				• I. •			<u> </u>
	UNCLASSIFIEI					407	(
SECURITY CLASSIFICATION OF THIS PAGE				AD-	-A252		
REPORT DOCUMENTATIO							• Approved • No. 0704-0188
1a. REPORT S	ECURITY CLASS			<b>(20</b> 18)			
2a. SECURITY	CLASSIFICATIO	N AUTHO	LECTE	3. DISTRIBUTION	AVAILABILITY O	F REPORT	
26. DECLASSIFICATION / DOWNGRADING JEDULE				APPROVED FOR PUBLIC RELEASE DISTRIBUTION UNLIMITED			
. PERFORMIN	NG ORGANIZAT	TON REPORTION BI	ER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)			
6a. NAME OF PERFORMING ORGANIZATION			6b. OFFICE SYMBOL (If applicable)	7a. NAME OF M	ONITORING ORGA	NIZATION	
Surface Dynamics Laboratory				OFFICE OF NAVAL RESEARCH PROPULSION AND ENERGETICS PROGRAM			
6c. ADDRESS (City, State, and ZIP Code)				7b. ADDRESS (Cit	ty, State, and ZIP	Code)	
WASHINGTON STATE UNIVERSITY Pullman, WA 99164-2814				SOO NO Arlin	RTH QUINCY STRI GTON, VA 22217	EET	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION (If applicable)				9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER			
8c. ADDRESS (City, State, and ZIP Code)				10 SOURCE OF	UNDING NUMBER	RS	
				PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
7. DEDCOMA		PARTICLE	EMISSION AND CHARGING	GEFFECTS INDUCED	BY FRACTURE		
L. FERSUNA.	L AUTHOR(S)		J. THOMAS I	ICKINSON			
3a. TYPE OF	REPORT	136. TIME C	J. THOMAS I	ICKINSON	RT (Year, Month,	Day) 15. PAG	
3a. TYPE OF	REPORT Final ENTARY NOTAT	13b. TIME C FROM <u>6/1</u> TION	J. THOMAS I OVERED /87 TO 6/34/92	ICKINSON 14. DATE OF REPO June 3	RT (Yesr, Month, 1992	<b>Day)</b> 15. PA(	GE COUNT 14
3a. TYPE OF 6. SUPPLEMI	REPORT Final ENTARY NOTAT	13b. TIME C FROM _6/1 TION	J. THOMAS I OVERED /87 TO 6/34/92	ICKINSON 14. DATE OF REPC June 3	RT (Ye <i>ar, Month,</i> <b>9, 199</b> 2	<b>Day)</b> 15. PÁ(	GE COUNT 14
3a. TYPE OF 6. SUPPLEMI 7. FIELD	REPORT Final ENTARY NOTAT	13b. TIME C FROM _6/1 TION CODES	J. THOMAS I	ICKINSON 14. DATE OF REPO June 3 Continue on revers FRACTURE PARTIC	RT (Year, Month, a, 1992 The if necessary and	Day) 15. PAG	SE COUNT 14 lock number)
3a. TYPE OF 6. SUPPLEMI 7. FIELD	E REPORT Final ENTARY NOTAT	13b. TIME C FROM6/1 TION CODES SUB-GROUP	J. THOMAS I OVERED /87 TO 6/34/92 18. SUBJECT TERMS ( CRACK PROPAGATION, ENERGETIC MATERIAL BREAKDOWN, MICROCI CRYSTAL DEFECTS, SC/	ICKINSON 14. DATE OF REPC June 3 Continue on revers FRACTURE, PARTIC S, RDX, RADIATION IACKING, LASER AB INVING TUNNELING	RT (Yesr, Month, , 1992 e if necessary and LE EMISSION, FRAM DAMAGE, INTERF, LATION, SURFACE I MICROSCOPY	Day) 15. PAG d identify by b CTO-EMISSION ACIAL FAILUR CHARGE, FRACT	GE COUNT 14 lock number) E, ELECTRICAL FOGRAPHY,
3a. TYPE OF 6. SUPPLEMI 7. FIELD 9. ABSTRACT	REPORT Final ENTARY NOTAT COSATI GROUP T (Continue on	13b. TIME C FROM _6/1 TION CODES SUB-GROUP reverse if necessary	J. THOMAS I OVERED /87 TO 6/34/92 18. SUBJECT TERMS ( CRACK PROPAGATION, ENERGETIC MATERIAL BREAKDOWN, MICROCI CRYSTAL DEFECTS, SC/ and identify by block m	ICKINSON 14. DATE OF REPC June 3 Continue on revers FRACTURE, PARTIC S, RDX, RADIATION IACKING, LASER ABI NNING TUNNELING umber)	RT (Year, Month, a, 1992 The if necessary and LE EMISSION, FRAM DAMAGE, INTERF LATION, SURFACE ( MICROSCOPY	Day) 15. PAG d identify by b CTO-EMISSION ACIAL FAILUR CHARGE, FRACT	SE COUNT 14 lock number) E, ELECTRICAL, FOGRAPHY,
ISA. TYPE OF	REPORT Final ENTARY NOTAT ENTARY NOTAT GROUP T (Continue on We summa fracture an capabilities and b) to atomic for scanning t UV laser i energetic mechanism (often invo inorganic a	13b. TIME C FROM 6/1 TION CODES SUB-GROUP reverse if necessary arize three rese and UV laser bo to a) detect a obtain high re- rce microscopy unneling micro- interactions with processes accors s such as disk- olving charge fa and organic ma	J. THOMAS I OVERED /87 TO 6/34/92 18. SUBJECT TERMS ( CRACK PROPAGATION, ENERGETIC MATERIAL BREAKDOWN, MICROCI CRYSTAL DEFECTS, SC/ and identify by block material BREAKDOWN, MICROCI CRYSTAL DEFECTS, SC/ and identify by block material solution topographi . Three princip scopy studies of f h surfaces. These mpanying fracture ocation motion and transfer processes) iterials.	ICKINSON 14. DATE OF REPC June 3 Continue on revers FRACTURE, PARTIC S, RDX, RADIATION FRACTURE, LASER ABI NNING TUNNELING umber) Ave focused on terials. These raticle release Cal information le areas of s racture surfac studies have f , particularly d plastic defo , and high et	RT (Year, Month, 9, 1992 The if necessary and LE EMISSION, FRAG DAMAGE, INTERFA LATION, SURFACE MICROSCOPY studies have from surfaces n utilizing sci study have h es of crystals focused on th those involver mation, phen hergy UV lass	Day) 15. PAG d identify by b CTO-EMISSION ACIAL FAILUR CHARGE, FRACT CHARGE, FRACT amics assoc e been bass is on fast ti anning tun been fracto s and poly te examinat ying beat nomena at sers interact	GE COUNT 14 lock number) E, ELECTRICAL FOGRAPHY, iated with ed on our me scales, heling and -emission, mers, and ion of the generating interfaces cting with
13a. TYPE OF 16. SUPPLEMI 17. FIELD 19. ABSTRACT 19. ABSTRACT 19. UNICLAS	REPORT Final ENTARY NOTAT ENTARY NOTAT GROUP T (Continue on We summa fracture at capabilities and b) to atomic for scanning t UV laser i energetic mechanismi (often invo inorganic a	I 3b. TIME C FROM 61 TION CODES SUB-GROUP reverse if necessary arize three rese and UV laser bo to a) detect a obtain high re- rce microscopy unneling micro interactions with processes accors such as disk olving charge to and organic ma	J. THOMAS I OVERED /87 TO 6/34/92 18. SUBJECT TERMS ( CRACK PROPAGATION, ENERGETIC MATERIAL BREAKDOWN, MICROCI CRYSTAL DEFECTS, SC/ and identify by block manual and characterize parts solution topographic . Three princip scopy studies of f h surfaces. These mpanying fracture ocation motion and transfer processes) iterials. RPT DTIC USERS	ICKINSON 14. DATE OF REPC June 3 Continue on revers FRACTURE, PARTIC S, RDX, RADIATION FRACTURE, PARTIC S, RDX, RADIATION INNING TUNNELING umber) NVE focused on terials. These raticle release cal information le areas of s racture surfac studies have f particularly d plastic defo , and high et UNCLASSIN	RT (Year, Month, , 1992 Te if necessary and LE EMISSION, FRAM DAMAGE, INTERF, LATION, SURFACE of MICROSCOPY surface dyna e studies have from surfaces n utilizing scu- study have have to of crystals focused on th those involver mation, phen hergy UV lass CURITY CLASSIFIC FIED	Day) 15. PAG d identify by b CTO-EMISSION ACIAL FAILUR CHARGE, FRACT amics assoc e been base is on fast ti anning tum been fracto is and poly be examinat ying beat a nomena at sers interact	GE COUNT 14 lock number) E, ELECTRICAL FOGRAPHY, iated with ed on our me scales, heling and beenission, mers, and ion of the generating interfaces cting with

.



Accesion For NTIS CRA&I

DTIC TAB

Unannounced

Justification

By

Distribution /

Dist

A-

Availability Codes

Special

d

 $\square$ 

#### OFFICE OF NAVAL RESEARCH Contract N00014-87-K-0514

Final Report June, 1992

#### PARTICLE EMISSION AND CHARGING EFFECTS INDUCED BY FRACTURE

J. Thomas Dickinson

Department of Physics Washinton State University Pullman, WA 99164-2814

Reproduction in whole or part is permitted for any purpose of the United States Government.

Approved for public release; distribution unlimited.



92 6 29 1.20

## I. Technical Summary

When a crack propagates through a material, a number of elementary processes can occur which lead to departures from equilibrium. These processes involve breaking chemical and physical bonds, the motion of atoms, molecules, electrons, and ionic species in the vicinity of the crack tip, and production of localized heating due to plastic deformation. The consequences of such microscopic processes can result in surface and near surface defects being created, non-equilibrium surface stoichiometry and charge distributions (involving electrons, holes, point defects and radicals, as well as elementary (and transient) excitations such as excitons, excited states of color centers, and various vibrational excitations. We have shown that a number of emissions can result from these circumstances; we call such emission fracto-emission, which includes the emission of particles such as electrons, ±ions, and neutral species, and photons before, during, and following the propagation of a crack in a stressed material. The major goals addressed in our emission work are: (1) characterization of fractoemission, (2) improving our understanding of the emission mechanisms in terms of microscopic processes accompanying fracture (idealized systems), and (3) applications of fracto-emission to understand the energetics of crack growth and its influence on the physical and chemical state of the fracture and the near fracture surface. The characterization studies include identification of specific emitted species, energy distribution measurements, studies of the fractal features of emission from brittle materials, and determination of the spatial distribution of the emission (through imaging). Mechanism studies include fundamental studies of temperature dependences of the emission, modification of excitations via optical stimulation, experiments on well defined interfacial failure, and time resolved spectroscopy of the photon emission. The application studies include experiments on model inorganic crystalline materials and propellents, energetic crystalline materials, and elastomers/polymers of interest to the Navy.

We have also been connecting the fracto-emission work with the microscopic features of the newly created fracture surface. We are employing the scanning tunneling microscope (STM) in conjunction with other microscopies to correlate fracto-emission properties to determine the topographical nature of the fracture surface over a wide range of sizes. Such information should aid in the development of atomic-scale models of deformation and fracture in brittle materials. Of particular interest is the use of topography to examine the consequences of cracks moving into regions of high densities of dislocations. Furthermore, we developed an atomic force microscope (AFM) to allow such studies to be done routinely on insulating materials.

We are also studying the interaction of radiation with materials under mechanical stress to explore possible synergisms in damage mechanisms due to they way mechanical and radiative energy couples. Recently, we have also been studying the emission products of UV laser irradiation on including a glassy inorganic material and RDX single crystals. The latter is of particular interest in terms of the decomposition paths and resulting plasma interactions the products can undergo. A somewhat esoteric application of this work is the potential use of lasers for micromachining explosive crystals into intricate shapes with submicron resolution. We have also proposed that thin films of energetic materials may be useful in the electronics processing industry as temporary coatings which could be readily etched with UV radiation.

Three areas have been pursued intensively utilizing our capabilities to a) detect and characterize particle release from surfaces on fast time scales, b) to obtain high resolution topographical information utilizing scanning tunneling and atomic force microscopy, and c) to analyze the consequences of high energy laser beams interacting with surfaces. The three areas of study have been:

a) fracto-emission,

b) STM and AFM studies of fracture surfaces, and

c) UV laser interactions with surfaces.

Briefly, our goals have been to examine the energetic processes accompanying fracture, particularly those involving heat generating mechanisms such as dislocation motion and plastic deformation, phenomena at interfaces (often involving charge transfer processes), and high energy UV lasers interacting with inorganic and organic materials. This work has shown that a variety of excitations can occur during deformation and fracture, that during

## **II.** Summary of Work Accomplished

<u>Creation of Free Charge Carriers with Fracture</u>: We developed a new technique for examining elementary excitations in a material during fracture, namely measurements of transient increases in conductivity in single crystal silicon due to a propagating crack. We observed rapid increases in conductivity due to the production of free charge carriers <u>during</u> crack growth. The band gap of Si is 1.1 eV, which appears to be bridged via electronic excitations induced by the bond breaking at the crack tip. This is the first measurement of this kind and offers insight into the types of mechanically induced excitations that can occur in crystalline materials during fracture. (See item 1 in list of publications--Section III, below).

Evidence of Chaos in the Photon Emission (phE) from Fracture: We have examined the fluctuations in the photons (acquired at 10 ns intervals) accompanying fracture of an epoxy and single crystal MgO and found that these signals show *chaotic* as opposed to stochastic, random behavior. The evidence for deterministic chaos comes from analysis of the autocorrelation function, the Fourier transform, a correlation integral (Grassberger and Procaccia), and the fractal box dimension. We have also proven the existence of a positive Lyapunov exponent and the presence of a low dimensional attractor. The fracture surfaces of this epoxy are shown to be fractal with equivalent fractal dimension. Thus, the dynamic process of creating a fracture surface results in topographical features which are simultaneously reflected in the intensity variations of the photons emitted. We were not able to determine the fractal dimension of the MgO (should be quite low) but did find that the photon emission was chaotic. The relation of such parameters as fracture toughness and other measures of dissipation to these photon emission correlation parameters may prove very useful for the application of phE measurements to the characterization of materials. It should be emphasized that recent work by Mecholsky and Passoja (e.g., J. Am. Cer. Soc. 72, 60 (1989)) have snown a strong correlation of fractal dimension of the fracture surfaces with the corresponding fracture toughness, thus providing us with strong motivation to make links to fracto-emission properties. (See item 2 in list of publications below). An extension and refinement of this work was carried out using particulate filled epoxy. We examined the phE and EE during crack propagation in a common epoxy, Shell Epon 828/Z Hardner, filled at 0, 20 and 40 % (by weight) with  $\sim 7 \,\mu m \, Al_2O_3$  particles. The particular measurement of interest involves examination of the fluctuations in the photons accompanying fracture of this epoxy (acquired at 5 ns intervals); measurements on this resin system support our earlier results showing that the phE exhibited chaotic as opposed to stochastic, random behavior. We examine in more detail these signals and discuss possible relations to fracture toughness and length scales involved. This work is presented in item 3.

**Spectra of Light Emitted During Peeling of an Adhesive Tape:** We have studied the visible light emitted from the region near the detachment zone during the peeling of pressure sensitive adhesives. This photon emission due to adhesive failure is a unique form of *triboluminescence*. We investigated the properties of this light from the peeling of a filament tape with a natural rubber-resin adhesive from its backing at various peel speeds. We have shown conclusively that small electrostatic discharges are the major source of the radiation. Total intensity vs time measurements show that the light consists of very intense bursts with

3

typical duration of 50 ns which frequently induce additional discharges for times as long as 50-100  $\mu$ s. Time resolved spectra of these emission show them to be dominated by the line spectrum of molecular nitrogen for both the initial bursts and those that follow in the next 0.1-100  $\mu$ s. Thus, the "after-emission" is not due to phosphorescence of the polymer(s), but due to these additional electrostatic discharges. This work is described in item 4.

Autographs of Photon Emission from Adhesive Failure in a Composite Tape: A study utilizing a very unique method for producing contact prints (autographs) of the photon emission produced during extremely slow peeling of a composite tape from Polaroid photographic film was carried out. We continue to see direct evidence of small electrostatic discharges which occur in this type of fracture involving interfacial failure. The failure mechanism of this particular tape involves fracture of the reinforcing glass filaments which results in fluctuations in the microscopic detachment rate. This produces modulations in the photon emission corresponding to several orders of magnitude. This work was discussed in item 5.

**Damage and Electron Emission in the Cleavage of Single Crystal LiF:** In the production of cleavage surfaces of LiF single crystals, we have discovered that the region of the crystal interacting strongly with the metal cleavage blade is the region of essentially all of the emission for this mode of loading. Using scanning techniques, microscopy, and varying loading conditions, we conclude that the damaged region where the cleavage blade and crystal come into contact is extraordinarily "hot" in terms of electron emission. Macroscopic particles (ejecta) from the damaged region which frequently cling to the fracture surface are also shown to be highly emissive. In contrast, the "untouched" cleave surface emits little, if any long lasting, intense emission. We propose that the high intensity emission originates from defects created during the production of higher index plane fracture surfaces.<sup>6</sup> This work was done primarily by an undergraduate physics major (J.P.M.).

**Fracto-Emission from MgF2:** Studies of the electron emission produced from the fracture of single crystal MgF2 were completed in a collaboration with K. C. Yoo (Westinghouse R & D) and R. G. Rosemeier (Brimrose Corporation). This work is described in item 7 in the list of publications. Here we were interested in the role of anisotropic effects due to the crystal structure of MgF2. We were able to observe considerable changes in the electron intensity with variation of the dominant orientations of the fracture surfaces. The separation of surfaces with  $\{110\}$  orientation. From elastic constant anisotropies, the production of  $\{110\}$  surfaces should require more fracture energy. In addition, we consider the possibility of higher defect densities on the  $\{110\}$  surfaces due to differences in local geometry and instantaneous rates of energy release in the region of the crack tip.

**Fracto-Emission from Fused Silica and Sodium Silicate Glasses:** We examined in great detail characteristic intensity vs time measurements of photon emission (phE), electron emission (EE), positive ion emission (PIE), and neutral emission (NE) due to the fracture of fused silica and sodium trisilicate glass. We show, for example, that the trisilicate is a copious emitter of atomic Na and both atomic and molecular oxygen. The phE, EE, and PIE from the two glasses share a number of properties. This work appeared in item 8. Utilizing time-of-flight techniques as well as mass spectroscopy we have succeeded in determining the masses of the positive ions emitted during the fracture of fused silica (SiO<sub>2</sub>).<sup>9</sup> The major positive particles emitted (in order of decreasing intensities) are: SiO<sup>+</sup>, Si<sub>2</sub>O<sup>+</sup>, Si<sup>+</sup>, and O<sup>+</sup>. We have proposed a sequence of bond breaking events which could lead to such species being liberated. Such species show unambiguously that non-equilibrium processes accompany bond breaking due to fracture. More importantly, in terms of composite fracture, we are obtaining unique signatures

for distinguishing the various failure modes. In this case, silica or silica glass fiber fracture would yield Si containing species, whereas organic matrices free of Si would not.

**Dislocation-related Emissions:** Some fracto-emission components from alkali halides appear to be related not to bond-breaking during the fracture event, but to the recovery of fracture-induced plastic deformation. We have shown that neutral emission from single-crystal NaCl and LiF is due to the emergence at the fracture surface of dislocations driven into the bulk material during crack growth. This emission is delayed by a few ms from the time of fracture. We have published the results for the alkali halides in item 10 As this process deposits considerable energy in a very small volume of material, this dislocation motion has important implications in the fracture could in principle result in unexpected ignition. Our results indicate that dislocation emergence deposits this energy on times scales of 1 ms or less, suggesting that the *rate* of energy deposition is also high. Results on a model energetic material, ammonium perchlorate, show delayed spikes of certain neutral molecules, suggesting that a similar process does indeed occur in important energetic materials.

A related study on a fundamental material, single crystal Ge, is described in reference 11, where we see the delayed emission of Ge and Ge<sub>2</sub>, again attributed to dislocation activity accompanying dynamic fracture. We were able to obtain a rough measurement of the velocity of the Ge atoms which is ~ 700 m/s and supports a *non-thermal* emission mechanism. This work has been extended to materials such as calcite (generating CO)<sup>12</sup> and to another mineral, K feldspar(generating K atom emission).<sup>13</sup>

An exciting and related study on alkali containing silicates shows that even in very brittle glasses, stored deformation related energy can be released in a concerted fashion to emit alkali atoms, thus relates nicely to the crystalline materials. (See item 14 below).

**Possible Fracto-Fusion Mechanism for Observed Neutrons in Deuterated Metals.** In the heat of excitement associated with the possibility that the observed bursts of neutrons seen by Jones, Scaramuzzi, and Menlove (separate groups) are due to microcrackinduced charge separation which accelerates deuterons-- we collaborated with workers at Los Alamos in examining the fracto-emission accompanying the fracture of deuterated Titanium. This was to explore the possibility that the so-called fracto-fusion model was the origin of such neutron emission. We showed that charged particles are in fact produced by fracture, both negative and positive and are pursuing measurements of energy as well as species of these emissions. No claim of observations of fusion products was made nor expected. It is our understanding to date that most of the neutron signals have not been reproducible; Thus, our study is of more interest in terms of a materials science interest. The work is described in reference 15.

**Photon Emission from Interfacial Failure at Embedded Interfaces**: By use of semitransparent materials, we have been able to detect interfacial failure at interfaces *inside* a polymer matrix. We have also used simultaneous electron emission measurements to determine the exact instant when cracks reach the surface of the sample relative to the internal failure. We have completed measurements include the pullout process of metal cylinder from an epoxy matrix. We also investigated the frictional failure of single rod pullout (following debonding) to determine if fracto-emission signals can be detected from this process where stick-slip behavior is observed. We see strong fluctuations in the stick-slip process indicating highly disordered mechanical interlocking. The analogy with a slip system such as a fault appears to be valid. One very significant observation is precursors in the photon emission prior to slip. These are due to "micro-slip" occurring before catastrophic slip. Thus, a "warning" can be achieved by this monitor. This work is published in references 16 and 17.. Measurements of Electrical Transients during Internal Debonding: We have used fast electrical measuring techniques to examine the transient currents generated in a steel rodepoxy matrix system, similar to that used above. Interfacial failure in the steel rod-epoxy matrix system was seen to be accompanied by distinctive voltage and current signals which are correlated with interfacial failure events inferred from small changes in rod strain. We have developed a model for the current generated during debonding as well as during the initial pullout event immediately following fracture. This work has led to a novel method for looking at interfacial failure on sub-microsecond time scales.<sup>18</sup>

**Fracto-Emission From a Model Interface:** Au-SiO<sub>2</sub>-Si: We have measured electron and photon emission during the detachment of gold films vapor deposited on oxidized Si, a system where energy levels and electronic structure has been well studied. We show that the resulting emissions are consistent with the effects of charge separation predicted from the initial formation of the Au-SiO<sub>2</sub> interface, yet greatly modified by charge transfer through the oxide layer to and from the Si substrate.<sup>19</sup>

### Electrical Charge on Electa from Impact Loading of Explosive Crystals:

We made measurements of the properties of small macroscopic particles (ejecta) released from the impact loading of single crystals of PETN. Total mass, total electrical charge, and approximate size distributions were determined. Long wavelength electromagnetic radiation was detected from the impact suggesting that microdischarges occurred during fracture. The charge on the surface was attributed to the electrostatics of fracturing a piezoelectric crystal. Similar results have been observed on single crystal quartz. This work appeared in ref. 20.

Scanning Tunneling Microscopy of Fracture Surfaces: In the fracture of semi-brittle materials, we expect that the fractography of the surface to be intimately related to energy dissipation and failure mechanisms. These can occur on a number of size scales, including the nanometer scale. We have finished studies of fracture surfaces of single crystal MgO<sup>21</sup> using scanning tunneling microscopy (STM) to examine topography of fracture surfaces on very small length scales. We made observations where considerable detail in the nanoscale motion of a crack tip are revealed. A number of crystal planes are found including very high energy planes. This work has led to current work on STM investigations of fracture surfaces of polymers [D. M. Kulawansa, S. C. Langford, J. T. Dickinson, and R. P. Dion, "Scanning Tunneling Microscope Observations of Polymer Fracture Surfaces," J. Mater. Res. 7, 1292 (1992)], silica based glasses, and metallic glasses.

Excimer Laser Interactions with Solid Surfaces. We have examined in the influence of UV Excimer radiation on Na<sub>2</sub>O  $3SiO_2$  glass. We have characterized the damage to the surfaces of this material as well as determinations of the type of particles and their velocities due to the pulsed laser bombardment. This includes measurements of the charged particle emission (photoelectrons,  $\pm ions$ , and neutral emission (both ground state and excited) as a function of photon flux. We examined in detail the onset of significant removal of matter from the glass (ablation), where we see evidence for laser *induced* absorption at 248 nm (thus a threshold in exposure for damage to occur), an electrostatic acceleration of positively charged particles interacting with laser heated electrons (inverse bremstrahlung) resulting in ~30 eV Na atoms in high lying Rydberg states.<sup>22</sup>

Most recently, we made a new discovery concerning the process of inducing etching of wide bandgap materials, namely the strong influence of the simultaneous application of beams of electrons *and* laser light. We showed direct evidence of a synergism between these radiation sources. In terms of sensitivity of materials to radiation, the role of interactions between two or more types of radiation should be an area of considerable interest. This work is presented in ref. 23 Related work on a mechanistic model describing the effects of intense UV radiation pulses on materials is outlined in item 24. Measurements of the negative charge emission accompanying laser bombardment of a silica glass are presented in ref. 25.

**Decomposition of RDX by Excimer Laser Radiation:** We completed a study of consequences of excimer radiation on single crystal RDX, an explosive molecular crystal, where we showed that decomposition of the crystalline material occurs and that <u>photochemical processes</u> dominate. Furthermore, the resulting etching of the molecular crystal is related to the induced chemical reactions, as seen in the product distributions coming from the crystal as a function of laser fluence. Finally, we showed that there was a sustained reaction following the laser pulse which we could quantify with the luminescence coming from the reaction products. This work is described in item 26 in the publication list.

Interaction of Excimer Laser Ultraviolet Radiation with KAPTON-H under Mechanical Stress: We examined the response of highly stressed polyimide films to excimer laser radiation (20 ns pulses @ 248 nm wavelength) in vacuum. We investigated changes in surface topology due to surface/near damage, crack initiation, and eventually crack growth over a wide range of applied stress. We showed that the morphology of the stressed material has a significant influence on the resulting damage and suggest that the regions of highest damage are those experiencing the highest local stress. Initial results are also presented on the effect of mechanical stress on yields of the photo-ablation products ejected from the polymer surface. This work appears in reference 27. A similar study performed in air is described in item 28.

# II. Technical Reports Issued

- Particle Emission and Charging Effects Induced by Fracture, Technical Report, June, 1989, by J. Thomas Dickinson.
- Particle Emission and Charging Effects Induced by Fracture, Technical Report, May 1991, by J. Thomas Dickinson.

#### **III.** Publications from This Work

- 1. S. C. Langford, D. L. Doering, and J. T. Dickinson, "The Production of Free Charge Carriers by Fracture of Single Crystal Silicon", Phys. Rev. Lett. <u>59</u>, 2795 (1987).
- 2. S. C. Langford, Ma Zhenyi, and J. T. Dickinson, "Photon Emission as a Probe of Chaotic Processes Accompanying Fracture", J. Mater. Res. <u>4</u>, 1272 (1989).
- 3. Ma Zhenyi, S. C. Langford, and J. T. Dickinson, M. H. Engelhard and D. R. Baer, "Fractal Character of Crack Propagation in Epoxy and Epoxy Composites as Revealed by Photon Emission during Fracture," J. Mater. Res. <u>6</u>, 183 (1991).
- 4. Ma Zhenyi, Fan Jiawen, and J. T. Dickinson, "Properties of the Photon Emission Accompanying the Peeling of a Pressure Sensitive Adhesive," J. Adhesion <u>25</u>, 63 (1988).
- 5. E. E. Donaldson and J. T. Dickinson, "Autographs from Peeling Fiber Reinforced Pressure Sensitive Adhesives: Correlation with Failure Mechanisms,"J. Adhesion <u>30</u>, 13 (1989).
- 6. J. P. Mathison, S. C. Langford, and J. T. Dickinson, "Concerning the Post Emission of Electrons from Cleavage Surfaces of Single Crystal LiF," J. Appl. Phys. <u>65</u> 1923 (1989).
- 7. K. C. Yoo, R. G. Rosemier, J. T. Dickinson, and S. C. Langford, "Anisotropy Effects in Fracto-Emission from MgF2 Single Crystals", Appl. Phys. Lett. <u>55</u>, 354 (1989).
- 8. J. T. Dickinson, S. C. Langford, L. C. Jensen, J. Kelso, C. Pantano, and G. McVay, "Fracto-Emission from Fused Silica and Sodium Silicate Glasses," J. Vac. Sci. and Technol. A <u>6</u>, 1084 (1988).
- 9. S. C. Langford, J. T. Dickinson, and L. C. Jensen and L. R. Pederson, "Positive Ion Emission from the Fracture of Fused Silica," J. Vac. Sci. Technol. A. 7, 1829 (1989).
- 10. J. T. Dickinson, L. C. Jensen, S. C. Langford, and J. P. Hirth, "Atomic and Molecular Emission Following Fracture of Alkali Halides: A Dislocation Driven Process," J. Mater. Res. 6, 112 (1991).
- 11. J. T. Dickinson, S. C. Langford, L. C. Jensen, "Atomic and Molecular Emission Accompanying Fracture of Single Crystal Ge: A Dislocation Driven Process," Phys. Rev. Lett. <u>66</u>, 2120 (1991).
- 12. J.T. Dickinson, L.C. Jensen, S.C. Langford, P.E. Rosenberg, and D.L. Blanchard, "CO<sub>2</sub> Emission Accompanying the Fracture of Calcite," Phys. Chem. Minerals <u>18</u>, 320 (1991).
- 13. J.T. Dickinson, L.C. Jensen, S.C. Langford, P.E. Rosenberg, and D.L. Blanchard, "Fracture Induced Emission of Alkali Atoms from Feldspar," Phys. Chem. Minerals <u>18</u>, 453 (1992).
- 14. S. C. Langford, L. C. Jensen, J. T. Dickinson, and L. R. Pederson, "Alkali Emission Accompanying Fracture of Sodium Silicate Glasses," J. Mater. Res. <u>6</u>, 112 (1991).

- 15. J. T. Dickinson, L. C. Jensen, S. C. Langford, R. R. Ryan, and E. Garcia, "Fracto-Emission from Deuterated Ti: Supporting Evidence for a Fracto-Fusion Mechanism," J. Mater. Res. 5, 109 (1990).
- 16. J. T. Dickinson and Ma Zhenyi, "Fracto-Emission Accompanying Adhesive Failure in A Model Fiber Pull-out System," Die Macromoleculare Chemie, Macromolecular Symposia <u>41</u>, 9 (1991).
- 17. Ma Zhen-Yi and J. T. Dickinson, "Fracto-Emission from Embedded Interfaces," J. Appl. Phys. <u>70</u>, 4797 (1991).
- 18. K. A. Zimmermann, S. C. Langford, and J. T. Dickinson, "Electrical Transients during Interfacial Debonding and Pullout of a Metal Rod from an Epoxy Matrix," J. Appl. Phys. <u>70</u>, 4808 (1991).
- 19. D. L. Doering, S. C. Langford, J. T. Dickinson, and P. Xiong-Skiba, "Fracto-Emission during the Interfacial Failure of a Metal-Oxide-Semiconductor System: Au-SiO<sub>2</sub>-Si," J. Vac. Sci. Technol. A. <u>8</u>, 2401 (1990).
- 20. E. E. Donaldson, M. H. Miles, and J. T. Dickinson, "Electrical Charge on Ejecta from Impact Loading of Explosive Crystals", J. Mat. Res. <u>24</u>, 4453, (1989).
- S. C. Langford, L. C. Jensen, Ma Zhenyi, and J. T. Dickinson, "Scanning Tunneling Microscopy Analysis of MgO Fracture Surfaces, J. Vac. Sci. Technol. A <u>8</u>, 3470 (1990).
- 22. P. A. Eschbach, J. T. Dickinson, S. C. Langford, and L. R. Pederson, "The Interaction of UV Excimer Laser Light with Sodium Trisilicate, "J. Vac. Sci. A 7, 2943 (1989).
- J. T. Dickinson, S. C. Langford, L. C. Jensen, P. A. Eschbach, L. R. Pederson and D. R. Baer, "Consequences of Simultaneous Exposure of Inorganic Solids to Excimer Laser Light and an Electron Beam," J. Appl. Phys. <u>68</u>, 1831 (1990).
- 24. P. A. Eschbach, J. T. Dickinson, S. C. Langford, L. C. Jensen, L. R. Pederson and D. R. Baer, "Precursors to the Photo-Ablation of Sodium Trisilicate Glass due to UV Excimer Irradiation", Mater. Res. Soc. Symp. Proc. <u>158</u>, (1990), pp. 463-469.
- 25. S. C. Langford, L. C. Jensen, J. T. Dickinson, and L. R. Pederson, "Negative Charge Emission due to Excimer Laser Bombardment of Sodium Trisilicate glass," J. Appl. Phys. <u>68</u>, 4253 (1990).
- J. T. Dickinson, L. C. Jensen, D. L. Doering, and R. Yee, "Mass Spectroscopy Study of Products from Exposure of RDX Single Crystals to KrF Excimer Laser Radiation," J. Appl. Phys. <u>67</u>, 3641 (1990).
- K. Tonyali, L. C. Jensen, and J. T. Dickinson, "The Interaction of Excimer Laser Ultraviolet Radiation with Kapton-H Under Mechanical Stress," J. Vac. Sci. Technol. A <u>6</u>, 941 (1988).
- 28. K Tonyali, L. C. Jensen, and J. T. Dickinson, "Excimer Laser Induced Damage in Stressed Polyimide Films Exposed in Air," Mat. Res. Soc. Proc. <u>100</u>, 665 (1988).

### **IV Invited Presentations on This Work**

- Fracto-Emission from Crystals and Interfaces," International Society for Optical Engineering, OE- LASE '88, Los Angeles, January, 1988.
- "Fracto-Emission: A New Way of Studying Failure," IBM-Almaden Research Center, San Jose, June, 1988.

"Fracto-Emission from Elastomers," Elastomer Gordon Conference, New London, July, 1988.

"Fracto-Emission from Inorganic Materials," Glass Science Gordon Conference, Tilton, August, 1988.

"Fracto-Emission from Interfaces," Science of Adhesion Gordon Conference, New Hampton, August, 1988.

Fracto-Emission as a Tool for Failure Analysis", ASM, Seattle, September, 1988.

"The Emission of Particles and Photons from the Fracture of Minerals and Inorganic Materials," American Chemical Society, Los Angeles, September, 1988.

"Fracto-Emission from Polymers and Interfaces," 20th Europhysics Conference on Macromolecular Physics: Physical Mechanisms in Polymer Failure," Lausanne, Switzerland, September, 1988.

"The Interaction of Radiation with Mechanically Deformed Materials," 9th International Symposium On Excelectron Emission and Applications," Wroclaw, Poland, 1988.

"Fracto-Emission from Materials," 9th International Symposium On Excelectron Emission and Applications," Wroclaw, Poland, 1988.

"Crack Initiation and Growth in Polymers Due to Radiation, "Materials Science And Engineering Society, Prague, Czechoslovakia, October, 1988.

"Fracto-Emission as a Probe of Failure Mechanisms", Macromolecular Chemistry Institute, Prague, Czechoslovakia, October, 1988.

"Fracto-Emission from Polymers and Interfaces," 3M Adhesion Technical Forum, November, 1988.

"The Emission of Particles from Deformation and Fracture of Composites," McDonnell Douglas Corporation, November, 1988.

"Fracto-Emission from Interfaces and Composites," DOW Chemical Co., January, 1989.

"Fracto-Emission from Polymers and Interfaces", Boeing Co, January, 1989

"Fracto-Emission from Cohesive and Adhesive Failure of Materials", Materials Science Dept. U. of Michigan, March, 1989.

"Fracto-Emission from Interfacial Failure", Symposium on Adhesion, Materials Research Society, San Diego, April, 1989. "Fracto-Emission from Elastomers", Frontiers in Elastomer Science Symposium, ACS, Mexico City, May, 1989.

- "Fracto-Emission Accompanying Adhesive Failure", Symposium on Adhesion, ACS, Seattle, June, 1989.
- "Fracto-Emission from Insulators and Interfaces", International Conference on Fracture, Irsee, Germany, June, 1989.
- "Fracto-Emission: Recent studies in Particle Emission Accompanying Fracture," Sandia National Laboratories, July, 1989.
- "Electrical Phenomena Accompanying Fracture," Sandia National Laboratories, July, 1989.
- "Localized Energetic Processes During Fracture," ONR-NIST Workshop on Fundamental Concepts in Theory of Fracture, Gaithersburg, 1989.
- "Fracto-Emission Accompanying Adhesive Failure", Case Western Reserve University, November, 1989.
- "Particle Emission Studies of Fracture," Ohio Section of American Vacuum Society, Cleveland, November, 1989.
- "Fracto-Emission: Recent studies in Particle Emission Accompanying Fracture," Dept. of Physics, University of Texas-El Paso, November, 1989.
- "Excimer Laser Ablation of Materials," Dept. of Physics, University of Texas-El Paso, November, 1989.
- "Fracto-Emission: Recent studies in Particle Emission Accompanying Fracture," Dept. of Physics, Montana State University, April, 1990.
- "Excimer Laser Interactions at Surfaces," Dept. of Physics, Montana State University, April, 1990.
- "Atomic and Molecular Processes Accompanying Fracture", BioSym Technology Symposium, Dallas, April, 1990.
- "Fracto-Emission from Polymer Surfaces and Interfaces," ACS Macromolecular Sectariat, Boston, April, 1990.
- "Fracto-Emission from Polymers and Interfacial Failure," Dow-Corning Co., Midland, MI, June, 1990.
- "Fracto-Emission from Ceramics and Glasses," Dow Chemical Co., Midland, MI, June, 1990.
- "Fracto-Emission From Glass Surfaces and Interfaces," Gordon Conference on Glass, June, 1990.
- "Fracto-Emission from Polymers and Composites," Prague International Conference on Polymers, Prague, Czechoslovakia, July, 1990.

Fracto-Emission from Thermoplastics," Dow Chemical Co., September, 1990.

"Characterization of Fracture Surfaces," Pacific Coast Meeting of American Ceramics Society Meeting, October, 1990.

- "Fracto-Emission: Recent studies in Particle Emission Accompanying Fracture," Xerox Corporation, Rochester, NY, October, 1990.
- "Excimer Laser Interactions at Surfaces," Dept. of Materials Science, University of Washington, October, 1990.
- "Fracto-Emission: Recent studies in Particle Emission Accompanying Interfacial Fracture," 3M Co., St. Paul, MN, February, 1991.
- "Give Me a Break: A Molecular View of Fracture, Washington State University Distinguished Faculty Address, February, 1991.
- "Energetic Processes and Mechano-Chemistry Accompanying Deformation and Fracture of Materials and Interfaces," Battelle Pacific Northwest Laboratory, May, 1991.
- "Fracto-emission: Recent Studies in Particle Emission Accompanying Fracture," Keynote Address: International Conferenc on Fracture Mechanics of Ceramics, Nagoya, Japan, July, 1991.
- "Fracto-Emission from Tribological Loading of Ceramics and Polymers", Mechanical Engineering Laboratory (MITI), Tsukuba, Japan, July, 1991.
- "Molecular Emissions From Bond-Scissions in Polymers," Dow Chemical Co., August, 1991.
- "Laser Ablation of Wide Bandgap Materials," SPIE Conference, San Jose, September, 1991
- Japan Defense Agency, Sept-Oct. 1991 : Eight Lectures on "Dynamic Processes at Surfaces".
- "Fracto-Emission: Recent Studies in Particle Emission Accompanying Interfacial Failure," Osaka University, Osaka, Japan, October, 1991.
- "The Origin and Evolution of Defects in Materials Under Stress," AFOSR Workshop on Defects, Wright-Patterson, October, 1991.
- "Fundamental Processes Accompanying Fracture of Polymers and Interfaces," 3M Corporation, October, 1991.
- "Fracto-Emission: Recent Studies in Particle Emission Accompanying Interfacial Failure," Dept. of Physics, Western Michigan University, Kalamazoo, Nov. 1991.
- "The Mechanisms of Ablation of Wide Bandgap Materials", American Chemical Soc., San Francisco, April, 1992.
- "Fracto-Emission from Ceramics and Glasses," American Ceramics Society, Minneapolis, April, 1992.

"Chaos and Fractals in Fracture", Gordon Conference on Fractals, June, 1992.

To be presented:

"Laser Ablation of Wide Bandgap Materials," Gordon Conference on Ion, Electron, Laser Beams, July, 1992.

"Laser Ablation of Wide Bandgap Materials," MRS Fall Meeting, Boston, 1992.

"Fracto-Emission from Polymer Interfaces," ACS, Chicago, August, 1993.

"Laser Ablation of Wide Bandgap Materials", International Workshop on Laser Materials Interactions, Oak Ridge, September, 1993.

1

# **Distribution List**

~ ~

	No. of Copies
Dr. Richard S. Miller Program Manager, Propulsion and Energetics OCNR CODE 1132P RM 619 800 N. Quincy Street Arlington, Virginia 22217-5000	1
Administrative Contracting Officer	1
Director, Naval Research Laboratory ATTN: Code 2627 Washington, D.C. 20375	1
Defense Technical Information Center Bldg. 5, Cameron Station Alexandria, VA 22314	2