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Szilard-Chalmers Effect in CdS and CdTe†

Chihiro KIKUCHI

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The neutron damage effect in crystalline CdS and CdTe has been investigated by measuring photoluminecence and conductivity change. The photoluminecence measurements for CdS show the ratio of the Cd concentration resulting from thermal and fast neutron irradiation to be about 28, different from the result by conducting measurements, about 40. Some theoretical aspects of these results are also given. For CdTe, two types of the crystals are studied, *i.e.* *n*-type and *p*-type CdTe. Changes of carrier concentration in CdTe crystal are measured before and after thermal neutron irradiation. In the case of *n*-type CdTe, it is concluded that thermal neutrons produce predominantly Cd defects in the crystal and no evidence for the Te-vacancies is observed. Although measurements on *p*-type CdTe indicate decreases of the hole concentration by thermal neutron irradiation, the value obtained is still large in comparison to the intrinsic value of the hole concentration.

I. INTRODUCTION

Although fast neutron damage in solids has been the subject of intensive investigation in many laboratories, the related problem of thermal neutron damage has to date received relatively little attention. Among the first to suggest recoil effects following capture gamma emission was H. P. Yockey,[1] whose comments appeared as a footnote in the paper by J. W. Cleland and J. H. Crawford. Subsequently, certain aspects of the problem were considered by H. C. Schweinler[2] and by R. M. Walker,[3] and the first measurements on resistivity changes in metals were carried out by R. R. Coltman *et al.*[4] at the Oak Ridge National Laboratory.

When the problem of thermal neutron damage also occurred to us, a somewhat different approach was taken because the suggestion grew out of discussions in an undergraduate nuclear engineering course. The material under discussion happened to be cadmium, so that the effect was looked for in CdS.[5] Of the possible physical measurements to make, it seemed that photoluminescence change would be the easiest to detect, and to our delight, we found that the CdS crystal "lit up like a Christmas tree" after being in the reactor for an hour or less!

The purpose of this report then will be to outline the problem of thermal neutron damage by considering certain aspects of nuclear physics not generally familiar to solid-state physicists, and conversely aspects of solid-state physics not familiar to nuclear physicist.

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* Department of Nuclear Engineering. University of Michigan Ann Arbor, Michigan, 48105, U. S. A.

II. SOLID STATE SZILARD-CHALMERS EFFECT

The chemical effects arising from the recoiling radioactive nuclei were first shown in 1934 by L. Szilard and T. A. Chalmers.[6] They demonstrated the existence of the effect by collecting and concentrating the free radioactive ^{128}I ions. Possibly several factors contributed to the success of this early experiment. One is the availability of the means to concentrate the recoil products. Another is the relative simplicity of the ^{128}I capture gamma spectrum. The spectrum consists of gamma rays in the range 3~5 MeV, for which the recoil energy is between 38 and 100 eV. Since the chemical binding energies are in the range 1~5 eV, the recoil energy is more than adequate to break the chemical bond. Another factor is the low probability of recombination, resulting in the relatively high yield of free iodine.

When the search for the corresponding effect in crystalline CdS compounds like Cds and CdTe was undertaken, several questions arose immediately, Obviously it is impossible to concentrate interstitial atoms and furthermore the vacancy-interstitial recombination rate is appreciable. Furthermore the threshold energy for displacement being about 25 eV, is appreciably larger than the chemical binding energies which lie in the 1 to 5 eV range. Since the recoil energy depends upon the square of the gamma ray energy, the probability of vacancy production depends significantly upon the probability of emitting energetic gamma rays. The crucial problem then is to see what information about nuclear recoil energy can be inferred from the capture gamma spectrum.

The first information is the energy distribution of the emitted gamma rays.[7] The capture gamma spectrum indicates the following results:

Photons/100 Capture Neutrons

E_γ (MeV)	0~1	1~2	2~3	3~5	5~7	7~9
N_γ	135	92	96	73	17	1

The numbers in the second row are the number of gamma photons emitted in the indicated energy range. Since measurements show that the average number of gammas[9] emitted per capture event is 4.1, we infer that at least one but sometimes 2 gammas are emitted in the 0~1 MeV range, two more gammas in the ranges 1~2 MeV and 2~3 MeV, and fourth one in the 3~9 MeV range.

The nuclear recoil energy can be estimated by the following arguments. If p_i is the recoil momentum associated with the gamma of energy $E_{\gamma i}$, then

$$E_R=\frac{1}{2M}(\Sigma p_i)^2$$

$$=\frac{1}{2M}[\Sigma p_i^2+\Sigma p_i\cdot p_s].$$

If this expression is averaged over all possible directions two successive gamma rays, then the second term is expected to be zero. The reason for this is that the directional correlation functions are even functions of cos θ_{ij}. In addition any residual anisotropy stemming from directional correlation can be expected to be obliterated by collisions of the recoiling ^{114}Cd with lattice atoms because the time

between successive collisions with lattice atoms is small in comparison with the radioactive lifetime. Even for a gamma ray of energy as low as 2 MeV, the collision time is about 10^{-14} sec compared to the lifetime is the range 10^{-12} to 10^{-14} sec. In other words the recoiling atom makes at least one collision with lattice atoms before the next gamma is emitted. Consequently we obtain

$$<E_R>_0=\frac{1}{2M}\Sigma p_i^2=\frac{1}{2Mc^2}\Sigma E_{\gamma i}^2.$$

Next averaging the above expression over all possible decay sequences, we obtain

$$T_R\equiv\overline{<E_R>_0}=\frac{1}{2Mc^2}\overline{\Sigma E_{\gamma i}^2}=143\text{ eV}$$

which is obtained by taking the weighted average of the capture gamma spectrum. A possible sequence of gammas is then 4.7, 2.5, 1.3, and 0.5 MeV, which give recoil energies of 104, 29, 8, and 1 eV, with a total of about 142.

Another relevant piece of information is obtained from the theory of gamma-decay from highly excited nuclear states. According to Blatt and Weisskopf,[10,11] the energy distribution of the primary spectrum, *i. e.* of the gammas emitted immediately after neutron capture, is determined by two competing factors, which favor the emission of high and low energy gamma photons respectively. The result is primary spectrum, which peaks near 1/3 to 1/2 of the maximum available energy, S_n. Applied to ^{114}Cd, this means that the first gamma is probably in the neighborhood of about 3 to 4 MeV and that the first gamma provides sufficient recoil energy for the decaying nucleus to escape from its lattice site.

A description that we obtain for the radiation damage mechanism then is as

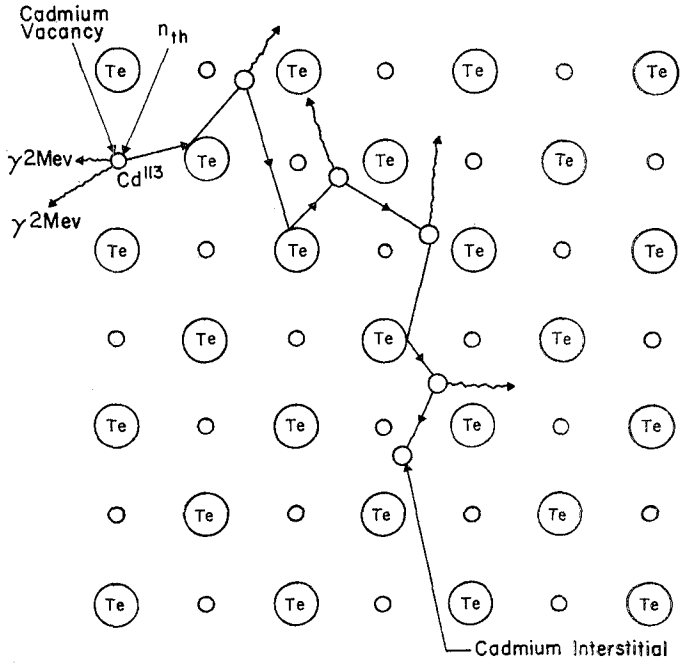

Fig. 1. Uncorrelated (n, γ) recoil mechanism in, for example, a crystal of CdTe.

follows: An energetic gamma ray is emitted so that the Cd recoils with an energy of the order of 100 eV. The collision time with other atoms in the lattice is of the order of 10^{-14} sec, and the radiative lifetime of the decaying nucleus is possibly in the range 10^{-14} to^{-12} sec. Consequently the recoiling atom bounces about in the lattice as it emits the remaining excitation energy. A graphic representation of a possible sequence of events is given in Fig. 1.

III. FAST VS THERMAL NEUTRON DAMAGE

For fast neutron damage, the damage mechanism is provided by the linear momentum and energy of the incoming neutron, which upon striking a lattice atom produces the so-called primary knock-ons of energy

$$\bar{T} \cong \frac{2E_0}{A}.$$

These in turn collide with other lattice atoms, resulting ultimately in a large number of displaced atoms. The general theory is discussed in many texts[12] on radiation damage so that here we shall consider a very simple theory applied specifically to binary materials like CdS and CdTe.

We consider CdS. The incoming fast neutrons produce two kinds of primary knock-ons, and each kind can be considered to produce secondaries, tertiaries, *etc.* The displacement energies of Cd and S are slightly different, being about 7.3 and 8.7 eV for Cd and S respectively, but we shall assume them to be equal. For S, $A=32$, so that the S primary knock-on energy is about ($E_0=2$ MeV)

$$E_p(\mathrm{S}) \cong \frac{4}{A} = 0.125 \text{ MeV}.$$

The bulk of this energy is dissipated in producing ionization. The energy range in which atomic displacements begin to dominate over ionization is taken to be $E_c=A$ (keV). Accepting this assumption, the average number of both Cd and S displacements produced by a single primary knock-on is

$$\bar{\nu}_s = \frac{32{,}000}{2E_d} = \frac{16{,}000}{E_d}.$$

Similarly by for Cd primary knock-on

$$E_p = \frac{4}{A} \cong 34 \text{ keV}$$

so that

$$\bar{\nu}_{cd} = \frac{34{,}000}{2E_d} = \frac{17{,}000}{E_d}.$$

Consequently, if n_0 is the number CdS molecules, per unit volume, then the concentration of Cd and S displacements is given by

$$\begin{aligned} N_d(f) &= n_0(\phi_f t)\sigma_{sc}(\mathrm{S})\bar{\nu}_s + n_0(\phi_f t)\sigma_{sc}(\mathrm{Cd})\bar{\nu}_{cd} \\ &\cong 20{,}000 n_0(\phi_f t)\sigma_{sc}(\mathrm{Cd})/E_d. \end{aligned}$$

To obtain the last result we made use of the fact that

$$\frac{\sigma_{sc}(\mathrm{S})}{\sigma_{sc}(\mathrm{Cd})} \simeq \frac{1}{7}.$$

In a similar manner the thermal neutron damage concentration is given by

$$N_d(th) = n_0(\phi_{th}t)\sigma_{th}(\mathrm{Cd})\frac{143}{E_d}$$

so that

$$\frac{N_d(th)}{N_d(f)} = \frac{\phi_{th}}{\phi_f}\frac{\sigma_{th}(\mathrm{Cd})}{\sigma_{sc}(\mathrm{Cd})}\frac{143}{20{,}000}$$

$$\cong 2.5\left(\frac{\phi_{th}}{\phi_f}\right).$$

The cross sections for Cd are

$$\sigma_{th} = 2450 \pm 50b$$

$$\sigma_{sc} = 7 \pm 1b.$$

Furthermore for the University of Michigan swimming-pool type reactor, the flux ratio is about 10, so that the damage ratio turns out to be about 25.

The above quantity is the ratio of the combined Cd and S vacancies produced by thermal and fast neutrons, so that some care is needed in comparing to any physical measurement. For fast neutron damage, the primary knock-ons are relatively energic, many collisions will take place before the energy is distributed among the displaced atoms. Hence it is not unreasonable to suppose that the Cd : S vacancy ratio is very nearly equal to 1. For thermal neutrons on the other hand, the initial moving particle is Cd, and as we have seen, its energy is never more than a few tens of electron volts. As it moves through the lattice, it will collide with other Cd and S atoms, but the fraction of energy transferred to S atoms will always be smaller than that to other Cd atoms. This is readily seen by noting that the average energy transferred is proportional to

$$\frac{2Mm}{(M+m)^2}$$

in which m and M are the masses of the moving and struck atoms respectively, so that

$$\frac{\bar{T}_{\mathrm{S}}}{\bar{T}_{\mathrm{Cd}}} = \frac{M_{\mathrm{S}}}{M_{\mathrm{Cd}}}\frac{(2M_{\mathrm{Cd}})^2}{(M_{\mathrm{S}}+M_{\mathrm{Cd}})^2} \cong 0.68.$$

If the displacement threshold energies are very nearly equal, as they are found to be so, the number of Cd vacancies can be expected to exceed the S vacancies.

These intuitive conclusions are supported by a more detailed analysis given by Baroody.[13] His theory indicates that for

$$\lambda \equiv \frac{4M_AM_B}{(M_A+M_B)^2} > 0.5$$

in which M_A and M_B are the masses of the two constituents, and

$$E_p \gg E_d$$

the A and B concentration defects are very nearly equal. However appreciable deviation from equality can occur for $\lambda < 0.5$ and for small values of E_p. For

example for $\lambda=0.25$ and $E_p<4E_d$, Baroody's calculations indicate that essentially only one type of defect is produced. For CdS, $\lambda=0.67$, so that specific calculation need to be made before any conclusion can be drawn. A study of materials like CdO with $\lambda=0.43$, may provide a critical test of Baroody's theory.

For CdTe (Cd At wt=112.40, Te At wt=127.60) λ is very nearly equal to 1, so that these ambiguities are not expected to arise.

IV. RESULTS FOR CdS

To search for the effects discussed above, it seemed to us that it would be best to look for luminescent changes in materials like CdS.[5] A relevant parameter, the so-called macroscopic cross-section for Cd metal and the two compounds CdS and CdTe are listed below.

	Mol. wt.	Density	no ($\times 10^{-22}$)	(cm^{-1})
Cd	112.41	8.642	4.63	113
CdS	144.48	4.82	2.01	49
CdTe	240.02	6.20	1.56	39

This means that the penetration depths of thermal neutrons are of the order of 10^{-2} cm, so that if changes in the mechanical properties of the samples were to be looked for, then in a specimen of linear dimension 1 cm only a thin outer surface will be affected by the radiation. Furthermore the precision of mechanical measurements, such as the elastic constants, is not very high, being of the order of 0.1 to 1 %. The situation for luminescent measurements, on the other hand, is quite different. For the excitation of luminescence ultra-violet radiation is needed, and the absorption coefficients are of the order of 10^{+5} to 10^{+6}/cm. This means that u. v. probes surface layers of the order of 10^{-5} cm thick. Assuming that the thermal flux of 5×10^{12} neutrons/cm^2/sec is completely absorbed in a layer of 10^{-2} cm and that each neutron produces one defect, we see that the defect production rate is about $5\times10^{14}/cm^3$/sec. A 30-minute reactor irradiation then is expected to produce defect concentration of the order of $10^{18}/cm^3$. Since the luminescence of CdS is sensitive to its stoichiometry and defect structure, this material was chosen for the initial experiments. As indicated changes in the red luminescence was detected on the first day the experiment was carried out.

Irradiation of the CdS samples was accomplished by placing the samples directly into the core of the University of Michigan Phoenix Project swimming-pool type reactor, operated at power levels varying from 100 kW to 2 MW. The irradiation time varied from 5 to 60 minutes. To separate the effects produced by fast neutrons, gammas, and thermal neutrons, samples packaged in polyethylene ampules with gold-foil thermal neutron monitors were irradiated with and without 40-mil cadmium sheath. The thermal neutron flux at a power level of 1 MW was typically 5.16×10^{12} n/cm^2/sec with a cadmium ratio of 10 to 1. The sample temperature during irradiation was less than 90°C.

The sample activity immediately after removal from the core was generally greater than 200 mR/hr at contact but less than 10 mR/hr one week later. Con-

sequently all mesurements were made about one week after exposure.

The crystals used were "pure" single crystals of the bulk and platelet types having different luminescent properties. The bulk crystals were cleaved from larges boules and varied in size but typically $10\times5\times1$ mm^3 with an initial resistivity of about 2 ohm cm. The platelet crystals were used in the "as-grown" condition, approximately $10\times4\times0.5$ mm^3 of initial resistivity of about 10^9 ohm cm.

The effects of neutron irradiation on the luminescence spectrum at 78°K of typical bulk is shown in Fig. 2. For such a crystal the luminescence spectrum consisted initially of exciton emission at 4880 Å, "edge" emission at 5140 Å, a low intensity band at 6000 Å and another low-intensity emission at about 7200 Å. Neutron irradiation produces a marked reduction of both the exciton and edge emission and the introduction of an intense broad emission band at 7200 Å.

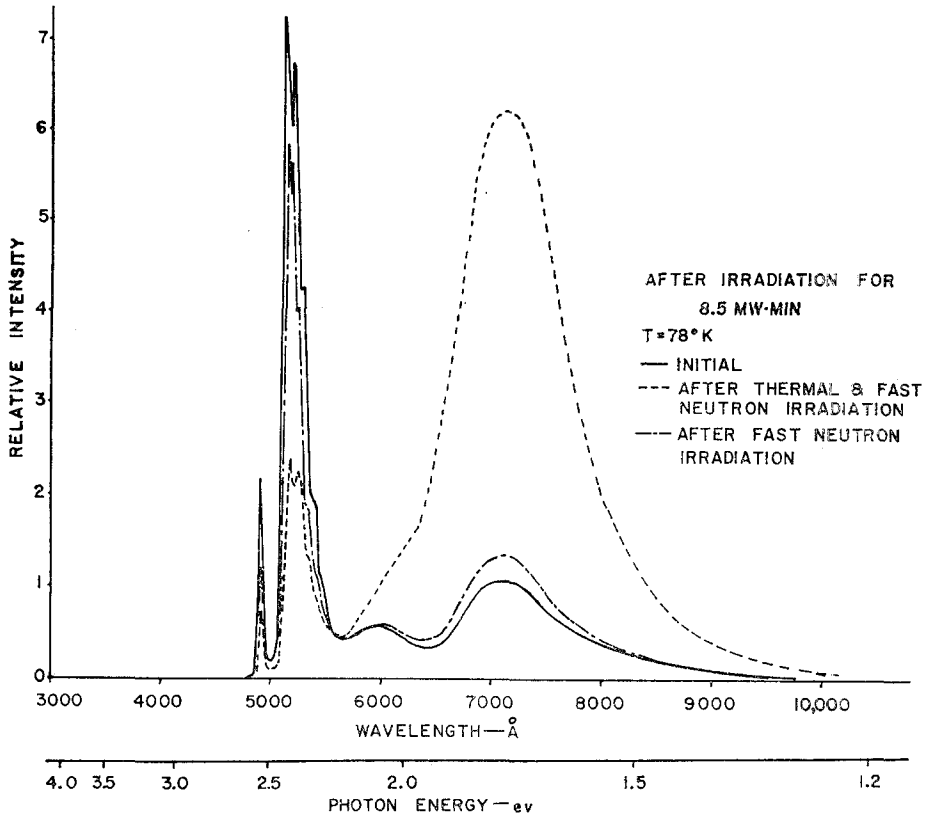

Fig. 2. Red luminescence (7200 Å) induced by thermal neutrons in CdS.

Figure 3 is presented to emphasize the relative importance of thermal and fast neutron effects. In Fig. 3 for example, it is seen that the red luminescence intensity produced by thermal neutrons is about 28 times that of fast neutrons.

The luminescence intensity, such as the exciton line at 4867 Å (2.5471 eV) also decreases. This line is possibly to be identified with the I_2 bound exciton discussed by Thomas and Hopfield.[14] From the analysis of the Zeeman structure they attributed this line to an exciton recombining at a neutral donor center.

Thomas and Hopfield showed that this is due to neutral donor. They suggested that the I_1 line 2.5359 eV (488.5 Å) may be due to cadmium vacancy.

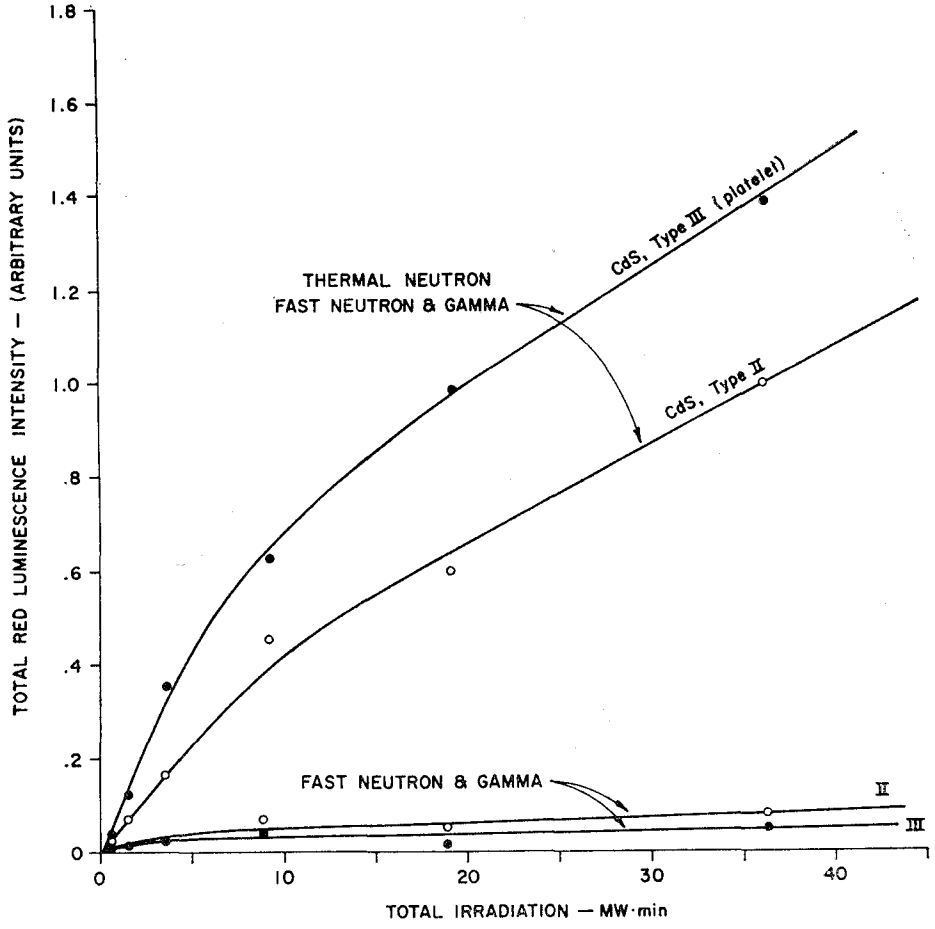

Fig. 3. Intensity of the 7200 Å luminescence produced in CdS vs total irradiation.

The thermal neutron irradiation results suggests that Cd Vacancies or interstitials are in some way related to the 7200 Å red luminescent center. Unfortunately conflicting results make definitive assignments difficult. Kroger *et al.*[15] studied this luminescence by varying the stoichiometry of CdS and attributed the center to Cd vacancies. On the other hand, Vuylsteke and Sihvonen[16] favor S-vacancy for the red luminescent center. Furthermore Kulp and Kelley[17] found that the red luminescence is enhanced under electron beam bombardment. The changes in luminescence begin to take place at electron beam energy of 115 keV, which is the threshold for S displacements. The threshold for Cd displacement comes at 290 keV (E_d(S) = 8.7 eV, E_d(Cd) = 7.3 eV).

More recently an interesting experiment was performed by Mitsuhashi, Chikawa, and Nakayama[18] whose results suggest that the red luminescence bands at 6350 and 7400 Å are due to Cd interstitials. The experiments were carried out by plastically deforming CdS crystals to produce Cd-rich and S-rich

dislocations respectively by bending CdS crystals in opposite directions about the c-axis. The sample is annealed after bending for 2 hours at temperature ranging from 350 to 750°C. The change in the luminescence spectrum is noted. It was found that for the specimen having S dislocation, *i. e.* dislocations in which the half-planes terminate in a row of Cd atoms, the red luminescence at 7400 Å decreased when annealed at 650°C and disappeared completely when annealed at 720°C. In contrast, for the Cd-dislocation specimen the intensity of the red band was essentially unaffected. Furthermore, the intensity of the 7400 Å band increased relative to that of the 6350 band after iodine doping of unbent crystal.

Typical results showing the effects of thermal neutron irradiation on the conductivity of CdS are given in Fig. 4. At room temperature before irradiation the sample conductivity was about 0.1/(ohm cm) which dropped to about 10^{-6}/(ohm cm) following thermal neutron fluence of the order of 10^{15}/cm^2. Fast neutron

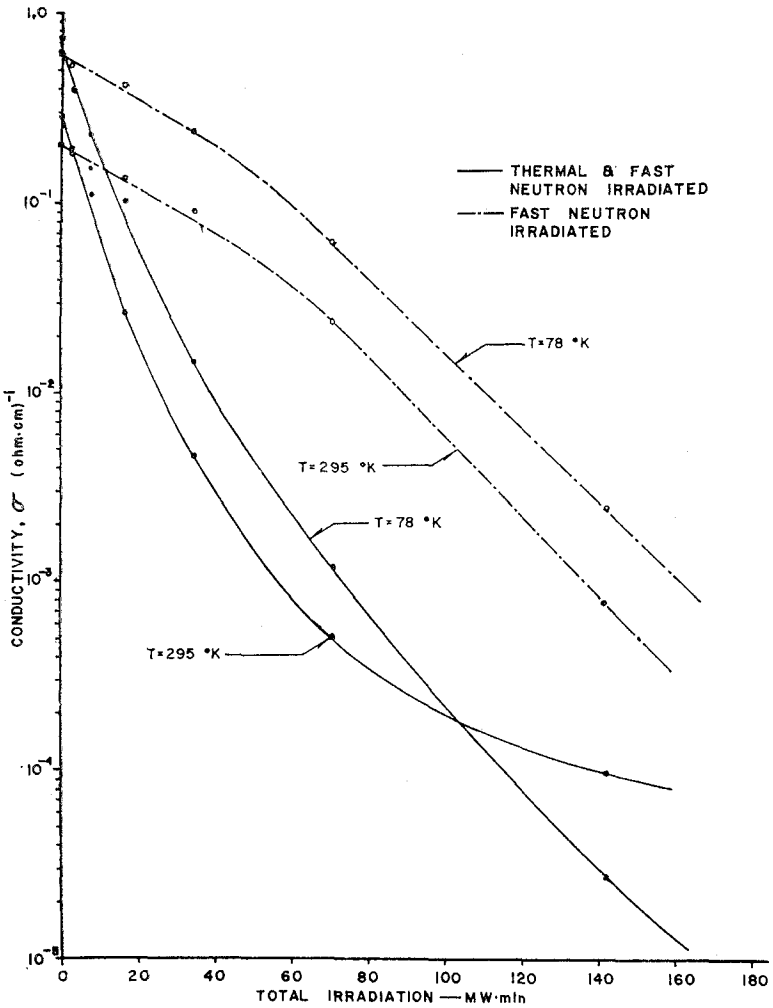

Fig. 4. Dark conductivity changes of CdS crystal at 78° and 295°K produced by reactor neutron irradiation.

irradiation also resulted in conductivity decrease, but the effect was smaller by a factor of about 40.

It was noted earlier that the photoluminescence changes are in the ratio of about 28 : 1, which is to be compared to the ratio 40 : 1 for the conductivity changes. The reason for the difference is that photoluminescence is determined by one type of defect, say Cd or S defects, whereas the conductivity is affected by both the Cd and S defects. The distinction can be put into a more quantitative form as follows. Let $[Cd]_{th}$ be the Cd defect concentration resulting from thermal neutron irradiation, and $[Cd]_f$ and $[S]_f$ the Cd and S defect concentrations produced by fast neutrons. Then photoluminescence measurements indicate that

$$\frac{[Cd]_{th}}{[Cd]_f} \sim 28$$

whereas conductivity measurements suggest that

$$\frac{[Cd]_{th}}{[Cd]_f - \alpha[S]_f} \sim 40.$$

The minus sign in the denominator comes about because Cd and S defects have opposite effects upon the carrier concentration, *i. e.* Cd defects act as acceptors and S defects as donors. The coefficient α is introduced to take into account the facts that Cd and S defect concentrations may not be equal and that the effectiveness of S defect as a donor may not be equal to the of Cd defect as an acceptor.

Fortunately or unfortunately there appears to be the need to re-examine both neutron and gamma radiation effects in CdS. According to the results just discussed, the conductivity always decreases and this decrease has been attributed to Cd defects that behave as acceptors. On the other hand, R. O. Chester[19] reports that the conductivity can increase or decrease depending upon the energy of the gamma radiation. She reported that under Co-60 gamma irradiation (1.17 and 1.33 MeV) the carrier concentration increased from about 5×10^{15} to about $8\times10^{15}/cm^3$. If, however, a sample is subjected to the less energetic Cs-137 gamma radiation (0.662 MeV) the carrier concentration was found to decrease. The increase in carrier concentration was attributed to the slight excess of Cd defects over S defects (Cd/S=1 : 1) due to the internal beta irradiation of Compton electrons for the Co-60 gamma rays, compared to excess of S defects (Cd/S=1/6.1) when irradiated with the less energetic Cs-137 gammas. However, it is not clear that all relevant displacement mechanisms have been proberly taken into account. At these energies it may be that other mechanisms, such as those suggested by Varley[33] and others, need to be considered. Furthermore, in may be that defect annealing is important; this possibillity is suggested by the recent investigations by L. P. Randolph and R. B. Oswald.[20]

The need of distinguishing the neutron radiation effects in high-conductivity specimens from those in low-conductivity specimens has been emphasized by R. T. Johnson.[21] Upon irradiating these samples of resistivities 10, 9, and 0.5 ohm cm, he found that the final resistivities after fluences of the order of $10^{14}\sim10^{17}$ neutrons $/cm^2$ increased to about 2×10^4 ohm cm. In contrast for high resistivity samples (in-

itially 9.4×10^{7} and 6.8×10^{8} ohm cm) the resistivities decreased, approaching a value of about 8×10^{4} ohm cm after neutron fluence of about 2×10^{17} neutron/cm^{2}. The limiting resistivities for both high- and low-resistivity samples are about 8×10^{4} ohm cm, corresponding to electron concentration of about 1.3×10^{12}/cm^{3} and the Fermi level 0.37 eV below the conduction band. That thermal neutron irradiation also decreases the resistivity of high resistivity CdS was reported earlier R. B. Oswald and C. Kikuchi.[22]

V. RESULTS FOR *N*-TYPE CdTe[23]

The radiation procedures were similar to those of CdS to prepare the samples for Hall and conductivity measurements, thin wafers were cut from CdTe ingots and polished to thicknesses of the order of 0.05 cm. Samples were then placed in glass vials, which were flushed with argon gas before sealing. This was done to avoid oxidation. Typical results are shown in Figs. 5 and 6.

We shall consider several experimental facts to guide us in constructing an appropriate model for CdTe. The crystals were zone-purified but the carrier concentrations were still of the order of 10^{15}/cm^{3}, suggesting that the impurity concentration was still quite high and that the donor levels lie above the Fermi

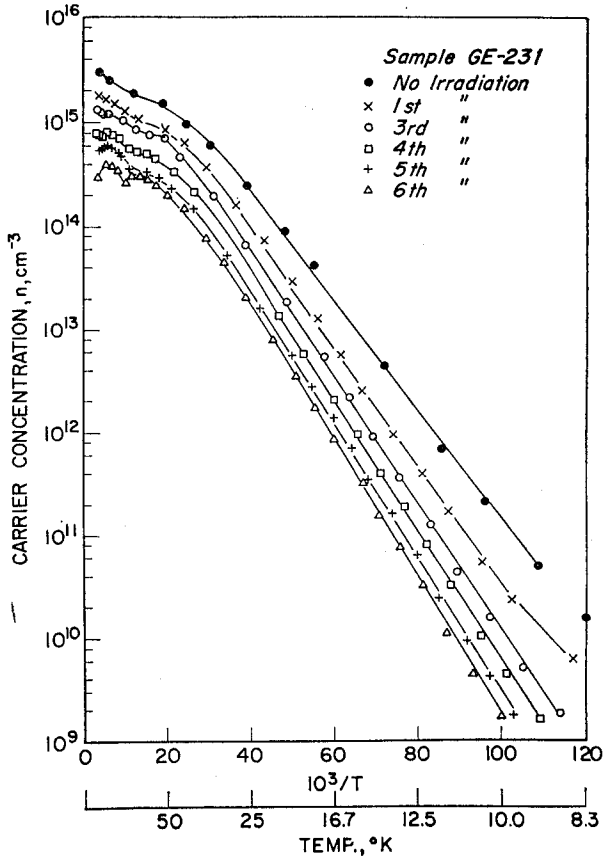

Fig. 5. Dependence of carrier concentration in CdTe crystal on thermal neutron.

level, possibly less than $kT=0.025$ eV below the edge of the conduction band. The position of the Fermi level is calculated from

$$n=N_C \exp\left(\frac{E_F-E_C}{kT}\right)$$

in which

$$N_C\equiv\frac{2(2\pi m_e^* kT)^{3/2}}{h^3}=1.778\times10^4 T^{3/2}$$
$$=9.3\times10^{17} \quad (T=300^\circ\mathrm{K}).$$

The effective mass m_e^* was taken to be $0.11m_e$. Then for $n=10^{15}/\mathrm{cm}^3$ we find that

$$E_C-E_F=0.17 \text{ eV}.$$

The carrier removal rate is in the neighborhood of unity, suggesting that deep traps are produced. These facts lead us then to the model

E_c ——————————

E_D ---------- $N_D\epsilon_D\equiv E_c-E_D$

E_F —·———·——

E_t ·····-------- $N_t\ \epsilon_t\equiv E_c-E_t$

in which N_D is the donor concentration and N_t is the trap concentration resulting from thermal neutron irradiation.

Assuming then that the donors are the suppliers of electrons, we find that

$$N_D=n+\frac{N_D}{1+\gamma_D\exp\left(\frac{E_D-E_F}{kT}\right)}+\frac{N_t}{1+\gamma_t\exp\left(\frac{E_t-E_F}{kT}\right)}.$$

If the trap levels are more than several kT below the Fermi level, then the exponential term in the denominator of the last term is small, so that we obtain

$$N_D-N_t-n=\frac{N_D}{1+\gamma_D\exp\left(\frac{E_D-E_F}{kT}\right)}+\frac{N_D}{1+\frac{\gamma_D N_c}{n}\exp\left(\frac{E_D-E_c}{kT}\right)}$$

which leads to

$$\frac{n(N_t+n)}{N_D-N_t-n}=\gamma_D N_c\exp\left(-\frac{\epsilon_D}{kT}\right).$$

In the so-called "freeze-out" region.

$$N_t,\ N_D\gg n$$

so that

$$n=\frac{\gamma_D N_c(N_D-N_t)}{N_t}\exp\left(-\frac{\epsilon_D}{kT}\right).$$

Thus a plot of ln n against $1/T$ gives ϵ_D, the position of the donor level below the conduction band edge.

Figure 5 shows such plots for an n-type CdTe grown at and given us from the General Electric Research Laboratory. The slopes suggest levels at $E_c-0.009$ eV before thermal neutron irradiation and at about $E_c-0.012$ eV after irradiation. These values agree well with those obtained by Segall, Lorenz, and Halsted.[24]

They reported E_D to be about 0.011 eV, except for one sample (B) for which $E_D = E_c - 0.007$ eV.

The conclusion that thermal neutrons produce predominantly Cd defects is based on the observation that the level $E_c - 0.06$ eV is not observed under low thermal neutron fluence. This level was found by the G. E. group in samples heat-treated with an excess of the cadmium component or subjected to 1.5 MeV electron bombardment and has been attributed to Te-vacancy. The electron dose required to reveal the level was about 6×10^{16} elections/cm^2. Under larger thermal neutron fluence ($\sim 10^{17}$/cm^2) a level appears at about $E_c - 0.059$ eV, as shown in Fig. 6.

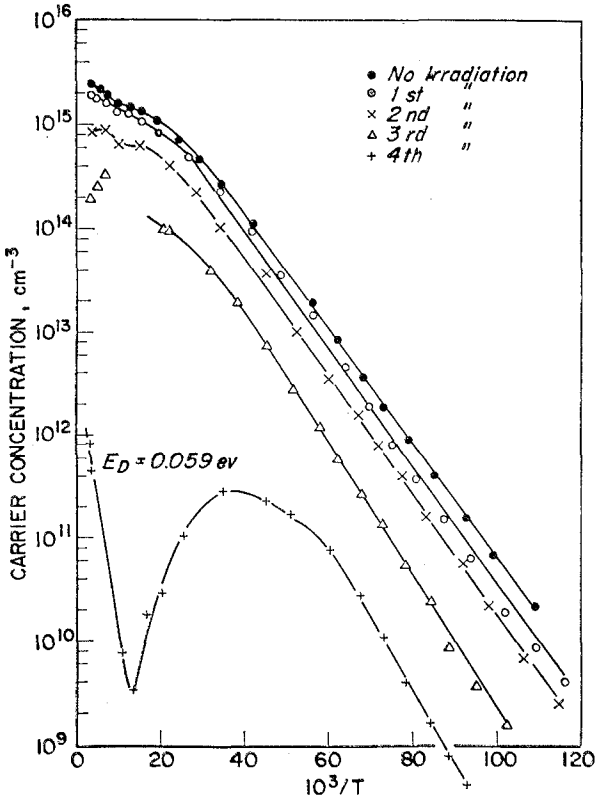

Fig. 6. Effect of high thermal neutron fluence on CdTe carrier concentration.

As both Figs. 6 and 7 show, after prolonged irradiation, the levels at $E_c - 0.059$ eV for CdTe and $E_c - 0.085$ eV for CdS are revealed. These values are within experimental errors of the double acceptor levels reported by Lorenz and Woodbury.[25] The unusual characteristic of these plots is that visible radiation was not needed to establish equilibrium with respect to the double acceptor level (See for example, Lorenz, Aven, and Woodbury[26]). A possible explanation is that the residual radioactivity of the sample is responsible for equilibrations. It would be of interest to check these ideas by examining the double acceptor level in ZnSe before and after thermal neutron irradiation.

The absence of evidence for the Te-vacancies in CdTe is rather surprising

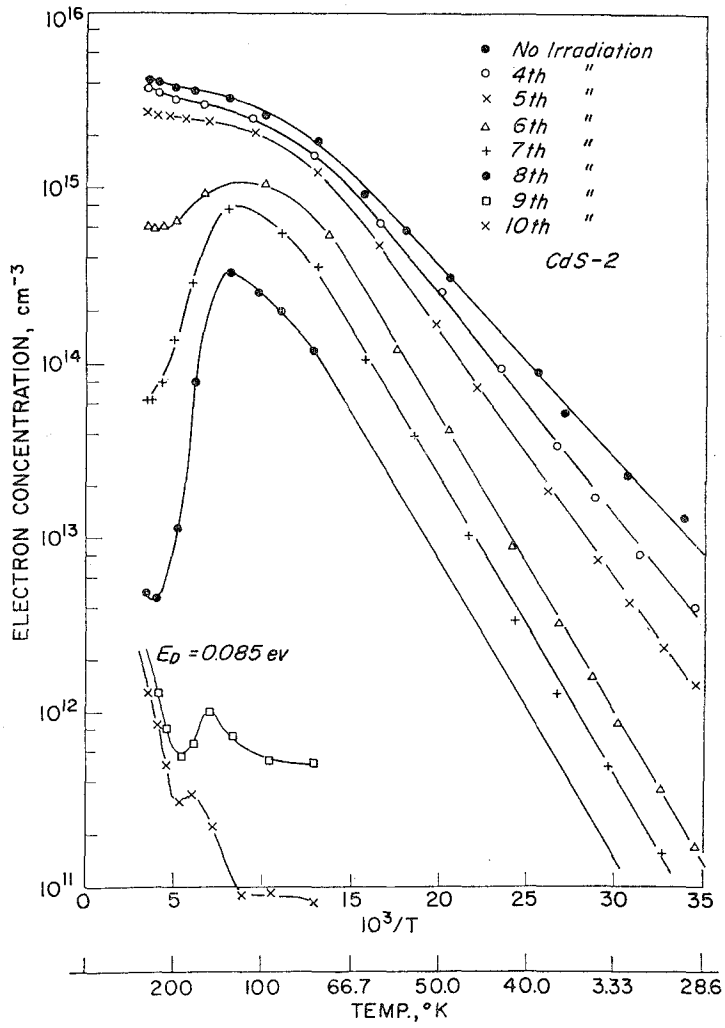

Fig. 7. Effect of thermal neutron fluence on the carrier concentration in CdS.

because as we have seen the cumulative Cd recoil energy is about 143 eV, which is appreciably larger than the threshold energy. The difference in the atomic weights (112.41 for Cd and 127.61 for Te) is small so that nearly equal concentrations of these vacancies are to be expected, if the displacement energies are equal. Measurements by F. J. Bryant and E. Webster[27] indicate that the displacement energies are 5.6 eV for Cd and 7.8 eV for Te. For CdS, the difference is appreciably smaller, being 7.3 eV for Cd and 8.7 eV for S, and as indicated earlier, there is evidence of appreciably annealing of S-defects for temperatures above 200°K.

VI. RESULTS FOR *P*-TYPE CdTe[28]

Measurements on *p*-type CdTe have also been carried out. Just as the electron concentration decreases upon irradiation for *n*-type material, the hole concentration decreases for *p*-type material upon thermal neutron irradiation. Measurements

were made on p-type samples whose initial hole concentrations were about 6×10^{15} /cm^3. At the end of the irradiation period the hole concentration dropped to a saturation value of about 5×10^9/cm^3. This value is still large in comparison to the intrinsic value of 1.4×10^6/cm^3. The dominating level before irradiation was $E_v+0.15$ eV, but successive irradiations revealed at $E_v+0.20$ eV, $+0.3$ eV, and also $+0.4$ eV.

A study of the effects of electron irradiation upon luminescence was carried out by Bryant and Webster.[29] They investigated luminescence in the neighborhood of 1.13 μm. The center emitting this radiation was generated by bombarding CdTe with electron beam of energy 340 keV or higher. Upon electron irradiation it was found that the emission at 1.13 μm was enhanced but that at 0.89 μm was reduced. This is very similar to the effect seen in CdS. The sample most suitable were found to be p-type sample, which had been fired at high temperatures for about 200 hours, showed strong luminescence emission at 1.13 μm initially and the increase in emission at this wave length after electron bombardment was small.

The samples for their studies were purchased from Semi-Element, Inc. The impurity concentrations appear to be relatively high. They reported that the samples contained 10^{16}/cm^3 of Zn, 2×10^{15}/cm^3 of S, 10^{15}/cm^3 of Se, and 10^{15}/cm^3 of Si. By Hall measurements the carrier concentrations were seen to be in the neighborhood of 10^{15}/cm^3.

Because of the relatively small difference in the atomic weights for Cd (112.41) and Te (127.61), it seems difficult, if not impossible to obtain the threshold energy for displacement by this method. Bryant and Webster[29] found that the threshold for 1.13 μm center is 340 keV. The energies transferred to Cd and Te at this electron beam energy are 8.9 eV and 7.8 eV respectively. The two workers did not report another threshold.

A related experiment was carried out by Matsuura, Itoh, and Suita,[30] who observed changes in the conductivity behavior at 250 keV electron beam energy. They found the conductivity to increase for beam energy below 250 keV, but above this value the conductivity to decrease. At this beam energy the Cd and Te receive 6.2 and 5.3 eV respectively. They indicated that their sample was obtained also from Semi-Element, Inc.

VII. DISCUSSION

In the following table we summarize the carrier removal rates for CdS and CdTe reported by several investigators.

We note first that our carrier removal rates are in good agreement with those obtained by R. O. Chester.[19] The second point to note is that the crarrier removal rate for CdTe is 1 or nearly so, whereas for CdS the value is about 0.1. The third point to note is the large positive value for high resistivity CdS, compared to about -1 for low resistivity CdS. Further investigations are needed for the explanation of these results.

It should perhaps be noticed that S. Tanaka and T. Tanaka[31] in a much earlier publication reported the effects of deuteron bombardment upon high resistivity CdS. The resistivity was initially about 10^{10} ohm cm and dropped to about 10^4 ohm cm. From the dependence of the resistivity a donor level, assigned to S-

Sample	Material	Type	no (10^{-15})	dn/d (nvt)	Radiation	Reference
GE-231	CdTe	*n*	2.3	−1.0	Thermal	a
GE-232	CdTe	*n*	1.7	−0.6	Tharmal	a
	CdTe	*n*	?	−0.6	Tharmal	b
MH-1						
MH-1A	CdTe	*p*	5.5	−1	Tharmal	c
MH-3						
MH-4						
	CdS	*n*	5	−0.098	Tharmal	d
	CdS	*n*	*n*	−0.048	Tharmal	b
LRC	CdS	*n*	1-10	−1	Fast	e
HRC	CdS	*n*	10^{-7}	13	Fast	e

a. C. Barnes and C. Kikuchi, *Nuc. Sci, and Eng.*, 31, 513, (1968).
b. R. O. Chester, *J. App. Phys.*, 38, 1745 (March 1967).
c. C. Barnes and C. Kikuchi, *Radiation Effects*, 2, 243 (1970).
d. C. Branes, Thesis, unpublished.
e. R. T. Johnson, *J. App. Phys.*, 39, 3517 (July 1968).

vacancies, was found at about $E_c-0.4$ eV. This level may possibly be the same as the ESR center attributed by K. Morigaki and T. Hoshina[32] to an electron trapped at a S-vacancy.

Although in this report attention is focussed on the nuclear recoil effects, we need to keep in mind that about 4 gammas are radiated for each capture event. The effect of these gammas upon the nearby negative ions needs detailed investigation. Effects related to the mechanisms proposed by Varley[33] or its modifications by C. C. Klick,[34] by J. Durup and R. L. Platzman,[35] and by R. E. Howard, S. Vasko, and Smoluchowski.[36]

The answer to the question on the effects internally emitted gamma rays may be provided by ESR study of $CaWO_4$: Cd or possibly $CdWO_4$. According to crystal structure analysis, Cd is surrounded by 8 nearest oxygens. If a gamma ray causes an oxygen to leave its site, then one of the W will lose an oxygen and become paramagnetic. Since the ESR properties of W associated with an oxygen vacancy is known, and since such centers are not produced in appreciable quantities by an external gamma source, the ESR signal intensity will provide a convenient indicator. Furthermore thermal neutron irradiation of $CaWO_4$ doped with Cd may also assist in the identification of fast neutron produced paramagnetic centers in $CaWO_4$ that have not yet been identified.

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