

HOLE DRIFT MOBILITY AND LIFETIME IN CdS CRYSTALS*

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(Received March 5, 1962)

In view of the considerable interest in the properties and applications of CdS, it is surprising to find that hardly any information is available on the transport properties of holes in these crystals. Low-field electroluminescence experiments, photoelectromagnetic effect,² and other measurements^{3,4} have led to the conclusion that holes must be mobile. A hole lifetime τ_h between 10^{-7} and 10^{-6} sec has generally been estimated.

By the use of fast-pulse techniques it has been found possible to study the drift mobility of holes in a very direct way and to obtain consistent values for both μ_h and τ_h . In the experiments a 40-keV electron pulse of a few nsec duration⁵ generates free carriers to within a depth of about 5μ below the top electrode. Holes are drawn out of this region by a pulsed applied field and drift across the specimen. The resulting charge displacement is integrated and displayed on wide-band electronic equipment. The success of the experiment depends largely on the choice of suitable electrodes. Work on the electron drift mobility in CdS⁶ suggested the use of a noninjecting top electrode and an injecting bottom electrode for the type of carrier drifting across the specimen. In the present investigation a thin blocking top electrode (transparent to the electron beam) and a Au or Ag bottom electrode were therefore used. The blocking electrode consisted of a 0.5μ blown Pyrex film gently pressed against the crystal.

The observed pulse shape gives the integrated charge displacement q as a function of time. It is shown in Fig. 1(a) for a low applied field ($E \approx 4 \times 10^3$ v/cm). The deviation from linearity of the rising edge indicates the loss of holes during transit into deep traps, possibly recombination centers, for which the thermal release time is far longer than the transit time t_t . The pulse shape corresponds to point A on curve (c), ($t_t \approx 2\tau_h$). With a large field ($\approx 13 \times 10^3$ v/cm⁻¹, point B) the rising edge of the pulse tends to become practically linear, as shown in Fig. 1(b) which was observed for $t_t \approx \frac{1}{2}\tau_h$. The intersection of the tangents at $t=0$ and $t \geq t_t$ defines t' which was measured as a function of E . It can be shown that

$$1/t' = (1/\tau_h)[1 - \exp(-t'/\tau_h)]^{-1}. \quad (1)$$

If d is the specimen thickness, $t_t = d/(\mu_h E)$.

Seven pure (i.e., undoped) high-resistivity crystals were investigated. They were obtained from three different sources: RCA, Princeton; AEI, Harlow; EMI, Hayes. Curves (c) and (d) show typical experimental results of $1/t'$ vs E/d for two of the specimens. The crystal orientation is such that the holes drift in a direction perpendicular to the c axis. At low E , t' tends towards τ_h and the experimental values of τ_h obtained all lie between 1×10^{-7} and 3×10^{-7} sec, in agreement with the above estimates. With the known value of τ_h , t_t can now be calculated from Eq. (1) for each value of E/d . This leads to curves (c') and (d') from which μ_h is obtained. The room-tem-

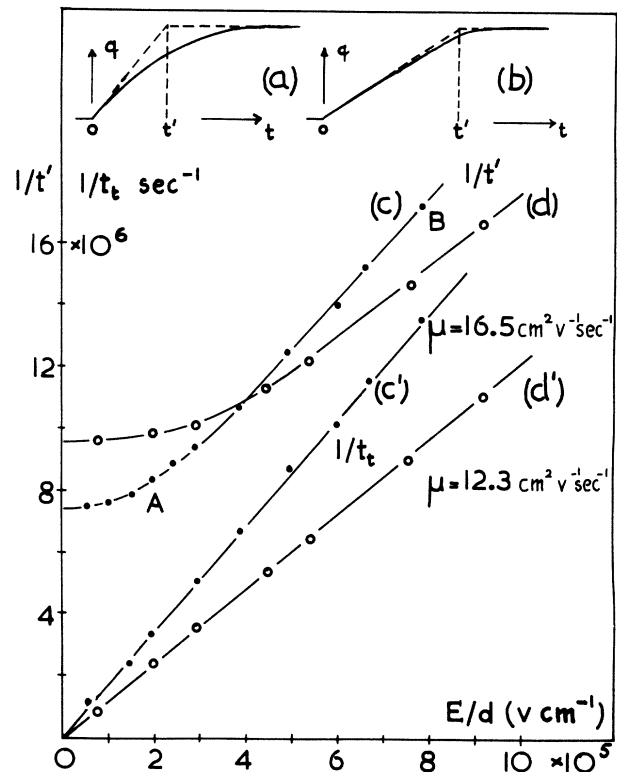


FIG. 1. (a) Typical pulse shape at low E when $t_t \approx 2\tau_h$, corresponding to point A on curve (c). (b) Pulse shape at high E when $t_t \approx \frac{1}{2}\tau_h$, corresponding to point B on curve (c). (c) $1/t'$ measured for EMI crystal, $d = 165 \mu$, $\tau_h = 1.4 \times 10^{-7}$ sec. (d) $1/t'$ measured for RCA crystal, $d = 40 \mu$, $\tau_h = 1.0 \times 10^{-7}$ sec. (c') and (d') $1/t_t$ curves calculated from Eq. (1).

perature values of μ_h for the seven crystals lie in a range between 10 and 18 $\text{cm}^2 \text{v}^{-1} \text{sec}^{-1}$ with a mean value of about 15 $\text{cm}^2 \text{v}^{-1} \text{sec}^{-1}$. The good linearity of the calculated curves supports the validity of the assumptions made in deriving Eq. (1).

The temperature dependence of μ_h has been investigated between 500°K and 77°K for five of the specimens. The agreement between different curves is very satisfactory. The interesting feature of the results is a mobility maximum at about 210°K after which all $\log \mu_h$ vs $1/T$ curves decrease linearly towards the lower temperatures with an activation energy of 0.019 ± 0.002 ev. It may be possible that this energy is associated with transitions of free holes between the upper two valence bands of CdS. Such an interpretation appears to be supported by recent work on the band structure of CdS,⁷ in which the dichroism of absorption edge is explained in terms of transitions from the upper two valence bands to the conduction bands. From the optical data it is concluded that the energy separation between these

bands is 0.02 ev at room temperature and 0.016 ev at 4.3°K, which agrees with the above activation energy, measured between 200°K and 77°K.

Further work on the possible interpretation of these results in terms of the valence band structure is in progress.

The authors wish to thank Dr. R. W. Smith of RCA, Dr. J. Franks of AEI, and Mr. McGill of EMI for kindly supplying the crystals.

*This work was supported by the European Research Office of the U. S. Army.

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FREE CHARGE CARRIER EFFECTS IN CADMIUM FLUORIDE

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(Received March 7, 1962)

We have found optical absorption and conductivity due to free electrons in single crystals of CdF_2 doped with several trivalent rare earth ions. CdF_2 has a band gap of¹ 6 ev and the fluorite structure. This is the first observation of a large concentration of conduction electrons in an ionic crystal with such a large band gap.

It was shown by the determination of the crystal field splitting of the low-lying Eu^{+3} levels as obtained from an analysis of the fluorescence spectrum of $\text{CdF}_2:\text{Eu}$ that, for concentrations of Eu in the range 10^{-3} to 10^{-5} mole fraction, charge compensation is ordinarily achieved by means of interstitial fluoride ions.² Earlier measurements of the x-ray lattice constant and density of $\text{CdF}_2:\text{Ce}^{+3}$ yielded the same conclusion at larger impurity concentrations.³ A similar conclusion holds for CaF_2 doped with trivalent ions.^{4,5} We have now found that charge compensation can also proceed by means of electrons in the conduction band or in shallow (0.06 ev deep) traps.

When $\text{CdF}_2:\text{Sm}^{+3}$ crystals of about 0.1 cm^3 are

heated in a saturated cadmium metal vapor at 500°C, for times as little as 15 minutes, the originally colorless crystals become colored blue uniformly and transmission measurements from 0.4μ to 6.0μ show a continuously rising absorption. In crystals containing 10^{-3} Sm the absorption coefficient varied as $\lambda^{3.5}$, and crystals containing 10^{-4} Sm yielded a $\lambda^{3.0}$ dependence.

The resistivities of these crystals, as obtained by a four-point probe method, were about 1 ohm cm. Both thermoelectric power and Hall measurements indicated *n*-type conductivity with a room-temperature mobility of 7 to 10 $\text{cm}^2/\text{volt sec}$ and carrier concentrations from 5×10^{17} to $10^{18}/\text{cm}^3$.

We propose that heating in Cd vapor results in the diffusion of the interstitial F^- ions to the surface and the diffusion of electrons in from the surface, CdF_2 being then formed at the surface. In $\text{CdF}_2:\text{Sm}^{+3}, \text{Na}^{+1}$, in which the substitutional Na^{+1} ion compensates the charge of the Sm^{+3} ion, no coloration was observed nor could pure CdF_2