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## The Fe<sup>2+/3+</sup> donor level in CdTe

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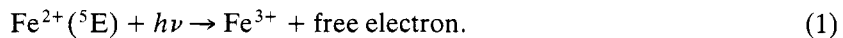
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**Abstract.** Photoconductivity, absorption and temperature dependence of conductivity were studied in CdTe:Fe crystals. The position of the Fe<sup>2+/3+</sup> donor level has been determined. It lies 130–150 meV above the top of the valence band. The value of the optical ionization energy has been confirmed as 1455 meV. The lattice relaxation energy has been found to be below 20 meV. The Auger photoconductivity originated by the <sup>5</sup>E → <sup>5</sup>T<sub>2</sub> intracentre transitions within the Fe<sup>2+</sup> centres has been observed.

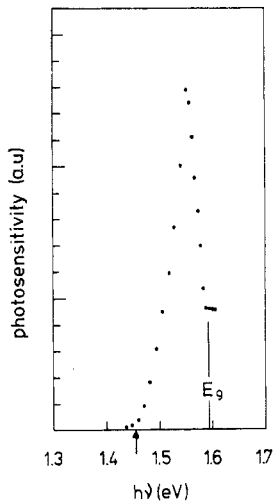
### 1. Introduction

Iron atoms are known to substitute cadmium atoms in the lattice of CdTe, and many properties of this impurity are very well described (Slack *et al* 1966, 1969 Baranowski *et al* 1967, Mahoney *et al* 1970, Brunthaler *et al* 1984). Nevertheless, information about some essential parameters is very scarce. Let us consider the ionization energy of the Fe<sup>2+</sup> centre and the corresponding lattice relaxation energy.

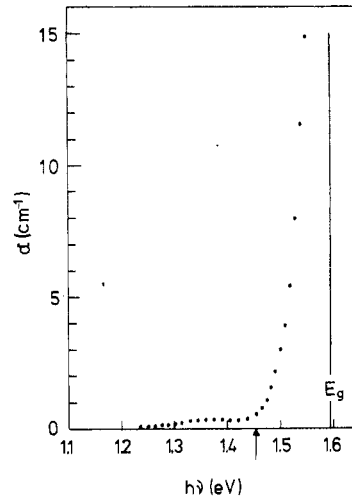
Vul *et al* (1972) maintained that iron does not introduce any level into the energy gap in CdTe. On the contrary, the photo-EPR experiments (Lischka *et al* 1985, Jantsch *et al* 1986) have shown the presence of the Fe<sup>2+/3+</sup> level in the gap. The observed increase of the Fe<sup>3+</sup>-related EPR signal, caused by illumination, was ascribed to the photoionization process



The energy threshold for the production of Fe<sup>3+</sup> centres can be seen at about 1420 meV (figure 1 of Lischka *et al* 1985) and 1450 meV (figure 2 of Jantsch *et al* 1986), giving the value of the optical ionization energy. However, photo-EPR experiments alone cannot prove that the production of Fe<sup>3+</sup> centres proceeds by the photoionization process (1). The observation of free carriers which are created by the photoionization seemed obviously important in order to confirm the validity of (1). With respect to this problem the present paper is complementary to the papers of Lischka *et al* (1985) and Jantsch *et al* (1986): we have observed the photoconductivity due to photoionization (1) and have confirmed the value of the optical ionization energy. Moreover, combining various experimental techniques we have been able to determine the thermal ionization energy



**Figure 1.** Photoconductivity spectrum of a CdTe:Fe crystal at 77 K. The DC steady state photoconductivity was measured and divided by the photon flux.



**Figure 2.** Absorption spectrum of the CdTe:Fe crystal at 77 K. A linear background, not exceeding  $0.8 \text{ cm}^{-1}$  has been subtracted. The peak at about 1380 meV corresponds to the  ${}^5\text{E} \rightarrow {}^3\text{T}_1$  intra-centre transitions within the  $\text{Fe}^{2+}$  centre.

(the position of the iron level) and to show, in disagreement with Jantsch *et al* (1986) that the lattice relaxation energy is very small.

## 2. Samples

The CdTe crystal was grown by a modified Bridgman technique. Iron was added to the melt, corresponding to a concentration of  $3 \times 10^{18} \text{ cm}^{-3}$ . The samples were cut, ground, polished and etched in a solution of bromine in methanol. Electrical contacts were prepared by the chemical deposition of gold.

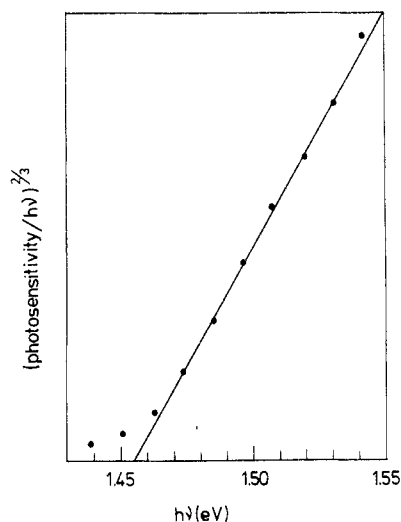
## 3. Experimental details

Standard experimental techniques were used to measure the absorption spectrum and the temperature dependence of conductivity. The DC steady state value of the photoconductivity was measured as a function of photon energy in the spectral region where the photoionization of  $\text{Fe}^{2+}$  occurred. For photon energies below 1 eV modulated photoconductivity was measured. Absorption and photoconductivity were measured at 77 K.

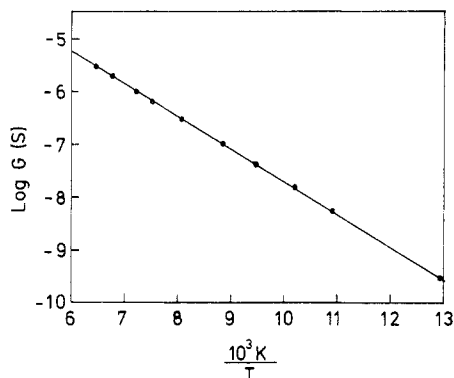
## 4. Results and discussion

### 4.1. Optical ionization energy

The photoconductivity (PC) and absorption spectra in the region 1.1–1.55 eV are presented in figures 1 and 2 respectively. Even without any mathematical treatment the



**Figure 3.** Determination of the photoionization threshold. The same data as in figure 1.



**Figure 4.** Temperature dependence of the conductivity of the CdTe:Fe crystal. The slope of the line corresponds to 125 meV.

onset of certain optical transitions is seen in both figures at about 1450 meV. After Lischka *et al* (1985) we ascribe these transitions to the photoionization of  $Fe^{2+}$  (formula (1)). The precise position of the photoionization threshold usually results from an analysis of the absorption curve. In our case the threshold is too close to the main absorption edge. The tail of the interband absorption may interfere strongly with the iron absorption, making any analysis hopeless. Fortunately, photoconductivity seems to be dominated by iron photoionization. The shape of the PC peak indicates that even for  $h\nu \geq E_g$  the intrinsic PC is smaller than the extrinsic PC caused by the photoionization of iron. (The mechanism of formation of an imperfection PC peak due to competition between the extrinsic and intrinsic PC has been described by Szadkowski and Lubomirska-Wittlin (1986).) For the left-hand side of the PC peak in figure 1 the PC components other than that connected with iron can be neglected. Because the sample was thin, the PC for  $h\nu < 1.55$  eV is simply proportional to the photoionization cross section ( $\sigma_{ph}$ ) of the  $Fe^{2+}$  ions. Theoretical models of the photoionization of deep impurities for the case of the transitions between d-orbitals and the conduction band (Allen 1969, Langer 1971) give the dependence

$$\sigma_{ph} \propto h\nu(h\nu - E_o)^{3/2} \tag{2}$$

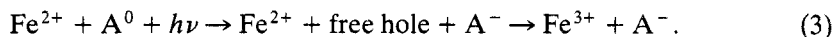
where  $E_o$  is the optical ionization energy.

In figure 3 the PC from figure 1 is presented on a scale suitable for comparison with the relation (2). The fairly good straight line which is obtained determines the value of the optical ionization energy:

$$E_o = 1455 \text{ meV.}$$

This value agrees well with that from the photo-EPR measurements (Jantsch *et al* 1986).

It should be mentioned at this point that the creation of the EPR active  $\text{Fe}^{3+}$  centres could also result from the process involving ionization of some unknown acceptor centres, e.g.



The threshold of such a process would be seen in both photo-EPR and photoconductivity (free holes) and could be mistakenly interpreted as the photoionization threshold of iron. An example of process (3) with a threshold at 950 meV has been described by Lischka *et al* (1985). Fortunately this threshold had previously been identified by them as belonging to nickel.

The agreement between our experimental data (figure 3) and formula (2) may be treated as evidence that the observed photoionization transitions are related to the conduction band. Process (3) involving the valence band would be described by a formula different from (2).

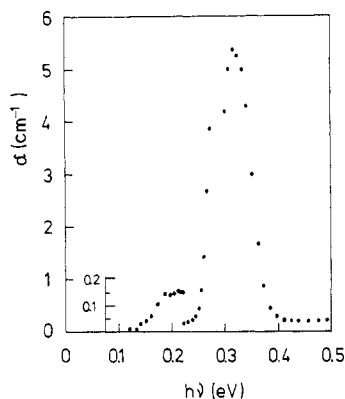
#### 4.2. Thermal ionization energy (location of the iron level)

The position of the  $\text{Fe}^{2+/3+}$  donor level is defined by the value of the thermal ionization energy ( $E_{\text{th}}$ ) of the  $\text{Fe}^{2+}$  centre in its ground state.  $E_{\text{th}}$  is the net energy required to transfer an electron from the  $\text{Fe}^{2+}$  centre to the bottom of the conduction band and to transfer the surrounding lattice to the new equilibrium configuration. The  $\text{Fe}^{2+/3+}$  level lies  $E_{\text{th}}$  below the conduction band, i.e.  $E_{\text{g}} - E_{\text{th}}$  over the valence band. We are going to determine the upper and lower limit for the position of the iron level in the energy gap of CdTe.

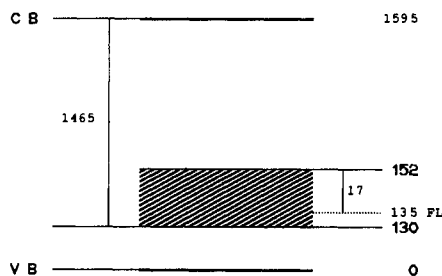
To set the upper limit we combined information about the Fermi level from the temperature dependence of conductivity and information about the concentration of the  $\text{Fe}^{2+}$  centres from the measurement of the characteristic intracentre absorption band.

The sample was p-type. The temperature dependence of conductivity is presented in figure 4. Taking into account the known temperature dependence of the mobility of holes and of the effective density of states in CdTe (Zanio 1978) we infer that the Fermi level was pinned 135 meV above the valence band.

The absorption spectrum in the region 125–500 meV is shown in figure 5. The characteristic band between 250 and 400 meV corresponds to the  ${}^5\text{E} \rightarrow {}^5\text{T}_2$  transitions within the  $\text{Fe}^{2+}$  centres. The cross section for those transitions (at the peak) was determined by Slack *et al* (1966) to be of about  $0.8 \times 10^{-18} \text{ cm}^2$  at room temperature. Vul *et al* (1972) obtained the value  $1 \times 10^{-18} \text{ cm}^2$ . The main problem in the precise determination of the cross section is the measurement of the concentration of the centres. This concentration is usually overestimated, i.e. the cross section is underestimated. Slack *et al* (1969), after thorough studies of the concentration of the iron centres, have found the value  $1.7 \times 10^{-18} \text{ cm}^2$ , which is twice as large as the previous one. For our purposes we need the *upper limit* of the cross section. Given the values quoted above, we believe that the true value of the cross section for the room temperature does not exceed  $3.4 \times 10^{-18} \text{ cm}^2$  (twice the largest quoted value). According to the results of Vul *et al* (1972) who measured the spectra at both 77 K and room temperature, the value  $3.4 \times 10^{-18} \text{ cm}^2$  at room temperature corresponds to  $5.8 \times 10^{-18} \text{ cm}^2$  at 77 K. Thus, the cross section at 77 K is smaller than  $5.8 \times 10^{-18} \text{ cm}^2$ . Applying this value to the peak absorption in figure 5, which is  $5.4 \text{ cm}^{-1}$ , we infer that the concentration  $[\text{Fe}^{2+}]$  of iron centres in the  $\text{Fe}^{2+}$  charge state is larger than  $0.93 \times 10^{18} \text{ cm}^{-3}$ . The amount of iron added to the melt was  $3 \times 10^{18} \text{ cm}^{-3}$ . Part of it could have been lost in the technological



**Figure 5.** Absorption spectrum of the CdTe:Fe crystal. The left part of the spectrum is shown in an expanded vertical scale.



**Figure 6.** Location of the  $Fe^{2+/3+}$  donor level in the energy gap of CdTe. See the explanation in the text. Energy is in meV.

process and consequently the remaining concentration of iron [Fe] is smaller than  $3 \times 10^{18} \text{ cm}^{-3}$ . If  $[Fe^{2+}] > 0.93 \times 10^{18} \text{ cm}^{-3}$  and  $[Fe] < 3 \times 10^{18} \text{ cm}^{-3}$  then  $[Fe^{2+}]/[Fe] > 0.31$ . As more than 31% of iron centres are in the  $Fe^{2+}$  charge state, the iron level cannot lie more than 17 meV above the Fermi level.

The  $Fe^{2+/3+}$  level is related to the ground state of the  $Fe^{2+}$  centre, i.e. to the  $A_1(\Gamma_1)$  level from the  ${}^5E$  group of five levels, split by spin-orbit interaction. The distance 17 meV has been calculated using statistics appropriate for this situation.

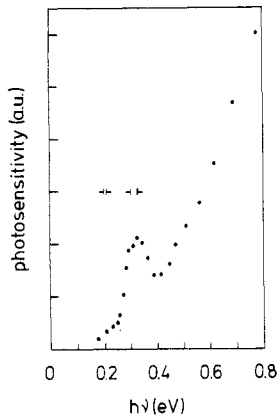
Adding 17 meV to 135 meV we find the upper limit for the position of the iron level. The  $Fe^{2+/3+}$  level must lie no more than 152 meV above the top of the valence band (in other words:  $E_{th} > 1443 \text{ meV}$ ). It is worth noting the relatively weak dependence of the upper limit on the value of the cross section. If we multiplied this value by ten, we would get 165 meV instead of 152 meV as the upper limit.

The absorption spectrum presented in figure 5 gives us additional information about the position of the Fermi level, confirming the conclusions from the measurements of the temperature dependence of conductivity. For photon energies below the  ${}^5E \rightarrow {}^5T_2$  peak one can see the onset of a weak spectrum which must be related to the transitions between the valence band and the empty levels in the gap. The onset is at about 150 meV which means that the levels lying only 150 meV above the top of the valence band may be empty. Thus, the distance between the Fermi level and the valence band should be rather smaller than 150 meV.

The lower limit for the position of the iron level is  $(E_g - E_o)$  over the valence band and results from the measurement of the optical ionization energy  $E_o$ . In the previous chapter we claimed that  $E_o = 1455 \text{ meV}$ . The accuracy of the determination of this value is seen directly in figures 1–3. We have estimated that  $E_o < (1455 + 10) \text{ meV}$ . The error in the opposite direction is difficult to estimate and is not important at this point. As the energy gap at 77 K is 1595 meV (Segall and Marple 1967) and  $E_o < 1465 \text{ meV}$ , we find that the lower limit for the position of the iron level is 130 meV over the valence band.

The situation is shown clearly in figure 6. The iron level must be in the shaded area between the established upper and lower limits.

The lattice relaxation energy  $E_L$  represents the difference between  $E_o$  and  $E_{th}$ . As  $E_o < 1465 \text{ meV}$  and  $E_{th} > 1443 \text{ meV}$ , we get  $E_L < 22 \text{ meV}$ .

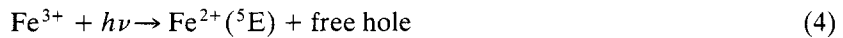


**Figure 7.** Photoconductivity of the CdTe:Fe crystal at 77 K. The modulated photoconductivity was measured and divided by the photon flux. Between 250 and 400 meV the photoconductivity is originated by an Auger process involving the  $\text{Fe}^{2+}$  centre.

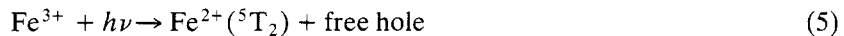
At this point it is convenient to summarize the main result of this work: the  $\text{Fe}^{2+/3+}$  donor level in CdTe lies 130–150 meV above the top of the valence band (in other words, the thermal ionization energy is 1445–1465 meV). The lattice relaxation energy is below 20 meV.

#### 4.3. The iron centre and the valence band

When iron donors are compensated by shallow acceptors, so that the Fermi level lies close to the iron level, the iron centres in both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  charge states exist in the crystal. In this case the optical transitions between the valence band and the iron levels are possible. For example, the processes



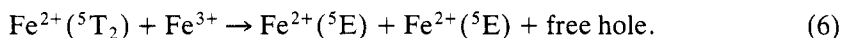
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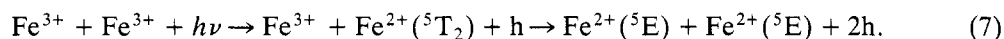
can create free holes and diminish the number of iron centres in the  $\text{Fe}^{3+}$  charge state. Jantsch *et al* (1986) observed quenching of the  $\text{Fe}^{3+}$  EPR signal and ascribed it to reaction (4). The threshold of the quenching seemed to be somewhere around 500 meV. The fact that this value is much higher than the difference  $E_g - E_o$  allowed the authors to assume a significant lattice relaxation energy. Our results, presented above, disagree with this assumption. We think that the threshold of quenching, observed by Jantsch *et al* (1986) was related not to process (4) but to process (5), which requires higher energy and results in the excited  ${}^5\text{T}_2$  state for the  $\text{Fe}^{2+}$  iron centre. The  ${}^5\text{T}_2$  level is about 280 meV above the  ${}^5\text{E}$  ground level. Process (4) was probably too weak to be detected. Such a situation where transition (5) to the excited state is more effective than (4) occurs for example in GaAs:Fe (Kleverman *et al* 1982) where the maximum cross section for process (5) is nearly an order of magnitude larger than that for process (4).

Creation of free holes by processes (4) or (5) should be seen as photoconductivity at low photon energies, but we found it difficult to distinguish this type of PC from the PC due to other impurities (certainly present in the crystal). The PC spectrum of the CdTe:Fe crystal for low photon energies is presented in figure 7. Beside the smooth spectrum which can be ascribed to either iron centres in the  $\text{Fe}^{3+}$  charge state or to other impurities,

there is an interesting feature between 250 and 400 meV. It turned out (Szadkowski 1988) to be the PC originated by an Auger process. The photons cause  ${}^5E \rightarrow {}^5T_2$  internal transitions within the d-shell of the Fe<sup>2+</sup> centre. The excitation energy is then transferred to any acceptor centre, where the hole is released to the valence band. In particular, the energy of the excited Fe<sup>2+</sup> centre can be transferred to another iron centre in the Fe<sup>3+</sup> charge state:



The Auger-type transfer of energy and the fact that the iron level is so close to the valence band make it possible for one photon with  $h\nu > 430$  meV to release two holes from two Fe<sup>3+</sup> centres:



As iron is a ubiquitous unintentional impurity in CdTe crystals, it is worth remembering the simple consequences of its presence. When iron is only partially compensated by shallow acceptors the Fermi level is pinned at the iron level and the p-type conductivity is governed by the distance between the valence band and the Fe<sup>2+/3+</sup> donor level. The photoconductivity of the crystal can be dominated by the transitions from the valence band to the Fe<sup>3+</sup> centres and from the Fe<sup>2+</sup> centres to the conduction band. While being a donor, the iron centre very much resembles an acceptor.

### Acknowledgments

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