

THE EFFECTS OF GAMMA-RAY RADIATION
ON THE ELECTRICAL PROPERTIES
OF ZnSe SINGLE CRYSTAL

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ABSTRACT

The effects of gamma radiation on the dark resistivity and Hall mobility in high purity ZnSe single crystals have been investigated at various temperatures. The gamma irradiation is conducted in a cobalt 60 gamma cell with an average dose rate of 1.2×10^6 rads/hr. Following radiation, the dark current decreases as the radiation dose increases. The resistivity of ZnSe crystal changes from $\sim 10^8$ ohm-cm to $\sim 10^{10}$ ohm-cm at room temperature. The Hall mobility decreases from ~ 500 cm²/V-sec to a limiting value of ~ 170 cm²/V-sec. Before radiation, a single donor ionization energy $E_D = 0.316$ eV below the conduction band edge is obtained from the result of the temperature dependence of the Hall coefficient. The corresponding concentration of donors and compensating acceptors are respectively $N_D = 1.19 \times 10^{11}$ cm⁻³ and $N_A = 3.94 \times 10^{10}$ cm⁻³. After gamma irradiation, the donor ionization energy level changes to 0.377 eV below the conduction band. The values of N_D and N_A in this level are 1.17×10^9 cm⁻³ and 3.71×10^8 cm⁻³ respectively. The results indicate that irradiation with gamma rays leads to predominantly acceptor type defects in ZnSe and the predominant scattering mechanism limiting the lattice mobilities is the polar interaction with the longitudinal optical phonons.

CHAPTER I

INTRODUCTION

The first research papers on II-VI compounds dated back to the middle of the Nineteenth Century. The early work was carried out on pressed, powdered or sintered specimens, which often led to confusing and conflicting results. Until a decade ago, successful growth of single crystals of II-VI compounds in high purity form has made it possible to apply new research techniques to old problems and to attack new ones. It is now possible to achieve very high photosensitivities in all II-VI compounds; the range of band gaps in II-VI compounds covers a range of maximum photosensitivities from the near ultraviolet to the near infrared. The successful application of scattering theory to the study of transport properties of n-type II-VI compounds has laid a solid foundation to the understanding of the electrical properties of these materials. Since the technology of single crystal growth has been extensively developed, actual or potential opportunities for commercial application have multiplied. From a materials research viewpoint, II-VI compounds combine all the challenges and fascinations of the more ionic I-VII insulators and the more covalent III-V semiconductors.

The purpose of investigating radiation effects in solids is twofold: first to use the radiation as a tool to study the properties of solids and second to study the radiation damage in solids under various radiation environments. Fast particle bombardment provides a means of controlled introduction of lattice defects into crystalline solids and hence is an

excellent method for studying in a general way the influence of lattice defects on the physical properties of solids. From an application point of view, it is important to investigate the behaviour of semiconductors which form part of solid state devices, under various radiation environments with a view to developing a better understanding of the mechanisms responsible for causing any change of electronic properties of such materials and a new approach to the design of solid state devices for use in radiation environments. Furthermore, a study of defect stability is extremely important from the practical point of view. It is obvious that if defects could give rise to new and desirable properties in a semiconductor, it is desirable to retain these properties throughout the service life of a device made from this semiconductor.

Many investigations have studied the effects of radiation in single elements in the past twenty years. However, the full interpretation of the radiation effects on II-VI compound semiconductors is still not available.

Although a much larger group of compounds could be referred to as II-VI compounds, the present work is confined specifically to the ZnSe (Zinc Selenide) because ZnSe is one of the II-VI compounds which has not been well investigated up-to-date. The effect of irradiation with 1.2×10^6 rads/hr. ^{60}Co gamma rays on the electrical properties in ZnSe has been studied by means of conductivity and Hall mobility measurements at various temperatures and fields. In this thesis, Chapter II gives a brief review of the previous

works on the general properties of some II-VI compound semiconductors. The theory of radiation effects is described in Chapter III, and the experimental methods and results in Chapter IV. Analysis and discussion of results are given in Chapter V and conclusions in the final Chapter.

CHAPTER II

LITERATURE REVIEW ON II-VI COMPOUND SEMICONDUCTORS

2.1 Some Important Factors Determining the Electrical Properties

2.1.1 Point Defects

The deviation from hypothetical perfect crystal structure can be described in terms of defects. Comparing with line defects and plane defects, the point defects of various types are more important in determining the electrical properties of II-VI compounds. In point defects, it can be classified into native point defects and the foreign (or impurity) point defects. For example, the native point defects are misplaced lattice atoms (or ions), interstitials, vacant lattice sites, and zero-dimensional associates between them, and electrons and holes. The isolated native point defects appear to be very unstable at room temperature, and they either tend to associate themselves with other defects, or precipitate out during the cooling of the sample.

The effect of those imperfections is to introduce discrete energy levels in addition to the levels for the perfect crystal, provided they are far enough apart to be treated as isolated centres of potential in the crystal. When there is a high density of impurity centres, the level will interact and may form sub-bands (impurity bands). Such sub-bands have a marked effect on the conductivity of certain semiconductors at low temperatures.

The binding energy ' ϵ_1 ' of the electrons and ' ϵ_2 ' of the holes, to the impurity centre, are given by

$$\epsilon_1 = m_e^* E_H / n_i^2 K^2 m \quad (2.1)$$

$$\epsilon_2 = m_h^* E_H / n_i^2 K^2 m \quad (2.2)$$

where ' E_H ' is the ionization energy of the ground state of the hydrogen atom ($\approx 13.6\text{eV}$), ' n_i ' is an integer, ' m_e^* ' is the effective mass of electrons in the conduction band, ' m_h^* ' is the effective mass of holes in the valence band, ' K ' is the static dielectric constant of the semiconductor, and ' m ' is the mass of an electron in free space.

Besides, the effective radius ' a ' of the impurity centre when occupied by an electron in the ground state is given by

$$a = \frac{m}{m_e^*} K a_0 \quad (2.3)$$

where ' a_0 ' is the Bohr radius which is $0.53 \times 10^{-8}\text{cm}$. In II-VI compounds, the effective masses are generally larger and dielectric constants smaller than those of the element semiconductors such as Ge and Si. Hence, the electrons are more tightly bound, the wave function does not spread as much and central cell corrections are more important in II-VI compounds than in

Ge and Si semiconductors.

Experimentally, De Nobel (1959) proposed that a donor level of 0.02eV below the conduction band edge of CdTe was due to interstitial Cd, and Lorenz (1964) showed that the n-type conductivity observed in the high purity CdTe was due to residual impurities. Woodbury (1964) has suggested that the concentration of any electrically active interstitial Cd even in the purest CdS crystals available is always lower than the residual concentration of shallow foreign donors. Reynolds and Stevenson (1966) have suggested that interstitial Te may act as a double acceptor in ZnTe on the basis of self-diffusion measurement. The native defects in II-VI compounds have been investigated; most are the Zn and Cd vacancies. Also, it has been suggested that isolated cation vacancies may act as a double acceptor in ZnTe (Aven and Segall, 1963) and CdTe (Lorenz and Segall, 1963).

2.1.2 Carrier Lifetime and Mobilities

The band structure is another important factor determining the electrical properties of II-VI compounds. For example, the behaviour of the mobility depends upon the effective mass which is inversely proportional to the curvature of the band. Consider the effect of collision on the motion of the electrons and positive holes in semiconductors under the influence of electrical and magnetic fields. For a certain assumption, the average time ' \bar{t} ' between collision is given by

$$\bar{t} = \frac{1}{n_0} \int_0^{\infty} \frac{nt}{\tau} dt = \tau \quad (2.4)$$

where ' n_0 ' is the number of electrons moving in a certain direction at $t = 0$, ' τ ' is the so-called mean free time. Suppose that the electrons are moving in the crystal under an applied electric field \bar{E} which is in x-direction. Its x-component of velocity, ' \bar{v}_x ' can be written as

$$\bar{v}_x = \bar{v}_{x0} - \frac{\bar{E}q\tau}{m_e^*} \quad (2.5)$$

where ' \bar{v}_{x0} ' is the velocity of electrons in the x-direction at $t = 0$, ' q ' is the electronic charge. Assuming $v_{x0} = 0$, we have

$$\bar{v}_x = - \frac{q\bar{E}\tau}{m_e^*} = - \mu_e \bar{E} \quad (2.6)$$

where ' μ_e ' is the electron mobility defined by

$$\mu_e = q\tau/m_e^* \quad (2.7)$$

Similarly, for positive holes,

$$\bar{v}_x' = q\tau'\bar{E}/m_h^* \quad (2.8)$$

The hole mobility is given by

$$\mu_h = q\tau'/m_h^* \quad (2.9)$$

where ' $\bar{\tau}$ ' is the mean free time for the holes. If there are 'n' electrons in the conduction band and 'p' holes in the valence band, the current density in the x-direction can be written as

$$\bar{J}_x = q(n\mu_e + p\mu_h)\bar{E} \quad (2.10)$$

and the conductivity is given by

$$\sigma = q(n\mu_e + p\mu_h) \quad (2.11)$$

For simplicity, the mean free time ' τ ' has been regarded as being the same for all electrons. In fact, ' τ ' depends on the velocity of the electron or hole being scattered, and may also depend on the direction of motion through the crystal. Generally, some correct weighing function which determines the average relaxation time $\langle\tau\rangle$ can be found. However, the drift velocity and mobility of electrons is more conveniently written in terms of $\langle\tau\rangle$ as

$$\bar{v}_x = q\bar{E}\langle\tau_e\rangle/m_e^* \quad (2.12)$$

and

$$\mu_e = q\langle\tau_e\rangle/m_e^* \quad (2.13)$$

When a magnetic field is applied to the crystal carrying a current in a direction at right angles to the current, an e.m.f. is produced across the crystal in a direction perpendicular to the current and to the magnetic field. This effect is well known as the Hall effect and it is one of the most powerful tools for studying the electronic properties of semiconductors.

The Hall coefficient for n- and p-type non-degenerate semiconductors is given by

$$R_H = - \frac{r_H}{nq} = - \frac{1}{nq} \frac{\langle \tau_e^2 \rangle}{\langle \tau_e \rangle^2} \quad (2.14)$$

and

$$R_H = \frac{r_H'}{pq} = \frac{1}{pq} \frac{\langle \tau_h^2 \rangle}{\langle \tau_h \rangle^2} \quad (2.15)$$

For mixed conductors, it can be shown that

$$R_H = - \frac{1}{q} \frac{r_H b^2 n - r_H' n}{(bn+p)^2} \quad (2.16)$$

where b is the mobility ratio μ_e/μ_h . The Hall factor is defined by

$$r_H \equiv nqR_H \equiv \frac{\mu_H}{\mu} \quad (2.17)$$

where 'n' is the carrier concentration, ' μ_H ' is the Hall mobility and ' μ ' is the drift mobility.

The relation of the motion of electrons and the external field of force can be written as

$$m_e^* \frac{d\bar{v}}{dt} = \bar{F} \quad (2.18)$$

where the velocity vector ' \bar{v} ' is given by

$$\bar{v} = \hbar^{-1} \nabla_{\mathbf{K}} E(\mathbf{K}) \quad (2.19)$$

When an electric field and a magnetic field are simultaneously applied to the semiconductor, \bar{F} is given by

$$\bar{F} = -q\bar{E} - q(\bar{v} \times \bar{B}) \quad (2.20)$$

where \bar{B} is the magnetic flux density. In general, the effective mass of the hole will not be the same as that of an electron since they arise from different bands. For the spherically symmetrical case, the effective mass tensor can be written as

$$\frac{1}{(m_e^*)_{ij}} = \hbar^{-2} \frac{\delta^2 E_c}{\delta k_i \delta k_j} \quad (2.21)$$

and

$$\frac{1}{(m_h^*)_{ij}} = -\hbar^{-2} \frac{\delta^2 E_v}{\delta k_i \delta k_j} \quad (2.22)$$

It can be noted that ' m_e^* ' and ' m_h^* ' are inversely proportional to the curvature of the constant energy surface in k-space.

In the presence of a magnetic field, the resistance depends upon the magnetic field, and it may be shown that the low field transverse magnetoresistance $\Delta\rho/\rho$ may be conveniently measured by a parameter ' ξ ' defined by

$$\xi \equiv \Delta\rho/\rho (\mu_H)^2 \quad (2.23)$$

This parameter is independent of the magnitude of the scattering and depends only on its energy dependence.

2.1.3 Scattering Mechanisms

The electrical properties of II-VI compounds depend also upon a combination of several scattering processes such as piezoelectric and polar optical mode scattering.

Most conventional scattering mechanisms can be described by a relaxation time $\langle \tau \rangle$ or mobility ' μ '. The theory of polar optical mode scattering has been reviewed by Frölich (1954) who showed that a perturbation theory is applicable for values of ' α ' [a coupling constant of the high frequency (or bare) mass and the low frequency (or polaron) mass] small compared with unity. The expression for mobility given by Frölich is

$$\mu_o = (16.91/z^{1/2}) \left(\frac{1}{n_r^2} - \frac{1}{K} \right)^{-1} \left(\frac{m}{m^*} \right)^{3/2} (e^{-z/T} - 1) \quad (2.24)$$

where ' n_r ' is the optical index of refraction and ' z ' ($=\hbar\omega/kT$) is the characteristic temperature and ' ω ' is the angular frequency of longitudinal optical phonons, ' m^* ' is the effective mass of electrons (or holes). The piezoelectric scattering can occur in a crystal which has a piezoelectric effect and it is due to the electric fields produced by acoustic phonons. Blatt (1957) has derived the expression for the piezoelectric mobility, and it is

$$\mu_p = \left(\frac{16}{3} \sqrt{2\pi} \right) \left\{ \hbar^2/qm^*{}^{3/2} (kT)^{1/2} \right\} \left\{ \sum_{\text{modes}} \frac{\langle \kappa^2 \rangle}{K\epsilon_o} \right\}^{-1} \quad (2.25)$$

where ' κ^2 ' is a suitable average of the piezoelectric electrochemical coupling constant, ' K ' is the static dielectric constant. Then, the

mobility due to the lattice scattering can be written as

$$\frac{1}{\mu_{\text{lattice scattering}}} = \frac{1}{\mu_o} + \frac{1}{\mu_p} \quad (2.26)$$

The mobility measured at 77°K is considerably lower than the value predicted theoretically for pure lattice scattering. The discrepancy is probably due to ionized impurity scattering which is important in impure and non-stoichiometric compounds. The expression for mobility due to ionized impurity scattering given by Brooks (1955) is

$$\mu_i = \frac{4(2/\pi)^{3/2}(kT)^{3/2}(4\pi \epsilon_o K)^2}{q^3 m^{*1/2} N_I [\ln(b) - 1]} \quad (2.27)$$

where

$$b = \frac{6m^*(kT)^2 (4\pi\epsilon_o K)}{\pi q^2 \hbar^2 n'} \quad (2.28)$$

in thermal equilibrium,

$$n' = n + (N_D - N_A - n)(n + N_A)/N_D \quad (2.29)$$

and

$$N_I = n + 2N_A \quad (2.30)$$

where 'n' is the carrier concentration, ' N_A ' is the acceptor concentration, and ' N_D ' is the concentration of the donors.

The theoretical mobilities of carriers in II-VI compound semiconductors at 300°K. are given in Table 2.1.

2.2 Electrical Properties

2.2.1 Cadmium Sulfide

Since the band gap in CdS which is 2.24eV at 300°K is quite large, the intrinsic carrier concentration is very low and the carrier concentration is therefore mainly determined by impurities or native defects. The effective mass has been obtained by a number of investigators with impurity concentration, binding energy and dielectric constants taken into account. Zook (1963) measured m_e^*/m to be 0.19 which is in good agreement with the theory. Devlin (1965) reported that $m_e^*/m = 0.20$ is the most reliable value when the effects of piezoelectric scattering and optical mode scattering on the Hall mobility are considered, and the temperature dependence of the static dielectric constant is taken into account. The temperature dependence of the Hall mobility in undoped n-type

CdS given by Devlin is shown in Fig. 2.1.

The energy bands are expected to be anisotropic at $K = 0$ due to the hexagonal structure of the CdS crystal. There have been several measurements of the anisotropy of the conductivity and the mobility. Masumi (1959) measured the conductivity anisotropy as a function of temperature. A similar result has also been reported on the anisotropy of the mobility by Zook and Dexter (1963). They concluded that the anisotropy of the magneto-resistance is consistent with a single anisotropy valley at $K = 0$.

Spear and Mort (1963) obtained the same values for the hole mobility of all their samples but the electron mobilities were considerably different from sample to sample.

In Figs. 2.2 and 2.3 are given some typical experimental results on the temperature dependence of conductivity and Hall coefficient in CdS obtained by Itakura and Toyoda (1963). The Hall mobilities ' μ_H ' calculated from 'R', also shown in Fig. 2.4 from which the activation energy ΔE is calculated to be 0.014eV for the temperature range from 200°K to 50°K, and 0.007eV from 50°K to 10°K. They interpreted these results as being due to two kinds of donor levels, one with a concentration of $1.5 \times 10^{17} \text{cm}^{-3}$ at 0.014eV and the other with more than 10^{16}cm^{-2} at 0.007eV below the conduction band. It can be seen from Fig. 2.4 that the Hall mobility is

TABLE 2.1

Theoretical Mobilities of Carriers (in cm²/V-sec) in II-VI Compound Semiconductors at 300°K [after Devlin (1965)]

	<i>CdS</i>	<i>CdSe</i>	<i>CdTe</i>	<i>ZnS</i>	<i>ZnSe</i>	<i>ZnTe</i>
μ_e (opt. mode)	330	630	1320	344	600	-
μ_h (opt. mode)	38.5	98	190	-	90	114
μ_e (piezo.)	4360	1.5×10^4	1.5×10^6	-	3.7×10^5	-
μ_h (piezo.)	406	1.23×10^3	2.1×10^5	-	5.5×10^4	1.5×10^5

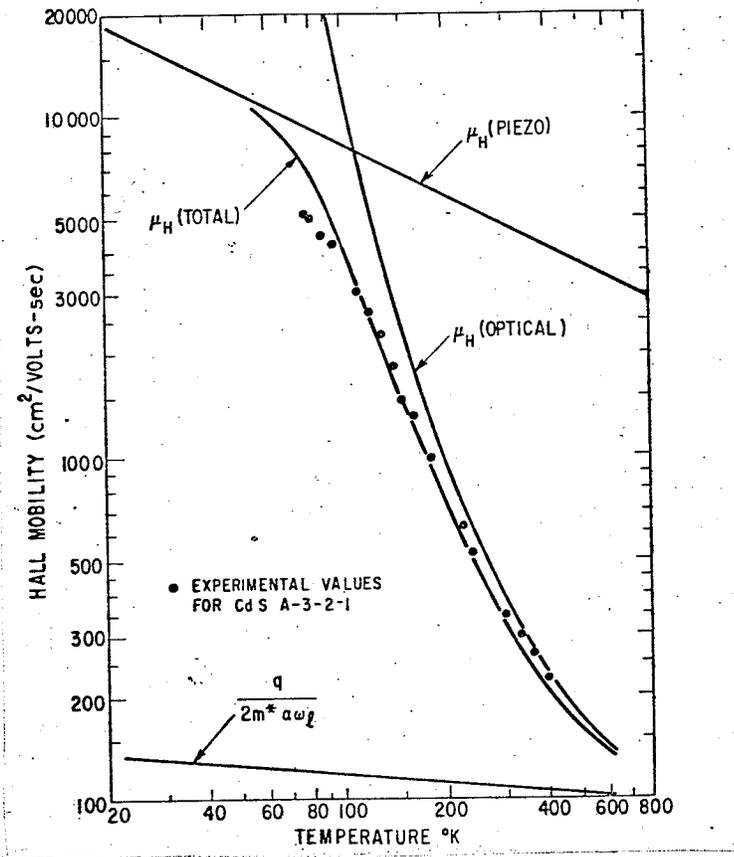


Fig. 2.1

The temperature dependence of the Hall mobility in undoped n-type CdS. The solid curve is the theoretical intrinsic Hall mobility due to piezoelectric and optical mode scattering assuming $m_e^*/m_e = 0.20$. The line at the bottom indicates the temperature dependence where μ_F is Fröhlich's (1954) low temperature approximation for the mobility and $Z = \hbar\omega_e / KT$, and α is the polaron coupling constant.

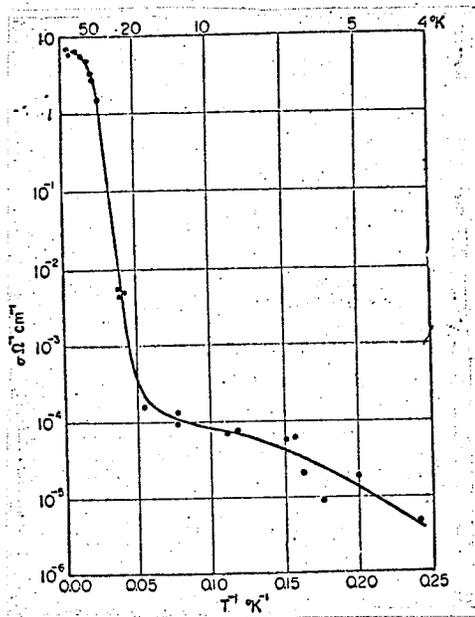


Fig. 2.2

Electrical conductivity as a function of temperature for CdS (Itakura & Toyoda, 1963)

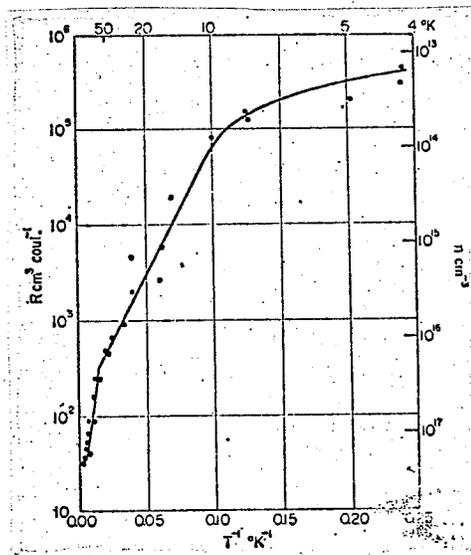


Fig. 2.3

Hall coefficient as a function of temperature for CdS (Itakura & Toyoda, 1963)

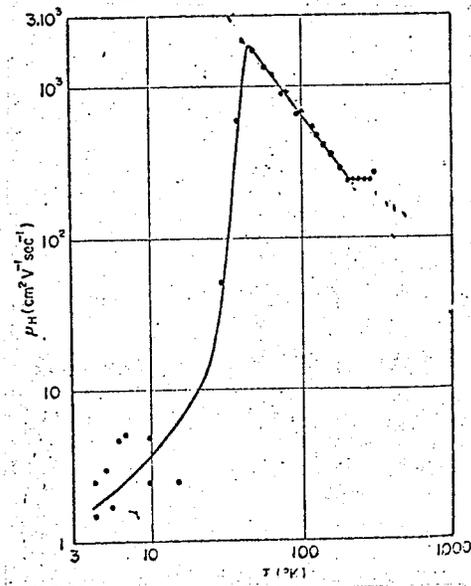


Fig. 2.4

Temperature dependence of Hall mobility of CdS crystals (Itakura & Toyoda, 1963)