

OPTICAL, INFRARED AND LASER RAMAN STUDIES
IN
HEXAGONAL LAYER SEMICONDUCTING COMPOUNDS

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By

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Thesis submitted to the
Indian Institute of Technology, Delhi
for the award of the Degree of
DOCTOR OF PHILOSOPHY

Department of Physics,
Indian Institute of Technology, Delhi

December, 1974

ACKNOWLEDGEMENTS

The author wishes to express his sincere gratefulness to Dr. O.P. Agnihotri of Physics Department, I.I.T., Delhi, for suggesting the problem and for his valuable and continued guidance. His kindness, patience and encouragement are also greatly appreciated without which this investigation would have never been completed.

The author is grateful to Professor K.L. Chopra and Professor C.L. Mehta as the successive Heads of the Physics Department, I.I.T., Delhi for providing the necessary facilities for the work. The author is grateful to the Director, S.P.L., Delhi for allowing him to use Cary 14 spectrophotometer. Sincere thanks are due to Professor M.S. Sodha for his kind interest in the progress of this work. The author is deeply indebted to Dr. R.C. Tyagi and Dr. H.K. Sehgal for their constant help and stimulating discussions during the course of the present investigation. Thanks are due to the Government of France for the gift of infrared and Raman spectrophotometers.

It is a great pleasure for me to acknowledge the cooperation and help rendered by my colleagues and friends. Financial supports from Director, I.I.T., Delhi and C.S.I.R., India is gratefully acknowledged.

Sincere appreciation is expressed to Mr. S.L. Aneja for efficient typing of thesis and Mr. N.S. Gupta for preparing the drawings.

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PREFACE

The MX_2 ($\text{X} = \text{S}, \text{Se}$ or Te) layer materials characterized by their high degree of anisotropy form a structurally and chemically well defined family known as dichalcogenides. Electrically however, they cover a wide spectrum of properties, from an insulator like HfS_2 , through semiconductors like MoS_2 and semimetals like WTe_2 to true metals like NbS_2 . During the past few years a wide spread interest in the structural, optical, electrical, magnetic and superconducting properties of these layer compounds has evolved as is evident from the recent literature survey. We concentrate here on four semiconducting compounds, three of which (MoS_2 , MoSe_2 and MoTe_2) belong to group VI, whereas the fourth one (SnSe_2) is a IV-VI compound. These compounds have very weak interlayer van der Waal's binding and therefore found to be very useful as solid lubricants.^{1,2} This interlayer gap can be increased to accept alkali metal atoms or ions.³⁻⁵ Recently, in SnSe_2 a notable polarity dependent memory switching has been observed.⁶ These further increased the interest of scientists in these materials. Although structure and semiconducting properties of these materials are known to some extent, there is a very little knowledge about their optical behaviour. The published work in electronic region is mainly concentrated on MoS_2 ⁷⁻¹² possibly because of its availability in nature. In case of MoSe_2 and MoTe_2 only a few papers are available at present. The data of SnSe_2 as reported by various workers¹³⁻¹⁶ are very divergent in nature. The observation of lattice vibrations of any of these layer compounds have not been reported until the

work on natural MoS_2 was published.¹⁷ No work has so far been done on infrared and Raman studies of MoSe_2 , MoTe_2 and SnSe_2 crystals.

In the present investigation single crystals of MoS_2 , MoSe_2 , MoTe_2 and SnSe_2 were grown in our laboratory, the structures of these crystals were established and their electronic and vibrational spectra were extensively studied. The reported work has been divided in six chapters.

In Chapter I basic concepts and theories of optical infrared and Raman spectra are discussed in brief. Methods used in the thesis for calculating optical constants from the observed spectra are also explained

Chapter II deals with the experimental methods. Good large single crystals have been grown by using vapour phase transport technique with and without a transport agent. For MoX_2 , bromine and for SnSe_2 , iodine were the suitable transporters. The crystal structures are analysed using optical microscopy, X-ray analysis and electron microscopy. Most of the crystals were identified as 2H-polytypes. However, effect of various growth parameters has not been studied in detail because the main aim was to get good quality large single crystals rather than to establish the growth mechanism. Experimental techniques involved in cleaving thin crystals, measuring their thickness and in recording their optical (visible and near infrared), infrared (down to $50\mu\text{m}$) and He-Ne gas laser excited Raman

spectra are discussed in this chapter. A brief description of spectrophotometers used is also included. Since all the crystals were in the form of thin sheets, no measurements were possible for $\bar{E} \parallel \bar{C}$ orientation.

Chapter III describes the crystal structure and the symmetry of single crystals in detail. Group theoretical analysis of the Γ point lattice modes is applied to two space groups D_{6h} and D_{3d} of our interest.

Chapter IV gives our results on optical spectra in visible and near infrared regions. The work is mainly concentrated on transmission measurements on these compounds. The optical constants are calculated from transmission data and compared with the published results. The behaviour of exciton bands in MoSe_2 and MoTe_2 is found to be similar to that already reported in case of natural MoS_2 . In SnSe_2 a detailed analysis of the shape of intrinsic absorption edge has been performed and the types of transitions responsible for it are identified. The existence of allowed direct transitions across an energy gap of 2.1 eV and forbidden indirect transition across an energy gap of 0.98 eV is established. However, the existence of two forbidden indirect transition energy gaps¹³ is not found. Further, no existence of forbidden direct transitions as reported earlier¹⁴ could be found. The wide differences among results of various workers on refractive index of SnSe_2 are thought mainly due to an inaccurate assignment of order number to an interference fringe.

Chapter V gives our results of infrared ($\leq 50 \mu\text{m}$) studies of molybdenum dichalcogenides. To-date only the 'reflectivity' measurements in Reststrahlen region on single crystals of natural MoS_2 ¹⁸ and on pressed pellets of MoS_2 and MoSe_2 ¹⁹ are reported. We studied the infrared 'absorption' of single crystals of MoS_2 , MoSe_2 and MoTe_2 . The infrared absorption of their KBr pellets and reflection of pressed pellets of these compounds are also studied. The fundamental absorption bands of single crystals of MoS_2 and MoSe_2 are fitted to a damped classical oscillator model and the various parameters of oscillator are estimated. Besides fundamental, the infrared spectra of MoS_2 , MoSe_2 and MoTe_2 showed a number of multiphonon absorption bands. In MoSe_2 an impurity band is also observed and attributed to oxygen impurity in the crystal. The index of refraction of MoX_2 ($X = \text{S}$ or Se) in Reststrahlen region is determined from interference fringes and fitted to a theoretical curve of oscillator model.

Chapter VI gives our results of laser excited Raman studies of MoX_2 ($X = \text{S}$, Se or Te) and SnSe_2 . In each case all the Raman active modes as predicted by theory have been identified. To-date Raman spectrum of MoS_2 is only available.¹⁸ On comparing our infrared and Raman results we find a mode degeneracy in MoS_2 as well as in MoSe_2 and MoTe_2 . SnSe_2 data however, show its absence as was expected from the difference between the two structures. Few elementary theoretical calculations of lattice vibrations of MoS_2 family are now available.^{20,21} A comparison between theory and experiment is therefore made and some of force constants are evaluated.

The publications resulting from the above investigation are listed below.

1. Laser Excited Raman Spectra of Gr. VI Semiconducting Compounds.

Solid State Communication, 12, 135 (1973).

2. Infrared Optical Properties of MoSe_2 .

Solid State Communication, 12, 1261 (1973).

3. Laser Raman Spectrum of SnSe_2 *

(Communicated).

4. Optical Constants of SnSe_2 *

(Communicated).

* Presented at Indo-German Conference on "Defects in Non-metallic Solids", I.I.T. Madras, 26-28 February, 1974.

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