FINAL REPORT

Research Grant NGR 05-010-001

National Aeronautics and Space Administration

and

University of California, Santa Barbara

ULTRAVIOLET SOLID STATE SPECTROSCOPY IN THE SPECTRAL REGION 3000 - 300 A

Grant Period: October 1, 1960 - December 1, 1969

Principal Investigator

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INTRODUCTION

Research Grant NGR 05-010-001 began October 1, 1960 and terminated December 1, 1969. During this period experimental research was carried out in the area of solid state spectroscopy on a variety of materials of interest to both ultraviolet optics and solid state physics. Studies were aimed principally at obtaining a detailed knowledge of fundamental electronic spectra and optical properties from near-normal incidence reflectance measurements obtained over a broad range from 3000 - 300 A (4 - 40 eV). In the course of the research, other techniques involving photoemission, luminescence, thin-film transmission, and modulation spectroscopy were also employed. This research was among the first to obtain low temperature highly resolved exciton and interband spectra for strongly ionic insulators and correlate them with specific electronic states in the solid. The most significant results of the research were:

a. A detailed understanding of the interband spectra of several alkali halides and alkaline earth oxides for which the first correlations were made of spectral data and empirical psuedo-potential band structure calculations in ionic solids,

b. Observation of exciton-phonon bound states in alkaline earth oxide spectra,

c. The first observation of valence band, spin-orbit splitting in metal oxides,

d. The development and early use of polarizers for far ultraviolet spectroscopy, and

e. Evaluation of the optical constants of a variety of ultraviolet optical materials above the fundamental absorption edge.

SUMMARY OF RESEARCH

The initial effort in the research was a thin-film transmission study of plasmon effects in In and Pb undertaken with the help of A. Alkezweeny. Plasmon induced transmission bands in both materials were observed and used to determine both plasmon energies and d-band excitations in these materials. The results were reported in J. Phys. Chem. Solids, Vol. 24, 1667 (1963).

Simultaneous with the above, J. Osantowski studied the fundamental spectra of CdS and ZnS in normal incidence reflectance. Both spectra were found to be rich in structure which was later identified with density-of-states maxima and interband edges. The results were reported to the American Physical Society in March 1964 and published in J. Phys. Chem. Solids, Vol. 25, 778 (1963) and J. Opt. Soc. Am., Vol. 53, 399 (1963).

X-ray irradiation effects near the absorption edge of LiF were studied by E. Schpansky. An irradiation induced absorption band at 11.1 eV was discovered and its relation to other color centers in LiF determined through bleaching experiments. The results were reported at the First International Conference on Vacuum Ultraviolet Physics, April 1962 and published in J. Quant. Spectrosc. Radiat. Transfer, Vol. 2, 613 (1962).

One of the important results of this research emerged from a comprehensive study of the fundamental spectrum of diamond begun by J. Osantowski and completed by R. A. Roberts. For this work, a low

temperature, vacuum reflectometer was constructed for use in the range 4 - 30 eV at 300 K and 4 - 12 eV at 80 K. Reflectance spectra of the three main diamond types (I, IIa, and IIb) were obtained and the spectral structure associated with specific critical points by comparison with band structure calculations. The results of this study which both substaniated and corrected various aspects of previously published spectra were published in Phys. Rev. Letters, Vol. 17, 302 (1966) and Phys. Rev., Vol. 161, No. 3, 730 (1967).

In about 1964, improvements in band structure calculational techniques and theoretical advances in the interpretation of fundamental spectra showed that a detailed determination of electronic states in insulators was feasible, provided accurate, low temperature reflectance spectra could be obtained from clean single crystals. From 1964 until the termination of the grant, the research was focussed on this problem. Measurements were undertaken on a variety of alkali halides (KI, RbI, LiF, NaCl, and KCl) and alkaline earth oxides (BeO, MgO, and CaO). New techniques, such as a pile-of plates polarizer for the far ultraviolet, an improved low temperature (10 K) reflectometer, and a pulsed high-energy light source were developed to carry out the research.

The explanation of the MgO spectrum by comparison with the empirical psuedo-potential calculation of M. Cohen and P. J. Lin proved to be the key to the problem and in rapid succession data taken by D. M. Roessler on NaCl and KCl were interpreted in terms of the MgO band structure. Later, detailed band structure calculations by Cohen and Fong agreed in their major aspects with our assignments.

The exciton spectra of the alkaline earth oxides (BeO, MgO, and

CaO) proved to present one of the most interesting problems of all. In addition to providing the first measurement of the spin-orbit splitting of the oxygen ion valence band, they showed additional doublet splitting with spacings near the optical phonon energy of the crystal. The suggestion by Toyozawa and Hermanson that these were exciton-phonon bound states opened up a new, fruitful field of research that is currently of considerable interest.

The results of the work since 1964 were published in several journals, co-authored with D. M. Roessler, E. Loh, and R. Whited.

PUBLICATIONS

A complete list of publications resulting from this research is attached. Reprints of most of these papers have already been submitted; those for the one outstanding paper will be submitted as soon as they are received by the author.

CONCLUSION

The present research project made fundamental contributions to solid state physics in general and to the field of ultraviolet optical materials in particular. These contributions range from the determination of plasmon and d-band energies in metals to a detailed understanding of electronic states in ionic insulators. In the course of the experiments, new ultraviolet spectroscopic techniques and instrumentation were developed which will provide the basis for continuing work in the field. The alkaline earth oxides were shown to be among the best materials for studies of the exciting new phenomena of exciton-phonon bound states.

PUBLICATIONS

William C. Walker, author

Extreme Ultraviolet Reflection Spectrum of LiF, J. Opt. Soc. Am., Vol. 52, 223 (1962) with J. Osantowski

Reflection Spectrum of Cubic Zinc Sulfide in the Interband Transition Region, J. Opt. Soc. Am., Vol. 53, 399-400 (March 1963) with J. Osantowski

Vacuum Ultraviolet Optical and Photoelectric Effects in Solids, J. Quant. Spectrosc. Radiat. Transfer, Vol. 2, 613-620 (1962). Also given as an invited paper at the "First International Conference on Vacuum Ultraviolet Radiation Physics", April, 1962

d-Band Transitions in Solids, J. Phys. Chem. Solids, Vol. 24, 1667-1669 (1963)

The Ultraviolet Reflection Spectrum of Cadmium Sulfide, J. Phys. Chem. Solids, Vol. 25, 778-779 (1963) with J. Osantowski

Ultraviolet Optical Properties of Diamond, Phys. Rev., Vol. 134, No. 1A, A153-A157 (1964) with J. Osantowski

Polarization Dependence of the Far Ultraviolet Optical Transitions in CdS, Phys. Rev. Letters, Vol. 13, 51 (1964)

Pile-of-Plates Polarizer for the Vacuum Ultraviolet, Appl. Opt., Vol. 3, 1457 (1964)

Fine Structure in the Direct Absorption Edge of Diamond, Phys. Rev. Letters, Vol. 17, 302 (1966) with R. A. Roberts and D. M. Roessler

Spin-Orbit Splitting of the Γ Exciton in MgO, Phys. Rev. Letters, Vol. 17, 319 (1966) with D. M. Roessler

Ultra-Violet Optical Properties and Electronic Band Structure of Magnesium Oxide, Phys. Rev., Vol. 155, No. 3, 992 (1967) with M. L. Cohen, P. J. Lin and D. M. Roessler

Exciton Structure in the Ultraviolet Spectra of KI and RbI, J. Opt. Soc. Am., Vol. 57, No. 5, 677 (1967) with D. M. Roessler

Electronic Spectrum of Crystalline Lithium Fluoride, J. Phys. Chem. Solids, Vol. 28, 1507 (1967) with D. M. Roessler

Publications (continued)

William C. Walker, author

Electronic Spectrum and Ultraviolet Optical Properties of Crystalline MgO, Phys. Rev., Vol. 159, No. 3, 733 (1967) with D. M. Roessler

Optical Study of the Electronic Structure of Diamond, Phys. Rev., Vol. 161, No. 3, 730 (1967) with R. A. Roberts

Optical Constants of MgO and LiF in the Far Ultraviolet, J. Opt. Soc. Am., Vol. 57, No. 6, 835 (1967) with D. M. Roessler

Electronic Spectra of Crystalline NaCl and KCl, Phys. Rev., Vol. 166, No. 3, 599 (1968) with D. M. Roessler

Phonon-Induced Splitting of Exciton Lines in MgO and BeO, Phys. Rev. Letters, Vol. 20, 847 (1968) with D. M. Roessler and E. Loh

Optical Constants of NaCl and KCl in the Far Ultraviolet, J. Opt. Soc. Am., Vol. 58, No. 2, 279 (1968) with D. M. Roessler

Electronic Spectrum of Crystalline Beryllium Oxide, J. Phys. Chem. Solids, Vol. 30, 157 (1969) with D. M. Roessler and E. Loh

Exciton Spectra of CaO and MgO, Phys. Rev. Letters, Vol. 22, 1428 (1969) with R. Whited

Exciton and Interband Spectra of Crystalline CaO, Phys. Rev., Dec. 15 (1969) with R. Whited (to be published)

RESEARCH PARTICIPANTS

Both postdoctoral and graduate research assistance were employed on the grant. A brief account of these personnel is given below in tabular form.

Name	Position	Date	Degree Awarded	Present Position
A. Matsui	Postdoctoral Fellow	1968-1969		Sano Electronics Tokyo, Japan
D. Roessler	"	1966-1968		Bell Laboratories
R. Roberts	Research Assistant	1964-1967	Ph.D.	Naval Research China Lake
R. Whited	"	1966-1969	Ph.D.	
J. Osantowski	"	1960-1964	M.A.	Goddard Space Flight
L. Hughey	"	1962-1965	M.A.	N.B.S.
E. Schpansky	"	1960-1963	M.A.	Colorado State University
A. Alkezweeny	"	1960-1962	M.A.	Meteorological Research, Inc.

DISSERTATION AND THESIS TITLES

Name	Title
Ph.D. Dissertations	
R. Whited	Exciton and Interband Spectra of Crystalline CaO and MgO
R. Roberts	Optical Study of the Electronic Band Structure of Diamond
M.A. Theses	
L. Hughey	Photoelectron Energy Distributions in the Far Ultraviolet
J. Osantowski	Reflectivity of Solids in the Vacuum Ultraviolet
E. Schpansky	Ultraviolet Color Centers in X-irradiated Lithium Flouride
A. Alkezweeny	Extreme Ultraviolet Photon Absorption in Metals