ELECTRICAL RESISTANCE OF MANGANESE SELENIDE AT LOW TEMPERATURE

by

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I Introduction

This paper presents the results of measurements made on the direct-current electrical resistance of manganese selenide (MnSe) in the temperature range from liquid air to room temperature. This substance displays the typical properties of a semi-conductor.

The term "semi-conductor" denotes a solid which shows electronic conductivity at sufficiently high temperature, but whose conductivity tends to zero as the temperature is lowered. Most semi-conductors have properties markedly dependent on the amount and kinds of impurities, but it is to be noted that an impurity in many cases is simply a stoichiometric excess of one of the constituents. For example, cuprous oxide (CuO) has a lower conductivity if oxygen is driven off by heating in a vacuum, and a higher conductivity if the sample is placed in an atmosphere of oxygen.

In any semi-conductor, the effect of the impurity is to disturb the lattice structure of the crystalline solid. By the band theory of A. H. Wilson®, this disturbance means that new energy levels are introduced in addition to the normal levels of the material.

The normal levels for a semi-conductor are two widely spaced bands—the lowest energy band and the conducting band. The region between bands is forbidden, so that no electron can leave the lower level until it has sufficient thermal energy to jump all the way to the conducting state. In this case, there would be no conduction at all for the substance at low temperatures.

The impurity levels, however, fall in the forbidden energy range. Much less energy is required to cause conduction from these levels. The

*See Bibliography.
substance, instead of becoming a perfect non-conductor at low temperature, becomes a semi-conductor—a conductor with a very high resistance. The behavior is strongly temperature dependent, and the resistance increases as the temperature is lowered, in contrast to the behavior of a metal.

Theoretical considerations, based on Fermi-Dirac statistics and a wave-mechanical approach to the problem, give the following equation for the resistivity of a semi-conductor with impurities. If $\mathcal{m} \ll N$ where

$\mathcal{m} = \text{no. of free electrons} / \text{cm}^3$

$N = \text{no. of impurity atoms} / \text{cm}^3$

$$R = a e \frac{E}{kT}$$

where $R = \text{resistivity}$

$a = \text{constant dependent on the material}$

$E = \text{Excitation energy for an impurity level}$

$k = \text{Boltzmann's constant}$

$T = \text{Kelvin temperature}$

This equation indicates that the logarithm of the resistance should be proportional to the reciprocal of the absolute temperature.
II Apparatus

A. Bridge and Thermocouple

Resistances were measured on a plug-type Wheatstone Bridge with a dial box connected in series with the variable resistance for finer adjustments. All correcting leads were soldered to copper strips to make good contacts at the bridge terminals, and a 1.5 volt battery was used. Deflections were observed on a galvanometer which had a resistance of 526 ohms and a sensitivity of .00057 a/mm. Ratios varying from 1000 to 1000 to 1-1000 were used. For greater accuracy, all readings were taken with the galvanometer connected in such a way that it joined the two highest resistances with the two lowest.

The samples were mounted as shown in the figure. The sample and holder fitted into a glass tube which contained an atmosphere of helium. The helium gas eliminated the possibility of liquid air condensing on the sample at low temperatures. The glass tube was suspended in such a way that a Dewar flask could be raised around it. When cotton was put around the top of the Dewar flask, it took approximately twelve hours for the temperature inside to rise from liquid air temperature to room temperature.

Temperatures were measured with a copper-constantin thermocouple, one junction of which was held in a large ice bath and the other junction of which was attached to the glass tube inside the flask. The thermocouple was calibrated against a pentane thermometer over the entire range.

B. Sample Mountings

The first sample was a porous bar of fused material. It was about 1 cm. long and 0.1-0.2 cm. in its other dimensions. It was cemented to a glass rod, and the leads were soldered to the copper-plated ends of the bar.

The later samples were very small particles of MnSe—perhaps about one millimeter in diameter. These were mounted by spot-welding two very fine
wires to the surfaces of the particle. Gold wire, .0005" in diameter was used. (Platinum wire was tried first, but gold worked better.) The spot welding was done by discharging a condenser through the wires and the sample.

Best results were obtained when the condenser had a capacitance of 8 or 10 microfarads, and was charged to 250 or 300 volts. Both leads could be welded at the same time by pressing the wires against the sample between glass plates. It was important to have the tips of the wires in contact with the material.

A third method of mounting samples was also used. This consisted simply in pressing two brass blocks firmly against one of the grains of material described above. The two blocks were turned on a lathe so that they fitted snugly inside a 3/8" glass tube, closed and flattened at one end. One block rested on the bottom of the tube, and the other block was pushed down on the sample by a spring. Details are shown in the figure.

C. Torsion Balance

A torsion balance was used to obtain a rough check on the magnetic susceptibility of a bar of MnSe. Details are shown in the figure. The bar was suspended by a delicate quartz fiber between the pole pieces of an electromagnet. A graduated scale on top of the mounting measured the angle through which the torsion head had to be turned to bring the mirror back to the zero position when a field was applied. Angles could be read fairly accurately to the nearest tenth of a degree.

Neglecting the susceptibility of the gas in the container, the susceptibility of the bar should be approximately proportional to the angle of twist for small angles.
TORSION BALANCE

180° SCALE

RAZOR BLADE

COUNTERWEIGHT

SET IN GREASE (FREE TO ROTATE)

QUARTZ FIBER

GLASS WINDOW

MIRROR

GLASS TUBE

RIGID ROD

POROUS BAR

DEWAR FLASK

POLE PIECES
III Experimental Procedure

A. Preparation of Manganese Selenide

The first samples of MnSe were prepared by the method given in Kelley's article. Pure selenium (99.99%) was obtained from Johnson, Mathey and Co., and manganese (99.95% pure) was obtained from the Rice Institute Chemistry Department.

The two materials were ground into a fine powder, thoroughly mixed (with 50% excess Se), and put in a 75 centimeter combustion tube so that the mixture filled about a third of the bottom part. The tube was of silica glass and was 2.5 cm. in diameter, with a constriction about 25 cm. from the top end. The tube was evacuated with a fore pump, filled with helium gas, and sealed off. The reaction was set off with a Bunsen burner, and then the tube was left in an electric oven for 20 hours at a temperature of 300°C. In order to drive excess Selenium past the constriction, the sealed end of the tube was then allowed to project from the furnace into the air for five more hours of heating at 500°C. After slow cooling, the tube was broken open and rough chunks and grains of MnSe were extracted. The pieces were extremely porous and some parts were blacker than others, as if the fusion process had not been complete. The black pieces were rejected. Three attempts of this kind were made in an attempt to get satisfactory samples.

B. Susceptibility Measurements

When this research was begun, one aim was to be the study of the magneto-resistance of MnSe. Susceptibility measurements have shown that the substance is anti-ferromagnetic, and it was thought that the effect of a magnetic field on the resistance at low temperatures might be correlated

*See Bibliography.
with the variation of susceptibility.

A rough check was made on the susceptibility of the material taken from the combustion tube to see if it was actually anti-ferromagnetic. Readings were taken at only three points: in air at room temperature, in a bath of dry ice and alcohol, and in a liquid air bath. When the sample had come to temperature equilibrium with the bath, a magnetic field was applied. Then the torsion head was turned until the mirror had returned to its zero position. The angle was measured. When the magnetic field was removed, the torsion head had to be turned in the opposite direction, and the angle was measured. If the two angles agreed to within 0.5 of a degree, the reading was accepted. At least three readings were made at each temperature.

These measurements showed that the susceptibility increased steadily as the temperature was lowered. Between room temperature and dry ice, the curve was reversible, but once the sample had been cooled to liquid air temperature, a hysteresis effect set in. Now if the substance were anti-ferromagnetic as Kelley observed, the susceptibility at -196°C should have been less than the susceptibility at -70°C. Therefore, it was concluded that the substance was not anti-ferromagnetic. Three attempts to produce anti-ferromagnetic MnSe ended in failure. The probable reason for this failure was incomplete combination of the Mn and Se. The reaction, once started, is supposed to proceed vigorously by itself with considerable heat evolution, according to Kelley. Actually, it did not behave this way in the present case, i.e., the reaction, while vigorous in local spots, did not traverse the whole material. The porous bar made from the material contained some uncombined Mn or Se which would account for the non-appearance of anti-ferromagnetism.

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Finally some MnSe prepared by Kelley was obtained, but it was found that the change in resistance caused by a magnetic field was too small to observe with the field strengths available. This phase of the project was finally abandoned.

C. Resistance Measurements

Except in special cases, the temperature of the samples was changed very slowly. It required from four to six hours to reach liquid air temperature from the starting point at room temperature. In the reverse direction, even longer times were allowed. Some complete runs lasted all day and all night. This precaution was taken to make sure that the sample had had time to come into phase equilibrium.

The accuracy of the resistance measurements was estimated by noting how much change in the variable resistance was required to produce a one centimeter deflection on the galvanometer scale, assuming that one centimeter deflection could certainly be detected. If

\[ X = \text{resistance of the sample} \]

\[ A, B = \text{ratio arm resistances} \]

\[ R = \text{variable resistance} \]

then

\[ X = \frac{B}{A} \cdot R \]

\[ \Delta X = \frac{B}{A} \Delta R \]

\[ \frac{\Delta X}{X} = \frac{\Delta R}{R} \]

Changes of two units in the third figure for \( R \) could always be detected, indicating an accuracy of about 2%.

Once a sample had been cooled to liquid air temperature, the curve of its resistance shifted to higher values by more than the experimental error.
An example is the difference between the two curves for the porous bar. In the case of the bar, this effect was observed every time the sample was cooled sufficiently, although all curves were reversible at least as far as -65°C. It was thought that the porosity of the bar and possibly poor contacts might be giving erroneous results.

Consequently, another method of mounting was tried. The spot-welded samples showed the same behavior. However, not more than two runs were obtained with any one sample because invariably the contacts would break loose. This could be detected immediately either by indications of an open circuit, or by the unsteadiness of the galvanometer deflections. It must be noted that for readings recorded, the galvanometer was steady. Moreover, no readings have been recorded from runs in which contact troubles developed before the run was finished.

In order to be sure that the very high resistances observed were not due to poor contacts, a third method of mounting samples was tried. With the pressure-contact method, the initial resistance was so high that no readings could be made below about -120°C. However, the curve had about the general shape as the other curves, which was interpreted as meaning that the strong variations were intrinsic to the material.
IV Experimental Results

The runs on the porous bar gave unsatisfactory results, but they indicated the wide range of variation of the resistance, and emphasized the experimental difficulties that would be faced.

Each of the runs on the spot-welded samples was intended to check some particular part of the curve. The first sample showed in particular that the curve was reversible between 27°C and -67°C. The run on the second sample was made with particular emphasis on detecting the hysteresis at liquid air temperature. The third sample represented an unsuccessful attempt to study the transition region.

Although no two curves have exactly the same shape, all exhibit somewhat similar behavior. Differences in the slopes may supposedly be attributed to the varying amounts of impurities in the different samples.

A break in a curve of this type is attributed to a change in crystal structure which affects the activation energy of the impurity level. The activation energy is the difference between the energy of the impurity level and the energy of the conduction band. The activation energies corresponding to the initial slopes of Samples #1 and #3 have been calculated:

\[
E_1 = 0.16 \text{ electron volts/degree} \\
E_2 = 0.09 \text{ ev/deg}
\]

These values are at least of the proper magnitude in comparison to values from other substances. No attempt has been made to calculate the slope of the high resistance phase for the following reason. Examination of the calibration curve for the thermocouple shows that in the region of liquid air, thermocouple readings very close to each other represent large changes in the value of \( \frac{1}{T} \).

\*See reference 6.
\*\*Silicon with boron impurity . . . . 0.08 ev/deg reference 5.
\*\*\Selenium with bromine . . . . 0.07 ev/deg reference 4.
Furthermore, the pentane thermometer showed a temperature of -192°C when it was totally submerged in liquid air. One might have expected it to read a few degrees lower, e.g., -196°C. This introduces a possibility that all points near the lower temperature end of the curve should actually be shifted 10-15 units to the right. This change, if true, would greatly decrease the value of the slope. However, it would not change the magnitude of the resistances observed nor the fact that a hysteresis occurs.
V Conclusions

1. The obvious conclusion is that the electrical resistance of MnSe is very strongly temperature dependent, increasing its value some 10,000 times in a range of 200°C. Moreover, there are discontinuities in the resistance curve in accordance with the hypothesis of lattice modifications in the material as its temperature is lowered.

2. There is good evidence of a lattice modification in the range between -77°C and -114°C. (Samples #1 and #3) There is less conclusive evidence of another phase change in the range between -156°C and -162°C.

3. A temperature hysteresis is observed if the sample is cooled below -162°C. The substance retains a higher resistance as it is warmed, until it returns to the region of the first phase change.

4. The calculated values for the activation energies of the impurity levels are of the same order of magnitude as values taken from similar data for other compounds.
## Sample Data

### I. Deflection of a bar of MnSe in a Magnetic Field

<table>
<thead>
<tr>
<th>Potentiometer readings (volts)</th>
<th>Time</th>
<th>Current in the coil (amps.)</th>
<th>Angle with No Field (degrees)</th>
<th>Angle with Field (degrees)</th>
<th>Angle with No Field (degrees)</th>
<th>Total Deflection</th>
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<tr>
<td>.1153</td>
<td>1.0</td>
<td></td>
<td>45.0</td>
<td>44.1</td>
<td>45.0</td>
<td>95.2</td>
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<tr>
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<td></td>
<td>45.0</td>
<td>45.5</td>
<td>45.0</td>
<td>89.5</td>
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<tr>
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<td>45.0</td>
<td>46.0</td>
<td>45.1</td>
<td>89.1</td>
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<td>1.0</td>
<td></td>
<td>45.0</td>
<td>42.0</td>
<td>42.0</td>
<td>107.0</td>
</tr>
<tr>
<td>.0004</td>
<td>1.0</td>
<td></td>
<td>45.0</td>
<td>42.0</td>
<td>42.0</td>
<td>107.0</td>
</tr>
<tr>
<td>.0004</td>
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<td>42.0</td>
<td>42.0</td>
<td>105.4</td>
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<td>42.0</td>
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<td>106.2</td>
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<tr>
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<td>1.0</td>
<td>45.0</td>
<td>42.0</td>
<td>42.0</td>
<td>107.0</td>
</tr>
</tbody>
</table>
## II. Resistance Measurements

Potentiometer reading in connection with the thermocouple

<table>
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<tr>
<th>Time</th>
<th>Resistance</th>
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<tr>
<td>3:00</td>
<td>506.1</td>
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<td>3:30</td>
<td>2063</td>
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<tr>
<td>4:00</td>
<td>2252</td>
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<tr>
<td>4:15</td>
<td>3139</td>
</tr>
<tr>
<td>4:40</td>
<td>3384</td>
</tr>
<tr>
<td>4:55</td>
<td>5202</td>
</tr>
<tr>
<td>5:00</td>
<td>7440</td>
</tr>
<tr>
<td>5:10</td>
<td>11,000</td>
</tr>
<tr>
<td>5:15</td>
<td>18,370</td>
</tr>
<tr>
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<td>32,570</td>
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<tr>
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<td>7440</td>
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<tr>
<td>5:40</td>
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<td>25,200</td>
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<td>7:00</td>
<td>5,100.0</td>
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<tr>
<td>7:10</td>
<td>1,720.0</td>
</tr>
<tr>
<td>7:30</td>
<td>718.5</td>
</tr>
</tbody>
</table>

*See Calibration Curve.*
Sample Calculation

I. Torsion Balance (taken from the first reading in the Sample Data)

\[
\begin{align*}
44.9 & \pm 44.6 \\
299.5 & 90.0 - 44.8 = 45.2 \\
44.8 & 90.0 - 55.7 = 34.3 \\
& \quad = 79.5
\end{align*}
\]

II. Activation Energies for the Impurity Levels (taken from the Initial Slope of Sample #1)

\[
R = a \exp\left( \frac{E}{kT} \right)
\]

\[
\ln R = \ln a + \frac{E}{kT}
\]

This is linear in \( \ln R \) versus \( 1/T \) where \( E/k \) is the slope.

Therefore \( E/k = \text{Slope} \)

\[
E = k(\ln 30000 - \ln 1000) / (.0051 \pm .0031)
\]

\[
E = k(\ln 30) / .0018
\]

\[
E = k(2.303 \log 30) / .0018
\]

\[
E = k(3.40) / .0018
\]

\[
E = 1888.88 \text{ k}
\]

\[
E = 1888.88 \ (8.69 \times 10^{-5})
\]

\[
E = 0.16 \text{ electron volts}
\]
Acknowledgement

I wish to express my indebtedness to Dr. C. W. Heaps, who suggested this problem and gave valuable counsel throughout the work.
Bibliography


3. Kelley *Journal of the American Chemical Society*, 61, 203 (1939)


5. Pearson and Bardeen *Physical Review*, 75, 865 March 1949


7. Frerichs and Siegert *Physical Review*, 74,2 Nov. 1948