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Classification

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Relations between structural parameters and physical properties in CdTe and Cd_{0.96}Zn_{0.04}Te alloys

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Résumé. — Des mesures électriques et des expériences de photoluminescence ont été réalisées sur des cristaux de CdTe et de Cd_{0.96}Zn_{0.04}Te, de densité de dislocations variant entre 5×10^4 et $6 \times 10^5 \text{ cm}^{-2}$. La variation de la mobilité électronique a été interprétée en termes de : diffusion sur les régions de charge d'espace entourant les dislocations, réduction correspondante du volume effectif des cristaux, diffusion en excès dans les alliages due à leur caractère non idéal. La largeur de raie de recombinaison d'excitons liés à des accepteurs neutres se décompose en contributions associées au désordre d'alliage et aux dislocations, cette dernière étant augmentée dans les alliages.

Abstract. — Electrical measurements and photoluminescence experiments were performed on several CdTe and Cd_{0.96}Zn_{0.04}Te crystals with dislocation density in the range $5 \times 10^4 - 6 \times 10^5 \text{ cm}^{-2}$. The observed variation in electron mobility has been interpreted in terms of scattering on space charge regions surrounding dislocations, a related reduction in the effective volume of the crystals, and excess scattering due to a non ideal alloy behaviour. The linewidth of the acceptor-bound exciton recombination line includes contributions due to alloy disorder and dislocations, the latter being enhanced in the alloys.

1. Introduction.

While the electronic properties of CdTe have been investigated for a long time, systematic studies related to the crystalline quality are rather recent : they mostly derive from the interest in CdTe as a substrate for the epitaxy of CdHgTe alloys. Then it has been realized that the crystalline quality of CdTe could be significantly improved by the addition of Zn atoms in the compound [1-3]. On the other hand the crystal lattice parameter decreases as Zn is incorporated so that an atomic Zn concentration of 4 % allows a perfect lattice match with the alloy Cd_{0.2}Hg_{0.8}Te which is the composition needed for infrared detection in the common 8-12 μm wavelength range.

The better crystalline quality of CdZnTe alloys compared to CdTe has been analysed by various workers in terms of bond stabilization [4, 5] and solution hardening [6]. Experiments on plastic deformation and microhardness measurements [6] have shown that the crystal lattice is actually made harder by the presence of Zn, in fair agreement with the model first applied to GaAs : In [7].

Little attention has been paid to the physical

properties of ZnCdTe alloys. However some physical parameters are quite sensitive to the presence of structural defects and could be used as a complementary way for assessing the crystalline quality of the material.

In this paper we present a study of electrical and luminescence properties of CdZnTe alloys compared to CdTe. From the analysis of electron mobility and excitonic luminescence spectra it is shown that useful and interesting correlations can be established between physical quantities and structural parameters. This leads to a better understanding of the influence of crystalline defects on the electronic properties of semiconductors.

2. Experimental.

All the crystals studied were grown using the modified vertical Bridgman method [8]. The Cd vapour pressure above the melt was controlled with a Cd reservoir to make the crystals electrically conductive n-type.

Several crystals were grown with different growth parameters which led to crystals of variable quality. Five representative crystals were selected for this

Table I. — Dislocation density (N_d) and X-ray rocking curve linewidth (Δ_{RC}) of the investigated crystals.

	C4 CdTe	C3 CdZnTe	C6 CdZnTe	C2 CdZnTe	C11 CdZnTe
$x \%$	0	3.4	3.2	3.3	2.7
N_d (10^5 cm^{-2})	5	0.5	0.8	3	6.2
Δ_{RC} (arc.sec)	100	25	30	70	250

study. They are indicated in table I with the corresponding chemical and structural characteristics. The Zn composition was deduced from photoluminescence experiments (see below). The etch pit density N_d was determined by using the E – A_g Inoue etch [9] on a (111) Cd face. The rocking curve width Δ_{RC} was measured from the (333) X ray reflection. Figure 1 shows that Δ_{RC} is proportional to the square root of the dislocation density in agreement with the model of Gay *et al.* [10] which gives confidence in the structural measurements. The point corresponding to crystal C11 has been disregarded because of some error or artefact in the measurement of Δ_{RC} .

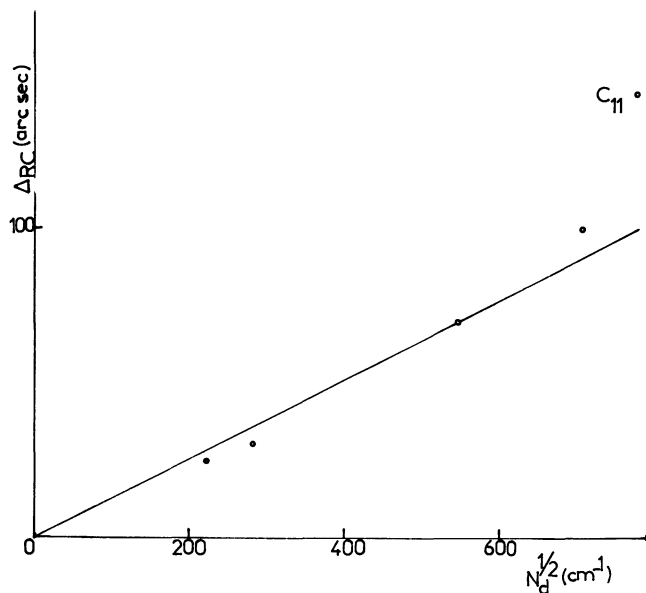


Fig. 1. — Double crystal rocking curve width Δ_{RC} as a function of the square root of the dislocation density.

Resistivity and Hall effect measurements were performed as a function of temperature using standard techniques.

Photoluminescence experiments were carried out at the temperature of 2 K. Excitation light was

provided by the 488 nm line of an Ar⁺ laser. The power density on the samples was about 50 W cm^{-2} . Luminescence analysis was done with a 1 m Jobin Yvon monochromator followed by a cooled GaAs photomultiplier.

3. Electrical properties.

The variations of electron mobility and carrier concentration are shown in figures 2 and 3 as a function of temperature for four crystals (C11 was semi insulating). The room temperature values are collected in table II.

The temperature dependence of carrier concentration was fitted by postulating the semiconductor is compensated. In this way we determine the donor ionization energy E_D and the concentration of donor and acceptor impurities, the values of which are given in table II. The measured samples show two distinct behaviours. A small ionization energy is determined for samples C2 and C4 in the range expected for effective mass donors. Samples C3 and C6 exhibit deeper donor levels which should be attributed to impurity complexes.

The analysis of electron mobility was conducted along the following lines. First, theoretical values of mobility μ_T were calculated by combining the effects

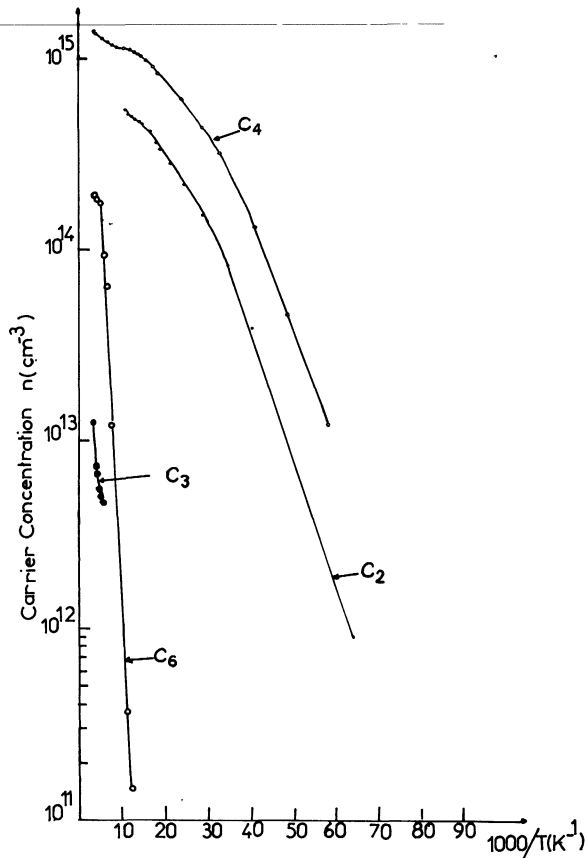


Fig. 2. — Electron concentration as a function of temperature as deduced from Hall measurements.

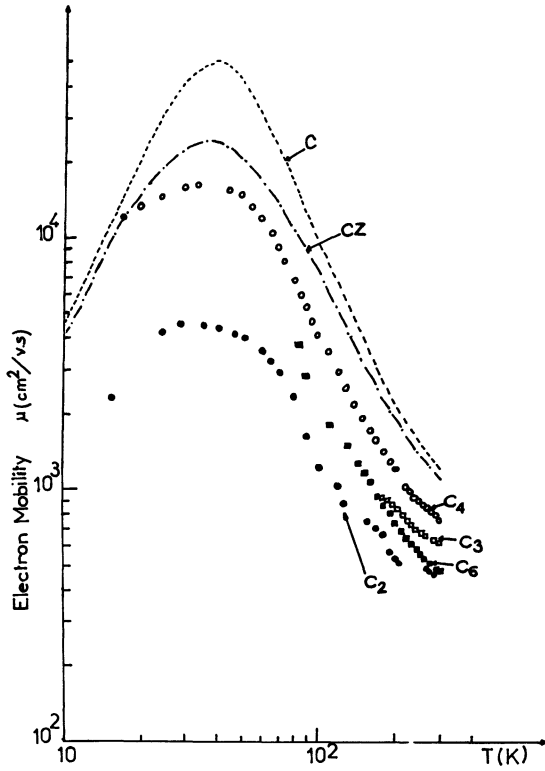


Fig. 3. — Electron mobility as a function of temperature as deduced from Hall and resistivity measurements. C and CZ designate the theoretical mobility μ_T calculated from formula (1) for CdTe and CdZnTe alloys respectively.

of various scattering mechanisms: polar optical scattering (μ_0), scattering on neutral impurities (μ_N) and on charged impurities (μ_I) disorder scattering (in case of alloys) (μ_R):

$$\frac{1}{\mu_T} = \frac{1}{\mu_0} + \frac{1}{\mu_N} + \frac{1}{\mu_I} + \frac{1}{\mu_R}. \quad (1)$$

The expressions of the first three terms were taken from Aleksenko *et al.* [11]. The last one is calculated from the formula [12]:

$$\mu_R = \frac{(2\pi)^{1/2} e \hbar^4 N_s}{3(kT)^{1/2} m_n^{5/2} (E_1 - E_2)^2 x(1-x)} \quad (2)$$

N_s is the concentration of atomic sites ($2.94 \times 10^{22} \text{ cm}^{-3}$ in CdTe), e is the electronic charge, m_n is the electron mass, $E_1 - E_2$ is the conduction band offset between CdTe and ZnTe taken to be 0.7 eV [13].

The variations of the theoretical mobility μ_T as a function of temperature are plotted in figure 3 with the parameters corresponding to sample C4 (CdTe, curve C) and C2 (CdZnTe, curve CZ). As these theoretical values are higher than the experimental ones, other mobility limiting processes have been considered. It is known that an inhomogeneous impurity distribution can greatly reduce the carrier mobility [14]. This is due to the formation of space

Table II. — Quantities determined from electrical measurements: n , electron concentration; μ_{ex} , electron mobility; E_D , donor ionization energy; $N_D(N_A)$, donor (acceptor) concentration; μ_{i0} , mobility related to excess scattering; f , function of the relative volume occupied by inhomogeneities.

	C4 CdTe	C3 CdZnTe	C6 CdZnTe	C2 CdZnTe
n (300 K) cm^{-3}	1.37×10^{15}	1.2×10^{13}	1.89×10^{14}	5.02×10^{14}
μ_{ex} (300 K) $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	750	600	460	450
E_D meV	7.5	43	88	9.1
N_D cm^{-3}	1.31×10^{15}			7.43×10^{14}
N_A cm^{-3}	1.67×10^{14}			2.43×10^{14}
μ_{i0} $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	4 000	3 030	2 040	2 000
f	0.44	0.74	0.64	0.63

charge regions surrounding local inhomogeneities. In the case these defects in concentration N_i are separated by a distance smaller than the electron mean free path they determine a mobility given by :

$$\mu_i = AN_i^{-1} T^{-5/6} \quad (3)$$

$$\mu_i = \mu_{i0} \left(\frac{T}{300} \right)^{-5/6} \quad (4)$$

Furthermore, because of the strong electric fields present in the space charge regions the latter can be regarded as impenetrable for electrons and a correction has to be brought to the volume of the crystal. Therefrom the experimental mobility is given by :

$$\mu_{ex} = \frac{1}{\frac{1}{\mu_T} + \frac{1}{\mu_i}} \cdot f(\varepsilon) \quad (5)$$

where ε is the relative volume occupied by inhomogeneities and f is a function of this volume : $f < 1$ [15].

The adjustment of this expression to the experimental curves gives the values of the quantities μ_{i0} and f gathered in table II.

4. Luminescence properties.

The low temperature photoluminescence spectra recorded on crystals C4, C3 and C11 are presented as examples in figures 4-6. These spectra exhibit typical exciton-related recombination lines : free exciton (X), exciton bound to neutral donors (D^0X), exciton bound to neutral acceptors (A^0X), optical phonon replica of the free exciton ($X-LO$) and of the acceptor-bound exciton (A^0X-LO) ; two electron transitions (D_2) seen on

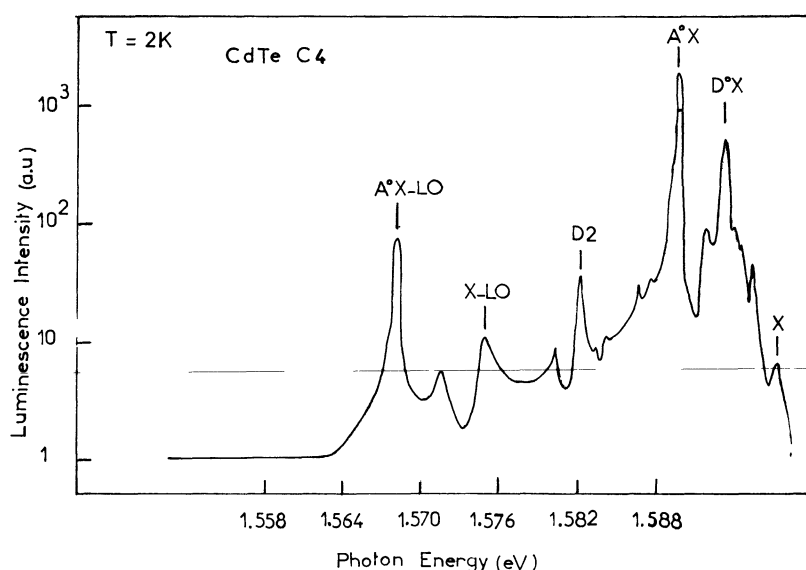


Fig. 4. — Low temperature photoluminescence spectrum of CdTe sample C4.

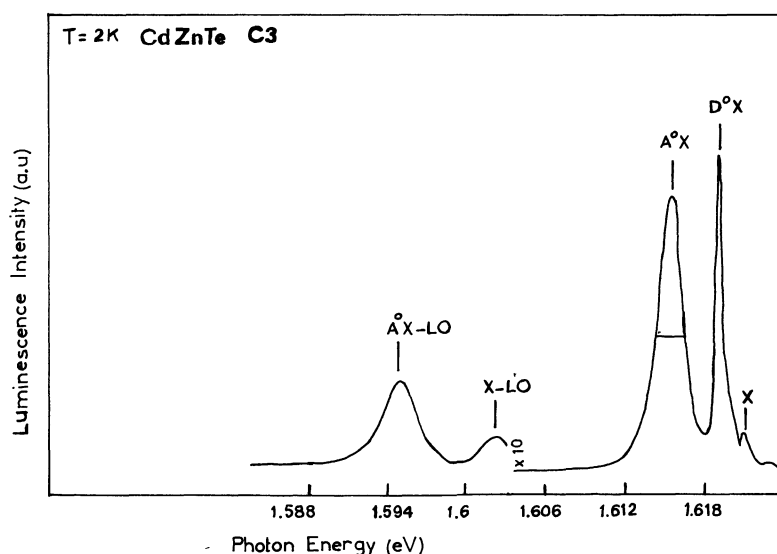


Fig. 5. — Low temperature photoluminescence spectrum of CdZnTe sample C3 with dislocation density $N_d = 5 \times 10^4 \text{ cm}^{-2}$.

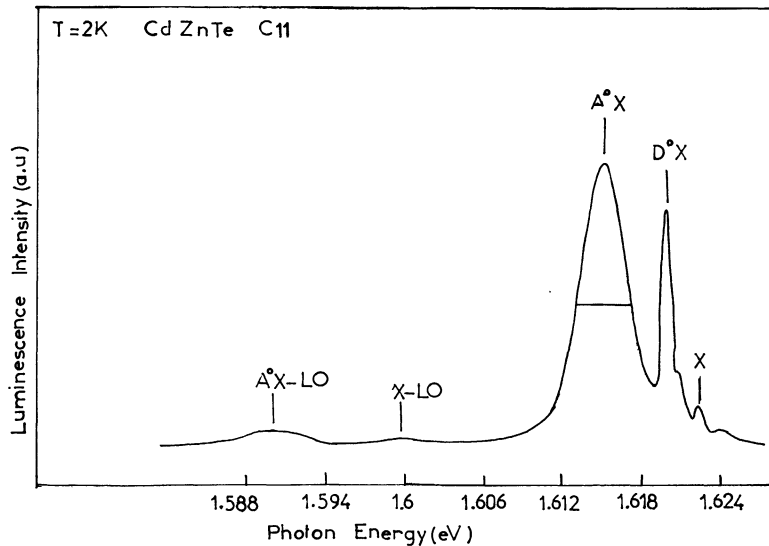


Fig. 6. — Low temperature photoluminescence spectrum of CdZnTe sample C11 with dislocation density $N_d = 6.2 \times 10^5 \text{ cm}^{-2}$.

CdTe only. The free exciton position can be used in conjunction with the variation of band gap as function of alloy composition [16] to determine the exact value of Zn concentration in the studied alloys. These composition values appear in table I.

A striking feature of the above photoluminescence spectra is the broadening of the A^0X line in the alloys. The full width at half maximum (FWHM) of the A^0X line is given in table III for the five crystals studied. The contribution of alloy disorder to this broadening can be evaluated with a model due to Goede *et al.* [17] and others [18]. This model starts from the mean alloy fluctuation in the volume V_X occupied by the excitons :

$$\sigma_X = \left(\frac{x(1-x)}{KV_X} \right)^{1/2} \quad (6)$$

where K is the concentration of cation sites in the

Table III. — Linewidth parameters for the acceptor-bound exciton photoluminescence line : FWHM, measured width value at half maximum ; ΔE_R , calculated contribution due to alloy disorder ; ΔE_c , remaining contribution.

	C4 CdTe	C3 CdZnTe	C6 CdZnTe	C2 CdZnTe	C11 CdZnTe
FWHM meV	0.35	2.45	2.8	3.3	3.5
ΔE_R meV	0	2.17	2.12	2.11	1.95
ΔE_c meV	0.35	1.14	1.83	2.53	2.9

crystals ($1.47 \times 10^{22} \text{ cm}^{-3}$ in CdTe). We consider the space occupied by the acceptor-bound exciton to be a sphere of volume :

$$V_X = \frac{4}{3} \pi \left[\left(\frac{m_0}{\mu} + \frac{m_0}{m_p} \right) \varepsilon_r a_B \right]^3 \quad (7)$$

where m_0 , μ , m_p are the free electron mass, the reduced exciton mass and the effective hole mass. ε_r is the static dielectric constant and a_B is the hydrogen Bohr radius. The sphere radius is thus expressed as the sum of the free exciton radius and of the neutral acceptor Bohr radius. Then the standard deviation of energy gap E_g is the volume V_X is :

$$\sigma_E = \frac{dE_g}{dx} \left[\frac{x(1-x)}{KV_X} \right]^{1/2} \quad (8)$$

For a Gaussian distribution the full width at half maximum is 2.36 times this standard deviation. We take this quantity $\Delta E_R = 2.36 \sigma_E$ to represent the part of the A^0X line broadening due to disorder. Table III gives the values of ΔE_R calculated with the following parameters : $\mu/m_0 = 0.083$; $m_p/m_0 = 0.6$; $\varepsilon_r = 10.2$; $dE_g/dx = 0.8 \text{ eV}$. These values can now be subtracted from the experimental FWHM to yield the excess broadening ΔE_c :

$$\Delta E_c = [(\text{FWHM})^2 - (\Delta E_R)^2]^{1/2} \quad (9)$$

The quantities ΔE_c are also indicated in table III.

5. Discussion.

We now intend to relate the physical parameters determined from the electrical and luminescence measurements to the structural characteristics of the

crystals, essentially the density of dislocations (Tab. I).

As for the electrical measurements a representative parameter is ε , the relative volume occupied by the regions impenetrable to electrons. Assuming spherical regions, ε is deduced from the factor f in table II by the expression [14]:

$$f(\varepsilon) = \frac{1 - \varepsilon}{1 + \varepsilon/2} \quad (10)$$

ε increases as the density of dislocations increases as

shown in figure 7. This relationship includes the alloys as well as CdTe. Thus it appears that the space charge regions surrounding dislocations are a major contribution to the reduction in the effective volume of the crystals.

Inhomogeneities also lead to an excess scattering represented by the mobility μ_i (3). After relations (3) and (4) μ_{i0}^{-1} is proportionnal to the concentration of scattering centers. Figure 8 shows the plot of μ_{i0}^{-1} as a function of the density of dislocations. The quantity μ_{i0}^{-1} tends to increase with increasing

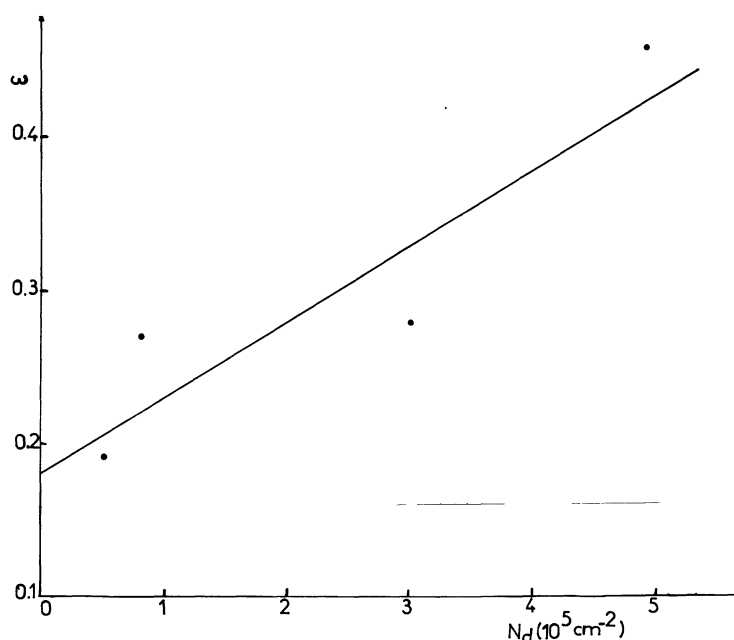


Fig. 7. — Relative volume ε occupied by regions impenetrable to electrons as a function of dislocation density.

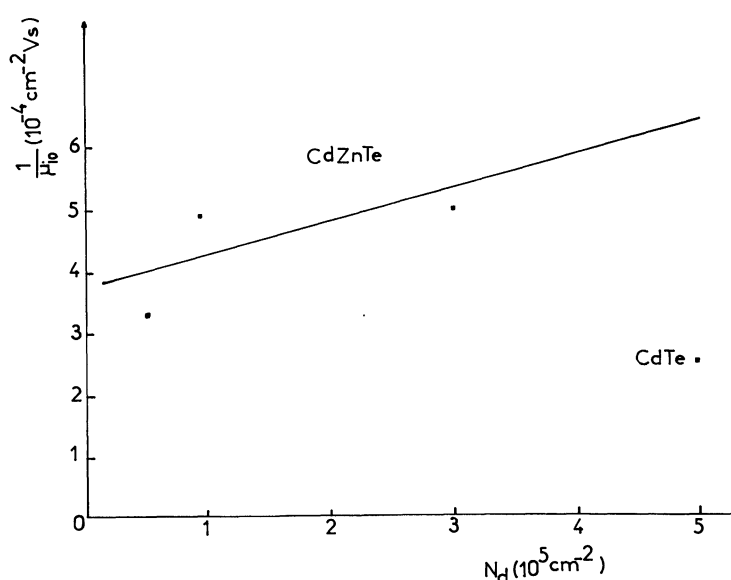


Fig. 8. — Relation between the room temperature mobility μ_{i0} limited by scattering on inhomogeneities and the dislocation density N_d .

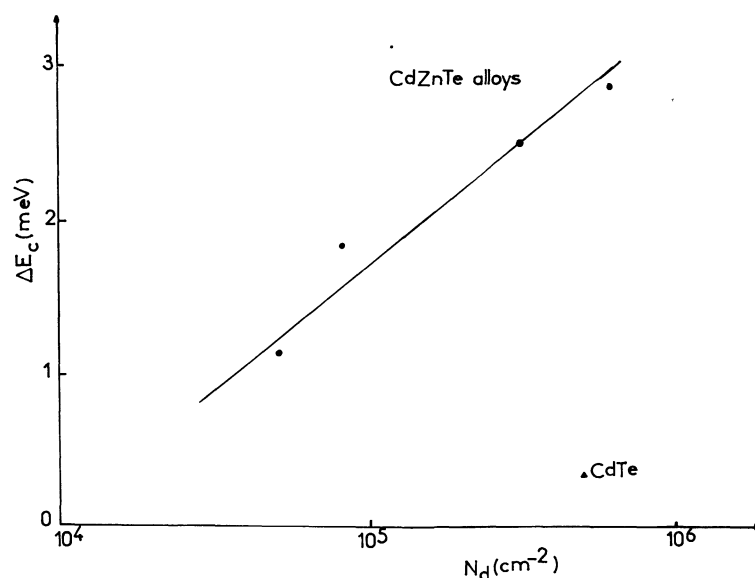


Fig. 9. — Linewidth of the A^0X recombination line ΔE_c (corrected from alloy disorder) as a function of dislocation density.

N_d in the alloys as shown by the best fitted straight line. However the main source of scattering does not depend on dislocation density and could be related to specific effects such as local strains and alloy clustering. The quantity determined for CdTe does not include this contribution and is due solely to dislocations. That particular value of $2.5 \times 10^{-4} \text{ cm}^{-2} \text{ V.s}$ appears to be in agreement with the value deduced from the straight line after subtracting the part due to alloying ($N_d = 0$). Thus the relation of figure 8 can be taken at a first approximation to express the effect of dislocations on scattering in the alloys as well as in CdTe.

As for the optical measurements the significant parameter is the width of the bound exciton recombination line A^0X . For the alloys the linewidth ΔE_c determined after deduction of the contribution due to disorder increases with the density of dislocations as shown in figure 9. However this relation does not account for the linewidth found in CdTe. Note that the latter is representative of a material of standard quality. Higher quality CdTe shows an A^0X linewidth as low as 0.1 meV [19].

It appears that the optical properties of the alloys are more sensitive to the presence of dislocations than the compound CdTe. Again this could be related to the non ideal character of the alloys, e.g.

some kind of interaction between Zn clusters and dislocations.

6. Conclusion.

The electronic properties of $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ alloys with x around 4 % have been analysed and related to the dislocation density. Several physical effects have been demonstrated. The space charge regions surrounding dislocations reduce the conducting volume of the crystals which leads to a smaller effective mobility. This effect has been separated from the dislocation induced scattering process affecting the electron mean free path.

Moreover the linewidth of the bound exciton recombination lines increases rapidly with the density of dislocations which could be related to the associated strain field. The same types of effects are also found in the compound CdTe. However the alloys exhibit additional contributions besides that due to alloy disorder. We suggest that these extra contributions could originate from aspects not included in the analysis of ideal alloys, such as local strains due to bond length misfit and Zn clustering. Deviation from a random distribution of substituted Zn atoms in CdZnTe was indeed observed in recent NMR experiments [20].

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