

XV-3. Optical Properties of α -MnS in the Fundamental Absorption Region*

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The optical absorption spectrum from 0.1 to 14 eV is presented based on measurements of transmission in the transparent range and reflectance in the opaque range. Discussion is given of various absorption features which include weak manganese $3d^{2+} \rightarrow 3d^+$ transitions, transitions from a wide $S^2-(3p)$ band to the narrow $3d^+$ band and to a broad $4s$ -like conduction band with associated excitons, and possible transitions at the Brillouin zone edge. A suggested band scheme is presented based on the observed absorption.

§ 1. Introduction

Simple compounds of the first transition series are interesting because of diverse electrical, optical, and magnetic effects connected with their electron energy band structure. The NaCl-structured transition metal compounds such as the oxides MnO, NiO, and CoO, and the higher chalcogenides of manganese are insulators (or semiconductors) despite an unfilled d shell of the cation. Apparently no band calculations have been made and very little experimental information from which to determine energy band structure is available, largely because of lack of single crystals of these materials. In this paper we report measurements of optical absorption over a wide photon energy range made on single crystals of α -MnS, and suggest a possible energy band scheme based on the observed effects.

§ 2. Experimental Method

Single crystals of α -MnS (hereafter denoted simply by MnS) were grown by the chemical transport method with iodine as the carrier.¹⁾ The usual growth habit of these crystals in thin platelets characteristically about 5 mm $\times$ 5 mm by 10 to 100 μ thick. Microscopic examination of the surfaces and analysis of the interference fringes observed in optical transmission show the surfaces to be of extremely high quality. Absorption coefficients have been determined from transmission measurements between the absorption edge near 3 eV and the Reststrahl absorption near 30 μ . In extracting absorption coefficients from transmission measurements use was made of reflectance values calculated from

index of refraction measurements taken from the interference fringe positions. Normal incidence reflectance measurements have been taken in the opaque region from 3 to 14 eV and analyzed by the Kramers-Kronig analysis²⁾ for the optical constants and hence the absorption coefficients. Machine evaluation of the integral was performed at 0.1 eV intervals to determine the phase shift, from which the optical constants n and k , and the absorption coefficient, $\alpha = 4\pi k/\lambda$, were computed. The method of Roessler³⁾ was used to extrapolate the data to infinite energies.

§ 3. Discussion of Results

Results of optical absorption coefficient determinations are shown in Figs. 1 and 2 plotted as a function of photon energy. Figure 1 encompasses the region where transmission measurements could be made, and Fig. 2 shows the results of the Kramers-Kronig analysis of reflectance data.

The three absorption peaks of Fig. 1 in the visible region between 1.8 and 3 eV have been observed in a diffuse reflectance spectrum by MnS by Ford, *et al.*⁴⁾ and explained as due to transitions from the ground state of the manganese ion ($^6S_{5/2}$) to higher states of the ion which are split by the crystal field. The sharp peak near 2.7 eV is independent of the crystal field strength in first order and hence is not broadened by lattice vibrational effects as are the other two peaks at 2.0 and 2.4 eV. Structure is resolved in the sharp peak which we assign to a splitting of the $^4A_{1g}$: 4E level which is degenerate in first order but has its degeneracy removed by partial covalency.⁵⁾ With this splitting in

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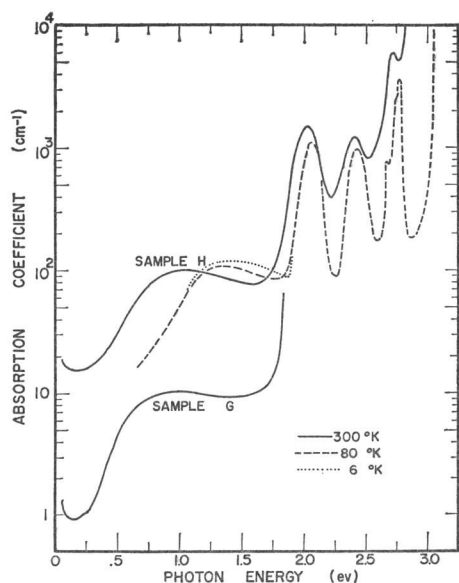


Fig. 1. Spectral dependence of the absorption coefficient of MnS in the transparent region.

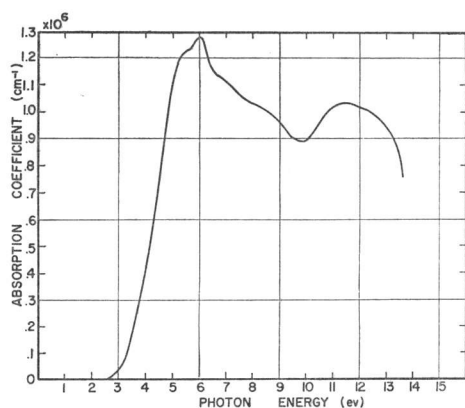


Fig. 2. Spectral dependence of the absorption coefficient of MnS calculated from reflectance data.

mind the maximum width of the $3d$ band is inferred to be 0.1 eV or less.

The broad absorption band centered near 1 eV at room temperature seems to be superimposed on a continuous background that increases steadily with energy. As the temperature is lowered the peak narrows and shifts toward higher energy, reminiscent of F -center absorption in ionic crystals⁶⁾ and impurity-to-impurity absorption in semiconductors.⁷⁾ Although it is difficult to be sure, the absorption seems to be intrinsic as it occurs in the several different crystals examined and does not depend on the heat treatment, despite large changes induced in the continuous background by annealing. We suggest that this

absorption is intrinsic but weakly allowed and takes place during excitation of an electron from one localized level to another. In view of the apparent narrowness of the $3d$ band already referred to, the intrinsic localized levels are assumed to be a filled manganese $3d^{2+}$ level and an empty manganese $3d^+$ level. Such an excitation would correspond to transfer of an electron from the $3d^{2+}$ level of the manganese to the $3d^{2+}$ level of another with a required energy of about 1 eV. The width of the absorption hump would therefore be caused by the participation of many phonons due to the strong coupling to the lattice of the highly localized initial and final states.⁸⁾

A strong absorption edge is seen to begin at about 2.8 eV (Fig. 1) with smoothly rising absorption to a maximum of greater than 10^6 cm^{-1} near 5 eV (Fig. 2). This magnitude suggests an intrinsic allowed transition. It is suggested that this absorption is due to transitions from the $3p$ band of sulfur to the $3d^+$ level, which are allowed electric dipole transitions. Two very sharp peaks have been observed in transmission measurements taken on the thinnest sample (about 5μ) at helium temperature. The peaks are barely but clearly separated from the rapidly rising absorption at energies of 2.96 and 3.05 eV. D. M. Eagles,⁹⁾ in discussing optical absorption due to transitions from a wide band to a narrow band in ionic crystals, suggests that exciton structure in the absorption edge will consist of a series of probably unresolved bands corresponding to excitons produced with different numbers of emitted and absorbed phonons. He suggests, however, that an exciton process involving no emission or absorption of phonons will be a line absorption. A likely interpretation for the two tiny peaks therefore seems to be a no-phonon exciton associated with $\text{S}^{2-}(3p) \rightarrow \text{Mn}^+(3d)$, the duality arising because of the spin-orbit splitting of the $3p$ band. Since sulfur is adjacent to chlorine in the periodic table, the spin-orbit splitting of the $3p$ band in the two cases should be similar. Considerable work on optical absorption in the alkali chlorides reveals splitting of I' exciton peaks by 0.1 eV due to the spin-orbit interaction.⁹⁾ The observed splitting of 0.09 eV for the MnS peaks in question is close enough to suggest the correctness of this explanation and to further indicate the participation of the $3p$ band edge in the 2.8 eV absorption edge.

Further structure in the high energy absorption

spectrum of Fig. 2 consists of a peak starting at about 5.8 eV and peaking near 6 eV, a break in the curve near 6.5 eV with a possible broad band extending to 10 eV, and a broad band starting near 10 eV with possible faint structure in it. The structure from 7 to 9 eV should not be taken too seriously as weak light source intensity magnified possible errors in this energy range. It can generally be concluded from the results that sharp exciton structure does not dominate the absorption spectrum as in the case of the alkali halides. However, one gets the impression that details of the structure between 5 and 8 eV may be washed out by overlap of adjacent peaks.

A simple correlation of the observed lowest energy exciton peaks with the inverse square of the lattice constant for the NaCl-structured alkaline earth chalcogenides suggests a prominent exciton peak should occur for the MnS lattice constant between 5 and 6 eV. It therefore seems likely that the peak at 6 eV may be due to an exciton associated with transitions from the $3p$ band to a broad $4s$ -like band of manganese. If this is correct, the broad absorption from 6.2 to 10 eV should be assigned to band transitions associated with these bands.

Lacking the guidance of any semblance of detailed band calculations pertaining to MnS, explanation of the higher energy structure is likely to be even more speculative. However, in the light of Phillips¹⁰⁾ review of the band structure deduced from numerous experiments on NaCl-structured alkali halides, a suggestion will be offered. If one assumes a nearly free electron model for the conduction band the next singularity in the density of states above the minimum of the conduction band (assumed to be at the Brillouin zone center) may be expected to occur at the symmetry point L in the (111) direction at the zone edge. A second critical point will be X in the (100) direction. The energy positions of these conduction band critical points relative to the minimum point of the conduction band, assumed to be at the zone center Γ_1 is given by Phillips as

$$E_f(X) = \hbar^2/2ma^2 = 5.3 \text{ eV},$$

$$E_f(L) = 3\hbar^2/8ma^2 = 4 \text{ eV},$$

where the energies have been computed for the lattice constant (a) of MnS. Thus, if the absorption band beginning near 6 eV is due to the onset of absorption at a minimum band gap located at Γ , additional bands might begin at

10 eV and 11.3 eV. This could be an explanation for the 10–14 eV absorption band.

§ 4. Summary of Suggested Band Structure

In Fig. 3 we summarize on a somewhat ima-

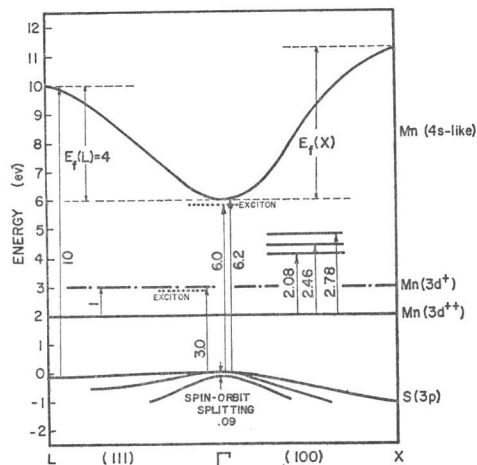


Fig. 3. Summary of suggested assignments for features of the optical absorption of α -MnS, based on a somewhat imaginative band diagram.

gative band diagram the results of the suggested optical transitions found in this work. The form of the valence and conduction bands is sketched by analogy with the bands of many NaCl-structured compounds surveyed by Phillips. The observed transitions in increasing order of their energy are as follows: (Number 2, 3 and 4 are based on helium temperature data where the structure is clearer. The others are for room temperature.)

1. Near 1 eV... $3d^{2+} \rightarrow 3d^+$ intrinsic but parity forbidden transitions between localized levels, with participation of many phonons.
2. 2.08, 2.46 and, 2.78 eV... $3d$ crystal field splitting transitions. The 2.78 eV peak suggests the $3d$ band is less than about 0.1 eV wide.
3. 2.96 and 3.05 eV...tiny, spin-orbit-split exciton peak associated with the $3p \rightarrow 3d$ transition.
4. 3.1 eV... $3p \rightarrow 3d$ absorption edge.
5. 6.0 eV...possible $3p \rightarrow 4s$ exciton peak assumed to be at Γ .
6. 6.2–10 eV... $3p \rightarrow 4s$ broad band-to-band transitions.
7. 10 eV...onset of transition possibly at L in the 100 direction at the Brillouin zone edge.

References

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DISCUSSION

Frederikse, H. P. R.: Is there any evidence of conduction in the Mn 3d-band (or levels) either from direct conductivity or photoconductivity measurements?

Callaway, J.: The conductivity has been studied extensively, and the results are reported in the PhD thesis of Dr. Huffman. Unfortunately, the results are not simple to interpret.

Fan, H. Y.: Do you have an interpretation for the low energy absorption?

Callaway, J.: We are inclined to interpret the low energy (~ 1 eV) absorption as due to charge transfer among the Mn^{++} ions.

Mitsubishi, H.: Could you observe optically any particular difference above and below the Neel temperature?

Callaway, J.: The three peaks in the optical absorption around 2 eV have a temperature dependence, involving a shift to higher energy with decreasing temperature. This has been studied in detail, and is largest at the Neel temperature. The temperature dependence of the sharp peak C can be accounted for in terms of the exchange interaction. In a simple model, the energy of this transition is proportional to the magnetic energy of a manganese ion interacting via a Heisenberg exchange mechanism with its neighbors. This can be determined from the specific heat curve after the lattice contribution has been subtracted. The agreement with the observed temperature dependence is quite good. A more detailed description can be found in the thesis of Dr. Huffman.