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Comparative optical absorption and photoreflectance study of n-type CuInSe₂ single crystals

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dependence of the electron concentration n of the samples the concentration of the electrically active donors is approximately equal to $N_D = N_A + n$. Thus we can also estimate the degree of compensation N_A/N_D , the resulting values are given in the last column of Table 2.

Concluding the discussion a few remarks concerning the nature of the donors and acceptors which we have identified in the CuInSe_2 single crystals. From the composition data of the samples it follows that the deviations from molecularity and from valence stoichiometry are in the ranges $\Delta m = -0.10$ to -0.12 and $\Delta s = -0.020$ to -0.025 . For this range of Δm and Δs values it can be supposed that copper vacancies V_{Cu} acting as acceptors and antisite defects In_{Cu} acting as donors are the predominant intrinsic defects in the crystals (KLUIN, MÖLLER; YAKUSHEV et al. and references cited therein). Other types of defects will be also present in the crystals but they are expected to play a minor role because of lower concentrations. If this defect model is correct the shallow donor dominating the electrical conductivity can be identified with the antisite defect In_{Cu} and the compensating acceptor with an ionisation energy of about 80 meV (see Table 2) with the copper vacancy V_{Cu} . It is interesting to note that the electrical conductivity of p-type CuInSe_2 single crystals with elemental compositions in the same range is dominated by an acceptor with an ionisation energy of 75 meV or slightly below this value (YAKUSHEV et al.). Obviously, this acceptor is identical with that found here as the compensating defect in n-type crystals. This result shows that the type of defects present in CuInSe_2 crystals is essentially determined by the elemental composition while the conductivity type and the carrier concentrations depend on concentration ratios of the intrinsic defects.

4. Conclusions

From the comparative investigation of optical absorption and photoreflectance spectra of n-type CuInSe_2 single crystals it is evident that the true gap energy of the samples can only be determined from photoreflectance spectra which are unaffected by impurity-induced absorption processes. The optical absorption spectra are essentially influenced by acceptor – to – conduction band transitions even in the photon energy range close to the fundamental edge. It is found that an analysis of the near-edge part of the optical absorption spectra can be successfully employed to determine the ionisation energy and the concentration of the main compensating acceptors if the true gap energy is known from an independent measurement like photoreflectance or photoacoustic spectroscopy.

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Moss et al.)

$$\alpha = \frac{B(h\nu - E_0 + E_A)^{1/2}}{h\nu[1 + (m_c/m_A E_A)(h\nu - E_0 + E_A)]^4}, \quad (4)$$

where B is a constant, m_c the effective mass of the electrons in the conduction band and m_A the mass of the electrons bound to the acceptor. Usually, the mass m_A is set equal to the heavy hole mass m of the valence band. The effective electron and heavy hole masses are $m_c = 0.09 m_0$ and $m_v = 0.71 m_0$ (NEUMANN 1986) which gives a mass ratio $m_c/m_v = 0.13$. Consequently, the expression in the squared brackets in the denominator of relation (4) only slowly varies with the photon energy and, therefore, can be assumed to be constant and approximately equal to one at photon energies that not essentially exceed the threshold energy $E_0 - E_A$. The error in the absorption coefficient (4) introduced by this approximation remains below 10% for photon energies $h\nu \lesssim E_0 - 0.8 E_A$ and still below 15% for $h\nu \lesssim E_0 - 0.7 E_A$ for the effective mass ratio given above. Therefore, if the photon energies remain below these limits the absorption coefficient spectrum due to acceptor-to-conduction band transitions given by relation (4) can be well approximated by relation (2) as found in our experiments (Fig. 2). Then the acceptor ionisation energy is given by $E_A = E_0 - E_g$. Using the gap energies E_0 determined from the photoreflectance spectra and the E_g values from Table 1 we calculate the ionisation energies compiled in Table 2. Furthermore, in this approximation we have $A \approx B$ which enables us to estimate the concentration N_A of the acceptors contributing to the absorption spectra. Since the crystals are n-type conducting the acceptors act as compensating defects. Therefore the ionised acceptor concentration can be set equal to the total acceptor concentration. The constant B of relation (4) is then given by (Dow et al.; Moss et al.)

$$B = \frac{32e^2 \hbar P^2}{3m_0 \epsilon_v c n} \left(\frac{m_c}{m_A E_A} \right)^{3/2} N_A \quad (5)$$

where ϵ_v is the permittivity of free space, c the vacuum velocity of light, n the refractive index of the material and P^2 the transition probability defined here by the relation

$$P^2 = \left(\frac{m_0}{m_c} - 1 \right) \frac{E_0(E_0 + \Delta_s)}{E_0 + (2/3) \Delta_s}. \quad (6)$$

Inserting in (5) the parameters $n = 2.9$ (ABOU-ELFOTOUH et al.; HÖRIG et al.), $P^2 = 10.8 \text{ eV}$ (NEUMANN et al. 1982), $m_c = 0.09 m_0$ and $m_A = m_v = 0.71 m_0$ (NEUMANN 1986) we obtained the acceptor concentrations given in Table 2. Finally, because of the negligible temperature

Table 2

Ionisation energies E_A (in meV) and concentrations N_A (in cm^{-3}) of the acceptors and degree of compensation N_A/N_D of the n-type CuInSe₂ single crystals investigated

Sample	E_A	N_A	N_A/N_D
1	79	$8.7 \cdot 10^{16}$	0.81
2	78	$1.1 \cdot 10^{17}$	0.79
3	77	$1.7 \cdot 10^{17}$	0.85
4	84	$1.3 \cdot 10^{17}$	0.81

Since the critical point energies derived from photoreflectance of semiconductors are always due to direct optical transitions between energy band states (CARDONA) and no other structures were observed at energies below those depicted in Figure 3 we come to the conclusion that the energies E_0 must be identified with the true fundamental edge of the CuInSe₂ single crystals investigated. There are several additional arguments that support this point of view. Firstly, comparing the electron concentrations of $2 \cdot 10^{16} \text{ cm}^{-3}$ to $3 \cdot 10^{16} \text{ cm}^{-3}$ and electron mobilities of 300 to 500 cm^2/Vs with related literature data for n-type CuInSe₂ single crystals (NEUMANN, TOMLINSON 1990) it follows that the defect concentrations should be in the range of $2 \cdot 10^{17}$ to $4 \cdot 10^{17} \text{ cm}^{-3}$. Theoretical estimates of defect concentrations in CuInSe₂ crystals with an elemental composition close to that of our samples gave even slightly lower values (KLUIN, MÖLLER). But then it follows from the band gap narrowing studies in n-type CuInSe₂ single crystals that the gap energy should be in the range between 1.000 and 1.005 eV (NEUMANN, TOMLINSON 1986). Secondly, optical absorption measurements on very thin n-type CuInSe₂ single crystal samples with low electron and defect concentrations gave a gap energy at room temperature of 1.008 eV (MEDVEDKIN et al.). Thirdly, a gap energy of 1.01 eV has been derived from photoconductivity spectra (SLIFKIN et al.) and of 1.008 eV from photoacoustic spectra (ZEGADI et al. 1992) of n-type CuInSe₂ single crystals having elemental compositions and electrical parameters close to those of our samples. Finally, the spin-orbit splitting of $\Delta_s = 0.237 \pm 0.010 \text{ eV}$ obtained from the photoreflectance spectrum of sample 3 (Fig. 3) is in good agreement with the most accurate previous experimental determinations of $\Delta_s = 0.233 \text{ eV}$ from electoreflectance spectra (SHAY et al.) and of $\Delta_s = 0.234 \text{ eV}$ from intervalence band absorption spectra (NEUMANN et al. 1981). Moreover, there are at least two arguments against the supposition that the characteristic threshold energies E_g deduced from the optical absorption spectra of the crystals by using relation (2) can be ascribed to the fundamental edge. Firstly, if gap narrowing effects are considered as the possible reason for the relatively low E_g values, it follows from a previous systematic study of this effect (NEUMANN, TOMLINSON 1986) that electron concentrations above $3 \cdot 10^{17} \text{ cm}^{-3}$ and ionised defect concentrations higher than $3 \cdot 10^{19} \text{ cm}^{-3}$ are required to explain the E_g values given in Table 1. These conditions are not fulfilled in the crystals investigated for both the electron and the defect concentration. Secondly, the values for the constant A of relation (2) determined from the optical absorption spectra of the crystals are below $10^3 \text{ cm}^{-1} \text{ eV}^{1/2}$ in all cases (see Tab. 1). On the other hand, the constant A for the fundamental edge has been found to be in the range $A = 3.7 \cdot 10^4 - 1.2 \cdot 10^5 \text{ cm}^{-1} \text{ eV}^{1/2}$ from optical absorption measurements on thin films (HERRERO, GUILLÉN; NEUMANN et al. 1982; VARELA et al.) and in the range $A = 8 \cdot 10^4 - 1 \cdot 10^5 \text{ cm}^{-1} \text{ eV}^{1/2}$ from photoacoustic spectra of single crystals (ZEGADI et al. 1993). Comparing with Table 1 we see that the true values of the constant A for the fundamental edge are about two orders of magnitude higher than those found in the present study which is well beyond the error limits in the experimental determination of this parameter.

If all these points are taken into account it is obvious that the threshold energies E_g derived from the optical absorption spectra must be ascribed to optical transitions with gap states involved. From Figure 2 it follows that in all samples the dependence on photon energy of the absorption coefficient can be well described by relation (2) in the range $h\nu = 0.93 - 0.95 \text{ eV}$. This result restricts the interpretation possibilities to optical transitions from ionised acceptors to the conduction band. Assuming a hydrogen-like acceptor with an ionisation energy E_A the corresponding absorption coefficient is given by (Dow et al.;

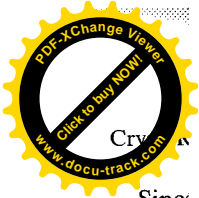
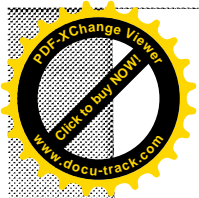


Table 1
Parameters E_g (in eV) and A (in $\text{cm}^{-1} \text{eV}^{1/2}$) of relation (2) for the n-type CuInSe₂ single crystals investigated

Sample	E_g	A
1	0.925	484
2	0.927	622
3	0.927	965
4	0.919	692

Since the lineshape of the two structures in the spectrum of Figure 3 corresponds to the limit of low fields the critical point energies E of the respective optical transitions can be determined with high accuracy using the relation of a broadened resonance line (ASPNES; NEUMANN, BOUAMAMA),

$$\Delta R/R = \text{Re} \{ C \exp(i\varphi) (h\nu - E + i\Gamma)^{-s} \}, \tag{3}$$

where C and φ are amplitude and phase factors, Γ is the broadening energy, and the exponent s depends on the type of the critical point. In CuInSe₂ both optical transitions in question give absorption spectra that can be described by relation (2) (NEUMANN 1986; TUTTLE et al.). This result corresponds to a three-dimensional critical point of type M_0 with an exponent $s = 5/2$ in the parabolic band approximation. Then, fitting relation (3) to the two structures of the photoreflectance spectrum of Figure 3 we find $E = E_0 = 1.004 \pm 0.005 \text{ eV}$ and $\Gamma = 64 \pm 5 \text{ meV}$ for the first structure and $E = E_0 + \Delta_s = 1.241 \pm 0.006 \text{ eV}$ and $\Gamma = 60 \pm 5 \text{ meV}$ for the second structure. Within $\Delta E_0 = \pm 3 \text{ meV}$ the same critical point energies E_0 were found for the other samples.

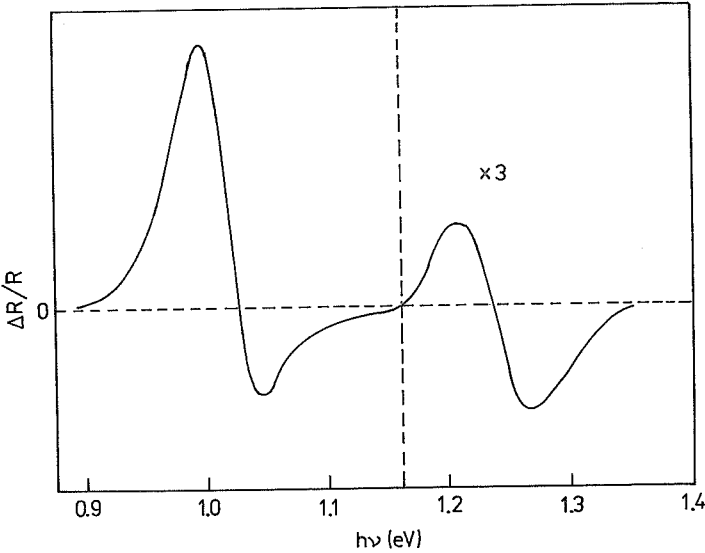


Fig. 3. Photoreflectance spectrum of an n-type CuInSe₂ single crystal (sample 3) at 300 K

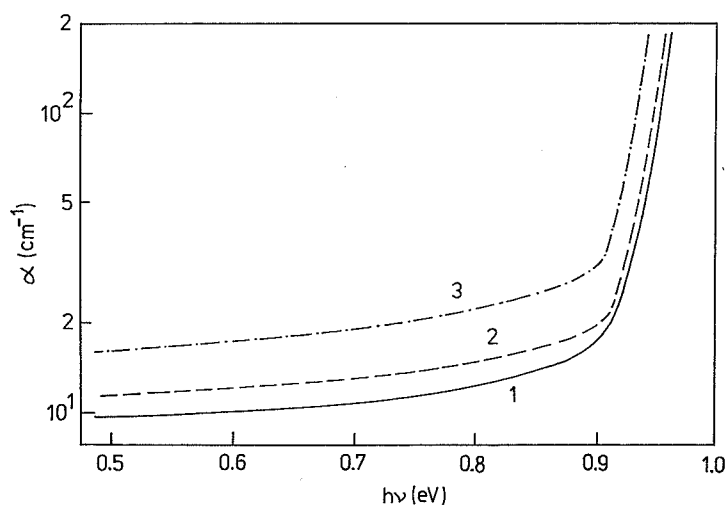


Fig. 1. Optical absorption spectra of n-type CuInSe₂ single crystals at 300 K

ranges $h\nu = 0.92 - 1.10$ eV and $h\nu = 1.15 - 1.35$ eV, respectively, without any indications of subsidiary Franz-Keldysh oscillations. Measurements on the other samples revealed only the first structure in the same energy range while the second weaker structure could not be detected. Comparing with existing literature data on the electronic band structure of CuInSe₂ (NEUMANN 1986 and references cited therein) it is evident that the first structure is due to the fundamental edge of the compound and the second one due to optical transitions to the lowest conduction band from the split-off valence band which is separated by the spin-orbit splitting Δ_s from the uppermost valence band.

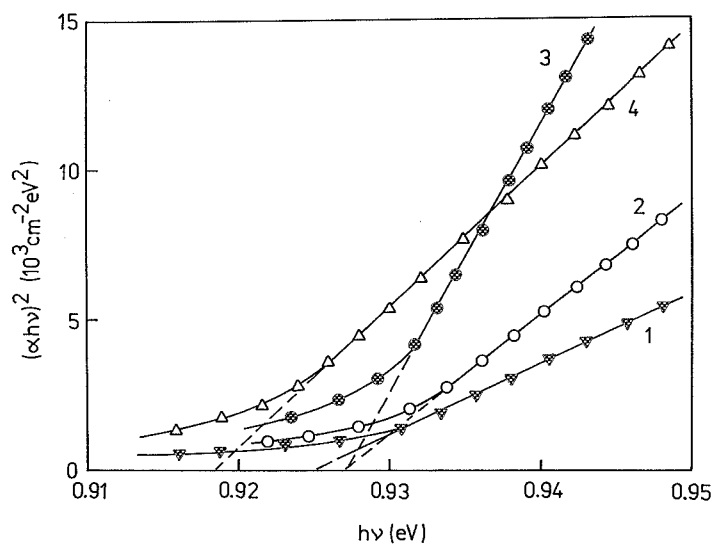
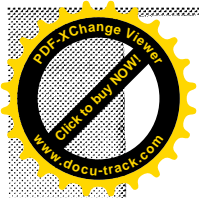


Fig. 2. Plot of $(\alpha h\nu)^2$ as a function of the photon energy $h\nu$ for the n-type CuInSe₂ single crystals investigated



2. Sample preparation and experimental details

The samples investigated were parallel-sided (112) — oriented CuInSe₂ single crystal specimens with diameters of 5–10 mm and thicknesses in the range $d = 300–900 \mu\text{m}$. They were cut from the middle part of ingots produced by the vertical Bridgman technique. All the samples had elemental compositions with a copper content around 24 at.%, an indium content around 26 at% and a selenium content always very close to 50 at.% as determined by electron microprobe measurements. The electrical parameters of the crystals were determined by temperature dependent Hall effect measurements using the method of van der Pauw. At room temperature the electron concentrations varied in the range from $2 \cdot 10^{16} \text{ cm}^{-3}$ to $3 \cdot 10^{16} \text{ cm}^{-3}$ and the mobilities in the range from 300 to $500 \text{ cm}^2/\text{Vs}$. All the samples showed a very weak temperature dependence of the electron concentration in the range from 77 to 300 K covered in the measurements. Ionisation energies of 2 to 5 meV were estimated for the electrically active donor dominating the conductivity.

Prior to the optical measurements the surface of the samples was mechanically polished through decreasing grades of diamond paste followed by a final vibratory polish with $0.05 \mu\text{m}$ alumina slurry and a subsequent chemical etch for 30 to 60 s in a 0.1% bromine in methanol solution. Optical transmittance spectra of the crystals were measured at room temperature in the photon energy range $h\nu = 0.4–1.2 \text{ eV}$ at normal incidence of radiation using a Perkin-Elmer spectrometer model Lambda 19. From the measured spectral dependence of the transmittance t the absorption coefficient spectrum was calculated using the relation

$$\alpha = \frac{1}{d} \ln \left\{ \frac{(1-R)^2}{2t} + \left[\frac{(1-R)^4}{4t^2} + R^2 \right]^{1/2} \right\}. \quad (1)$$

The reflectivity R was calculated from the spectral dependence of the optical constants of CuInSe₂ reported in the literature (ABOU-ELFOTOUH et al.; HÖRIG et al.; LÖSCHKE et al.).

The photoreflectance spectra were recorded at room temperature using an experimental arrangement analogous to that described elsewhere (NEUMANN et al. 1992). To produce the probe beam we used a tungsten halogen lamp and a grating monochromator model MDR 3 (LOMO, St. Petersburg). The reflected radiation was measured with an InAs photodetector cooled with liquid nitrogen and using the usual lock-in detection technique. As the pump beam an argon laser (457.9 nm line) was used. The pump beam was mechanically chopped with a frequency of 170 Hz, and neutral density filters were used to attenuate the laser power to appropriate levels.

3. Results and discussion

Optical absorption spectra were measured on four different samples, the results for samples 1 to 3 are depicted in Figure 1. At photon energies below about 0.85 eV all the spectra exhibit a nearly constant effective residual absorption which varies from sample to sample in the range from 10 to about 20 cm^{-1} . At photon energies above about 0.9 eV a steep increase of the absorption coefficients sets in. Usually this part of the absorption spectrum is ascribed to the fundamental edge of the compound and is analysed using the relation for the spectral dependence of the absorption coefficient above the fundamental edge of a semiconductor with a direct gap due to allowed optical transitions between parabolic bands,

$$\alpha = (A/h\nu)(h\nu - E_g)^{1/2}. \quad (2)$$

Here E_g is the gap energy and A a constant. Figure 2 shows a plot of the quantity $(\alpha h\nu)^2$ as a function of the photon energy $h\nu$ for all the four samples investigated. It is obvious that relation (2) can be used to describe the absorption spectra of all the crystals at photon energies above about 0.93 eV. The resulting values of the energy E_g and the constant A are compiled in Table 1.

Figure 3 represents the photoreflectance spectrum of sample 3 measured at room temperature. The spectrum exhibits two relatively broad structures in the photon energy

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Comparative Optical Absorption and Photoreflectance Study of n-Type CuInSe₂ Single Crystals

Optical absorption spectra in the photon energy range from 0.4 to 1.2 eV and photoreflectance spectra in the range of the fundamental edge are measured on n-type CuInSe₂ single crystals. Photoreflectance spectroscopy yields the true gap energy while the near-edge absorption spectra are dominated by acceptor – to – conduction band transitions, the acceptor ionisation energy being about 80 meV. Based on intrinsic defect chemistry considerations this acceptor is ascribed to copper vacancies.

An n-leitenden CuInSe₂-Einkristallen wurden optische Absorptionsspektren im Photonenenergiebereich von 0,4 bis 1,2 eV und Photoreflexionsspektren im Bereich der fundamentalen Absorptionskante gemessen. Die Photoreflexionsspektroskopie liefert die wahre Breite der verbotenen Zone, während die kantennahen Absorptionsspektren durch Akzeptor – Leistungsband – Übergänge dominiert werden, wobei die Akzeptorionisierungsenergie etwa 80 meV beträgt. Auf der Grundlage von Überlegungen zur Eigendefektchemie wird dieser Akzeptor Kupfervakanzen zugeschrieben.

1. Introduction

Although the optical properties of the ternary chalcopyrite semiconductor CuInSe₂ have been extensively investigated there is still some controversy concerning the true gap energy of bulk single crystals of the compound. Earlier optical absorption studies of thin films prepared by flash evaporation, r.f. sputtering and spray pyrolysis gave a direct fundamental edge and a gap energy at room temperature of 1.01 ± 0.01 eV (NEUMANN 1986 and references cited therein). Later experimental investigations on thin films deposited by other techniques like co-evaporation of the elements (CHATTOPADHYAY et al.; SZOT, HANEMAN; TUTTLE et al.; VARELA et al.), electro-deposition (GARG et al.; HERRERO, GUILLÉN), single source evaporation (FOUAD, YOUSSEF; SOLIMAN et al.) and close-spaced vapour transport with iodine as transporting agent (DJESSAS, MASSÉ) confirmed these results. On the other hand, the gap energies at room temperature of single crystals derived from optical absorption spectra vary from 0.932 to 1.008 eV (BELEVICH et al.; MEDVEDKIN et al.; NAKANISHI et al.; NEUMANN, TOMLINSON 1986; QUINTERO et al.), and a similar variation of the gap energies between 1.005 and 1.052 eV has been found at liquid helium temperature (ABDULLAEV; NAKANISHI et al.; RINCÓN, BELLABARBA; RINCÓN et al.). Possible explanations of these discrepancies can be narrowing of the band gap due to high concentrations of free carriers and ionized impurities (NEUMANN, TOMLINSON 1986) or the dependence of the gap energy on the elemental composition of the crystals (BELEVICH et al.; SHARMA et al.). In the present work we report results of a comparative optical absorption and photoreflectance study of n-type CuInSe₂ single crystals which require an alternative third interpretation model. It is found that optical transitions with shallow impurities involved must be taken into consideration in analysing the near-edge optical absorption spectra of the compound.