OPTICAL AND ELECTRONIC TRANSPORT PROPERTIES OF LUMINESCENT SEMICONDUCTORS, AMORPHOUS MATERIALS AND METASTABLE SOLIDS

FINAL REPORT

FERD WILLIAMS, MICHAEL MARTENS AND DAVID BERRY

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PHYSICS DEPARTMENT, UNIVERSITY OF DELAWARE, NEWARK, DE 19711

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OPTICAL AND ELECTRONIC TRANSPORT PROPERTIES OF LUMINESCENT SEMICONDUCTORS, AMORPHOUS MATERIALS AND METASTABLE SOLIDS.

Ferd Williams, Michael Martens, and David Berry

Physics Department, University of Delaware
Newark, DE 19711

Experimental and theoretical studies are included. The photoelectric threshold of lead azide and of amorphous ice and the electron affinity of lead azide were measured. Ammonium nitrate single crystals were grown and their polarized Raman spectra measured. The temperature dependences of zero-phonon pair spectra and their phonon replicas in gallium phosphide were measured. Line widths were explained by coupling with acoustical phonons and non-radiative...
de-excitation attributed to thermal ionizations of electron and positive hole. From esr measurements a chromium-vacancy pair in zinc sulfide was identified, and the anomalous near infrared absorption was explained by the Jahn-Teller effect. D. C. electronic transport and optical properties of amorphous semiconductors with intermediate range order were analyzed theoretically, and dependence on temperature and on model parameters predicted. Configuration interaction and electron-phonon coupling were included in the theoretical spectra of donor-acceptor pairs. The effects of hydrostatic pressure on impurity spectra were investigated theoretically; errors in the literature noted; and application to experiment made. The dependences of the adiabatic potentials and of the intensities and energies of zero-phonon and phonon-assisted transitions on pressure were predicted.
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I. Introduction

The general goal of the research of these grants has been to increase the understanding of the physical properties of compound semiconductors, both crystalline and amorphous, and of metastable solids. The emphasis is on properties which depend on electronic states. In fact this emphasis provides the unifying theme for the research described herein on such diverse materials as lead azide and zinc sulphide and on different phenomena such as photoelectric emission and spin resonance. In some cases the electronic states are of direct interest, for example, for the radiative transitions responsible for luminescence; in other cases, of indirect interest, for example, as structural probes in amorphous materials.

Both experimental and theoretical techniques are used in the research of these grants. Experiment and theory are used in combination and strongly interact in the solution of problems. For example, in subsections II C and III B, respectively, both experimental and theoretical research are reported on the electronic states and radiative transitions of donor-acceptor pairs in order to increase our understanding of associated defects.

Some of the work of these grants has involved close collaboration with laboratories of the U.S. Army. During the early part of the period
covered by this report we had a concurrent grant DA-ARO-D-31-72-G175 funded by the Picatinny Arsenal through ARO-D for research on thin films of lead azide - an important primary explosive. Under that grant we showed, from changes in the ultraviolet and near and far infrared absorption spectra, that the crystal becomes amorphous during initial stages of decomposition, thus monitoring structural changes by observations on electronic states. Under the grants reported on herein we continued research on lead azide, completing the measurement of photo-electric emission (see subsection II A) and more recently shifted our attention to the secondary explosive, ammonium nitrate (see subsection II B). The collaboration continues with Drs. H. Fair and J. Sharma and their colleagues at the Picatinny Arsenal.

More specific goals of the program of the two grants include the following: 1) to characterize the electronic states of metastable solids relevant to possible new techniques for initiation to detonation; 2) to investigate the optical transitions and electronic transport in amorphous materials in order to clarify their structure; 3) to study the radiative and non-radiative transitions of donor-acceptor pairs in semiconductors relevant to improved display devices and 4) to clarify the effects of applied stresses such as hydrostatic pressure on impurity spectra so as to more fully understand electron-phonon interaction.
of dopants. In Sections II and III, respectively, the experimental and theoretical research are reviewed; Section IV summarizes the achievements and conclusions.
II. Experimental Research

A. Photoelectric Emission from Lead Azide

In the following we report improved values of the photoelectric threshold, Fermi level and electron affinity of PbN₆. These quantities are important relevant to the effects of electronic states on initiation and on other explosive characteristics.

The measurements were done in ultrahigh vacuum, 10⁻⁸ torr or better. A retarding potential is applied to the electron collector. From the potential which just allows all photoemitted electrons to be collected, we can obtain the difference in work functions of the PbN₆ and of the gold collector electrode; from the retarding potential which just allows the most energetic electrons to be collected, combined with the photon energy, we can obtain the photoelectric threshold, that is, the energy from the valence band edge to the vacuum level. We thus find for PbN₆ the photoelectric threshold to be 4.4 eV and the Fermi level to lie 0.8±0.2 eV above the valence band edge. The value of the threshold is confirmed by measurements of photoelectric yield, that is, number of electrons emitted versus photon energy. Using the value of the band gap reported by Harry Fair of Picatinny we then find the electron affinity to be 0.6±0.2 eV.
These quantities can be used in the theoretical study of electronic processes in explosive solids and may contribute to evaluation of possibilities for electronic initiation.

B. Preparation and Optical Properties of Single Crystals of Ammonium Nitrate

The emphasis of the part of the research program concerned with the properties of metastable solids was shifted from primaries to secondaries, specifically, from PbN₆ to NH₄NO₃.

Most previously reported studies of NH₄NO₃ have been restricted to polycrystalline material. Therefore, a program to determine the best method for the preparation of single crystals of NH₄NO₃ was initiated. Undoped, single crystals of phase IV (room temperature phase) NH₄NO₃ were grown successfully by two methods: 1) temperature depression of supersaturated solutions of NH₄NO₃ in water and methanol and 2) solvent evaporation from solutions in water and methanol. The largest crystals (1/2 cm)³ were made by solvent evaporation from methanol solution. The absorption spectra of these samples indicated that no residual water was present and were the same for all samples independent of method of preparation.
The optical absorption edge at room temperature was measured to be at 340 μm. Fairly strong absorption was observed at 1.570 and 1.640 μm. Very strong absorption was seen at 2.3 μm.

Raman spectra taken on the crystals as well as on aqueous and methanol solutions showed most of the reported modes of the \( \text{NH}_4\text{NO}_3 \). The low energy lattice modes of the crystal were evident and all lines had widths appreciably narrower than those of the solution.

The pressure dependence of the polarized crystal spectra will be investigated under the continuation of this grant.

In addition, the optical properties of \( \text{NH}_4\text{NO}_3 \) protonated for better chemical stoichiometry in terms of the final reaction products will be actively investigated. A 2.5 MeV van de Graaf will be used for the protonation. The radiation damage associated with the \( \text{H}^+ \) implantation is predicted to make the material amorphous and possibly to affect the phase transitions characteristic of crystalline ammonium nitrate.
C. Effects of Electron-Phonon Interaction on Donor-Acceptor Pair Spectra

The donor-acceptor pair luminescence spectra from shallow impurities in gallium phosphide were studied. The temperature dependence of the near pair lines and the broad distant pair bands for vapor phase epitaxially grown layers of gallium phosphide with sulfur donors and carbon, zinc and cadmium acceptors were investigated.

Initial work was done on a fixed temperature liquid He cryostat utilizing a mercury lamp as the excitation source. The cryostat was replaced with a variable temperature cryotip capable of covering the range of temperatures from 5 K to 300 K. The sample holder was redesigned for these studies. The signal-to-noise of the spectra was considerably improved by the acquisition of an Argon ion laser for the primary excitation source. Resolution was improved by replacing the 0.5-meter Jarrel-Ash scanning monochrometer with a Spex 1702 0.75 meter monochrometer. Computer software for data analysis was developed and improved. This included an overlapping component deconvolution with variable function capability and surface projection graphics for fast data interpretation. Data was digitized to allow faster data analysis.

The principal scientific results of these studies are the following: the so-called zero-phonon lines are zero-phonon only with respect to optical phonons and are phonon-assisted and
broadened by acoustical phonons; two thermally-activated, non-radiative processes compete with the radiative de-excitation of near pairs and are identified as the thermal ionizations of the first and second electronic particles captured by the pair; and a pronounced temperature-dependence of the distant pair bands is attributed to changes in the relative intensities from the pairs contributing to these bands.

D. Spin Resonance and Optical Properties of Chromium-doped Zinc Sulfide

Work was completed on the electron spin resonance (esr) of ZnS:Cr. Through the use of esr studies, a center consisting of a nearest neighbor pair of Cr\(^{3+}\) at a cation site and a sulfur vacancy was found. The variation in the esr spectra before and after heat treating in a sulfur atmosphere at 950\(^\circ\) C was used to identify the center. From the orientational studies of the intensities and spacings of the esr lines a spin Hamiltonian was determined.

The analysis of our earlier measurements of the near infrared absorption of ZnS:Cr crystals was also completed. The band at 5700 cm\(^{-1}\) corresponds to the \(^5T_2 + ^5E\) transition of Cr\(^{2+}\) and has an anomalous temperature dependence. The half-width and peak position increase linearly with temperature. These dependences are interpreted as originating from a large difference in the frequency of Jahn-Teller modes between the excited and ground states.
E. Photoelectric Emission from Amorphous Ice

X-ray photoelectric emission measurements were made on amorphous ice. Samples were made with an evaporated gold dot on the surface for a reference potential. From these measurements the photoelectric threshold was found to be 9 eV.

In order to obtain a more accurate value of the photoelectric threshold, vacuum ultraviolet photoelectric emission measurements were made. Very thin films of ice on a gold substrate were used. The surface potential of the amorphous ice was probed by the photoemission from a gold dot on the ice surface. A method was developed to analyze the data, which allows for the separation of the photoemission from the ice and the photoemission from the substrate through pinholes in the ice. It was found that the photoelectric threshold of amorphous ice is 8.7±0.07 eV. These results show that the electronic states of the water molecules are strongly perturbed upon condensation. The perturbation is dependent on structure as evident from spectral changes in the photoelectric emission which were seen when the amorphous ice had been annealed at 147 K and converted to cubic ice.
III. Theoretical Studies

A. Amorphous and Graded Semiconductors

The investigation of the electronic and optical properties of mixed, graded semiconductors done under previous grants was extended to certain well-defined amorphous systems, those having medium range order. Mixed crystals in which the components formed either globular inhomogeneities or superlattices were investigated. Globular inhomogeneities are viewed as arising from spinodal separation, a process known to occur in many mixed systems. A metastable phase of the mixed system can be formed in which the concentration profile has a spatially periodic character. In such systems the band edge will be position dependent and can be described in terms of two types of grading functions: 1) electrostatic grading, in which the band gap remains position independent, and, 2) deformational grading, in which variations in the conduction and valence band edges result in a band gap that varies with position.

The solutions of the one electron Hamiltonian were found using the WKB approximation for the globular systems and the Mathieu solutions for a sinusoidal super-lattice.
From these investigations the following results were obtained:

1) The details of the absorption edge, of the band tailing and densities of states for both extended and localized states were found. Predictions were made as to the dependence of the optical absorption on model parameters. It was shown that an Urbach-like tail would arise in systems with electrostatic grading but none for those with deformational grading.

2) D.C. electronic transport properties for specific three dimensional systems with graded, globular inhomogeneities were investigated. The mobility was found to have a $T^{-1/4}$ dependence as is characteristic of many amorphous semiconductors. The temperature range over which this dependence occurred was found to depend upon the size of the inhomogeneities. A connection was made between the limits of validity and inhomogeneity size.

3) Properties of the electronic states were determined. The states near the crests of the undulating band edge and the localized states of the system were obtained. The dependence of the minigaps on the grading function was determined.

4) Some work was done on the Landau levels in graded systems. Here, combination of the interactions of the magnetic field perturbation and the grading perturbation was determined.
B. Electronic States and Radiative Transitions of Donor-Acceptor Pairs

The continuing theoretical work on donor-acceptor pairs and higher associates is focused at bringing the theory to a level which provides predictions comparable in accuracy with that of current experimental results. The amount of delocalization and attenuation of the effective mass states of the donor and acceptor between their cores was determined. The effect of the interaction Hamiltonian on effective mass functions was calculated, and thus effects on the radiative transition energies and on transition probabilities were evaluated. Also electron-hole correlation energy was estimated.

Effective Hamiltonians for donor-acceptor pairs were constructed and used to determine the electronic energies. These investigations confirm that the static dielectric constant can be measured from pair spectra; one can also obtain the energies for isolated dopants. Second quantization was used to construct an effective Hamiltonian that includes the interaction of phonons with the pairs.
III. Achievements and Conclusions

The principal achievements in experimental research under the two grants are the following: 1) the determination of the electron affinity of lead azide as 0.6±0.2 eV and of its Fermi level as 0.8±0.2 eV above the valence band edge; 2) the successful growth of large single crystals of ammonium nitrate and measurements of their polarized first order Raman scattering and its temperature dependence near the phase III-phase IV transition temperature; 3) the measurements of the temperature dependences of the detailed line and band shapes and intensities of the photoluminescent emission of donor-acceptor pairs in gallium phosphide and the interpretation of these results in terms of acoustical phonon broadening, non-radiative recombination involving thermal ionizations of the first and second electronic particle captured by the near pairs, and changes in the relative intensities from the different pairs participating in distant pair emission bands; 4) identification and characterization of Cr$^+$ and Cr$^{+2}$ defects in chromium-doped zinc sulfide; and 5) determination of the photoelectric threshold of amorphous ice as 8.7±0.07 eV and observation of changes in photoemission spectra on crystallization.

The principal achievements in theoretical research under the two grants are the following: 1) solutions for the electronic states, optical absorption and electronic transport of amorphous semiconductors
with ordered, graded globular inhomogeneities, originating from spinoidal separation, and of graded periodic multilayer films, separating in both cases effects due to "electrostatic" and "deformation" graded band edges;

2) application of polaron theory to the associated defects in semiconductors, in particular, to calculate the spectra of donor-acceptor pairs rigorously including the effects of electron-phonon interaction;

and 3) formulation of a general theory of the effects of hydrostatic pressure on electronic states and on optical spectra of molecular and atomic defects in solids, including anharmonicity and the direct effect of pressure on transition energies at a given configuration, as well as the well-known effect of pressure on the probability distribution of atomic configurations, and prediction of the effects of pressure on zero-phonon lines and their phonon replicas and on vibronic spectra.

The general conclusion on the work of these two grants is that the structure of defects in solids and structural changes in luminescent and metastable solids can be investigated by combined experimental and theoretical research on electronic states including effects of electron-phonon interaction. The methods and results reviewed in this report provided the basis for a new program on thin film electroluminescence, for proposed research on the effects of pressure and of pressure gradients on the initiation of metastable solids, and for continued research on optical phenomena in some stoichiometric laser materials.
Appendix I

Publications Completed Under Grant Since 1973


Appendix II

Degrees Granted and Personnel Supported by Grant 1973—present

Present Affiliation shown in parentheses

Bill Baron (Institute for Energy Conversion)
D. Berry (Part-time Postdoctoral Fellow)
D. Hoover (current Graduate Student)
K. Hunter (U.S. Navy)
G. B. Inglis (Massachusetts General Hospital)
T. Kottke (current Graduate Student)
L. Mehrkam, M.S. (1967), Ph.D. (1974) (U.S. Coast Guard Laboratory)
R. Morillo-Soto (current Graduate Student)
A. Oduwole, M.S. (1975) (Nigerian Army)
P. Sotak, M.S. (1976) (Analysis and Technology, Inc.)
S. Varma, Ph.D. (1974) (National Physical Laboratory, New Delhi, India)