Collision Induced Optical Spectra of Solids

Final Technical Report

by

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The purpose of this project was to study emission spectra of solids induced by the impact of energetic (5 to 200 keV) ions. The original proposal was prompted by our preliminary observations of continuous or broad band emission when certain metals and insulators were bombarded. These continua emanate from the solid and represent transitions between bands; electron-hole or electron-defect recombination mechanisms can be responsible. During the course of our studies we discovered also broad band emission from particles ejected from the surface; this appears to be restricted to the transition metals and involves very long lived states that travel up to one centimeter from the surface before emitting. We have shown that these continua from transition metals occur only when contaminant oxygen is present and that the ejected species is a metastable Mo O^* molecule. In studies of luminescence from alkali halides we have discovered a vibrational molecular spectrum; this has been identified as due to CN radicles formed by some ion induced chemical reaction of surface contaminants. The observed spectra lines have considerable intrinsic breadth due to the interaction of the CN radicle with the surface.

The research program commenced originally with a study of intrinsic luminescence; this phenomenon may be properly termed "ionoluminescence". Unexpectedly this lead to the identification of ejected transition metal oxides;
conventional spectroscopic sources provide no information on these species since the ground state (e.g. of Mo 0) is apparently repulsive over large ranges of internuclear separation. Finally the project lead also to the first identification of an ion induced chemical reaction.

An significant information generated by this project has now been published in the open literature. Consequently it is appropriate to report the scientific results by reproducing the abstracts of the more important publications.

A. Intristic Luminescence of Metals

The first study under this grant was of the intristic luminescence of certain metals. We concentrated particularly on the emission from Al induced by 10 to 30 keV H⁺ and He⁺; we predicted the spectrum theoretically on the basis of electron-hole recombination. The results have been reported: M. Zivitz and E. W. Thomas, Phys. Rev. B., 13, 2747 (1976) and the abstract is as follows:

Impact of 10- to 30-keV H⁺ and He⁺ ions on polycrystalline Al, Cu, and Mo targets induces broad-band light emissions in the photon energy range of 2-6 eV; these emissions emanate from the target. For aluminum the emission is particularly intense, increases linearly with incident beam current, and is invariant in relative shape with projectile energy and angle of incidence. The dominant peak is at a photon energy of 2.4 eV; and a weak shoulder is observed at 3.3 eV. An electron-hole recombination model is shown to account for the general form of the emission band. We also calculate the electron density of states and the complex part of the dielectric constant ε₂; the energy-band structure based on Ashcroft's Al pseudopotential is presented in tabular form.

B. Ion Induced Luminescence of Alkali Halides

We have studied extensively the broad band emissions resulting from light ion (H⁺ and He⁺) impact on alkali halides (LiF, NaCl, NaF, KBr, KF). The results have been reported: A. I. Bazhin, E. O. Rausch and E. W. Thomas, Phys. Rev. B, 14, 2583, (1976). The abstract is as follows:
A study has been made of luminescence induced by 25-keV H\textsuperscript{+} ion impact on pure alkali halides. The spectra generally exhibit two wide bands, the position of which depend on the type of crystal. A detailed investigation was made of the temperature and dose dependence of luminescence, and the effect of bleaching, in KCl and KBr. The peak intensity in the luminescent spectrum is independent of temperature from -160 to -70°C, rises to a maximum at about 10°C then falls monotonically for further increase in temperature. The dependence of intensity on dose is similar to published observations of \textit{V\textsubscript{3}} center formation. The ion-induced luminescence is not influenced by irradiating the crystal with light in the F band or by irradiating with white light. We propose that the ion-induced luminescence is due to the recombination of electrons from the conduction band with \textit{V\textsubscript{3}} and \textit{V\textsubscript{4}} hole centers. This proposed model is consistent with the known energies of \textit{V\textsubscript{3}} and \textit{V\textsubscript{4}} centers. After the surface was deliberately exposed to \textsuperscript{3}O\textsubscript{2} we also observe an additional band characteristic of \textsuperscript{3}O\textsubscript{2}.

C. The Broad Band Optical Emission from Mo, Nb, and W Bombarded by Heavy Ions

The most puzzling aspect of ion-induced emission from solids has been the continuum emission induced by impact of heavy ions (Ne\textsuperscript{+}, Ar\textsuperscript{+} etc.) on certain metals; the transition metals all show the phenomenon and Mo has been the case most frequently studied. These spectra were reported by at least three groups but no definite explanation of its origin was provided. We have shown quite conclusively that the spectrum occurs only in the presence of oxygen. A paper on this phenomenon has been published: E. O. Rausch, A. I. Bazhin, and E. W. Thomas, J. Chem. Phys. 65, 4447 (1976). The abstract is as follows:

Continuum emission has been observed when Mo, W and Nb targets were bombarded with 10 to 30 keV, Ne\textsuperscript{+}, and Ar\textsuperscript{+}. The emission occurs only when the environment of the target chamber contains an oxygen partial pressure of 2 \times 10\textsuperscript{-9} torr or above; for lower pressures the emission is absent. Identical continua are also observed when the metal oxides are bombarded with Ne\textsuperscript{+} and Ar\textsuperscript{+}; similar spectral features, though with changed relative intensities, are seen when the targets are bombarded with O\textsuperscript{+} and O\textsubscript{2}\textsuperscript{+} ions in the absence of O\textsubscript{2} gas in the vacuum environment. A significant feature of these continua is that the emitting species extend for some mm beyond the bombarded surface. We suggest that the source of the emission is sputtered oxides of the target. The variation of emission intensity with oxygen partial pressure and bombarding ion beam current is consistent with a mechanism where the oxide is formed by the simultaneous sputtering of an absorbed oxygen atom and a metal atom from the bulk material.
D. Ion Induced Luminescence of CN Molecules on Alkali Halide Surfaces

Impact of light ions on alkali halides produces a distinct band spectrum in the wavelength region 230-350 nm; which has the features of a vibrational structure of an electronic transition in a molecule; the source of the emission is located at the surface. We have concluded quite definitely that the emission is from CN radicals on the surface, whose origin lies in adsorbed contaminants. A paper on this phenomenon is published. A. I. Bazhin, E. O. Rausch and E. W. Thomas, J. Chem. Phys. 65, 3897 (1976). The abstract follows:

During a study of luminescence induced by low energy (20 keV) light ion \( \text{H}^+ \), \( \text{He}^+ \) impact on certain alkali halides (LiCl, NaBr, NaCl, KBr, KCl) we have observed a band spectrum in the region 230 nm to 350 nm. The bands are separated by 0.26 eV and have a half width of 0.12 eV; no fine structure is observed. Identical bands of much increased intensity are observed when samples deliberately doped with CN are bombarded. The phenomenon is not found with KBr crystals. We suggest that the observed bands are due to transition in the CN molecules, the \( \text{D}^2\Pi_1 \rightarrow \text{X}^2\Sigma^+ \) transition that is observed as a very weak transition in discharges. The mechanism whereby CN is formed on the samples remains unclear but appears to be influenced by the presence of adsorbed water.

E. General Conclusion

The original objective of the project was to understand the continuum or broad band luminescence of certain metals and alkali halides; this was accomplished quite readily. In the course of the work we successfully explained for the first time the continuum emission observed outside transition metal surfaces. Also we detected the formation of CN on alkali halides; probably the first published example of an ion induced surface chemical reaction.

VIII. Publications


IX. Invited Papers at Conferences


X. Other Seminars and Contributed Papers


XI. Theses


XII. Inventions or Discoveries

We claim no patentable inventions. However there are two major discoveries that should be recognised.

1. A method for producing, by sputtering, long lived excited transition metal oxides which produce continuum emission. This is the first effective mechanism for producing spectra of transition metal oxides; since there is an inherent population inversion there is some potential for use as a tuneable laser mechanism.

2. Discovery of the process of ion induced (or catalyzed) chemical reactions on a surface leading to formation of cyanide.

XIII. Scientific Collaborators

The following have collaborated in this NSF funded project although in some cases no direct financial support of income was provided.


3. Anatoli I. Bazhin. Faculty member of Donetsk University in the USSR. Visiting faculty member at Georgia Tech. under the USA-USSR young faculty exchange program.

XIV. Comments

The principal investigator has secured funding under NSF grant DMR77-04110 (effective 8/1/77) for further work on certain aspects of this program. Specifically the grant will cover a study of the chemical reaction which leads to CN formation (see VII. D) and similar reactions leading to CH formation.

XV. Signature

E. W. Thomas
E. W. Thomas
Professor
Principal Investigator

10/4/77
Date
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Attachment to Form 98A (Grant DMR 73 02317)

List of Publications


