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INVESTIGATION OF LASER-INDUCED
PRE-BREAKDOWN MATERIAL MODIFICATIONS

Final Report
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ABSTRACT

A new mechanism is presented for dielectric breakdown of wide gap materials in intense fields of photons having wavelengths in the visible region of the electromagnetic spectrum. It is based on multiphoton generation of free carriers and energy deposition from the photon field to the lattice via electron-photon-phonon collision processes. This laser breakdown model represents an alternative to the so-called avalanche ionization mechanism.

It is further demonstrated that laser pulses with peak fluxes below the single-shot threshold for both bulk and surface damage of sodium chloride crystals modify the properties of this material. As a result of multiphoton exciton generation primary defects are formed which lead to intense directional emission of neutral halogen and alkali atoms. As a consequence, the crystal surface is severely perturbed. We have developed the technique of thermally stimulated exoemission of particles to assess the degree of surface perturbation after laser exposure. Ongoing experiments present for the first time evidence that the single-shot laser surface damage threshold decreases with laser-induced surface perturbation.

FOREWORD

The work sponsored under this contract was concerned with certain aspects of the physics of dielectric breakdown at optical frequencies which so far have been neglected by the proponents of the traditional avalanche theory. These effects include pre-breakdown material modifications together with alternative mechanisms for energy deposition to the lattice. Two papers on the latter subject have been published or made available in pre-publication form to the dominant proponents of the avalanche mechanism, however, they still appear to be misinterpreted.⁽¹⁾ Therefore, some clarifying remarks seem to be in order at this point as an introduction to these papers (see below).

Pre-breakdown material modifications of halide surfaces exposed to laser pulses have been studied experimentally in two ways. i) We have attempted to establish a relative measure of the degree of surface perturbation inflicted by intense laser pulses having a peak flux below the single-shot damage threshold. The method of thermally stimulated exoemission of particles was shown to be a sensitive indicator for the complex processes involved in photochemical surface reactions. ii) We monitored the total amount of halogen emitted in certain well defined directions during the laser pulse and correlated this with the deterioration of the surface which leads to a distinct reduction in the surface damage threshold.

The experiments to ii) are still in progress and their results will be reported later.

The so-called "polaron" model of dielectric breakdown is described in the subsequent two papers. It was and is intended to be solely a discussion of free carrier (called polarons in ionic materials) absorption as a means to deposit energy, absorbed from the laser photon field, to the lattice without requiring these carriers to gain sufficient energy to ionize the

lattice. Since this removed the avalanche mechanism from consideration for free carrier production, the latter is replaced by multiphoton absorption.

The results obtained were rather surprising. If one excludes the limiting case computed (Nd-photons, eight-photon absorption in NaCl), not only were reasonable breakdown thresholds obtained, but their frequency dependence was not as severe as commonly expected for a multiphoton process. Additional aspects discussed were the change in refractive index due to the generation of free carriers and the ensuing deformation of the laser beam, which we expect to be a possible explanation for the small damage vestiges observed by Smith.⁽²⁾ By the way, independent of how free carriers are produced (whether via an impact ionization avalanche or otherwise), large densities of them, produced during a damaging pulse, will result in beam deformation, the details of which are presently under investigation.⁽³⁾ The "polaron" model does not address any statistical properties of laser damage, which may be introduced later by considering, e.g., the formation of primary defects in the bulk or on the surface.⁽⁴⁾

Contrary to Smith's arguments,⁽¹⁾ we are presently not convinced beyond any doubt, that many observed breakdown phenomena can only be caused by the avalanche process and that, on the other hand, the lack of other observations (e.g. multiphoton absorption of order $N > 3$ was not found by directly measuring the transmission of laser beams through wide gap solids⁽¹⁾) are proof for the absence of multiphoton phenomena in the breakdown process. This requires further comments, which are presented below on a case by case basis.

a) Statistical Damage Properties

Two different types of statistics are observed in dielectric breakdown. One concerns the number of shots required for a given fixed and

reproducible spatio-temporal pulse shape to produce damage.^(5,6) The arguments that may be used to explain these observations on a basis other than the statistically varying initial concentration of starting electrons have been advanced before.⁽⁴⁾ The other one concerns statistical distributions of micro damage sites in the laser focal volume. The only experimental evidence for reasoning in favor of a statistical avalanche process is provided by a set of pictures of damage sites taken by Smith et al.⁽²⁾ Just above threshold, a very limited number of small vestiges can be identified which, according to the authors, are statistically distributed along the laser beam axis in the focal volume. Closer examination reveals that this is not necessarily so. Instead, these damage sites have clearly a monotonically increasing separation between each other.

Only far above threshold ($\geq 40\%$ above) appear these sites to be statistically distributed, however, we feel that material modifications (refractive index gradients due to melting, ionization, etc.) have deformed the beam and, thus, modified the beam flux far beyond the point where the overall damage site can be analyzed any longer with a reasonable degree of confidence. Therefore, we tend not to place as much emphasis on these experiments as Smith et al.⁽²⁾ do. However, until beam deformation due to refractive index changes prior to the onset of damage are explained, we would like to see this issue treated as undecided rather than using it prematurely in favor of any damage mechanism. Our feeling is that the regularly spaced vestiges obtained just at the damage threshold can be explained by the interplay between self-focusing and self-defocusing beam deformations. Computer simulations, presently in progress, will shed more light on this very important point.⁽³⁾

b) Measurement of Multiphoton Absorption

The measurement of cross sections for multiphoton absorption in wide gap materials is difficult for a high order ($N \geq 3$) process particularly if one monitors the transmission or absorption directly by measuring the difference between incoming and transmitted photon flux.⁽¹⁰⁾ All of the data reported and reviewed by Smith⁽¹⁾ are based on this method which appears to be limited to $N = 2$. The measurement of processes $N > 3$ has to be performed indirectly by calorimetric⁽⁷⁾ or photocurrent⁽⁸⁾ methods. The reason for this becomes obvious if one considers direct measurements (e.g. transmission). Let us take a situation that is deliberately in favor of the transmission technique and assume that it is possible to directly measure the removal of 10^{-4} of the incoming flux, $F(\text{in})$. That is, the measurement is accurate down to $\frac{F(\text{in}) - F(\text{out})}{F(\text{in})} = 10^{-4}$. Since the cross sections for multiphoton absorption decrease drastically with order N , it becomes clear that, in order to remove 10^{-4} of the flux, one must operate at an increasingly higher flux with increasing N . Let us look at an example. The total number of absorption events in a volume of area A and length ℓ is

$$R^{(N)} = \Delta t F^N \sigma^{(N)} n_v A \ell \quad (1)$$

where Δt is the laser pulse width, F is flux, $\sigma^{(N)}$ the generalized cross section for N -photon absorption, and n_v the number of valence electrons. $NR^{(N)}$ is the number of photons removed during the absorption process. Let us assume we remove $10^{-4} \cdot AF(N)\Delta t$ photons total:

$$NR^{(N)} = 10^{-4} F(N) \Delta t A = N \Delta t F(N)^N \sigma^{(N)} n_v A \ell \quad (2)$$

The ratio of fluxes required to remove the same number of photons for multiphoton processes of order N_1 and N_2 becomes

$$\frac{F(N_1)}{F(N_2)} = \frac{N_1}{N_2} \frac{F(N_1)^{N_1}}{F(N_2)^{N_2}} \cdot \frac{\sigma^{(N_1)}}{\sigma^{(N_2)}} \quad (3)$$

Example 1: $N_2 = 2$ (two-photon absorption)

$N_1 = 3$ (three-photon absorption)

One finds from (3):

$$F(3) = \left(\frac{2}{3} F(2) \frac{\sigma(2)}{\sigma(3)} \right)^{1/2}$$

This means, it takes a flux $F(3)$ that is considerably larger than $F(2)$ to remove the same percentage of photons from the flux in both cases. Assume $F(2)$ was only 10^{-2} times the breakdown threshold flux (which is approximately 10^{+29} photons/cm²sec for a 30 psec pulse^(1,9)), again biased in favor of the transmission method (which actually works with fluxes that are quite close to the damage threshold). Assume further $\sigma(2) \approx 10^{-49}$ cm⁴sec¹ and $\sigma(3) \approx 10^{-80}$ cm⁶sec².⁽⁹⁾ One needs to operate with a flux $F(3) = 8.2 \times 10^{28}$ photons/cm²sec to see a 3-order process with the assumed high sensitivity (0.01% of all incoming photons are absorbed) of this experimental method.

Example 2: $N_2 = 2$ (two-photon absorption)

$N_1 = 4$ (four-photon absorption)

Eq. (3) yields:

$$F(4) = \left(\frac{2}{4} F(2) \frac{\sigma(2)}{\sigma(4)} \right)^{1/3}$$

Assume⁽⁹⁾ $\sigma(4) = 10^{-111}$ cm⁸sec³. One obtains

$$\begin{aligned} F(4) &= \left(\frac{1}{2} 10^{27} \cdot \frac{10^{-49}}{10^{-111}} \right)^{1/3} = \left(\frac{1}{2} 10^{27} \times 10^{62} \right)^{1/3} \\ &= 0.79 \times 4.6 \times 10^{29} \end{aligned}$$

$$F(4) = 3.7 \times 10^{29} \text{ photons/cm}^2\text{sec.}$$

That is, one has to operate at a flux around the damage threshold^(1,9) to absorb 0.01% of the photons. Clearly then, the removal of this small fraction of a very high flux means deposition of sufficient photons to melt the lattice, thus, a 4-photon process cannot be measured by the transmission method as used by Liu et al.^(1,10) without the risk of damage, no matter which damage mechanism prevails. Considering the chosen examples, the failure to measure even a 3-photon process because the sample suffers optical breakdown at the required fluxes is not surprising. It is therefore no valid argument in favor of the avalanche mechanism, in contrast to Smith's interpretation⁽¹⁾ of observed breakdown during attempts to measure with this technique multiphoton absorption of order $N > 2$.

Therefore, instead of measuring multiphoton cross sections in this way, it is mandatory to monitor the amount of deposited energy per unit volume. The equipment to do so must be sensitive enough to detect deposited energy densities below those that produce damage. The measurement of multiphoton-generated photoconductivity is the only method used so far,⁽⁸⁾ but it runs into serious space-charge problems at high carrier densities and may therefore be unreliable.⁽¹¹⁾

c) Damaging Free Carrier Density

We have shown that the free carrier density, built up during a pulse of a flux equal to the damage threshold, can reach 10^{21} cm^{-3} for psec pulses.⁽⁹⁾ The avalanche model requires to reach about $10^{18} - 10^{19} \text{ cm}^{-3}$ to explain experimental damage features. Alysassini and Parks⁽¹²⁾ have measured similar densities at the onset of damage in glass, but Auston and Shank⁽¹³⁾ found densities as high as 10^{21} at damage onset in Ge. Be it as it may, neither of these numbers is any direct evidence for the validity of the avalanche model. In order to deposit sufficient energy to the lattice either via inverse bremsstrahlung or polaron absorption, densities of this magnitude are simply required in either model. A serious consequence of these high densities is the reduction of the

refractive index, which deforms the beam and, thus, impairs the extraction of exact values for the laser peak flux or rms field strength at the damage threshold.^(9,14)

d) Polaron Absorption

Several proponents of the avalanche model were quick to demonstrate that the "polaron" model must be wrong, because it seemingly relies on the generation of optical phonons to deposit energy to the lattice. All that had to be done is measure damage in the absence of optical phonons, e.g. in a monoatomic covalent lattice such as diamond. The experiments were performed by Liu et al.⁽¹⁵⁾ Again, most of the features that are customarily taken to be typical for avalanche ionization were found and thus, the polaron model was judged to be invalid. It is, of course, almost trivial to point out that a photon-electron-phonon collision process is not restricted to optical phonons, chosen just as an example in our case^(9,14) and therefore, we again reject these measurements as evidence against our model.

In conclusion, we like to state that, in our opinion, the mechanism of dielectric breakdown at visible laser frequencies is not clear. Instead of arguing which model is correct we must now concentrate on experiments which are carried beyond the present state of the art.⁽¹⁾ The deposited energy, the free carrier densities and the beam deformation have to be determined directly and simultaneously in order to unravel various possible mechanisms for free carrier generation and energy deposition. In addition, much more work is needed to clarify the influence of primary defect formation and photochemical surface decomposition on the intrinsic damage behavior of such optical materials as halides.

REFERENCES

1. W. Lee Smith: Optical Engineering 17, 489 (1978).
2. W. Lee Smith, J. H. Bechtel, N. Bloembergen: Opt. Commun. 18, 592 (1976).
3. P. Kelly, D. Ritchie, P. Bräunlich, A. Schmid: "Computer Simulation of Laser Damage Morphology in the Alkali Halides," Boulder Laser Damage Symposium, Sept. 1978.
4. N. L. Boling, P. Braunlich, A. Schmid: Appl. Phys. Lett. 27, 191 (1975).
5. M. Bass, H. H. Barrett: IEEE J. Quant. Electron. QE-8, 338 (1972).
6. D. Milam, R. A. Bradbury, R. H. Picard: in Laser-Induced Damage in Optical Materials (NBS Special Publication No. 435, p. 347, 1975).
7. M. Bass, E. W. Van Stryland, A. Stewart: Laser Damage Symposium, Boulder, Sept. 1978.
8. I. M. Catalano, A. Cingolani, A. W. Minafra: Phys. Rev. B5, 1629 (1976).
9. P. Kelly, A. Schmid, P. Bräunlich: Phys. Rev. B16, 4569 (1977) (attached).
10. P. Liu, W. Lee Smith, H. Lotem, J. H. Bechtel, N. Bloembergen, A. Adhav (in press, cited in 11).
11. R. T. Williams: private communication.
12. N. Alyassini, J. H. Parks: NBS Special Publication 435, 356 (1975).
13. D. H. Auston, C. V. Shank: Phys. Rev. Lett. B2, 1120 (1974).
14. P. Kelly, A. Schmid, P. Braunlich (submitted to Phys. Rev., copy attached).
15. P. Liu, R. Yen, N. Bloembergen: IEEE J. Quantum Electr. QE-14, 574 (1978).

Optical breakdown in alkali halides*

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A theory of optical breakdown in dielectrics is presented and applied to NaCl and NaBr for wavelengths $0.172 \leq \lambda \leq 1.0642 \mu\text{m}$. It is based on multiphoton carrier generation and energy transfer from the radiation field to the lattice via polaron-photon absorption. This mechanism represents a clear alternative to avalanche breakdown models as no lattice impact ionization is involved. Breakdown field strengths calculated for various laser pulse lengths and frequencies, are fully corrected for the nonlinear refractive index n_2 as well as for contributions to the refractive index resulting from a sharp increase in polaron density during a damaging pulse. The results are in good agreement with experimental data obtained with nanosecond laser pulses.

I. INTRODUCTION

The electron avalanche model, since its introduction by Zverev *et al.*,¹ has apparently been remarkably successful in describing several experimentally observed optical-breakdown phenomena in dielectric solids. Although many details of the original concept have been modified extensively in recent years, the basic features remained: in the presence of an intense radiation field, electrons that are either initially available² in the conduction band or generated by single- or multiphoton carrier generation³ are accelerated by simultaneously interacting with the photon field and the surrounding lattice vibrations. They may gain sufficient energy in successive photon-electron-phonon collisions to create additional free electrons by impact ionization of either impurities or lattice constituents (e.g., transitions of valence electrons into the conduction band). The ensuing increase in the free-electron concentration will in turn increase the total production rate of those electrons whose kinetic energy reaches the ionization limit ("hot" electrons). This process repeats itself until the resulting electron avalanche has reached such proportions that dielectric breakdown is inevitable.

The detailed processes that are expected to lead to hot electrons in a dielectric exposed to an intense flux of optical photons are presently still subject to much debate. Most theoretical approaches advanced in the literature have serious problems in explaining the magnitude of the avalanche ionization rate as a function of the optical field strength and, as a consequence, the breakdown field strength E_B .^{2,4}

"Inverse bremsstrahlung" is commonly thought to be a mechanism by which, in the presence of

an electric field E and of electron-phonon collisions, electrons are capable of gaining energy at a rate

$$\frac{d\epsilon}{dt} = \frac{e^2 \tau_c E^2}{m(1 + \omega^2 \tau_c^2)}, \quad (1)$$

where e is the charge of the electron, m its effective mass, τ_c the electron-phonon collision time, and ω the laser frequency.^{5,6}

Inelastic electron-phonon collisions prevent rapid acceleration of the electrons and, as a result, almost all the energy absorbed from the radiation field is deposited into the lattice of the dielectric. According to Sparks,⁴ the simple avalanche model suffers from its inability to simultaneously determine the magnitude of the ionization rate and its frequency dependence. To circumvent this considerable problem, Yablonoivitch and Bloembergen⁷ derived the ionization rate $W_i(E)$ for NaCl from experimental dc breakdown data. Their procedure was justified by measurements of the breakdown field strength E_B of various alkali halides at the CO₂ frequency which exhibited remarkable similarities with the dc data.⁸ Surprisingly, the measured values of E_B in the same materials exhibited a dependence on the laser pulse length that could straightforwardly be explained by the very same $W_i(E)$ even at the Nd and ruby frequencies.^{9,10} One simply had to assume dielectric breakdown occurred as soon as the electron avalanche had grown to a carrier density of about 10^{18} cm^{-3} . Similar behavior was observed in a number of other wide-band-gap materials (mostly alkali halides). As a consequence, the semiempirical ionization rate obtained by Yablonoivitch and Bloembergen subsequently became one of the main arguments in favor of the avalanche model.^{11,12}

The frequency dependence of E_B enters this clas-

sical avalanche theory through the rate at which conduction electrons gain energy via inverse bremsstrahlung as well as through the probability for the electron energy to reach the ionization limit. The former can be shown to be related to the dc breakdown field via⁸

$$E_B = E_B(\text{dc})(1 + \omega^2 \tau_c^2)^{1/2}. \quad (2)$$

Since in alkali halides $\tau_c \leq 10^{-15}$ sec, one expects very little change of E_B up to the ruby frequency, again in apparent agreement with recent experimental observations.^{10,12} Thus, by using $W_i(E)$ from dc data and by independently extracting the ω dependence of E_B from Eq. (2), the avalanche model apparently provided a suitable description of dielectric breakdown in alkali halides at optical frequencies ω up to about 10^{15} sec⁻¹.

The dependence of E_B on frequency, which one obtains in NaCl on closer examination of the probability for free electrons to be accelerated to the ionization limit in a sequence of electron-photon-phonon collisions is, however, characterized by a rapid decrease with increasing ω . Therefore, as Sparks pointed out, avalanche formation by that mechanism in NaCl may well be impossible at optical or near-ir frequencies.⁴ An electron will, on the average, just oscillate in an ac field rather than continuously gain energy unless it suffers backscattering collisions during the short time interval in which the E vector changes direction. The very same electron which has accelerated with the aid of such a backscattering collision must repeat this process until its energy is sufficient to generate a second one by impact ionization. Such a sequence of reversing collisions is so unlikely at optical frequencies⁴ that the theory has been appropriately named "lucky reversing electron theory."¹³⁻¹⁵

The lucky electron theory was thought to be the logical explanation for the observed statistical nature of damage by Q-switched lasers^{16,17}; since the interval between the start of the laser pulse and the initiation of avalanche by at least one "lucky electron" will not be constant, the avalanche may or may not have sufficient time left during the remaining duration of the pulse to reach breakdown proportions. Thus, for constant laser peak power and otherwise identical experimental conditions, some shots will result in damage and others will not. Recently, however, experimental artifacts and several prebreakdown material modifications have been shown to be responsible for some features of the observed laser damage statistics.¹⁸⁻²⁰ Careful experimentation does indeed yield a distinct threshold behavior of the breakdown field strength.^{11,12} Therefore, at the present time, it appears that the lucky electron theory is

not valid for optical breakdown.

Sparks⁴ introduced the Holstein process and various vertical intraconduction-band transitions to amend the avalanche idea at optical frequencies. These processes let the electron absorb a quantum $\hbar\omega$ with reasonably high probability that it may reach the ionization limit in one or more Holstein steps or intraconduction-band transitions or combinations of both. This theory, while still in a very preliminary state, appears to explain the main features of avalanche breakdown at photon frequencies up to the far uv, although its prediction of breakdown field frequency dependence has recently been shown by Smith *et al.*¹² to contradict experimental findings.

A fundamental concept, first pointed out by Hellwarth,²¹ was widely overlooked during the debate about the physical processes involved in breakdown. Instead of concentrating on how a few fortunate "hot" electrons may be generated during the interaction, he suggested that attention be focused on all the other electrons that absorb energy: which energy, being insufficient for impact ionization, is nevertheless dumped into the lattice. The resulting increase in temperature may cause irreversible lattice modifications (breakdown) before the onset of an avalanche. The absorbed energy can be transferred by the photocarriers via Joule heating of the lattice in a time much shorter than the laser pulse length. This notion of almost instantaneous energy deposition into the lattice seems particularly persuasive in view of the fact that electrons in ionic crystals interact strongly with the lattice via the electrostatic coupling.

In the present paper, the Hellwarth picture of optical breakdown in dielectrics is adopted in an attempt to compare its features with experimental laser breakdown data as a function of laser frequency and pulse length for representative alkali halides. An important aspect of such a breakdown model is the generation of a sufficient density of charge carriers, in the absence of impact ionization. Single- and multiphoton photocarrier generation are obvious mechanisms. The present theory can therefore be viewed as an attempt to deal with multiphoton absorption as a damage mechanism as was first suggested by Bloembergen.⁶ Without going into specific detail, he argued that at laser frequencies $\omega \sim E_g/2\hbar$ (E_g is the band-gap energy), multiphoton absorption, instead of just providing starting electrons for the avalanche,¹⁰ begins to dominate impact ionization as the more effective mechanism for charge carrier production. In this context the frequency dependence of the multiphoton breakdown theory presented in this paper is of particular interest. According to Bloembergen and his co-workers,¹² we

should expect it to fail for $\omega < E_g/2\hbar$ or, in other words, whenever a multiphoton process of order $N > 2$ is required for the transition across the forbidden gap. In the following, we will attempt to test this expectation for order $N=2$ up to the order $N=8$ required for band-to-band transitions in NaCl at the Nd wavelength.

The criteria for breakdown are not well defined. However, it has proven quite useful to assume that breakdown occurs as soon as the material melting point has been reached.³ We maintain this criterion for the following discussion in which laser breakdown of dielectrics is treated on the basis of multiphoton-generated charge carriers which, "dressed" as polarons (instead of as free carriers as before), absorb energy from the field and heat the lattice. Such a system of electrons coupled electrostatically to the lattice and moving under an external field together with their induced lattice distortion is well known from polaron theory.

II. MULTIPHOTON POLARON ABSORPTION MECHANISM

The theory of laser-induced damage presented here is based on (i) polaron generation via single- or multiphoton absorption whereby valence electrons are excited into the conduction band and (ii) single- or multiphoton absorption in polaron-phonon collision processes. This approach differs from the one used by Sparks¹ mainly in not requiring that the electrons be accelerated to the ionization limit. *A priori*, therefore, avalanche is ruled out and damage is assumed to occur only by polaron Joule heating. As stated before, the incentive for such an investigation was given by the difficulties in explaining avalanche at photon frequencies in the visible and the realization that, with

increasing photon energy, multiphoton photocarrier generation is expected to somehow take over as the dominant breakdown mechanism.⁶

The analytical formalism we use is a set of differential equations for the concentration of polarons and for the lattice temperature. The required multiphoton cross sections $\sigma^{(N)}$ for carrier generation are taken from the literature. Though well known for lower orders, the cross sections for higher orders are uncertain. We will try to take account of this fact by discussing results obtained for a range of cross sections. The absorption coefficient K , for photons in the polaron-phonon collision process, which in turn is responsible for the temperature increase, requires some further discussion.

The computational methods employed to obtain K were originally derived by Feynman *et al.*,²² to calculate the mobility of low-energy electrons in polar crystals. This method has proven very powerful for all problems in which moving electrons interact simultaneously with many phonons such that the individual collisions cannot be separated in time. Based on a path-integral method,²² the polaron conductivity tensor with²³ and without²⁴ a magnetic field present, the optical absorption of polarons,²⁵ and the polaron conductivity tensor in the presence of an intense laser field have all been studied. Recently Pokatilov and Fomin²⁶ applied this technique to the problem of multiphoton absorption by polarons for different types of interaction mechanisms between the polaron and the surrounding lattice. With the variables V and μ defined by the respective electron-phonon scattering mechanism they arrive at the following expression for the N -photon polaron absorption coefficient as a function of the local laser field strength E :

$$K_N = \frac{2\pi N n_c}{F(t)\hbar} \left(\frac{2\pi m}{k_B T} \right)^{1/2} \sinh(aN) \left(\frac{\hbar}{2m\omega} \right)^{\mu-1} \frac{V(0.5\beta)^N}{(N!)^2(2N+1)} \sum_{P=0}^{\infty} \frac{(-1)^P (2\beta)^P (0.5+N)^2_P}{(P!)(1+N)_P(1+2N)_P(1.5+N)_P} \\ \times \{ (N+\xi)^{-\mu+N+P+1} K_{-\mu+N+P+1}[a(N+\xi)] \\ + |N-\xi|^{-\mu+N+P+1} K_{-\mu+N+P+1}[a|N-\xi|] \}, \quad (3)$$

where $a = \hbar\omega/k_B T$, $\beta = e^2 E^2 / 2m\hbar\omega^3$, $K_\nu[\]$ is the MacDonald function, $\hbar\omega$ the laser photon energy, m the polaron mass, k_B the Boltzmann constant, n_c the polaron density, $\hbar\omega_0$ the respective phonon energy, and $\xi = \omega_0/\omega$. For acoustical-phonon scattering, $\mu=0$ and $V = k_B T \delta_1^2 / 4\pi^3 \hbar u^2 \rho$, while for optical-phonon scattering, $\mu=1$ and

$$V = \frac{\alpha(\hbar\omega_0)^{3/2}}{\pi^2(2m)^{1/2} \sinh(\hbar\omega_0/2k_B T)}.$$

Here u , is the speed of sound, α the optical coupling constant, ρ the mass density, and δ_1 the deformation-potential constant. The total absorption coefficient K is given by

$$K = \sum_{N=1}^{\infty} K_N.$$

The method used to obtain Eq. (3) contains several simplifications. Firstly, the electrons' disper-

sion is assumed quadratic. Secondly, the interaction between electrons and lattice vibration modes is such that only one particular mode (either the optical or the acoustical) is selected in each instance and, for the chosen mode, dispersion is neglected. Furthermore, all parameters are considered temperature independent. In the case of optical-phonon scattering the coupling constant α is chosen to represent weak or intermediate coupling. Thirdly, no crystallographic anisotropy is taken into account and the laser field is assumed linearly polarized. Consequently, with all these assumptions, the calculations presented below are not expected to exactly reproduce observed breakdown data. However, we do expect them to indicate trends and provide long-wavelength limits for the validity of the multiphoton-polaron mechanism.

The variables n_c and T in Eq. (3) are obtained from the appropriately modified differential equations used in our previous breakdown studies.³ As before, the change in conduction carrier density n_c as a function of photon flux F (and of time for pulsed laser fields) is assumed to result from multiphoton carrier generation:

$$n_c(t) = n_v(0) \left[1 - \exp \left(-\sigma^{(M)} \int_0^t F^{(M)}(t') dt' \right) \right], \quad (4)$$

where M is the order of the multiphoton process, $\sigma^{(M)}$ the generalized cross section, and $n_v(0)$ the density of valence electrons in a given material at time $t=0$. The laser pulse shape is assumed to be $F(t) = A^* \sin^2(\pi t/t_p)$. A^* is the peak flux and t_p the total pulse duration.

The increase in temperature T is calculated from

$$\frac{dT}{dt} = \frac{FK\hbar\omega}{c_0\rho}, \quad (5)$$

where c_0 is the specific heat of the dielectric.

For the acoustical- and optical-phonon scattering modes it is necessary to correct for the change in the refractive index as a function of polaron density when calculating K and converting optical fluxes into rms field strengths. In the case of optical phonons the phonon contribution to the polaron part of the permittivity as opposed to the pure lattice part has been analyzed by Gurevich *et al.*²⁷ in the limit of small α , resulting in the relation

$$\epsilon_p(\omega) \equiv \epsilon_{p1} + i\epsilon_{p2} = 4\pi i\sigma(\omega)/\omega, \quad (6)$$

where $\sigma(\omega)$ is the conductivity. In this case the real part of the conductivity becomes, for $\hbar(\omega - \omega_0) \gg k_B T$,

$$\text{Re}\sigma(\omega) = \frac{2n_c e^2 \alpha}{3m\omega_0} \left(\frac{\omega_0}{\omega} \right)^{5/2} \left(1 - \frac{\omega_0}{\omega} \right)^{1/2}. \quad (7)$$

Following similar procedures and replacing the matrix element for free-electron-optical-phonon

interaction by that for the deformation potential for free-electron-acoustic-phonon interaction²⁸

$$|C_q|^2 = \epsilon_1^2 k_B T / 2q V u_s^2,$$

(V is here an integration volume), we arrive at the following relation again, with $\hbar(\omega - \omega_0) \gg k_B T$:

$$\text{Re}\sigma(\omega) = \frac{e^2 \epsilon_1^2 (k_B T)^{1/2} m^{1/2} n_c}{\hbar^3 \pi^{3/2} \omega \rho u_s^2} \left(1 - \frac{\omega_0}{\omega} \right)^2 \times \left[\exp \left(\frac{\hbar\omega_0}{k_B T} \right) + 1 \right]. \quad (8)$$

As has been explained already, our calculations presume the polarons not to acquire sufficient energy from the radiation field to enter into an energy range where the deformation-potential scattering occurs predominantly with zero-point lattice oscillations.²⁸ Thus, the real part of the conductivity as expressed by Eqs. (7) and (8) is valid over the whole energy range of interest here. An additional term $\text{Im}\sigma(\omega)$, required to calculate the polaron permittivity, has been derived²⁷:

$$\text{Im}\sigma(\omega) = n_c e^2 / m\omega. \quad (9)$$

The total permittivity can be separated into the polaron portion and the lattice portion:

$$\epsilon(\omega) \equiv \epsilon_p(\omega) + \epsilon_L(\omega) \equiv \epsilon_I + i\epsilon_{II}, \quad (10)$$

with

$$\epsilon_L(\omega) \equiv \epsilon_\infty \frac{\omega_T^2 - \omega^2 - i\omega\gamma}{\omega_L^2 - \omega^2 - i\omega\gamma} \quad (11)$$

(ω_L and ω_T represent longitudinal and transverse optical vibration frequencies, and γ acts as a damping parameter for optical vibrations and was considered negligibly small in our calculations, $\gamma \ll \omega_L$). Substituting Eq. (7) or Eqs. (8) and (9) in Eqs. (6) and (10), one easily derives the real and imaginary parts of the total permittivity and in turn the linear refractive index n_0 , defined by

$$n_0 = \frac{1}{2} [\epsilon_I + (\epsilon_I^2 + \epsilon_{II}^2)^{1/2}]^{1/2}. \quad (12)$$

To allow for the response of the nonlinear lattice polarization to very intense fields the nonlinear refractive index n_2 is included as well. Thus the total refractive index n is given by

$$n = n_0 + n_2 E^2, \quad (13)$$

and n_0 is identical with the usual linear refractive index in the absence of free carriers.

Having obtained all the necessary formalism, we will now proceed to study breakdown fluxes for different laser wavelengths and pulse durations. From our previous calculations we retain the temporal laser pulse shape as $F = A^* \sin^2(\pi t/t_p)$, with F being the momentary and A^* the peak photon flux and t_p the total pulse length.^{3,10,10} Further-

more, we retain the condition that breakdown occurs at a time $\frac{1}{2}t_p$ when the local temperature at that time is the melting point of the material under study. These conditions have been discussed at length.³ The polaron density $n_c = 0$ at $t = 0$ and $T = 300$ K.

It is intuitively satisfying to study breakdown within two limits: (i) the polaron should be allowed to absorb just as many photons as necessary to gain energy sufficient for cascade ionization, thus allowing for "hot" polarons, and (ii) the polaron absorption mechanism should be limited to "low-order multiphoton absorption" so as to avoid impact ionization. Either one of these pictures will provide a criterion for determining whether an avalanche assumption in optical breakdown is indispensable at all or only for a limited frequency range. In effect, this distinction within one model either stresses the existence and necessity of "hot" carriers on the one hand, or concentrates solely on the contribution of all the other carriers to produce breakdown on the other. However, calculations of a complete polaron avalanche pose a serious problem, since no cascade ionization rates or cross sections consistent with the present formalism are known up to now. Results presented in the following apply therefore only to the "low-order multiphoton absorption" limit. The question of what constitutes "low order" was decided by requiring that our results (breakdown fluxes at $\frac{1}{2}t_p$) maintain a precision of about 1% for consecutive stepwise increases in the order of polaron multiphoton absorption. In all examined cases of both scattering mechanisms for different wavelengths and laser pulse lengths only $N = 1$ contributed to K with sufficient precision. As a consequence, *all our results represent damage events due to single-photon absorption by polarons and instantaneous energy transfer to the lattice.*

IV. RESULTS AND DISCUSSION

A. Beam deformation

The purpose of this section is to briefly discuss the present calculations in the light of very recent experiments on optical-breakdown morphology in alkali halides, as well as to establish a link between the formalism at hand and the problems of beam deformation via self-focusing and self-defocusing. Actual breakdown experiments inevitably are difficult to perform and to interpret because of the intricate role beam deformation plays in determining the effective local breakdown field strength. Measured breakdown field strengths normally must be corrected for self-focusing,¹⁰⁻¹² which results from the increase in refractive index due to the nonlinear term $n_2 E^2$. Yablonovitch and

Bloembergen,⁷ however, have pointed out that this local increase in refractive index can be counterbalanced by a decrease due to the presence of an increasing number of free carriers. These may be generated either by an avalanche or by other mechanisms. In principle, then, corrections to measured breakdown fields should take into account both contributions to the refractive index. However, the actual density of free carriers at breakdown has never been measured in optical-breakdown experiments. The time evolution and the value at breakdown of the decreasing part of the refractive index are in general unknown. It might be for this reason that self-focusing corrections to breakdown data have attracted far greater attention than self-defocusing corrections. The latter are nevertheless required because of the sharp increase in the free carrier concentration prior to and at breakdown. Calculations of the refractive index based on Eqs. (12) and (13) show, for different laser wavelengths and pulse lengths, a consistent slight increase in total refractive index during the early stages of a damaging pulse. This is followed by a sharp decrease, still early in the pulse, once the photon flux is sufficiently high to efficiently pump carriers from the valence band via the respective multiphoton absorption processes.

Figure 1 illustrates a typical case of this behavior for NaCl for a 30-psec ruby pulse. In this figure as in all other figures presented herein, calculations were performed for the acoustical-phonon scattering mechanism using the parameters listed in Table I. Breakdown occurs at the center of the pulse (15 psec) with a flux of 8.4×10^{29} photons/cm² sec. Obviously, the onset of drastic changes in the local refractive index occurs far below these breakdown fluxes (see inset). However, the density of absorbing polarons monotonically increases up to breakdown. As a result, the competing effect of n_2 is completely overpowered above a certain threshold field strength, in agreement with earlier expectations.⁷ In view of this result the contribution of polarons to the total local refractive index within the breakdown volume cannot be neglected, and local field corrections to breakdown data cannot be limited to self-focusing alone. One must deal with beam deformation caused by initial self-focusing, followed by defocusing as soon as the free carrier density is large enough ($\sim 10^{16}$ cm⁻³).

Consider a laser beam, having a peak flux F just sufficient to damage at $\frac{1}{2}t_p$, being focused into a dielectric. Early in the pulse the focal waist will be reduced in diameter owing to the dominance of $n_2 E^2$ over the negative free carrier contribution n_c to the total refractive index. As soon as the free-carrier density exceeds about 10^{16} cm⁻³, defocusing will

FIG. 1. (a) Time evolution of the refractive index n , the density of polarons n_c , and the temperature $\Delta T = T - 300$ K during a 30-psec laser pulse of the form $F = 8.4 \times 10^{29} \sin^2(\pi t/t_p)$ (photons cm $^{-2}$ sec $^{-1}$) for which breakdown occurs at $t = \frac{1}{2}t_p = 15$ psec. The inset shows details of the initial increase of the refractive index due to the nonlinear refractive index n_2 . (b) Time evolution of the photon flux F and the local rms field strength E under the same conditions as in (a). The breakdown field strength is $E_B = E(\frac{1}{2}t_p) = 9.2$ MV cm $^{-1}$. These and all subsequent figures are based on calculations using the acoustical-phonon-scattering mechanism in NaCl for which the parameters are listed in Table I.

occur because now $|n_p| > n_2 E^2$. This in turn will reduce F and, therefore, n_c just behind the location of this initial focal waist reduction. At some point, n_c will again be small enough to make self-

focusing possible, leading to increased concentrations n_c and, as a consequence, to self-defocusing, etc. Thus, one can speculate that, owing to the interplay of the two competing beam-forming mechanisms, a spatially periodic sequence of zones with alternating high magnitudes in carrier densities is generated. Extending this speculation a bit further, it may well be that the breakdown morphology observed for peak powers just above the laser damage threshold is a manifestation of periodic changes in total n_c .¹²

B. Acoustical-phonon scattering

For the reason discussed in the previous section, local breakdown fields are meaningful only if corrections for the nonlinear refractive index as well as those for the breakdown carrier density are considered. We therefore will abandon the custom of investigating breakdown fields as a function of laser pulse length in favor of local breakdown photon fluxes. This does not rule out estimations of properly corrected breakdown fields. In order to determine the value of local breakdown fields corresponding to our breakdown fluxes, we first calculate the effect of polarons on the local refractive index and convert, in a subsequent step, the photon fluxes to rms field strengths by making use of this local refractive index. Thus, we ascertain a master-slave relationship between the driving photon flux which can be measured experimentally and the induced local rms electric field which is experimentally inaccessible. If under certain conditions, as will be shown below, e.g., in the nanosecond regime, the polaron density at breakdown does not exceed 10^{19} cm $^{-3}$, its influence on the total refractive index remains minor and a comparison between experimentally found breakdown fields and the ones estimated here will be possible. Note in passing that this polaron density agrees well with the 10^{18} -cm $^{-3}$ electrons chosen in earlier laser breakdown work as a damage criterion¹⁰ for nanosecond pulses as well as with pre-breakdown electron density measurements in borosilicate crown glass (BSC-2).²⁹ This situation changes drastically in the picosecond regime where polaron densities larger by two orders of magnitude are calculated at the time of breakdown. Again, a similarly high density in free carriers has been shown³ to be necessary for avalanche breakdown, although later experimental determinations of picosecond breakdown fields have not taken into account the consequences resulting from it.^{11,12} Thus, a comparison of the present results with experimental data remains confined to the nanosecond regime. We shall demonstrate the importance of this distinction between breakdown field and flux by plotting for a 30-psec pulse the

TABLE I. Parameters for NaCl.

Symbol	Meaning	Value	Multiphoton cross sections $\sigma^{(M)}$ ($\text{cm}^{2M} \text{sec}^{-M-1}$)	
ρ	mass density	$2.165 \text{ g cm}^{-3} \text{ }^a$	$\sigma^{(2)} = 4 \times 10^{-49} \text{ }^b$	
c_0	specific heat	$2.0 \text{ cal g}^{-1} \text{ K}^{-1} \text{ }^b$	$\sigma^{(3)} = 1 \times 10^{-80} \text{ }^b$	
α	coupling constant	3.50	$\sigma^{(4)} = 1.45 \times 10^{-111} \text{ }^b$	
ϵ_∞	high-frequency permittivity	2.35 ^c	$\sigma^{(5)} = 5 \times 10^{-141} \text{ }^b$	
ϵ_0	static permittivity	5.62 ^c	$\sigma^{(8)} = 1.5 \times 10^{-225}$	
$\hbar\omega_L$	longitudinal optical phonon	$3.25 \times 10^{-2} \text{ eV }^d$		
$\hbar\omega_T$	transverse optical phonon	$2.05 \times 10^{-2} \text{ eV }^e$		
$\hbar\omega_0$	longitudinal acoustic phonon	$1.61 \times 10^{-2} \text{ eV }^e$		
u_s	velocity of sound	$4.67 \times 10^5 \text{ cm sec}^{-1} \text{ }^a$	λ (μm)	Initial refractive index n_0 ^k
m	polaron mass	$0.75m_0$ (free mass)		
δ_1	deformation-potential constant	8.9 eV	1.0642	1.53
n_2	nonlinear refractive index	$6.4 \times 10^{-13} \text{ esu }^f$	0.6943	1.54
n_0	initial valence electron density	$2.24 \times 10^{22} \text{ cm}^{-3}$	0.5321	1.55
T_M	melting point	1074 K	0.3471	1.58
E_g	band-gap energy	8.6 eV ^g	0.1720	1.90

^a From Ref. 34.^b From *Handbook of Chemistry and Physics* (Chemical Rubber Co., Cleveland, 1973).^c See Ref. 35.^d See Ref. 36.^e See Ref. 37.^f From Ref. 11.^g From Ref. 33.^h See Ref. 38.ⁱ See Ref. 39.^j From Ref. 31.^k See Ref. 40.

local refractive index and the local rms field as a function of time up to breakdown at $\frac{1}{2}t_b$. Figure 1 shows an initial increase of n due to the absence of any free carriers or polarons simply as a result of the additive effect of the nonlinear term $n_2 E^2$. The importance of this increase to self-focusing is evident. We note, however, that with increasing flux and, as a consequence, with increasing probability for band-to-band excitation the population of the conduction band begins first to counterbalance and later to completely overpower this positive contribution to the refractive index. As can also be seen in Fig. 1, this occurs early in the damaging pulse. Once the refractive index has started to dwindle, there is no reason to expect a reversal trend before breakdown, since both the photon flux and the band-to-band excitations continue to increase monotonically. The rapidly falling refractive index then forces the local electric field up according to $E \propto n^{-1/2}$. Therefore, the rms field strength at breakdown depends on the refractive index and the number of polarons necessary for breakdown at a particular laser wavelength and pulse length. Without knowledge of this polaron density the exact value of the local breakdown field strength cannot be determined.

After having established that the polaron density is a crucial quantity in optical breakdown, the polaron generation rate attains significance as well. Cross sections for multiphoton band-to-band ex-

citation, particularly those of higher orders, are not widely investigated in solids. The present calculations attempt to accommodate this fact by using a range of plausible cross sections. However, all cross sections used here (Table I) are the smallest published in the literature, with the exception of that for Nd photons. In this case, an eight-photon process is necessary to bridge the band gap of NaCl. No values for $\sigma^{(8)}$ in solids are available from the literature, and therefore a trial cross section was taken from multiphoton ionization experiments on Kr.³⁰ This value was arbitrarily modified so that a reasonable value of E_g was obtained for a 30-nsec pulse and this cross section was used henceforth. In case of the ruby frequency, reasonable agreement with measured data^{10,14} for nanosecond laser pulses was obtained with the cross section $\sigma^{(5)} = 5 \times 10^{-141}$ used in previous calculations.³ In order to demonstrate the dependence of the breakdown parameters on this cross section we also arbitrarily increased its value by one order of magnitude (Table I). This was also done for the doubled frequency of ruby. As we will see later, the cross sections significantly control general breakdown behavior and, as one would expect, are crucial in the present theory. The remaining parameters employed in the breakdown flux calculations, e.g., acoustical-phonon frequency and deformation-potential constant, are listed in Table I as well.

FIG. 2. (a) Breakdown photon flux A_B^* in NaCl vs inverse laser pulse length. t_p^{-1} calculated for different laser frequencies: Nd, neodymium laser frequency; 2Nd, doubled frequency of neodymium laser; Rb, ruby laser frequency; 2Rb, doubled frequency of ruby laser; Xe, xenon laser frequency. (b) Breakdown field strengths E_B under the same conditions as in (a).

In Fig. 2(a) we display breakdown fluxes A_B^* as a function of inverse pulse length for various laser frequencies. We observe a straight-line dependence on a double logarithmic scale. Indeed, the relation $t_p^{-1} \propto (A_B^*)^{(M+1)/2}$ is easily derived from Eqs. (4) and (5). In Fig. 2(b), we display the breakdown field strength E_B as a function of the reciprocal pulse length, in order to illustrate the effect of the changing refractive index on the conversion of flux to field strength.

If one rearranges the calculated data as in Fig. 3, such that for a set of identical pulse lengths the breakdown flux is plotted against the photon energy, a breakdown frequency dependence appears which qualitatively resembles the frequency dependence expected from the avalanche model in the region between the Nd and double Nd laser frequencies. Note that lack of a considerable frequency dependence in this range seems to rule out multiphoton processes as the dominant mode of optical breakdown in dielectrics.^{11,12} By exclusively considering the vast difference in cross sections (see Table I) one would expect a steep decline in breakdown fluxes with increasing laser frequency if multiphoton processes were to play a significant role. This decline was never observed experimentally, nor is it corroborated by our present calculations.

In Fig. 4 we compare experimental breakdown field strengths for a $t_p = 60$ nsec pulse¹⁰ with our wavelength-dependent data. Unfortunately, other published experimental data^{11,12} down to $0.34 \mu\text{m}$ cannot be strictly compared for reasons stated above. As is evident from Figs. 3 and 4, damage field thresholds decrease markedly only for laser photon energies larger than 3 eV in NaCl. However, the decrease is not as dramatic as expected solely on the basis of multiphoton band-to-band excitation cross sections. The reason for that becomes evident upon examination of the normalized

FIG. 3. Breakdown flux A_B^* in NaCl vs the energy of the laser photons for different pulse length t_p .

FIG. 4. Breakdown field strength E_B in NaCl vs photon energy for a $t_p = 60$ nsec pulse. Experimental data from Ref. 10.

polaron absorption coefficient and its wavelength dependence. This is shown in Fig. 5, where the ratio of K/n_c is plotted versus laser photon energy at breakdown. In effect, the influence of increasing probability for free carrier generation with increasing photon energy on the breakdown flux is weakened by a sharp decrease in the polaron absorption coefficient.

FIG. 5. Polaron photon absorption coefficient K divided by polaron density n_c in NaCl at breakdown ($t = \frac{1}{2}t_p$) vs photon energy for a 30-nsec and a 300-psec pulse. K/n_c in units of 10^{-17} (cm^2).

FIG. 6. Polaron photon absorption coefficient K of NaCl at breakdown ($t = \frac{1}{2}t_p$) vs laser pulse length for different laser photon energies.

The calculated polaron absorption coefficient at breakdown as a function of pulse length and wavelength is illustrated in Fig. 6. Of particular interest at this point is the large absorption coefficient at breakdown for a 30-psec Nd pulse. It should be possible to observe beam depletion by polaron absorption in this particular case at peak powers at or slightly below breakdown. Such an experiment would test the validity of the polaron optical-breakdown model at the Nd frequency. On the other hand, it seems very unlikely to observe beam depletion in commonly found experimental arrangements (tightly focused beams) for all the other frequencies discussed here.

Beam depletion or attenuation should be considered carefully. Two mechanisms are responsible: (i) the removal of photons due to carrier generation and (ii) photon absorption by the generated carriers in heating the lattice. Let us consider first the former, which is simply a consequence of the creation of a large density of charge carriers. This density assumes its highest value right at the moment of damage and, as previous calculations have shown,³ this peak density increases from around 10^{18} cm^{-3} for nanosecond pulses to over 10^{20} cm^{-3} for picosecond pulses. Thus we expect that beam depletion, if it exists, will be most pronounced for extremely short pulses. Attenuation due to charge carrier generation may be characterized by an absorption coefficient $\alpha(A_B^*)$ at $\frac{1}{2}t_p$ of a just damaging pulse: for pure avalanche,

$$\alpha_A(A_B^*) \geq E_c n_c W_i(A_B^*) / F \hbar \omega;$$

for multiphoton polaron generation,

$$\alpha_M(A_B^*) = \sigma^{(M)} A_B^{*M-1} n_v.$$

Some simple calculations show that $\alpha(A)$ may indeed reach large values. Consider a 15-psec full width at half maximum (FWHM) Nd-laser pulse. For pure avalanche breakdown, according to calculations by Kelly *et al.*,¹⁹ $A_B^* = 10^{31}$ photons $\text{cm}^{-2} \text{sec}^{-1}$ at the damage threshold, and $n_c = 1.3 \times 10^{20} \text{ cm}^{-3}$. For this case $W_i(A_B^*) = 10^{12} \text{ sec}^{-1}$ is obtained from the work of Fradin and co-workers.^{9,10} The resulting value for the free carrier generation absorption coefficient is $\alpha_A \approx 110 \text{ cm}^{-1}$.

Another example is multiphoton polaron generation at the ruby frequency for the same 15-psec FWHM pulse. With³¹ $\sigma^{(5)} n_v = 1.12 \times 10^{-118} \text{ cm}^{10} \text{ sec}^4$ and $A_B^* = 1.44 \times 10^{30}$, for which damage occurs again at $\frac{1}{2}t_p$, we obtain $\alpha_5 \approx 75 \text{ cm}^{-1}$. Remembering that $\sigma^{(5)}$ is known only within an order of magnitude, we have again obtained an absorption coefficient for this case that is comparable to α_A .

This peak absorption coefficient increases with decreasing order of the multiphoton excitation process somewhat, but even for a three-photon process it remains at values comparable to those above. On first sight, then, beam attenuation due to charge carrier generation alone appears to be a real problem in the picosecond regime, irrespective of the damage mechanism. Note that the energy absorbed in this process remains almost completely in the crystal in the form of electronic excitation during the duration of the pulse. The excited states (electrons in the conduction band) relax during a time that is much larger than t_p via radiative and nonradiative transitions and thus do not contribute to lattice heating for $t \leq \frac{1}{2}t_p$.

Let us now turn briefly to the absorption coefficient associated with heating of the lattice. It is widely agreed⁴ that energy transfer to the lattice from absorbing carriers happens via Joule heating. This can simply be expressed as the rate of increase of energy per unit volume⁴:

$$\frac{dW}{dt} = \sigma E^2 n_c = \frac{e^2}{m} \tau_c (1 + \omega^2 \tau_c^2)^{-1} E^2 n_c, \quad (14)$$

where the conductivity σ is written in terms of parameters used previously in Eqs. (1) and (2). Balancing this energy density increase per unit time by the corresponding absorption term from the photon field,

$$\frac{dW}{dt} = \alpha_f F \hbar \omega, \quad (15)$$

we arrive at an expression for the Joule heating absorption coefficient α_f :

$$\alpha_f = \frac{e^2}{m} \tau_c (1 + \omega^2 \tau_c^2)^{-1} n_c \frac{4\pi}{cn} \quad (16)$$

(c is the speed of light, n the refractive index). As long as $\omega \tau_c$ is not very much larger than 1 and $\tau_c \leq 10^{-15} \text{ sec}$, we find at the damage threshold for a reasonable $n_c \sim 10^{20} \text{ cm}^{-3}$ and $n \sim 1.5$ that

$$\alpha_f \leq 1.1 \times 10^4 \text{ cm}^{-1}.$$

As we can see from Fig. 6, with the exception of the 1.0642- μm line, the absorption coefficient K at breakdown consistently remains smaller than 10^4 . In view of possible beam attenuation the comparison of absorption coefficients for (i) generation of carriers and (ii) heating of the lattice by those absorbers leads us to conclude that neither model—inverse-bremsstrahlung avalanche or multiphoton-generated polarons—will *a priori* prevent or enhance beam attenuation as argued previously.¹² We therefore do not believe that eventual beam attenuation will offer a means of distinguishing between the two models. The only time this might become possible would occur for very short pulses at the Nd frequency.

Figure 7 shows the refractive indices at breakdown for different frequencies as a function of pulse length. For a given laser frequency the refractive index decreases with decreasing pulse length owing to the increase in polaron density as shown in Fig. 8. We reemphasize in this connection the necessity to properly account for the changing refractive index when transforming laser fluxes to local rms electric field strengths. Obviously this becomes more important the larger the relative change, e.g., at the longer wavelengths, where most of the experiments have been performed up to now.

FIG. 7. Total refractive index of NaCl at breakdown ($t = \frac{1}{2}t_p$) vs laser pulse length for different laser photon energies.

FIG. 8. Density of polarons in NaCl at breakdown ($t = \frac{1}{2}t_p$) vs laser pulse length for different laser photon energies.

Beam attenuation, self-focusing, and self-defocusing determine the local photon flux or the local rms field strength in a largely unknown and complicated fashion that has never been completely appreciated in experimental or theoretical laser breakdown work. For a pulse having a peak power right at the damage threshold we can conceive that damaging concentrations of charge carriers exist in a few very small zones of the self-focusing-self-defocusing pattern, located along the axis in the focal volume of the beam such that the total length of highly absorbing vestiges is very small (a few microns, as indicated by the damage morphology observed by Smith *et al.*¹²). Since the diameter of these areas is very small as well (e.g., a fraction of the beam waist diameter), rather small depletion of a beam with a flux that corresponds to the damage threshold will occur and then only at the maximum of the TEM₀₀ laser intensity profile. This will remain largely unnoticed using conventional beam diagnostic techniques which measure the temporal pulse behavior and its total energy. Of course, right after damage occurs, the usual beam depletion is observed caused by hot plasma formation.¹⁷

C. Optical-phonon scattering

Since it is not immediately evident which of the two polaron-scattering mechanisms, the optical or acoustical, would result in breakdown data that are in better agreement with experimental ones, we recalculated all steps outlined in the previous section for the optical-scattering mechanism as

well. The parameters used are also listed in Table I. It turned out that the polaron density at breakdown in the optical case is consistently higher, and breakdown under otherwise identical conditions occurs at significantly higher fluxes or local rms field strengths as compared to the acoustical case. We therefore believe that acoustical-phonon scattering dominates optical breakdown in dielectrics for the frequency range pertinent to this paper and that a future theory which allows for both phonon-scattering modes simultaneously would not yield results that are significantly different from those presented in the previous section.

D. Extension to NaBr

In Sec. IV B we discussed the pulse length dependence of the breakdown peak flux A_B^* and found it to obey the relation $t_p^{-1} \propto (A_B^*)^{(M+1)/2}$. We then tested the theory against the dependence of the breakdown field strengths on the laser frequency which were not found to decrease as rapidly as one would expect on first sight from a pure multiphoton mechanism. This behavior is in remarkable agreement with measured data for nanosecond pulses in the wavelength region $0.5321 \leq \lambda \leq 1.0642 \mu\text{m}$. These data had previously been taken as a strong indication for avalanche breakdown in NaCl and other alkali halides.

In this section we describe results of yet another test of our breakdown theory by considering materials other than NaCl with the goal of investigating the influence of different band gaps on the breakdown flux. We chose again alkali halides for this comparison because in this way the effect of parameters such as specific heat, mass density, phonon energy, etc., other than the band gap will be minimized and because there are experimental data available in the nanosecond regime. Comparison with materials of different band gap is complicated by the uncertainties in high-order multiphoton absorption cross sections. As stated in Sec. IV B, the value of $\sigma^{(M)}$ is of considerable influence on the breakdown peak flux and, therefore, accurate values for A_B^* or E_B cannot be calculated. But not only are the cross sections fairly unreliable, but also exact band-gap data are not always available.

To reduce the $\sigma^{(M)}$ uncertainty somewhat, we chose NaBr, a material with a smaller band gap than that of NaCl. In this way, the multiphoton order M is lowered to 7 at the Nd wavelength and 4 at the ruby wavelength. An additional problem in this connection is, of course, the absolute value of the band gap, which is stated in the literature as low as 7.1 eV,³² and as high as 7.7 eV.³³ The parameters used in the calculation of breakdown data

TABLE II. Values of the constants of NaBr used in the calculations.

Symbol	Meaning	Value
$\sigma^{(7)}$		$4.64 \times 10^{-197} \text{ cm}^{14} \text{ sec}^6$
ρ	mass density	3.2 g cm^{-3}
c_0	specific heat	$1.19 \text{ cal g}^{-1} \text{ K}^{-1}$
ϵ_∞	high-frequency permittivity	2.64^a
ϵ_0	static permittivity	5.78^a
$\hbar\omega_1$	longitudinal optical phonon	$2.7 \times 10^{-2} \text{ eV}^b$
$\hbar\omega_t$	transverse optical phonon	$1.82 \times 10^{-2} \text{ eV}^a$
$\hbar\omega_0$	longitudinal acoustical phonon	$1.57 \times 10^{-2} \text{ eV}^c$
u_s	velocity of sound	$4.3 \times 10^5 \text{ cm sec}^{-1}$
m	polaron mass	$0.87m_e$ (free mass)
$\mathcal{E}_1$	deformation-potential constant	7.92 eV
n_2	nonlinear refractive index	$9.6 \times 10^{-13} \text{ esu}^d$
n_v	initial valence electron density	$1.882 \times 10^{22} \text{ cm}^{-3}$
T_M	melting point	1028 K
	Initial refractive index at $1.0642 \mu\text{m}$	$= 1.62$
	Initial refractive index at $0.6943 \mu\text{m}$	$= 1.63$

^aSee Ref. 35.^bSee Ref. 36.^cSee Ref. 41.^dSee Ref. 12.

in NaBr are listed in Table II. Again, for the case of acoustical-phonon scattering, we find for ruby that the ratio $E_B(\text{NaBr})/E_B(\text{NaCl}) = 0.87$, which compares with the measured value¹⁶ of 0.82. And then using the Nd ratio of 0.7 from experiment,¹⁷ we obtain a reasonable value of $\sigma^{(7)}$ as shown in Table II.

E. Discussion of parameters

In order to investigate the influence on the calculated breakdown data of several parameters listed in Tables I and II, particularly of those whose values are known with less certainty, test runs were performed in which their values were changed. Aside from principle considerations, it is important to evaluate whether or not the agreement between computed results and experiments is merely fortuitous.

In the case of acoustical scattering the parameter least certain in value in alkali halides is the deformation-potential constant $\mathcal{E}_1$. In all initial calculations a value of $\mathcal{E}_1 = 8.9 \text{ eV}$ for NaCl was used which is close to the value of 9.95 eV suggested by Evseev and Tolpygo³⁴ for NaCl. Sparks⁴ derived a value of 4.5 eV from the theory of monovalent metals. In view of this smaller value we performed all calculations with $3^{-1/2}\mathcal{E}_1$. The results are compared with the original results in Table III for a selection of representative pulse lengths. Breakdown fields consistently increase by around 20%, whereby the increase appears somewhat more pronounced for damage at the shorter wavelengths than in the red and ir. Altogether the changes solely due to $\mathcal{E}_1$ are not spectacular for any of the other breakdown variables, and one can safely assume that within the uncer-

TABLE III. Dependence of breakdown values for NaCl on choice of deformation-potential constant $\mathcal{E}_1$. For each wavelength values are given for $t_p = 30 \text{ psec}$ (top line) and $t = 30 \text{ nsec}$ (bottom line). The left column for each variable refers to $\mathcal{E}_1 = 8.9 \text{ eV}$ and the right column to $\mathcal{E}_1 = 8.9/\sqrt{3} \text{ eV}$.

$\lambda (\mu\text{m})$	A_B^*		n_c		E_B		K	
1.0642	1.9×10^{29}	1.9×10^{29}	1.4×10^{20}	1.5×10^{20}	33.0	39.0	8.0×10^5	5.88×10^5
	5.1×10^{28}	5.8×10^{28}	4.3×10^{18}	1.1×10^{19}	1.54	1.66	1.4×10^2	1.23×10^2
0.6943	8.4×10^{29}	9.4×10^{29}	1.7×10^{20}	3.1×10^{20}	9.2	16.6	4.9×10^3	6.86×10^3
	8.7×10^{28}	1.0×10^{29}	2.0×10^{18}	5.1×10^{18}	2.47	2.71	4.1×10^1	3.41×10^1
0.5321	1.0×10^{30}	1.2×10^{30}	1.4×10^{20}	3.1×10^{20}	10.4	12.9	2.5×10^3	2.31×10^3
	6.5×10^{28}	8.1×10^{28}	2.4×10^{18}	5.8×10^{18}	2.44	2.77	3.7×10^1	2.97×10^1
0.3471	5.9×10^{29}	7.6×10^{29}	4.1×10^{18}	4.5×10^{20}	9.3	11.2	2.3×10^3	1.83×10^3
	1.9×10^{28}	2.5×10^{28}	6.9×10^{18}	1.6×10^{19}	1.6	1.84	7.0×10^2	5.29×10^1
0.1720	1.2×10^{29}	1.7×10^{29}	7.1×10^{20}	1.4×10^{21}	5.35	6.57	3.6×10^3	2.53×10^3
	1.2×10^{27}	1.7×10^{27}	1.3×10^{19}	1.5×10^{20}	0.59	0.63	3.5×10^2	2.44×10^2

tainty ranges still common to both experimental and theoretical work on laser damage, the present model suffers no serious deficiency because of lacking precision in ϵ_1 .

As stated in Sec. II, one of the most serious simplifications of our model is neglect of phonon dispersion. It seems therefore indispensable to analyze to what extent the proper choice of phonon energy influences our breakdown results. Assuming that our averaged phonon energies were in error by $\pm 20\%$ for both cases, we recalculated all our results outlined in Sec. IV B.

For a 20% increase in phonon energy the largest relative change observed is a change of breakdown field of +7% for a 30-nsec pulse at 0.5321 μm and acoustical scattering. The largest relative change for a 20% decrease in phonon energy occurs for a 30-psec pulse at 0.5321 μm and acoustical scattering where the breakdown field decreases by almost 10%. This then is an indication of the accuracy of the calculated breakdown data presented here. Improvements are, of course, only possible by considering the phonon spectrum, and by exact knowledge of $\sigma^{(M)}$ as well as ϵ_1 .

V. CONCLUSIONS

In conclusion, we find that optical dielectric breakdown at wavelengths between 1.06 and 0.172 μm can be explained quite successfully by the theory outlined above. This is achieved by assuming multiphoton band-to-band excitations to be the only charge-carrier-generation mechanism in NaCl and NaBr. Transfer of energy from the photon field to the lattice occurs exclusively via a polaron-photon absorption mechanism, whereby single-photon absorption by the polarons proves sufficient to explain NaCl measured breakdown behavior within a factor of 2. Thus, no lattice ionization process has to be involved. The concept of an electron

avalanche damage started by a few hot electrons is replaced here by the concept of damage by many electrons, none of which has sufficient energy for lattice ionization but which collectively produce irreversible material changes.

We readily admit that many of the above considerations remain speculation as long as the breakdown event is not modeled in a complete space- and time-dependent manner. It should be appreciated that the breakdown model described herein cannot, in its present form, provide the necessary quantitative beam-forming and attenuation corrections. It simply assumes a local flux to be present irrespective of whether it is the result of self-focusing or any other beam-forming and attenuating mechanism. What in essence we have done, then, is to simply restrict the calculations to a crystal volume that was sufficiently small so as to neglect all these effects. We retained only the correction of the refractive index for the conversion of photon flux into rms optical field strength and vice versa.

As a consequence, direct comparison of presently available experimental and calculated breakdown data was somewhat problematic. Additional uncertainties arose from the fact that our model made use of a number of simplifying assumptions (see Sec. II); nevertheless, the polaron breakdown model appears to provide a genuine alternative to avalanche breakdown. In fact, the success of the present formalism, aside from indicating that the experimental determination of breakdown fields will have now to take into account the change in refractive index, also justifies its extension (i) to space- and time-dependent laser-beam profile analysis and (ii) to the CO_2 wavelength region. It is our intent to proceed in these areas and simply note in conclusion that the present work contains no reference to $\lambda > 1 \mu\text{m}$ because of the uncertainty in the multiphoton generation rates.

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¹G. M. Zverev, T. N. Mikhailova, V. A. Pashkov, and N. M. Soloveva, *Zh. Eksp. Teor. Fiz.* **53**, 1849 (1967) [*Sov. Phys. JETP* **26**, 1053 (1963)].

²L. H. Holway and D. W. Fradin, *J. Appl. Phys.* **46**, 279 (1975).

³P. Bräunlich, A. Schmid, and P. Kelly, *Appl. Phys. Lett.* **26**, 150 (1975).

⁴M. Sparks, ARPA Report No. DAHC 15-73-C-0127, 1975 (unpublished).

⁵Yu. P. Raizer, *Usp. Fiz. Nauk* **37**, 29 (1965) [*Sov. Phys. Usp.* **8**, 650 (1966)].

⁶N. Bloembergen, *IEEE J. Quantum Electron.* **QE-10**,

375 (1974).

⁷E. Yablonovitch and N. Bloembergen, *Phys. Rev. Lett.* **29**, 907 (1972).

⁸E. Yablonovitch, *Appl. Phys. Lett.* **19**, 495 (1971).

⁹D. W. Fradin, N. Bloembergen, and J. P. Lettelier, *Appl. Phys. Lett.* **22**, 635 (1973).

¹⁰D. W. Fradin, Harvard University Technical Report No. 643, 1973 (ONR-372-0012) (unpublished).

¹¹W. L. Smith, J. H. Bechtel, and N. Bloembergen, *Phys. Rev. B* **12**, 706 (1975).

¹²W. L. Smith, J. H. Bechtel, and N. Bloembergen, Harvard University Technical Report No. 665, 1976 (ARPA F 44620-75-C-0038) (unpublished).

¹³M. Bass and H. H. Barrett, *IEEE J. Quantum Electron.* **QE-8**, 338 (1971).

¹⁴M. Bass and H. H. Barrett, *Appl. Opt.* **12**, 690 (1973).

- ¹⁵M. Bass and D. W. Fradin, IEEE J. Quantum Electron. QE-9, 890 (1973).
- ¹⁶D. W. Fradin and M. Bass, Appl. Phys. Lett. 22, 206 (1973).
- ¹⁷D. W. Fradin, E. Yablonovitch, and M. Bass, Appl. Opt. 12, 700 (1973).
- ¹⁸N. L. Boling, P. Bräunlich, A. Schmid, and P. Kelly, Appl. Phys. Lett. 27, 191 (1975).
- ¹⁹P. Kelly, P. Bräunlich, and A. Schmid, Appl. Phys. Lett. 26, 223 (1975).
- ²⁰D. Milam, R. A. Bradbury, and R. H. Picard, Natl. Bur. Stand. (U.S.) Spec. Publ. 435, 347 (1976).
- ²¹R. Hellwarth, Natl. Bur. Stand. (U.S.) Spec. Publ. 341, 67 (1970).
- ²²R. P. Feynman, R. W. Hellwarth, C. K. Iddings, and P. M. Platzman, Phys. Rev. 127, 1004 (1962).
- ²³A. A. Klyukanov and E. P. Pokatilov, Zh. Eksp. Teor. Fiz. 60, 312 (1971) [Sov. Phys.-JETP 33, 170 (1971)].
- ²⁴N. I. Balmush, A. A. Klyukanov, and E. P. Pokatilov, Phys. Status Solidi B 67, 387 (1975).
- ²⁵J. Devreese, J. DeSitter, and M. Goovaerts, Phys. Rev. B 5, 2367 (1972).
- ²⁶E. P. Pokatilov and V. M. Fomin, Phys. Status Solidi B 73, 553 (1976).
- ²⁷V. L. Gurevich, I. G. Lang, and Yu. A. Firsov, Fiz. Tverd. Tela (Leningrad) 4, 1252 (1962) [Sov. Phys.-Solid State 4, 918 (1962)].
- ²⁸E. M. Conwell, Solid State Phys. Suppl. 9 (1967).
- ²⁹N. Allyasini and J. H. Parks, Natl. Bur. Stand. (U.S.) Spec. Publ. 435, 356 (1976).
- ³⁰A. Gold and H. B. Bebb, Phys. Rev. 143, 1 (1966).
- ³¹V. S. Dneprovskii, D. N. Klyshko, and A. N. Penin, JETP Lett. 3, 251 (1966).
- ³²D. Fröhlich and B. Stagninus, Phys. Rev. Lett. 19, 496 (1967).
- ³³S. Nakai and T. Sagawa, J. Phys. Soc. Jpn. 26, 1627 (1969).
- ³⁴Z. Ya. Evseev and K. B. Tolpygo, Fiz. Tverd. Tela (Leningrad) 10, 1678 (1968) [Sov. Phys.-Solid State 10, 1325 (1968)].
- ³⁵R. P. Lowndes and D. H. Martin, Proc. R. Soc. London Ser. A 308, 473 (1969).
- ³⁶F. C. Brown, in *Polarons and Excitons*, edited by C. G. Kuper and G. D. Whitfield (Oliver and Boyd, London, 1962), p. 323.
- ³⁷G. Raunio and S. Rolandson, Phys. Rev. B 2, 2098 (1970).
- ³⁸A. Schmid, Ph.D. thesis, Technical University of Vienna, 1975 (unpublished).
- ³⁹I. M. Catalano, A. Cingolani, and A. W. Minafra, Phys. Rev. B 5, 1629 (1972).
- ⁴⁰H. H. Li, J. Phys. Chem. Ref. Data 5, 329 (1976).
- ⁴¹J. S. Reid, T. Smith, and W. J. L. Buyers, Phys. Rev. B 1, 1833 (1970).

Addendum to
OPTICAL BREAKDOWN IN ALKALI HALIDES

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ABSTRACT

Damaged thresholds in NaCl are calculated for photon energies between 2 and 8 eV with pulse lengths in the nanosecond and picosecond regimes using our polaron model. It is assumed that breakdown can occur either at the temporal center of a (clipped gaussian) pulse or at its end. We conclude that changes in the refractive index (negative lensing effects) while much smaller at the end than at the center are still not negligible and must, like self-focusing effects, be carefully considered in threshold studies.

Efforts to elucidate the mechanism of intrinsic optical breakdown in nominally transparent materials have yielded different model descriptions, all of which appear to explain certain features of experimental observations. One of them, avalanche ionization, has been invoked for years as the basic process by which crystalline wide gap insulators fail during exposure to intense laser pulses at wavelengths from the far IR to the visible.⁽¹⁻¹⁹⁾ Free carriers, produced by electron impact ionization of the lattice constituents, facilitate deposition of laser beam energy to the lattice via inverse bremsstrahlung and electron-phonon collisions. Difficulties in explaining how conduction electrons can acquire sufficient kinetic energy from the photon field to launch an ionization avalanche led us to propose a somewhat different picture of laser damage.⁽²⁰⁾ In it multiphoton photocarrier generation replaces the avalanche process and the somewhat qualitative inverse bremsstrahlung mechanism, borrowed from the theory of photoionization of gases,⁽²¹⁾ is now specified to be free carrier absorption via electron-photon-phonon collisions,⁽²²⁾ the cross section of which was calculated for ionic insulators by Pokatilov and Fomin⁽²³⁾ both for optical and acoustical phonon scattering. Since in polar materials such as the alkali-halides the conduction electrons are strongly coupled to the lattice ions, it is appropriate to term them polarons rather than "free" electrons.

Even in purely covalent crystals "free" carrier absorption is the fundamental process of energy transfer from the photon field to the lattice. The lack of optical phonons in such materials for dressing "free" carriers does not prevent carrier interaction with acoustical

phonons. Consequently, a model⁽²⁰⁾ which incorporates this interaction correctly should not be rejected⁽²⁴⁾ simply because it applies the term polaron to electron-acoustical phonon interaction while the term's initial meaning was confined to the optical phonon interaction.⁽²⁰⁾

Crucial for comparison of experimental results with theoretical predictions is the precise definition of what exactly constitutes an irreversible modification of the material. It is now commonly accepted that rapid temperature pile-up during the laser pulse leads to phase transformations (e.g. local melting) and/or to shock waves resulting in rupture of the lattice structure.⁽²⁶⁾ Thus, for damage to occur, the lattice temperature in the interaction volume has to reach, during the duration of the laser pulse, a critical value which may be assumed to be close to the melting point. If we here disregard pre-breakdown material modifications, as discussed by Schmid et al.⁽²⁵⁾ and Kabler and Williams,⁽²⁷⁾ and remember that laser damage has been shown to be a threshold phenomenon,^(5,10,11) then a laser pulse of a certain minimum peak flux must exist for a given pulse length, wavelength and initial temperature, for which the critical temperature is reached (in a previously unexposed interaction volume of a pure and well annealed crystal) precisely at the end of this pulse.^(3,18) This minimum peak flux F_{bm} , or the equivalent peak rms optical field strength $E_{Bm} = \left(\frac{4\pi}{cn} F_{Bm} \right)^{\frac{1}{2}}$, is called the single-shot damage threshold⁽¹⁷⁾ (here n is the refractive index of the material, given by $n = n_0 + n_2 E^2 + n_3 (n_c)$, where n_0 is the linear, n_2 the nonlinear refractive index and n_3 the negative contribution to n due to "free" carriers n_c ⁽²⁰⁾).

It should be clear then that the measurement of damage thresholds requires not only the detection of irreversible material modification in a minute region of maximum local laser flux within the focal volume but that it also requires confirmation that the time of damage occurrence coincides with the end of the laser pulse.

Measurement of breakdown times in the nsec regime⁽⁹⁾ appeared to favor damage at the temporal center of the pulse; no damage was observed to occur toward its end. We feel now that this observation may be caused by the particular mode of damage detection chosen in those experiments, namely visible registration of hot sparks after the critical temperature was reached. The lack of breakdown toward the end of the pulse simply meant that insufficient photon energy remained available to heat the phase-transformed (damaged) region to hot, luminous plasma.

Experiments with psec pulses are further complicated because it is difficult to ascertain the time of damage occurrence. However, the observation of well-defined threshold damage behavior in alkali halides by Smith et al.^(10,11) may be taken as a strong indication that, according to the definition of F_{Bm} , failure must have occurred very close to the end of the pulse.⁽²⁸⁾ In these experiments damage was diagnosed via the appearance of small localized breakdown vestiges rather than the occurrence of visible sparks.

The so-called "polaron breakdown mechanism" was discussed by Schmid et al.⁽²⁰⁾ to demonstrate that the development of an electron avalanche may not be a necessary condition for optical breakdown of wide-gap materials. Being unaware of Smith's deductions concerning the time

of damage occurrence in his psec experiments, they chose, for the sake of simplicity, the time of failure to coincide with the temporal center of the pulse, in accord with earlier observations in the nsec regime. (9)

Considering breakdown at the end of the pulse would only be a trivial extension of these calculations. However, as Smith⁽²⁸⁾ pointed out, several conclusions concerning beam deformation via n_3 -contributions to the refractive index may have to be revised because F_{Bm} or E_{Bm} are expected to be considerably smaller compared to the values F_B and E_B obtained for breakdown in the middle of the pulse. In addition, since n_c is now likely to be large only toward the end of the pulse, the conversion of F_{Bm} to E_{Bm} , or vice versa, may be less affected by the associated (smaller) change in the refractive index. It is the purpose of this paper to present calculated values of E_{Bm} together with n_3 for a variety of laser wavelengths and pulse lengths in order to examine these points.

Aside from minor changes in the code to economize computations, the same physical model as in ref. (20) was used. However, we choose a more realistic temporal pulse shape to replace the original $\sin^2(\pi t/t_p)$ -form (t_p is the total length of the pulse). A Gaussian temporal flux profile is used which has been clipped at its $1/e^3$ -value:

$$F(t) = F_0 \exp \left[- \ln 16 \left(\frac{t}{\tau_p} - \frac{3}{\sqrt{\ln 10}} \right)^2 \right], \quad (1)$$

where τ_p is the full width at half maximum (extension of the pulse even further out into the wings does not significantly alter the results). Thus, direct comparison with previous calculations⁽²⁰⁾ is not immediately

possible. Damage thresholds E_B and E_{Bm} in NaCl were calculated for pulses having a FWHM between 30 psec and 30 nsec and photon frequencies corresponding to the Xenon eximer and the ruby laser together with the doubled ruby and doubled Nd laser frequencies (Fig. 1).

The relative changes of the refractive index at the center of the pulse are listed in Table 1 for breakdown occurrence at the center as well as at the end. The negative contribution n_3 dominates n_2E^2 , however, as expected by Smith,⁽²⁸⁾ it is considerably smaller if one considers failure at the end. Nevertheless, given a Gaussian spatial beam profile, negative lensing effects are still not completely negligible and must be carefully considered in addition to the smaller positive (self-focusing) contributions. We re-emphasize at this point that all our calculations assume a local flux to be present irrespective of whether it is the result of self-focusing or any other beam-forming mechanism. Computer simulations of the complete spatio-temporal problem are presently in progress.⁽²⁹⁾

TABLE I

Relative change of refractive index $\frac{n_o - n(t_p/2)}{n_o}$ (in percent) at the peak of
a damaging pulse for different pulse lengths

Laser Frequency	30 nsec		3 nsec		300 psec		30 psec	
Xe	1.10	0.42	2.31	0.89	4.47	1.8	7.78	3.80
2 R ₂	0.50	0.19	1.58	0.44	4.68	1.33	13.1	4.05
2 Nd	0.38	0.13	1.48	0.32	5.74	1.35	19.0	5.16
Rb	0.58	0.13	2.47	0.52	10.4	2.20	28.3	9.48

The left column for each pulse length refers to breakdown at the temporal center of the pulse and the right column to damage occurrence at the end of the pulse.

REFERENCES

- (1) G. M. Zverev, T. N. Mikhailova, V. A. Pashkov, and N. M. Soloveva, Zh. Eksp. Teor. Fiz. 53, 1849 (1967) [Sov. Phys. JETP 26, 1053 (1968)].
- (2) L. H. Holway and D. W. Fradin, J. Appl. Phys. 46, 279 (1975).
- (3) P. Bräunlich, A. Schmid, and P. Kelly, Appl. Phys. Lett. 26, 150 (1975).
- (4) M. Sparks, ARPA Report No. DAHC 15-73-C-0127, 1975 (unpublished).
- (5) N. Bloembergen, IEEE J. Quantum Electron. QE-10, 375 (1974).
- (6) E. Yablonovitch and N. Bloembergen, Phys. Rev. Lett. 29, 907 (1972).
- (7) E. Yablonovitch, Appl. Phys. Lett. 19, 495 (1971).
- (8) D. W. Fradin, N. Bloembergen, and J. P. Lettelier, Appl. Phys. Lett. 22, 635 (1973).
- (9) D. W. Fradin, Harvard University Technical Report No. 643, 1973 (ONR-372-0012) (unpublished).
- (10) W. L. Smith, J. H. Bechtel, and N. Bloembergen, Phys. Rev. B 12, 706 (1975).
- (11) W. L. Smith, J. H. Bechtel, and N. Bloembergen, Harvard University Technical Report No. 665, 1976 (ARPA F 44620-75-C-0088 (unpublished)).
- (12) M. Bass and H. H. Barrett, IEEE J. Quantum Electron. QE-8, 338 (1971).
- (13) M. Bass and H. H. Barrett, Appl. Opt. 12, 690 (1973).
- (14) M. Bass and D. W. Fradin, IEEE J. Quantum Electron. QE-9, 890 (1973).
- (15) D. W. Fradin and M. Bass, Appl. Phys. Lett. 22, 206 (1973).
- (16) D. W. Fradin, E. Yablonovitch, and M. Bass, Appl. Opt. 12, 700 (1973).
- (17) N. L. Boling, P. Bräunlich, A. Schmid, and P. Kelly, Appl. Phys. Lett. 27, 191 (1975).
- (18) P. Kelly, P. Bräunlich, and A. Schmid, Appl. Phys. Lett. 26, 223 (1975).
- (19) D. Milan, R. A. Bradbury, and R. H. Picard, Natl. Bur. Stand. (U.S.) Spec. Publ. 435, 347 (1976).
- (20) A. Schmid, P. Kelly, P. Bräunlich, Phys. Rev. B 16, 4569 (1978).
- (21) Yu. P. Raizer, Usp. Fiz. Nauk 87, 29 (1965) [Sov. Phys. Usp. 8, 650 (1966)].

- (22) R. Hellwarth, Natl. Bur. Stand. (U.S.) Spec. Publ. 341, 67 (1970).
- (23) E. P. Pokatilov and V. M. Fomin, Phys. Status Solidi B 73, 553 (1976).
- (24) P. Liu, R. Yen, and N. Bloembergen, IEEE, QE-14, 574 (1978).
- (25) A. Schmid, P. Bräunlich, P. Rol, Phys. Rev. Lett. 35, 1382 (1975).
- (26) S. I. Zakharov, Yu. N. Lokhov, and Yu. D. Fifeiskii, Sov. Phys. Dokl. 19, 779 (1975).
S. I. Zakharov, Sov. Phys. JETP 44, 978 (1976).
- (27) M. N. Kabler, R. T. Williams, private communication
- (28) W. L. Smith, private communication
- (29) P. Kelly, D. Ritchie, P. Bräunlich, A. Schmid, Symposium on Optical Materials (Laser Damage Symposium), Boulder, Colorado, Sept. 1978 (to be published).

Fig. 1. Breakdown field strength of 30 psec laser pulses in NaCl vs. photon wavelength once for breakdown at temporal center of Gaussian pulse (dotted data points) and once at temporal final clipping point (crossed data points).

COLOR CENTER PROCESSES ON NaCl SURFACES AFTER ELECTRON BOMBARDMENT
OR EXPOSURE TO INTENSE PHOTON BEAMS

INTRODUCTION

Halide crystals, and in particular alkali halides, exhibit unique and characteristic properties when exposed to ionizing radiation. In contrast to other ionic materials, efficient production of structural defects occurs at kinetic energies of the incident particles down to less than 13 eV for charged particles¹ and 2 eV for photons.² The generation of excitons (electron-hole pairs) has been established as the fundamental process for the production of V_k , F, and H centers.³ Through a number of secondary reactions involving electron release (or trapping) and migration of primary centers, aggregate centers of the type F_2^+ , M, M', I, etc. may be produced as well.⁴

This extraordinary low stability to radiation poses a considerable problem in attempts to study the surface properties of halides. It prevents the use of any of the modern UHV techniques such as Auger Electron Spectroscopy (AES), Secondary Ion Mass Spectroscopy (SIMS), Electron Spectroscopy for Chemical Analysis (ESCA), Low Energy Electron Diffraction (LEED), etc. All of these employ probing beams having kinetic energies far in excess of the threshold energy for e-h pair production. In the process, efficient emission of halide atoms is observed. This effect is referred to as sputtering.

Sputtering of halide surfaces with electron beams¹ or intense photon (laser) beams² severely alters the exposed material. Not only is the crystal-line structure distorted but the stoichiometric composition is changed as well.

In most cases the material becomes alkali rich after e-beam sputtering since halogen atoms are the main sputtering products. This enrichment of the surface with alkali metal during electron sputtering has been identified as the rate-limiting process for sputtering of alkali halides.⁵ At elevated temperatures (e.g. above 450 K in NaCl), the produced layer of alkali metal is expected to desorb, resulting in greatly enhanced sputtering yields.¹

Photon sputtering (or photochemical surface decomposition) requires intense fluxes because the mechanism of e-h pair production is a multiphoton absorption process at the wavelengths used in our investigation (6934 Å or 3472 Å). In order to produce the same sputtering yield, a comparably much smaller flux is required at the doubled ruby frequency as compared to the flux at the ruby frequency, where we have established the process to be of fourth order.² The sample temperature turned out to be less critical for the sputtering yield at 6943 Å. An Na-enriched surface layer apparently evaporated easily during exposure of the sample to a pulse from the Q-switched Rb-laser. This is not so at 3472 Å, where Na tends to accumulate at laser peak fluxes sufficient for Cl-removal from the surface. It should be emphasized that in both cases photochemical surface decomposition is observed at fluxes considerably lower than the one-shot surface damage threshold.

Sputtered surfaces are obviously not in thermodynamic equilibrium because of their non-stoichiometric composition. Characterization of this non-equilibrium state is extremely difficult because of the reasons stated above. Yet, a grossly distorted or perturbed surface is expected to behave not like a "theoretically" clean one as far as its susceptibility to damage by photon pulses is concerned.

The problem of characterizing the degree of perturbation of such a photon-sputtered surface can be investigated in two ways:

- a) The single-shot damage threshold of a previously perturbed surface can be measured. This can conveniently be done, e.g., by measuring the total sputtering yield of a number of $N-1$ pulses of fixed spatio-temporal properties. Assume the N th pulse produces damage. The total sputtering yield is a measure of the "degree of perturbation" and the N th shot is equivalent to a single shot producing damage of this perturbed surface. Such experiments are presently in progress in our laboratory.
- b) We have shown that the method of thermally stimulated exoemission of particles provides a sensitive means of assessing the degree of perturbation of a halide surface.

This part of the report is concerned with a description of this new method.

For convenience we have performed all our experiments with e-beam sputtered surfaces instead of using photon pulses. The method is independent of how the surface was perturbed and, therefore, all results obtained are relevant for laser-perturbed halide surfaces as well. Clearly, in a further step actual laser-exposed surfaces have to be used and many engineering aspects (e.g. methods of preparing the optical surface before laser exposure, or whether and how a halide-substrate dielectric coating interface is perturbed by photochemical decomposition etc.) have to be investigated. At this point we will concentrate only on thermally stimulated exoemission of particles as a new potentially useful tool to characterize sputtered halide surfaces. NaCl is chosen as an example.

The formation of primary defects (color centers) has been established to occur according to the following reactions^{1,6}:

(1) Energy absorption $\rightarrow$ excitons (e-h pairs)

(2) hole self-trapping $\rightarrow V_k$ center

(3) trapping of an electron by a V_k center $\rightarrow$ F-H pair

Step three has been shown to be very fast (several picoseconds) and highly competitive with two other possible channels of energy deposition during electron trapping by a V_k center, namely luminescence or heat generation.⁶

While the formed F center may be stable up to 500 K in NaCl, the H center (a Cl interstitial) moves quickly to the surface or recombines with an F center above 70 K. V_k centers⁴ (Cl_2^- molecules, occupying two Cl lattice sites in the $\langle 110 \rangle$ direction) are known to decompose at about 165 K, with an activation energy of 0.27 eV.¹ This process may be considered as thermal release of the self-trapped hole. Continued re-trapping and release of holes can be considered V_k center migration.

Emission of halogen atoms has been identified as the most efficient mode of sputtering. Sputtering of halogen molecules or halogen ions occurs with vastly lower efficiency.⁷ The emission of atomic halogen during electron bombardment has been explained as the result of a replacement collision sequence.^{1,8,9} V_k centers, recombining with electrons, are believed to be able to impart sufficient kinetic energy to a neighbor Cl^- ion along a $\langle 110 \rangle$ direction to leave a vacancy (F center). The observation of strong atomic halogen emission in other directions (notably $\langle 211 \rangle$) has recently led us to believe that such a sequence may consist of only one step.^{2,10} On the surface, an arriving or freshly formed V_k center simply decomposes into a regular Cl^- ion bound to the lattice and a surplus Cl atom which can be emitted. The kinetic energy of the ejected Cl atom is so small that this process may be considered a desorption.⁷ The emission is, however,

directional because the Cl_2^- molecule (V_k center) decomposes along its bonding direction. Apparently it is not only oriented in a $\langle 110 \rangle$ direction but, on the surface, it may possibly be found also in $\langle 211 \rangle$ directions.²

Similar considerations are valid for H-centers (Cl_2^- molecules occupying only one lattice site). These may also be oriented not only along $\langle 110 \rangle$ directions, expected to be the case in the bulk, but also along $\langle 211 \rangle$ directions on the surface. However, their decomposition, again strongly directional, yields far larger kinetic energies (up to 1.3 eV).⁷

After formation of the primary defects F, H, and V_k , secondary defects can be produced upon continuing irradiation of the material. For example, F-centers may form clusters starting with F_2 (called an M center), F_3 etc. Similarly, the F-H pair production in the surface layers may form interstitial H-center clusters or H-centers close to other structural defects.³ While the uppermost surface layer may consist entirely of metallic alkali after sputtering, at a temperature below the alkali desorption temperature, rapid migration of H-centers above 70 K can deplete a layer that may be several lattice distances thick, leaving surplus alkali metal behind. This metal will migrate toward the surface only above a certain temperature and then evaporate. Although this temperature may be below the Na-desorption temperature, strong Na-gradients may prevent sodium migration until the surface overlayer starts to evaporate.

The recent discoveries of directional emission of halogen atoms during laser or e-beam sputtering, together with new insight in the mechanism of primary defect formation prompted us to re-investigate the complex questions concerning the origin of thermally stimulated exoelectron emission after bombarding a halide with ionizing radiation. Except for

Brunsmann and Scharmann¹¹ and Krylova,^{12,13} none of the workers in this field had ever searched for emission of particles other than electrons. On the other hand, clear correlation e.g. with the annealing temperature of the V_k center and the appearance of a characteristic exoemission peak at about 165 K has led Bichevin and Kämbre¹⁴ to conclude that electrons are emitted in a process that involves the release of a self-trapped hole. They believe that this in turn recombines with a trapped electron and, in an Auger transition, imparts the energy to a surface electron trap which releases the electron into the vacuum.

The formation of alkali rich surface layers had led us to expect that a pronounced Na desorption peak must be observed during a programmed increase with time of the sample temperature. Also, we expected that V_k center annealing (or migration) should yield atomic chlorine emission during the appearance of the V_k center exoemission peak.

In order to study these aspects, we have investigated the emission of particles (electrons, neutrals, and ions) from NaCl during the thermal anneal of the disturbed surface layer to equilibrium with the bulk. While we observed a number of still unexplained emission phenomena, we were able to prove, for the first time, that V_k center annealing can lead to atomic chlorine emission and that indeed a metallic Na layer is formed which evaporates at about 400 K. At the same time, we confirmed that all of the observed emission peaks are accompanied by the simultaneous emission of exoelectrons.

It is the purpose of this paper to report the experimental results and to attempt an explanation for a number of the measured emission peaks. Additional techniques used to gain information were Auger Electron

Spectroscopy and Cl_2 dosing. The first, applied to halide surfaces, may be more appropriately termed chemical analysis of the surface during steady-state sputtering. This steady-state situation was investigated during a slowly increasing sample temperature up to 600 K. Dosing the sample with Cl_2 molecules after sputtering at liquid nitrogen temperature permitted us to study a sputtered surface on which the exposed Na layer had reacted with chlorine. At the same time, we made use of the fact that the exothermic reaction between metallic sodium and chlorine gas yields readily detectable emission of electrons with an efficiency of about 10^{-6} per reaction.⁵ We propose that a V_k center arriving at the surface via migration can react with an excess Na atom and may lead to emission of an exoelectron. This provides an explanation for the observed electron emission during V_k center annealing and other processes that involve the migration of interstitial chlorine or sodium to the surface. We further propose that this electron emission could be used as a monitor of the migration of other highly reactive species in similar situations.

EXPERIMENTAL

The experiments were carried out at 10^{-7} Pa. (10^{-9} Torr) in a UHV system equipped with a quadrupole mass spectrometer and an Auger cylindrical mirror analyzer.⁶ In addition, we added a Channeltron electron multiplier for detection of charged particles with coils for magnetic discrimination between electrons and negative ions.¹⁷ These coils, by providing crossed E and B fields, sufficiently alter the trajectory of electrons to deflect them from the channeltron detector. Negative ions are not as readily deflected and thus are detected. Calibration of the discrimination

efficiency indicated that an upper limit of 2% of the electron emission may be detected when electrons are deflected out.

The (100) NaCl crystal ($1 \text{ mm} \times 36 \text{ mm}^2$, Harshaw Laser grade) was clamped to a 0.5 mm thick piece of tantalum that was cooled conductively to 100 K and heated resistively. A W-5% Re/W-26% Re thermocouple was attached to the Ta base directly beneath the NaCl crystal. Its contact with the sample assured that we were measuring the sample temperature within reasonable error. For the particle emission experiments, the sample was bombarded with 1.5 KeV electrons using a defocussed beam from the Auger electron gun. A standard dose consisted of 1 μA electron current to the sample face for a time of one minute. The sample was then heated at a linear rate of 0.5 K/second while the particle emission was monitored as a function of sample temperature. For the experiments concerning the temperature dependence of the Auger spectra, the sample was necessarily bombarded continuously with a focussed electron beam while the sample was heated as described.

Due to the complicated peak structure, activation energies were determined as follows: the emission intensity was recorded at increased sensitivity as a function of sample temperature during the portion of the emission where the initial rise of the curve takes place. The sample was then cooled and the process repeated. The natural log of the intensity was then plotted as a function of inverse temperature in an Arrhenius plot. For a process with kinetics given by $\dot{n} = f(n) \exp(-E_a/kT)$, the slope of such a plot yields the activation energy. This is referred to as the method of initial rise.

RESULTS

Figure 12 shows the emission of all observed particles following electron bombardment at 100 K. The curves are plotted so that the total negatively charged emission and the ion emission are to the same scale; however, the neutral sodium emission is not to scale. In addition to the well-studied thermally-stimulated exoelectron emission (TSEE),¹⁸ we have observed thermally-stimulated emission of negative Cl ions and neutral Na. No positive ions or other neutral particle species were observed for temperatures less than 650 K.

Emission Following Electron Bombardment

The large peak at 165 K, labeled e_1 , dominates the thermally-stimulated exoemission spectra.^c The intensity of this peak is approximately twenty times the intensity of the smaller peaks shown at 200 K and 240 K. Emission during this peak consists primarily of electrons, although negative ions cannot be ruled out entirely. Approximately 5% of all charged particles emitted at this temperature were found to be ions. It has been well documented that this peak corresponds to the decomposition of V_k color centers.¹⁹ The activation energy we obtain is 0.29 eV, which is in good agreement with the value of 0.27 given by Townsend et al.¹

At 200 K and 240 K we observe two small TSEE peaks. The first is composed entirely of electrons, and is denoted as e_2 . Approximately 30% of the negative particles emitted during the occurrence of the second (labeled c_1)

^cPeak labeling follows this procedure:

e denotes peaks that are due to electron emission.

c denotes peaks that have significant ion emission components.

Na denotes the neutral Na peak.

The peaks are numbered in order of increasing peak temperature.

Fig. 12. Thermally stimulated emission of neutral and negatively charged particles following electron bombardment at 100 K.

are ions. Due to their small size, their activation energies cannot be as reliably determined as for the stronger peaks. The same value, 0.14 ± 0.10 eV, was obtained for both e_2 and c_1 . No successful correlation of the e_2 peak with any color center decomposition has been made in the thermoluminescence or thermally-stimulated exoelectron literature. A TL peak that is similar to our c_1 peak has been attributed to the decomposition of M' color centers.²⁰

At 300 K an unusually broad peak (labeled c_2) appears, which consists of equal parts negative ions and electrons. The activation energy for the c_2 peak was determined to be 0.75 eV by the method of initial rise. Ion emission has not been observed before, although Brunsmann and Scharmann¹¹ could not exclude negative ion emission from NaF at temperatures corresponding to this peak by the Molwo-Ivey relation.²¹

An additional small peak, not resolved in Fig. 12, was sometimes observed at 340 K. Its existence was, however, confirmed by its behavior in the experiments to determine activation energies by the initial rise method. The binding state corresponding to this peak was observed to refill, after a small increase in temperature and subsequent cooling, in contrast to all the other binding states. Its activation energy was determined to be 0.85 eV. Some controversy exists in the TL and TSEE literature as to assignment of this peak to color center decomposition. It has been attributed to the decomposition of V_f color centers,¹⁴ as well as to the decomposition of F' centers.²⁰

Neutral Na was observed to desorb in a single first order flash desorption peak at 405 K, with an activation energy of 1.01 eV. This is in good agreement with the value of 1.07 eV calculated by Jammal and Townsend for ionic desorption of Na from a metallic Na surface,⁵ a value that is also close to the heat of formation (1.12 eV) of gaseous Na from metallic Na.²²

A strong emission peak, consisting of 90% electrons and 10% negative ions, occurred at 500 K. Its shape and the increase of the peak temperature

with electron bombardment time indicates a zero order emission process. The activation energy was determined to be 1.4 eV. This appears to be due to a bulk effect rather than a surface effect, in that the peak did not saturate with electron bombardment as did the surface related peaks (e_2 , c_1 , c_2). The e_3 peak also did not anneal directly during the thermal scan, but became negligible only after 15 minutes at 550 K. No successful correlation of this peak with color center migration or ionic conductivity effects was possible.

TSEE Following Electron Bombardment and Cl_2 Adsorption

To test the hypothesis that some of the emission is due to excess Na or surface defects created by the preferential sputtering of Cl during electron bombardment of the crystal, the crystal was dosed with Cl_2 gas after the electron bombardment and before thermal stimulation. The adsorbed Cl was expected to bond to the excess Na and possibly neutralize certain kinds of surface defects (e.g. Cl^- vacancies). The results of these experiments are shown in Fig. 13. The Cl_2 dose was approximately 5×10^{-6} Torr seconds. It is interesting to note that during the dose, intense chemi-emission of electrons was observed, which, according to Kasemo and Wallden is due to recombination of Cl with the excess Na.¹⁵ This emission continued for approximately the time needed for monolayer coverage.

The thermally-stimulated charged particle emission peak e_1 (165 K) was not affected by this dose, although the emission of neutral atomic Cl was observed at this temperature. Molecular Cl_2 (mass 70) was observed in a single peak at about 110 K which is interpreted as arising from a condensed layer of Cl_2 . However, atomic Cl (mass 35) emission was resolved into two peaks in this region. One peak corresponds to the cracking fraction (approximately 40%) of the Cl_2 observed at 110 K, the other to the e_1 peak (165 K).

Fig. 13. Thermally stimulated emission of neutral and negatively charged particles following electron bombardment and Cl_2 dose at 100 K.

This is direct evidence that the decomposition of V_k centers on or near to the surface produces emission of atomic Cl.

The emission peaks e_2 (200 K) and c_1 (240 K) were practically eliminated by the adsorption of Cl_2 . This implies that a necessary step for this emission is passivated by the adsorption of Cl. The ion emission peak at 300 K (peak c_2) did not change appreciably, while the electron emission approximately doubled. We also observed emission of atomic Cl at this temperature.

The neutral Na emission at 405 K was almost entirely removed by exposure to chlorine. This suggests that the adsorbed Cl reacts with the excess Na produced by electron bombardment, thus making the sodium unavailable for thermal desorption. The emission that remained may also indicate that interstitial Na has diffused to the surface during the heating of the sample to 400 K.

The 500 K emission peak e_3 is dramatically changed by the Cl_2 dose. The ion component increases by a factor of ten while the electron component remains at about the previous emission level observed without Cl_2 dose. A summary of the particle emission data is presented in Table 2.

Temperature Dependence of Auger Emission

The surface composition was studied as a function of sample temperature by Auger Electron Spectroscopy. The ratio of the major Na Auger peak (990 eV) to the Cl Auger peak (181 eV) for temperatures above 550 K indicated that the ratio of Na to Cl in the surface layers was 1:1.²³ Using this assumption the traces of the Na and Cl Auger peak height curves are shown in Fig. 14. It should be noted that the experiments were necessarily done under continuous electron bombardment, therefore the curves represent steady-state concentrations of the elements while sputtering, rather than a direct thermally-stimulated annealing process as discussed previously.

TABLE 2

Characteristics of Thermally Stimulated Emission from NaCl

Peak Label	Peak Temperature	Activation Energy	Composition	Effect of the Cl ₂ Dose
e ₁	165 K	0.29 eV	95% e ⁻ (5% Ion ⁻)*	No change in charged particle emission, atomic Cl emission observed.
e ₂	200 K	(0.14 eV)*	100% e ⁻	Removed.
c ₁	240 K	(0.14 eV)*	70% e ⁻ 30% Ion ⁻	Removed.
c ₂	300 K	0.75 eV	50% e ⁻ 50% Ion ⁻	Ion emission remains the same, electron emission doubles, atomic Cl emission observed.
	340 K	0.85 eV	(100% e ⁻)*	
Na	405 eV	1.01 eV	Na	Removed.
e ₃	500 K	1.4 eV	90% e ⁻ (10% Ion ⁻)*	Ion emission increases from 10% of total emission to 50%, electron emission remains the same.

*Data shown in parenthesis are less certain.

Fig. 14. Temperature dependence of the Auger peak-peak heights for Na and Cl. The relevant particle emission curves from Fig. 1 are shown for comparison to the Auger peak height curves.

For temperatures between 100 K and 220 K the surface concentrations remain roughly constant but the surface is Na rich. From 220 K to 310 K, the Cl peak is seen to decrease in two steps at 220 K and 275 K. As the Auger peak height is proportional to the relative concentrations in the surface layers, the negative derivative of the peak height is proportional to the loss of that element from the surface. The drop in the Cl peak height correlates well with the observed ion emission (shown in Fig. 3, for reference), thus indicating that the observed negative ion emission is a Cl species and also that a new channel in addition to V_k decomposition for Cl loss from the surface has been added at these temperatures. Above 400 K the desorption of Na is also indicated. The correlation between the observed emission peaks and the Auger curves is excellent.

These points are further illustrated in Fig. 15 where we have plotted the ratio of the Na:Cl Auger peak heights. It is easily observed that at temperatures below 450 K the surface composition of the NaCl during electron bombardment is Na rich. The exact composition is difficult to determine by Auger spectroscopy as the sampling depth is larger for the 990 eV Na line than the 181 eV Cl line. It is known however that the majority of the Auger signal comes from the first 2-3 atomic layers even for the 990 eV Na signal.²⁴ On the assumption that the Auger signal originates in the first two atomic layers of the NaCl crystal, the surface composition may be determined as follows. In the temperature range from 100 K to 240 K a ratio of 3Na:2Cl is indicated. This may be due to a 2Na:1Cl in the surface layer, caused by the sputtering of Cl by electron bombardment, covering the next atomic layer which is of the usual 1Na:1Cl composition. In the temperature range 330 K to 380 K the composition ratio is approximately 2Na:1Cl. In the same manner, this may be attributed to a monolayer coverage of Na above the NaCl lattice, due to

Fig. 15. Temperature dependence of the Na:Cl ratio on the surface as indicated by the Auger peak heights. The relevant particle emission curves are shown for comparison.

the emission of Cl ions from the previously 2Na:1Cl surface layer. As the temperature increases above 400 K the surface composition is seen to return to the nominal 1Na:1Cl composition.

DISCUSSION

As already mentioned in the introduction, one of the direct consequences of exposing NaCl to ionizing radiation is the formation of V_k centers. These may capture free electrons and as a result, F centers and H centers are formed.⁶ H center and V_k center migration to and/or decomposition on the surface is the source of atomic Cl emission observed during sputtering. If the electron bombardment occurs below the temperature at which V_k centers become mobile, only those produced directly at the surface will contribute to Cl emission.^{2,6} Others may not capture electrons and, thus, remain immobilized in the surface layer effected by the electron beam. Sputtering at 100 K will leave this surface layer in a condition which will be characterized in more detail below.

Most F centers formed during sputtering will have captured one of the electrons available during electron beam exposure to form F' centers. Heavy bombardment may have produced M centers or similar aggregates, again converted to M' centers by electron capture.

Most V_k centers have been converted to F-H pairs and their products. However a measurable concentration of these V_k centers remain and is long lived after sputtering, because now no free electrons are available for capture. These are the origin of the 165 K emission peak (e_1) observed during thermal stimulation. The identification of this peak with V_k center annealing is possible by correlating our results with experimental evidence provided by independent TSEE measurements¹⁴ and bleaching of the V_k adsorption band.¹⁹ An activation energy of 0.27 eV has been found to be necessary for V_k center

migration by Townsend et al.¹ Our value of 0.29 eV, determined by the initial rise method, is in good agreement with this result. V_k centers arriving at a non-sodium rich surface will then yield atomic Cl emission just as we observed after Cl_2 dosing which was carried out to convert the metallic Na overlayer to NaCl. The mechanism of electron as well as Cl^- emission during V_k center migration and annealing remains to be discussed. We propose that the following reactions may occur:

- i) When the V_k arrives at the surface where there is some metallic Na, it will react via

This is an exothermic reaction which may provide electron emission, and possibly even Cl^- emission due to the energy released. In fact, Kasemo and Wallden¹⁵ have observed up to 10^{-5} electrons per reaction for

which is less exothermic than (3). Another possible reaction is:

The F' center is expected to be the most prevalent of the vacancy centers on the surface at this temperature. Reaction (5) is also expected to be exothermic, and provides a direct mechanism for electron release.

- ii) When a V_k center arrives at a surface that has been dosed with Cl_2 , reaction (3) is no longer considered probable because the Cl_2 dose has converted the Na overlayer to

NaCl. However, the Cl_2 dose is not expected to passivate the F' surface center due to its relatively high negative charge concentration. Thus, reaction (5) must still be considered probable. This is supported by the observation that the emission of electrons at 165 K remains relatively unchanged after Cl_2 exposure.

Our observation of thermally-stimulated emission of atomic Cl from NaCl surfaces following Cl_2 dosing provides direct experimental evidence that the decomposition of V_k centers on the surface is indeed one of mechanisms for halogen emission observed during electron beam and laser sputtering of alkali halides. As mentioned before, the presence of a metallic alkali overlayer at temperatures below the alkali desorption temperature prevents atomic halogen emission because of the chemical reaction between the two species. Thus in our case, the necessary condition for the observation of Cl emission during V_k center annealing is to passivate the highly reactive alkali metal layer on the surface.

Before we attempt to shed some light on the mechanisms responsible for some of the other emission peaks and on the temperature dependence of the Auger signal, we point out that the curves shown in Figs. 12-14 represent results obtained under different conditions. While the same basic mechanisms--e.g. color center annealing, release or capture of electrons from some of these centers, etc.--occur in all three of these different situations, we point out that the first two curves are obtained after the formation of e-h pairs, while the Auger spectrum is measured during ongoing e-h pair production. Both types of experiments must, however, be influenced by the possibility of color center annealing at various temperatures. In addition, particle emission before and after Cl_2 dosing must be affected by the differences in the properties of the surface layers. To turn the argument

around, the differences may then be used as an indication of the properties of these layers.

As we have shown, the metallic alkali layer may simply be desorbed by heating the sputtered sample to the appropriate desorption temperature. In our case, Cl_2 dosing the sample below this temperature and after sputtering converts this layer to NaCl which is expected to be of a non-crystalline or at least a rather imperfect nature. Impurities are not expected to play a major role because of the low residual gas pressure in the UHV system. For example, formation of NaOH in the presence of water vapor is unlikely. However, surplus chlorine is most likely present after dosing with Cl_2 . This is indicated by the observed Cl_2 desorption. The presence of atomic Cl weakly bound in the surface layers is also possible. This is in sharp contrast to the chlorine deficient outer layers produced during low temperature electron beam sputtering.

During the temperature scan used in the particle emission experiments, both of these layers are, therefore, expected to behave differently despite the fact that in both similar color center migration and annealing processes occur. The difference in the concentrations of Na and Cl and, thus, also in the reactions involving the defect centers are expected to produce the observed characteristic differences in the nature of the emitted particles.

We have attempted to interpret the particle emission peaks and the changes in the Auger signals on the basis of well known color center annealing characteristics and on those qualitative differences in the surface layers. No correlation of the e_2 peak with color center decomposition has been offered by the TL and TSEE literature. The c_1 peak at 240 K has been identified as due to the decomposition of M' color centers.²⁰

There are two possible routes for this decomposition,

and also, because α center migration is observed to begin in the temperature range 200 K - 250 K,

It is noted that the migration of α centers to the surface and subsequent reaction as in Eq. (7) implies a mechanism for Cl removal from the surface as indicated by the Auger temperature dependence (Fig. 14). Also, the final migration step bringing the α center to the M' center will transfer a Cl ion to an electrostatically more stable bonding position which will yield energy of up to 7.9 eV.²⁶ It will, therefore, provide a possible mechanism for the observed ion emission through this energy release by exciting a nearby Cl ion into an antibonding state.

F' centers are more stable thermally than M' centers. The reaction:

is known to occur around 300 K in NaCl.⁴ Similar to the mechanism suggested for M' centers, this implies a second route for Cl loss from the surface layers as indicated in the Auger curves (Fig. 14). The charge distribution near an F' center is even more negative than near the M' center. The energy released by the Cl^- rebonding at the final α center migration step should thus be at least as large, and similarly provide a mechanism for the observed ion emission.

The surface composition of the sputtered NaCl is changed by Cl_2 dosing. Following electron bombardment it is observed that there is an excess Na overlayer (Fig. 14). The Cl_2 dose changes the surface composition to having an excess of Cl. Bonding of Cl_2 to Na has been proposed by Kasemo and Wallden¹⁵ and is also indicated by our results. As the F' center is highly negatively charged with respect to the lattice it is expected that this surface center may not

be affected by the adsorption of Cl. This appears to be supported by our data, in that the c_2 emission was not decreased by the Cl_2 dose. The additional emission of atomic Cl is another possible route of energy release which is probable only when there is an excess of surface Cl. The M' center has less negative charge to distribute among its nearest neighbors. Thus, it is plausible that this center is passivated by the adsorption of Cl_2 whereas the F' center is not.

The assignment of the exoemission peak at 340 K to color center decomposition is somewhat controversial. Scaramelli has studied this peak by correlating optical adsorption and photostimulated thermoluminescence.²⁰ She concludes that the peak at 340 K in NaCl is due to the annealing of F' color centers, through

with an activation energy of 0.91 ± 0.06 eV. Bichevin and Käämbre have studied the same peak by TSEE and have concluded that it may be due to the annealing of V_f color centers.¹⁴ As a V_f color center is a Na^+ vacancy in the lattice, the deciding point of this controversy is that the activation energy for Na^+ vacancy motion has been measured by ionic conductivity experiments as 0.65 ± 0.01 eV.²⁵ In contrast to this, the activation energy we observe for this peak is 0.85 ± 0.05 eV, which is in agreement with the value of 0.91 ± 0.06 eV for electron release from F' centers. Therefore, the interpretation that this peak is due to the decomposition of F' color centers is favored on the basis of this work.

Another prevalent annealing process takes place at around 500 K at which F centers start to become mobile and either form aggregates or diffuse into the bulk.²⁷ This process is equivalent to Cl diffusion from the bulk into the surface layer, where it is expected to react, and release energy in

a manner similar to the mechanism that was mentioned for M' center decomposition. This, again, may produce the observed electron and ion emission.

It is important to note that all four of these migration processes are manifested as structure in the steady-state Auger chlorine and sodium signals (Figs. 14,15).

An additional feature of the presented emission curves is the thermal desorption of Na, observed in a first order peak at 405 K. The temperature dependence of the Auger spectra also confirms this and indicates that at temperatures below 400 K a metallic Na overlayer is formed. The observed activation energy of 1.01 eV is in fair agreement with the value of 1.07 eV calculated by Jammal and Townsend for ionic desorption of Na from a Na metallic surface.⁵ This is also near the heat of formation (1.12 eV) for Na(gas) from Na(metallic).²² It should be noted that Jammal and Townsend concluded that the rate limiting step for electron sputtering was the desorption of Na from the NaCl surface with a calculated activation energy of 0.24 eV which agrees with their experiments. This is true above a substrate temperature of 400 K. At temperatures below 400 K a Na overlayer will be formed upon sputtering and the rate limiting step would then be Na desorption from metallic Na. This increase in activation energy as realized in a lower sputtering rate below 400 K has been observed.¹

More work is needed to truly understand these phenomena. Possible experiments which will aid in the interpretation of these results include:

- i) Photo-bleaching of the M' centers and/or ionization of the M centers. This should result in a decrease and/or increase of the c_1 emission similar to the effects on the TL peak associated with M' centers as observed by Scaramelli.

ii) Photo-bleaching of the F' centers and/or ionization of the F centers, this experiment should similarly effect the intensity of the c_2 peak.

iii) Full correlation of the optical absorption of the various color centers as a function of temperature. This would provide information on the decay of all relevant color centers which could then be used with confidence to analyze the various emission peaks. This would most effectively be done on thin film samples to emphasize the observation of surface defects with respect to bulk centers.

iv) Calculation of the energy released corresponding to the recombination mechanisms mentioned, and of the energy needed to emit atomic Cl and Cl^- from the various surface conditions. This would provide a direct measure of the probability of the emission due to the mechanisms proposed.

CONCLUSIONS

Even though the details of most of the processes occurring during thermal annealing of a perturbed surface are not understood at the present time, it has become obvious that sputtering by intense laser pulses (of a peak flux far below the laser damage threshold) or e-beams alters the exposed surface area. The deeply entrenched notion that any optical material remains completely unaffected as far as its structure, chemical composition or in general its "non-electric" properties are concerned, as long as it has not been damaged (a visible damage site has appeared), must be considered incorrect at least in NaCl and, with high probability, any other halide lattice. The emission of neutral particles and ions at the high rates observed in our work² is direct evidence for the fact that the surface can be considerably removed from a "theoretically" clean one in thermodynamic equilibrium by exposure to intense laser pulses.

REFERENCES

1. P. D. Townsend, et al., Rad. Eff. 30, 55 (1976).
2. A. Schmid, P. Braunlich, and P. Rol, Phys. Rev. Lett. 35, 1382 (1975).
3. N. Itoh, Crys. Latt. Defects 3, 115 (1972).
4. E. Sonder and W. Sibley in Point Defects in Solids Vol. 1 (Ed. J. H. Crawford and L. M. Slifkin, Plenum Press, N.Y.-London, 1972).
5. Y Al Jammal and P. D. Townsend, J. Phys. C: Sol. St. Phys. 6, 955 (1973).
6. M. N. Käbler and R. T. Williams, Phys. Rev. B 18, 194 (1978).
7. H. Overeijnder, Rad. Eff. 36/(1-2), 63 (1978).
8. D. Pooley, Proc. Phys. Soc. 87, 245 (1966).
9. H. Hersh, Phys. Rev. 148/2, 928 (1966).
10. P. D. Townsend, Phys. Rev. Lett. 36, 827 (1976).
11. U. Brunsmann and A. Scharmann, Phys. Stat. Sol. (a) 43, 519 (1977).
12. N. I. Konyushkina and I. V. Krylova, Sov. Phys. Solid State 1516 (1973).
13. I. V. Krylova, Russ. Chem. Rev. 45/12, 1101 (1976).
14. V. Bichevin and H. Kämbre, Phys. Stat. Sol. (a) 4, K235 (1971).
15. B. Kasemo and C. Wallden, Surf. Sci. 53, 393 (1975).
16. L. R. Danielson, M. J. Dresser, E. E. Donaldson, and J. T. Dickinson, Surf. Sci. 71, 599 (1978).
17. B. Z. Rosenblum, J. P. Carrico, P. F. Bräunlich, and L. Himmel, J. Phys. E, Sci. Instrum. 10, 1056 (1977).
18. K. Becker, CRC Critical Reviews in Solid State Sciences, 339 (March 1972).
19. F. Fischer, Z. Physik 163, 401 (1961).
20. P. Scaramelli, Nuovo Cimento 45B/2, 119 (1966).
21. P. D. Townsend and J. C. Kelly, Color Centers in Insulators and Semiconductors (Crane, Russak, and Co. Inc., N.Y., 1973).

22. Handbook of Chemistry and Physics, 48th Ed. (Chemical Rubber Co., 1968).
23. P. Palmberg, et al., Handbook of Auger Electron Spectroscopy (Physical Electronics Ind. Inc., 1972).
24. T. E. Gallon, Surf. Sci. 17, 486 (1969)
25. R. G. Fuller in Point Defects in Solids Vol. 1 (Ed. J. H. Crawford and L. M. Slifkin, Plenum Press, N.Y.-London, 1972)
26. C. Kittel, Introduction to Solid State Physics (4th Ed., John Wiley and Sons, Inc., 1971).
27. K. Kobayashi, Phys. Rev. 102, 348 (1956).