably not affect the results too much.

[19] See for instance: R. B. Brode, Rev. Mod. Phys. **5**, 257 (1933).

Remembering our former results it is easily seen that the factors multiplying $E\lambda$ in both formulae are equivalent and that their value is approximately 0.75. Putting then (16′) or (19) into (15), we have:

$$\int_0^\infty x\epsilon(x)dx \sim 5.5\times 10^{-10}\gamma_1 \times (1+7.3\times 10^{-4}V)V^2 \text{ volts cm.} \quad (24)$$

γ_1 includes: the correction 0.75, as mentioned above, a factor <1, if the incidence is not normal, and the possible contribution (factor >1) of outgoing electrons to (15); γ_1 is expected to be of the order of $\frac{2}{3}$. We call γ_2 the fraction of incoming energy absorbed within the crystal, i.e., not taken away by re-emitted electrons; γ_2 is constant if (A) or (B) is fulfilled and has to be very near to 1. Then (6) becomes:

$$W \sim \gamma_1/\Delta \cdot 5.5\times 10^{-10}(1+7.3\times 10^{-4}V)V^2 + \gamma_2 CV. \quad (25)$$

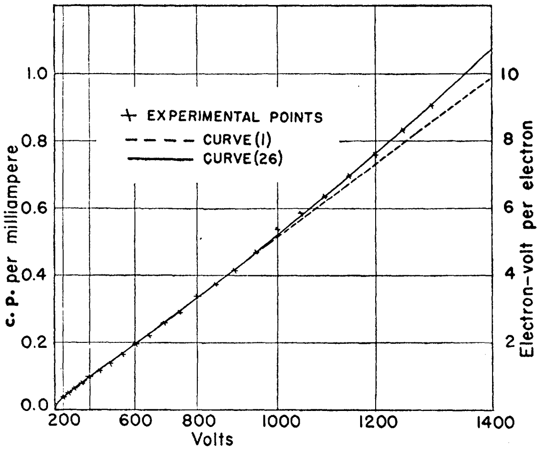

FIG. 5. Luminescent energy emitted by willemite when bombarded by cathode rays, as a function of electron energy, expressed both as brightness and as energy output. The theoretical curve (26) agrees with the experimental points still better than the empirical interpolation (1). Two parameters have been adjusted to fit the points at 200 volts and 800 volts.

6. CONCLUSION

The results of the quantitative discussion seem to justify the following picture of the luminescent phenomenon. The average penetration of slow electrons in a crystal is essentially given by their effective free path of scattering λ (defined in formula (13)). Because of characteristics of the atomic field as represented by the Thomas-Fermi model, λ is nearly proportional to the energy of slow electrons. A better approximation is given in Fig. 4 and formula (23).

Slow electrons undergo multiple scattering and diffusion within the crystal, but it is not necessary to calculate this process in detail. One may calculate directly $\int_0^\infty x\epsilon(x)dx$, which is the product of the energy lost by the electrons within the crystal and the average depth of energy loss. A careful discussion is necessary to show, that $\int_0^\infty x\epsilon(x)dx$ may be considered as proportional to the voltage of the electrons and to their penetration λ. The efficiency of production of luminescence is proportional to the average depth of production of excitons (i.e., of energy loss by electrons) as stated in §2. Thus one finds finally, that the efficiency may be considered as a linear function of the penetration λ of the electrons. Formula (25) is then obtained, which gives the amount of luminescent energy, that is, the efficiency times the incident energy.

γ_1 and γ_2 may be considered constant and slightly smaller than 1. Δ is the range of diffusion of excitation energy within the crystal. C is a physical constant defined by formula (5′) and still to be determined. The third term of (25) corresponds to the constant term in the linear representation of the efficiency as a function of the penetration of the electrons (see formula (5)).

Comparison of (25) with (1), neglect of the second and third term of (25) and the second term of (1), gives:

$$\gamma_1/\Delta \cdot 5.5\times 10^{-10}V^2 \sim 5\times 10^{-6}V^2;$$

$$\Delta \sim 1.1\gamma_1 10^{-4} \sim 0.7\times 10^{-4} \text{ cm.}$$

This comparison corresponds to a rough theory aiming to show that the efficiency is *proportional* to the energy of impinging electrons. The agreement is improved, if one tries to compare the complete expressions (25) and (1) by suitable determination of the unknown constants Δ and C:

$$aV^2+7.3\times 10^{-4}aV^3+bV \rightarrow 5\times 10^{-6}V^2+0.17.$$

Numerical evaluation shows that these two analytical expressions may be made nearly coincident over a wide range of values of V by suitable choice of a and b. If we take, for instance:

$$a=\gamma_1/\Delta\cdot 5.5\times 10^{-10}=2.28\times 10^{-6},\qquad b=C\gamma_2=0.133, \tag{26}$$

in order to fit the points at 200 and 800 volts exactly, that is:

$$\Delta\sim 1.6\times 10^{-4}\text{ cm},\quad C\sim 0.14, \tag{26'}$$

then the discrepancy between (25) and (1) never becomes larger than 0.03 volt in absolute value, or 5 percent in relative value, between 200 and 800 volts (Fig. 5). This agreement is as good as one could expect. Above 800 volts (25) correctly represents the faster increase of W (see §1). Equation (25) is certainly not very reliable below 200 volts, but it is important that the theory indicates $W=0$ for $V=0$ since the extrapolation of (1) to $V=0$ is obviously incorrect.

The interpretation of the experimental results now becomes slightly different from the simple one outlined in §2. The theory does not consider that the experimental points of the plot $W(V^2)$ lie on a straight line as represented by (1). Instead it yields an S-shaped curve which fits the experimental points as well as a straight line between 200 and 800 volts and still better than a straight line above this interval.[20] The result is essentially due to the approximate constancy of λ/E, but the apparent linear dependence of W on V^2 is due to the opposite action of two different factors. The slight increasing trend of λ/E tends to bend the curve $W(V^2)$ upwards, whereas the constant term C in the efficiency tends to bend it downwards. The accuracy of the agreement with the experimental results appears not to be due to accidental relations among the numerical constants, since it is only slightly affected by rather large changes of the numerical values (26′).

From the formulae (5′), (26′):

$$C=l/\Delta+r\sim 0.14$$

we may obtain further information. The free path of diffusion of excitons l should not be larger than λ, according to the assumptions of our theory; now, since $\lambda/\Delta\ll 0.14$, one concludes, that:

$$l/\Delta\ll C\sim 0.14.$$

Hence we obtain an evaluation of the probability that an exciton impinging on the surface is *not* absorbed by it:

$$r\sim C\sim 0.14.$$

I am very much indebted to Dr. E. Teller, who suggested this work to me and supported me with encouragement and advice in many discussions. Dr. T. B. Brown kindly furnished me with additional information and data on his experiments.

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[20] No important deviation of λ from (23) is likely to take place above 800 volts, since the slope of λ/E already corresponds to its asymptotic value given by the theory of Rutherford scattering.