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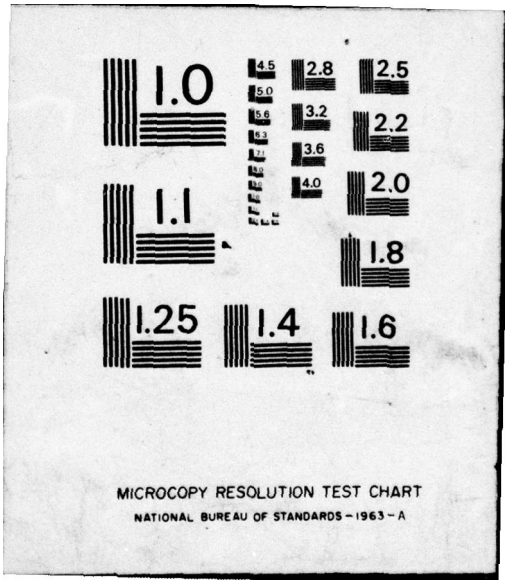
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EXPERIMENTAL AND THEORETICAL STUDY OF THE OPTICAL AND ELECTRONIC PROPERTIES OF SEMICONDUCTORS AND TRANSITION METAL COMPOUNDS

by

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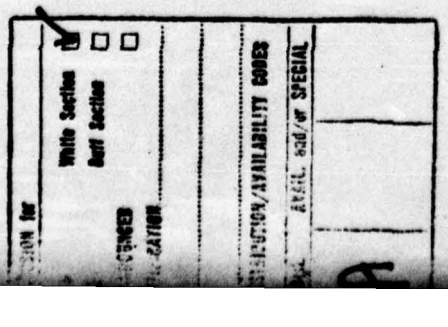
This research was supported by the Air Force Office of Scientific Research (AFSC) under grant No. AF-AFOSR-72-2353

The research project (grant no. AF-AFOSR-72-2353) comprised mainly experimental and theoretical studies of the electronic and optical properties of four families of interesting compounds: Two transition metals Pd and Pt; the four transition metal compounds TiC, TiN, ZrC, and ZrN; the three ternary simiconductors SbSI, SbSBr, and SbSeI; and the four chalcopyrites $CdSnP_2$, $CdSnAs_2$, $CdSiP_2$, and $CdSiAs_2$. Since the theoretical calculations on two metals are similar to the four compounds, the following report presents an overview of the efforts and accomplishments completed during the period of July 1973 - June 1976. However, reference should be made to publications and reports (both published and planned) associated with the grant for further details on the techniques and results. The research undertaken can be divided chronologically into two periods: July 1973 - September 1974 and October 1974, June 1976.

I. July 1, 1973 - September 30, 1974:

On the experimental side our efforts encompassed sample preparation and measurements of the optical reflectivities of the four transition metal compounds. Wafers of these compounds were hot-pressed at about 2200°C and 3000psi, then polished with diamond paste down to 1/4-μm grit. The optical reflectivity measurements extended from 0.1eV in the IR up to 8eV in the vacuum UV.

Except for the spectrum of TiC, the spectra of the other compounds represent the first accurate optical measurements on these compounds. Moreover, by comparing the reflectivity of



TiC with the previous measurements of Lye et al[1], we find more structures that are predicted by the theoretical calculations. The appearance of these structures is an evidence of high accuracy and performance on the part of our experimental apparatus. Further details of the experimental apparatus and features of the resulting spectra are given in references 2 and 3. Theoretically, we have completed the empirical pseudopotential calculations of the electronic band structures pertinent to the four transition metal compounds.[2,3] In the process of the computation we were able to derive a closed form for the matrix elements of the nonlocal d-pseudopotential; thus no numerical integration routine was needed and an appreciable amount of computer time was saved. We subsequently derived the corresponding reflectivity spectra using a direct transition model from the band structure. These spectra show good agreement with their experimental counterparts; thus providing the first successful understanding of the optical properties of the f.c.c. transition metal compounds and their microscopic origins. We found that the structures in the reflectivity spectra are not contributions from critical points but are rather due to contributions from large regions in the BZ, the so-called volume effect. Another interesting result was the test of the general applicability of previously proposed rigid band model to extrapolate the band properties of the nitrides from those of the carbides. Our results have revealed the inadequacy of such a model since the separation in energy of the d and p states were shown to differ

by about 2eV in going from the carbides to the nitrides. However, the model was found to work moderately well for compounds involving the same nonmetal ion and transition metal ion that belong to the same column of the periodic table.[3]

The pursuit of our theoretical investigations proceeded through the computation of the electronic charge distributions in these compounds, based on the wave functions obtained from the band structure calculations.[4,5] In the carbides the charge distributions showed strong metal-nonmetal bonds. The nitrides, however, showed slightly weaker metal-nonmetal interactions but had stronger metal-metal bonding. The metal-like component, characterized by a uniform spread in charge, is very low in the carbides and slightly higher in the nitrides. Furthermore, a charge distribution based on simple linear combination of atomic charge densities of Ti and C was computed and compared with that of TiC. The comparison indicated a partial transfer of charge from Ti to C sites, confirming the partial ionic nature of the bond mentioned above.

In addition to the above efforts the following accomplishments were achieved: 1) Theoretical studies on photoemission properties in CdSe,[6] based on an earlier band structure calculation by Bergstresser et al, were completed. The distribution of photoemitted electrons based on both direct and nondirect processes were calculated. The scattering processes have also been accounted for. The results indicated that both processes are equally important in this semiconductor. 2) In collaboration

with Dr. M. L. Cohen, Department of Physics, U.C. Berkeley, a study involving the comparison of charge distributions in copper and silver[7] and the calculation of the band structure of $NbSe_2$[8] were undertaken. 3) In collaboration with Dr. Y.R. Shen, a theoretical investigation aimed at understanding the nonlinear optical properties of GaAs, InAs and InSb was pursued. The results of these investigations are given in reference 9 and can be extremely useful in the design of electronic circuits at optical frequencies. 4) We have also completed calculations on the angular resolved photoemission from GaAs.[10] Since the angular resolved spectrum can provide more detailed information about the region in $\bar{k}$ space where the electrons are photoemitted, this work represents the first such detailed calculation on the III-V components. Results show the Umklapp process with the surface reciprocal lattice vector is important to understand the photoemission spectra of these materials.

II. October 1, 1975 - June 30, 1976

During this period of time our research was involved with the three ternary semiconductors and the four chalcopyrites. The main problem that confronted us all along was the procurement of single crystals with sizes suitable for optical measurements. This led us to carry out extensive experimental research concerning the possibility of growing good size single crystals. Throughout our investigation we were trying to focus on the most appropriate crystal growing scheme for obtaining the desired crystals. The first phase of our research was concerned with the Sb... series; after trying several growing

methods pertinent to these crystals we focused mainly on two techniques: growth from the melt and vapor transport. The latter method proved to be more convenient and appropriate for our purposes. To optimize our work we had to abandon commercial temperature controllers and ovens, and design a complete high performance system that is capable of accommodating both vapor growth and growth from the melt. The system comprises a two-zone oven with a vacuum jacket and an observation slit extending over its whole length; as well as high stability and high accuracy temperature controllers with a constant cooling rate capability - at a rate less than 1°C/hr. With the two zones we were able to establish the desired temperature gradient for vapor growth. During the course of experimental researching we found that the presence of traces of water vapor inside the sealed and evacuated ampoules prevented the nucleation of crystals within the appropriate temperature range (300-400°C) and consequently supercooled liquid solidified rather instantaneously and yielded very tiny crystallites. We thus found that it is necessary to bake the ampoules for 3 to 4 days during evacuation. Using the apparatus described above we were able to grow single crystals of SbSI and SbSBr with dimensions of about 2 x 1 x 10 mm. To the best of our knowledge the SbSBr crystals are the largest of their kind yet to be grown. By mounting three crystals side by side on a sample holder we obtained the reflectance spectra of SbSBr and SbSI in the range $1.8 < \hbar\omega < 6.0$eV using polarized light parallel and normal to their $\hat{c}$-axes.

In the second phase of our research, we used our past experience in growing the Sb... series to develop and build another crystal growing system suitable for the chalcopyrites. This system operates in the ranges 600° - 1000°C (In contrast to 250° - 500°C for the Sb... series) and has a full cycle of about 30 days; during the cooling phase a controlled cooling rate of less than 11°C/day was achieved. The method of solution growth was used to grow the $CdSnP_2$ and $CdSnAs_2$ (ratios of 94% Sn and 6% $CdAs_2$ or CdP_2 were used). The compounds were placed in a quartz boat inside an evacuated quartz ampoule. However, we were not successful in obtaining large enough crystals for optical measurements. While facing such difficulties in trying to procure suitable size crystals of the chalcopyrite structure we were able to contact Mr. K. J. Bachmann at Bell Labs who promised to supply us with three of the chalcopyrite crystals. Except for $CdSnP_2$, Mr. Bachmann has not yet been successful in growing crystals of sufficient size for our use. The $CdSnP_2$ crystal has been shipped to us but we have not yet received it.

On the theoretical side, our efforts were concentrated along three main lines: 1) Improving an earlier EPM band structure calculation on SbSI by Fong, et al.[11] During that time an automated technique for converging on the most accurate set of pseudopotential form factors has been developed and applied to the SbSI calculation. The improved results did not indicate any significant change near the band gap. However, the magnitude of reflectivity around 4eV has been reduced thus yielding a more acceptable resemblence to experimental data. 2) An elab-

orate group theoretical program has been developed. This program has the capability of generating all the symmetry information pertinent to any of the 230 symmorphic and nonsymmorphic space groups. The symmetry information include the group's classes, characters, and irreducible matrix representations, as well as the symmetrization of the electronic wave functions which leads to block diagonalization of the Hamiltonian matrix. This information is also of great importance in symmetrizing the lattice dynamical form factors and diagonalizing the dynamical matrix.

This program was used in a preliminary computation of the charge distribution in SbSI crystals in 3 planes normal to the $\hat{c}$-axis. The wavefunctions used were obtained from the improved band structure mentioned above. The computation involved the highest 12 valence bands and the lowest 8 conduction bands. The main purpose of this study was to determine the nature of bonding between Sb and S, since the bands considered are mainly derived from the 5p states of antimony and the 3p states of sulphur. On the other hand, bands 1-24 are expected to be derived from 5s(I), 3s(S), 5s(Sb), and 5p(I) states. The results confirmed our anticipations, showing very little contribution around the iodine site. The most interesting result, however, was the clear display of covalent bonding between Sb and S ions. This work was presented together with the associated band structure at the APS meeting in Washington, D.C. last spring.[12] The extensive study of these crystals reported here is essential

in unraveling a variety of potential applications ranging from microwave oscillators and turnable IR detectors to piezoelectric devices. 3) A computer program of the energy band structure of the crystals with the chalcopyrite structure has been developed. This program has been used to calculate the band structure and the derived reflectivity of $CdSnAs_2$, which was fitted to the reflectance data of Stokowski.[13]

In addition to the above investigations the following achievements were completed during the same period: a) A nonrelativistic band structure of the bcc transition metal tantalum has been calculated by the EPM method.[14] States near the Fermi energy agree well with two earlier APW calculations; however, the higher energy conduction bands are lower by leV. In addition, the reflectivity spectra based on both the direct transition and the nondirect transition models showed good agreements with the experimental data of Weaver et al.[15] However, we suggested that the derivative of the reflectivity should provide the decissive information about the validity of either model. b) Similar results on Nb and V were also obtained. Furthermore, we utilized the method of projection operator to calculate the s, p, d parts of the density of states, the so-called partial density of states. Since the present status of the experimental results on partial density of states is restricted only to the simple metals, the present results should stimulate X-ray measurements on transition metals, in order to better understand the deep core state excitations. c) Since the earlier calculations on photoemission, we have found the band structure

of CdSe obtained by Bergstresser and Cohen can be improved. Such improvement has been made. The important improvement is in the high energy conduction bands. Spectrum (reflectivity with electric field $\vec{E}$ parallel to the c-axis of the crystal, with $\hbar\omega \geq 6.$eV agree much better with the experimental data than the earlier results).

All the above calculations were done in collaboration with NASA Ames Research Center at Moffett Field, Calfornia.

d) In collaboration with Shen's group at Berkeley, we have completed the bend structure of HfS_2. This is a layered crystal with octahedral coordination. The spectrum derived from the band structure explains almost all the structure appeared in the measured data. It represents the first realistic comparison between the theory and the experiment for this class of materials which have been subjected to intensive study recently. The program thus developed can further be used to calculate the electronic properties of Zr and Ti dichalcogenides. By systematic study, we should be able to understand the bonding properties of these materials.

By combining the program developed for $NbSe_2$, we are able to study all the layer compounds whose electric, magnetic and superconducting properties are of great interest.

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List of Coupling Activities

1. M. L. Cohen, U. C. Berkeley
   Electronic Properties of
   a. Semiconductors
   b. Transition Metal Layer Compounds
   c. Noble Metals
   d. Pseudopotential Formalism

2. Y. R. Shen, U. C. Berkeley
   A. Electronic Properties of Semiconductors
   B. Nonlinear Optics

3. [illegible]. E. Whiting, NASA Ames Research Center, Moffett Field
   [illegible]ctronic Properties of
   a. Semiconductors
   b. Transition Metals

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Maged El-Batanouny

Staff Research Associates

Theodore R. Hillyer
William Elsholz

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Submitted

1. M. El-Batanouny, F. Wooten, J.F. Alward, and C.Y. Fong, (Optical Properties and Energy-Band Structures of TiN and ZrN).

2. J.F. Alward, C.M. Perlov, C.Y. Fong and C.G. Sridhar (Calculated Electronic Properties and Reflectivity of Tantalum).

Publications, continued

In preparation

1. M. El-Batanouny, F. Wooten, J.F. Alward, and C.Y. Fong, "Comparison of Charge Distributions and Bonding in the Carbides and Nitrides of Titanium and Zirconium" to be submitted to Phys. Rev.

2. J.F. Alward, C.M. Perlov, C.Y. Fong and C.G. Sridhar (Calculated Electronic and Optical Properties of V and Nb).

3. C.M. Perlov, J.F. Alward, C.Y. Fong (Empirical Pseudopotential Band Structure and Calculated Reflectivity in Rh).

4. C.G. Sridhar, E.E. Whiting and C.Y. Fong(Band Structure and Optical Properties of CaSe).

5. "Electronic Properties and Charge Distributions in the Semiconductors SbSI, SbSBr, SbSeI".

6. "Optical Properties, Electronic Band Structure, and Charge Distributions in Crystals with the Chalcopyrite Structure".

Thesis

J.F. Alward, Theoretical Studies of the Electronic Properties of Transition Metals and Transition Metal Compounds.

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

(18) (19) **REPORT DOCUMENTATION PAGE**

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: AFOSR - TR-76-1136
2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER: (9)

4. TITLE (and Subtitle): (6) Experimental and Theoretical Study of the Optical and Electronic Properties of Semiconductors and Transition Metal Compounds.
5. TYPE OF REPORT & PERIOD COVERED: Final Report, 3
6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s): (10) C. Y. Fong, Frederick Wooten
8. CONTRACT OR GRANT NUMBER(s): (15) AF-AFOSR-2353-72

9. PERFORMING ORGANIZATION NAME AND ADDRESS: Department of Physics, University of California, Davis, CA 95616
10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: (16) 9763, 61102F, 68130

11. CONTROLLING OFFICE NAME AND ADDRESS: AFOSR - NE, Bolling Air Force Base, Washington, D.C. 20332
12. REPORT DATE: (11) 30 Aug 76
13. NUMBER OF PAGES: 9

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office): (12) 18 p.
15. SECURITY CLASS. (of this report): UNCL
15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Semiconductors, SbSI, SbSBR, CdSnAs, TiC, TiN, ZrC, ZrN, Transition metal compounds.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The optical reflectivities of face-centered-cubic TiC, ZrC, TiN, and ZrN have been measured in the range 0.1<ħω<8.0eV. Subsequently, the electronic-energy-band structure for these compounds have been calculated using a modified empirical-pseudopotential method, and the structures in the reflectivities derived from these band structures show one-to-one correspondence to the structures in the experimental data; the agreement is to within 0.2eV. The charge distribution of these transition metal

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compounds were then calculated using the wave functions of the EPM calculations. The charge distribution (CD) explicitly shows a partial transfer of charge from the metal to the nonmetal that is more pronounced in the carbides than in the nitrides. In general the CD's show an ionic-covalent bonding between the metal and nonmetal, which the metal-metal bonds are weaker. We have developed a high accuracy and performance crystal growing system and were successful in obtaining crystals of SbSI and SbSBr suitable for optical measurements. Optical measurements of reflectivities were completed on these crystals in the range $1.8<\hbar\omega<6.0$eV. An improved band structure of SbSI was calculated together with the derived reflectivities. The resulting wave functions were used in computing the charge distribution in SbSI, which displayed a clear covalent bonding between Sb and S, and confirmed the anticipated ionic behavior of the iodine atoms. Furthermore, a program for calculating the band structures of crystals with chalcopyrite structure was developed and used in calculating the band structure of $CdSnAs_2$. Finally, an elaborate group theoretical program was also developed. This program has the capability of generating all the symmetry information pertinent to any of the 230 symmorphic and nonsymmorphic space groups.