



Photoemission investigation of the electronic structure of manganese
by Gary Joel Stensland

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in Physics
Montana State University
© Copyright by Gary Joel Stensland (1969)

Abstract:

Photoemission measurements in the spectral range from 4.1eV(threshold) to 11.8eV have been obtained from evaporated films of Mn. The nondirect transition model is used to obtain the optical density of states. The filled d-like states have a prominent peak 0.9±0.2eV below the Fermi energy, a shoulder at approximately 3.5eV below the Fermi energy, and an estimated width of 4.8eV. No structure was observed in N_c for energies above the vacuum level. The reflectance of Mn for angles of incidence of 12.5°, 40°, and 60° is measured from 2eV to 11.5eV, and is found to be structureless, except for a very broad and weak peak centered about $h\nu=7.0\text{eV}$.

PHOTOEMISSION INVESTIGATION OF THE ELECTRONIC
STRUCTURE OF MANGANESE

by

GARY JOEL STENSLAND

A thesis submitted to the Graduate Faculty in partial
fulfillment of the requirements for the degree

of

MASTER OF SCIENCE

in

Physics

Approved:

N. S. Moise

Head, Major Department

Gerald J. Lapuyre

Chairman, Examining Committee

A. Goering

Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana

June, 1969

ACKNOWLEDGMENT

The author wishes to express special thanks to Dr. Gerald J. Lapeyre, his thesis advisor, for his patience, guidance, and constructive criticism which made this thesis possible. The helpful guidance of other committee members, Dr. Georgeanne Caughlan and Dr. V. Hugo Schmidt, was also appreciated. Informative discussions as well as technical aid and advice rendered to the author in the course of this investigation by Kenneth A. Kress were very helpful. The author wishes to express his gratitude to this fellow student. The contributions of C. Badgley, F. Blankenberg, and Dr. E. Holversen in the design and construction of apparatus was appreciated. Thanks also to my wife for typing this thesis and being so patient and understanding.

TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
II. THEORY	3
III. APPARATUS AND PROCEDURE	11
A. Photoemission	12
B. Reflectance	15
IV. RESULTS	19
A. Reflectance Data	19
B. Photoemission Data	22
C. Optical Density of States Analysis	28
D. Summary	32
LITERATURE CITED	34

LIST OF FIGURES

	Page
Fig. 1 Side View of Reflectometer Used for Reflectance Measurements	16
Fig. 2 Spectral Reflectance of Mn Sample B at Three Angles of Incidence and the Effect of Exposure to the Atmosphere	20
Fig. 3 Spectral Reflectance of Mn Sample C at Three Angles of Incidence	21
Fig. 4 Quantum Yield and Determination of the Work Function of Mn	23
Fig. 5 Sample Dependence of Energy Distribution Curves at $h\nu=10.2\text{eV}$ Plotted as a Function of $E-h\nu+\phi$	25
Fig. 6 Energy Distribution Curves for Sample VI for $h\nu=6.2\text{eV}$ to $h\nu=9.8\text{eV}$ Normalized to the Quantum Yield	26
Fig. 7 Energy Distribution Curves for Sample VI for $h\nu=10.2\text{eV}$ to $h\nu=11.8\text{eV}$ Normalized to the Quantum Yield	27
Fig. 8 Valence Band Optical Density of States of Mn	29
Fig. 9 Effective Final Optical Density of States of Mn	31

ABSTRACT

Photoemission measurements in the spectral range from 4.1eV(threshold) to 11.8eV have been obtained from evaporated films of Mn. The nondirect transition model is used to obtain the optical density of states. The filled d-like states have a prominent peak 0.9 ± 0.2 eV below the Fermi energy, a shoulder at approximately 3.5eV below the Fermi energy, and an estimated width of 4.8eV. No structure was observed in N_c for energies above the vacuum level. The reflectance of Mn for angles of incidence of 12.5° , 40° , and 60° is measured from 2eV to 11.5eV, and is found to be structureless, except for a very broad and weak peak centered about $h\nu=7.0$ eV.

I. INTRODUCTION

The electronic structure studies of metals have been subjects of both experimental and theoretical investigations for many years. Methods such as de Hass-van Alphen, cyclotron resonance, and anomalous skin effects are useful in studying electronic properties near the Fermi surface of the metals. Photoemission measurements, however, have the attribute of giving information about the electronic properties over wide energy ranges centered about the Fermi level. And in contrast to other optical measurements, photoemission studies allow one to measure the energy of the electrons after excitation and thus obtain information on the initial and final states.

The optical constants which can be determined from reflectance measurements are related to the response of the electrons integrated over all final states at a given photon energy. As a result, only energy differences are determined for the excitation process. Reflectance measurements do, however, depend on a simpler physical process since electron scattering in the excited states does not contribute to the process, and information can be obtained for all photon energies. Thus determination of the optical constants does provide a useful correlation with photoemission results besides having its own intrinsic value.

The purpose of this work was to use the photoemission

process to study the metal manganese. The photoemission technique has been used to study the first series transition metals Cu,^{1,2} Ni,^{3,4} Co,^{4,5} and Fe.^{4,6} Lapeyre and Kress of this laboratory studied Cr.^{4,7} Since Mn lies between Cr and Fe on the periodic chart, it was chosen for this investigation.

Section II will summarize the photoemission theory necessary to interpret the data. Section III will present the apparatus and procedure used, and Section IV will present, interpret and summarize the results of this study.

II. THEORY

The energy of the photoemitted electrons, the quantum yield, and the reflectance are the quantities measured in this study. This chapter will show how these measurements lead to information on the electronic structure of manganese.

The photoemission experiment involves the measurement of the kinetic energy distribution of the electrons emitted from a clean metal surface when irradiated by a monochromatic beam of photons. What must be established is the relationship between the kinetic energy distribution of the emitted electrons and the properties of the electronic states in the metal.

The theory will show that the kinetic energy distribution of the electrons that have escaped is proportional to the product of the initial optical density of states (ODS) and the final ODS of the electrons inside the metal. But the crucial point is that the initial and final ODS have different functional dependence which permits their characteristics to be separated.

To establish the basic relationships, photoemission is considered a three step process.^{1,8} The first step involves the photoexcitation of the electrons. In the second step the electrons migrate to the surface and may suffer energy losses due to scattering. In the third step, electrons with

sufficient kinetic energy and the proper momentum escape into the vacuum.

The data in this study show no optical selection rules except energy conservation. When this occurs the optical excitations are called nondirect.* The internal energy distribution of the excited electrons produced in the first step of the photoemission process, is given by⁹

$$M^2 N_c(E) N_v(E-h\nu) \quad (1)$$

where M is the matrix element for the transition, $N_c(E)$ is the optical density of empty final states (conduction band) and $N_v(E-h\nu)$ is the optical density of filled initial states (valence band). Since the experiment measures the kinetic energy (KE) of the electron after it is emitted, the variable E is referenced to the vacuum level. The vacuum level is the minimum energy required for an electron to escape.

The matrix element M is taken to be constant because the data in this investigation show M has no strong energy dependence. This has been frequently observed in other transition metal studies.¹⁰

In the second step of the photoemission process the photoexcited electrons migrate to the surface. During this process a large fraction of the electrons are emitted with

*In some solids the Bloch state wave vector is conserved in the optical transition and the transition is called direct.

no energy loss. However, some of the electrons suffer inelastic collisions and produce two effects. First, electrons are scattered out of the state E and second, the scattered electrons may have sufficient energy to escape. The latter are called secondary electrons.

The energy distributions of the photoexcited electrons inside and outside the metal are now different. A simple model can be used to correct Eq. (1) for the electrons scattered out of the internal energy distributions. Taking the probability for an electron escaping from the metal without losing energy to be given by $e^{-x/L(E)}$ the correction factor is found to be¹¹

$$S(E, \nu) = \frac{\alpha(\nu)L(E)}{1 + \alpha(\nu)L(E)} \quad (2)$$

where $\alpha(\nu)$ is the optical absorption coefficient and $L(E)$ is the escape depth.

In the third step of the photoemission process the electrons leave the surface of the metal. But the excited electrons must have the proper momentum component perpendicular to the surface if they are to escape. This escape function or threshold function $T(E)$ is in general a complicated function.¹ In the simplest case where one assumes the photoexcited electrons are described by plane waves and the surface is atomically clean, the threshold function is¹

$$T(E) = \frac{1}{2} \left(1 - \frac{P_c}{P}\right) \text{ if } P > P_c \quad (3)$$

$$T(E) = 0 \text{ if } P < P_c \quad (4)$$

where P_c is the critical minimum momentum of the electron, and the vacuum level is taken as the zero of energy. Whether this free electron model for the threshold function is valid or not, two things are true. The maximum value of $T(E)$ is $\frac{1}{2}$ because electrons excited with a momentum component away from the surface cannot escape. Also $T(E)$ is a monotonically increasing function of E and zero for energies less than the vacuum level.

Combining the above three steps the expression for the energy distribution curve (EDC) becomes

$$n'(E)_{h\nu} \propto M^2 T(E) S(E, \nu) N_c(E) N_v(E-h\nu). \quad (5)$$

Upon normalizing the EDCs to the number of photons observed, Eq. (5) becomes

$$n(E)_{h\nu} = \frac{M^2 T(E) S(E, \nu) N_c(E) N_v(E-h\nu)}{\int_{E_F}^{E_F+h\nu} M^2 N_c(E) N_v(E-h\nu) dE}, \quad (6)$$

since the denominator gives the total number of transitions.

The quantum yield (Y) is defined as the total number of photoemitted electrons divided by the number of absorbed

photons. The relation between the energy distribution curves and the quantum yield is

$$Y(\nu) = \int_{E_F + \phi}^{E_F + h\nu} n(E) h\nu dE \quad (7)$$

where ϕ is the work function.

Since it is not practical to measure the light flux during EDC measurements the yield is measured by a separate experiment. In measuring the yield only the incident light flux can be measured. Thus the reflectance has to be determined in order to calculate the number of absorbed photons.

The denominator in Eq. (6) is directly related to the imaginary part of the dielectric constant ϵ_2 by the relation^{1,2}

$$\epsilon_2(\nu) = \frac{B}{\nu^2} \int_{E_F}^{E_F + h\nu} M^2 N_c(E) N_v(E - h\nu) dE. \quad (8)$$

The constant B is given by

$$B = \frac{8}{3} \frac{e^2 h}{m^2} \quad (9)$$

where e and m are the electron charge and mass respectively, and h is Planck's constant. Thus Eq. (6) can be written

$$n(E) h\nu = \frac{BM^2 T(E) S(E, \nu) N_c(E) N_v(E - h\nu)}{\nu^2 \epsilon_2(\nu)} \quad (10)$$

Typical values for the transition metals of $\alpha^{-1} \sim 100 \text{ \AA}$ and $L(8\text{eV}) \sim 10 \text{ \AA}$ are quoted in the literature¹² so $\alpha L \sim 0.1$. When $\alpha L \ll 1$, Eq. (2) reduces to $S(E, \nu) = \alpha(\nu)L(E)$ and Eq. (10) becomes

$$n(E)_{h\nu} = BM^2 C(\nu) N_c^{\text{eff}}(E) N_V(E-h\nu) \quad (11)$$

where

$$C(\nu) = \frac{\alpha(\nu)}{\nu^2 \epsilon_2(\nu)} \quad (12)$$

and

$$N_c^{\text{eff}}(E) = T(E)L(E)N_c(E). \quad (13)$$

Eq. (11) is valid for primary electrons, that is, those that escape without being inelastically scattered. The emission of secondary electrons, that is those which suffer inelastic collisions but still escape, makes an additive contribution to Eq. (11) and distorts the EDCs.^{1, 13} Most of the secondaries do not have sufficient energy to escape the surface barrier. As the photon energy increases, however, increasing numbers of secondaries have sufficient energy to escape. The energy distribution of secondaries is a monotonically decreasing function of the electron energy. Based on other studies the secondaries contribute on the order of 20 to 40 per cent at $h\nu = 11.0\text{eV}$.^{1, 4} Certain models have been

used in the literature^{1,13} to account for the contribution of these secondary electrons to the EDCs but they were not utilized in this study because significant information was obtained without them.

The important point to note about Eq. (11) is the functional dependence of N_c^{eff} and N_v . The energy position of the structure found in the EDCs originating from N_v has E-h ν dependence. Structure with E dependence is due to N_c^{eff} . Letting P_c and P_v be the kinetic energy values of the peaks in N_c and N_v respectively, the above properties can be represented by the equation

$$\Delta P_v(h\nu) = \Delta h\nu \quad (15a)$$

$$\Delta P_c(h\nu) = 0. \quad (15b)$$

The spectral reflectance (R) is measured in this work and as noted above is used in the yield study. Furthermore, the spectral reflectance data can be used to obtain the optical constants, eg. α and ϵ_2 . Two methods are available. One, using the Kramers-Kronig relations to reduce normal incidence reflectance data, requires that the reflectance data extend essentially over the whole spectral range. The second method, making use of the Fresnel equations, requires the reflectance at two angles, preferably more, for each energy at which the optical constants are desired.

The optical constants will not be determined in this study but either of the methods above could be used to analyze the data.

III. APPARATUS AND PROCEDURE

If Mn samples were prepared and studied in low vacuums, many impurities would adhere to the surface chemically or otherwise. Also impurities would be trapped in the sample during the evaporation itself. In particular Mn forms many stable oxide compounds.

The impurities have the effect of changing the spectral reflectance, especially in the ultraviolet region. Also almost all of the photoemitted electrons from a metal surface covered with impurities are scattered by the impurities. The typical EDCs obtained from a badly contaminated sample consist of one large peak at low energies. The intrinsic structure resulting from the properties of metal is no longer apparent.

To avoid such impurities, since the electronic structure of pure Mn is desired, the Mn samples were prepared and studied in ultra high vacuum systems. The samples were prepared by vapor deposition.

The Mn samples used for all the measurements were of ultra-high purity.* The main impurity was 250 parts per million of sulphur.

Mn has four crystal structures in the solid state.¹⁴ The room temperature structure for bulk samples is the α form

*Manganese was purchased from Electronic Space Products, Inc., Los Angeles, California.

which is a complex cubic structure.¹⁴ An X-ray diffraction analysis of a Mn film deposited at 10^{-4} to 10^{-5} Torr on a glass slide by heating a tungsten basket containing the source material showed predominately Mn α present. If Mn β or γ were present the lines were not distinct enough to be identified. Other investigations have obtained similar results for evaporated films of Mn.¹⁵

The kinetic energy distributions of the photoemitted electrons (EDCs) and quantum yield measurements are described in Section A. In Section B the apparatus and procedure to measure the spectral reflectance is described. Existing photoemission instrumentation was used in this study. The construction of the reflectometer was part of this thesis work and is therefore described in detail.

A. Photoemission

Most of the photoemission and quantum yield data were taken in an all metal ultra-high vacuum system pumped by an 800 L/s Orb-ion pump. The system contained a LiF window for transmission of the exciting radiation which permitted photon energies up to 11.8eV (1033\AA) to be utilized. A tungsten basket containing the source material was resistively heated until evaporation was accomplished. Base pressure of the system was typically in the 10^{-10} Torr range while evaporation brought the pressure up to the lower 10^{-8}

Torr range. These pressures were measured by an ion gauge.

The primary light source used for all the measurements was a one-meter McPherson model 225 vacuum ultraviolet monochromator which is equipped with a Hinteregger type, DC discharge lamp.

The photodiode geometry used has been described in the literature.^{16,17} Basically it consists of a cylindrical collector and a flat polished cathode which is approximately one inch in diameter. Both were made of stainless steel. The cathode could be moved out of the collector for sample preparation.

The electronics used to measure the EDCs for the electrons photoemitted from the cathode has been fully described in the literature.¹⁸ Basically, for a diode of the above design the current as a function of the retarding bias is an integral energy distribution. The energy distribution is thus obtained by differentiation. A retarding potential varying linearly with time was applied to the collector while photons of fixed energy impinged on the cathode. The electron current from the cathode to the collector was monitored by a Cary Model 401 vibrating reed electrometer. The electrometer output was differentiated by an operational amplifier differentiator.

To determine the quantum yield the total electron

emission was measured with an electrometer and the photon flux was detected by a sodium salicylate coated EMI 9514B photomultiplier tube. The fluorescence from the sodium salicylate permitted detection of the photon flux at energies above the transmission cut off of the tube's glass envelope. The spectral response of fresh sodium salicylate is considered constant. Since the response did vary with age, at the completion of an experiment the sodium salicylate film was compared with a freshly prepared film so that appropriate corrections could be made. The maximum variations were on the order of 10 per cent.

A second method used to study the quantum yield of Mn was to deposit a Au film inside the collector and on the cathode. The quantum yield of Au is reported in the literature.² Therefore by measuring the photoemitted electrons versus incident photon frequency for both a Mn and a Au sample, the shape of the Mn yield curve could be determined and the calibration also made.

The deposited Au films had other uses. By depositing a film of a metal of known work function on the collector, the shifts to expect in the EDCs due to contact potential effects was determined. The Au deposited on the cathode between the Mn films retarded peeling of the Mn films and also indicated when an adequate depth of Mn had been deposited for the

photoemission studies.

B. Reflectance

The optical reflectance $R(\nu)$ is the number of reflected photons divided by the number of incident photons. The ultra-high vacuum reflectometer used to make this measurement is shown in Fig. (1). Its design permits the reflectance to be measured at angles of incidence from 10° to 70° so either method of analysis described in Chapter II could be used to determine the optical constants.

The reflectometer consisted of a 10-inch stainless steel chamber with a LiF window. A Varian e-Gun evaporation source was used to form the thin film to be studied.

As illustrated in Fig. (1), both the substrate, on which the sample was deposited, and the detector, could be rotated. The substrate was mechanically coupled to an Ultek direct-drive rotary motion feedthrough. The detector was connected to a 6-inch ring gear. A permanent magnet outside the system was magnetically coupled to a permanent magnet inside the system which was connected by a shaft and pinion gear to the 6-inch ring gear. About .050 inch of stainless steel separated the two magnets which rotated easily on ball bearings. The number of teeth in the pinion and ring gears were such that 6.9 revolutions of the external magnet moved the detector through one revolution. The design allowed the

