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Impurity States near the Fundamental Absorption Edge in p-CuInS<sub>2</sub>

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The ternary compound CuInS<sub>2</sub>, which belongs to the chalcopyrite structure is of considerable technological interest. Because this compound has a direct energy gap of about 1.5 eV at room temperature, which is very near the optimum value for solar energy conversion, makes CuInS<sub>2</sub> a strong candidate for the fabrication of photovoltaic devices.

However, although the optical, electrical, and thermal properties of CuInS<sub>2</sub> have been receiving considerable attention lately, the related problem of the impurity states in CuInS<sub>2</sub> is not well understood, only scarce information can be found in the literature and some uncertainty is observed in the data reported by several authors /1 to 5/.

In this note, an attempt has been made in order to clarify this point by analyzing the experimental results of the absorption coefficient near the fundamental edge at 76 K on p-type CuInS<sub>2</sub>.

CuInS<sub>2</sub> single crystal were grown by a iodine vapour transport technique similar to that described elsewhere /5/. X-ray diffraction analysis and DTA did not show the presence of any secondary phase and the lattice parameters  $a = 5.52 \text{ \AA}$  and  $c = 11.27 \text{ \AA}$  are in close agreement with the accepted values /6/. The optical transmission of the sample was measured with unpolarized light at normal incidence in the range of interest (8000 to 9000  $\text{\AA}$ ). Details of the optical equipment are published elsewhere /7/ and will not be repeated here. The absorption coefficient spectra of p-CuInS<sub>2</sub> single crystals for three samples: as grown, annealed in vacuum (at 773 K for 36 h), and annealed in an S atmosphere (at 773 K for 36 h), curves A, B, and C, respectively, are shown in Fig. 1. The rise of  $\alpha$  above about 1.5 eV is suggested to be mainly due to the fundamental absorption edge and can be described by the relation /8/

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

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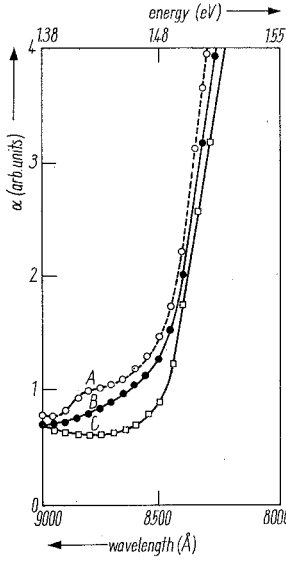


Fig. 1. Absorption spectra for p-CuInS<sub>2</sub> single crystal at 76 K: (A) as grown; (B) annealed in S atmosphere (773 K, 36 h); (C) annealed in vacuum (773 K, 36 h)

which corresponds to an allowed direct transition between parabolic bands. We find that the direct energy gap is  $E_g = (1.48 \pm 0.01)$  eV at 76 K in good agreement with the values published by other authors /3, 5/.

However, for  $h\nu \leq 1.5$  eV,  $\alpha$  does not follow relation (1) indicating, especially in the as-grown sample, a residual absorption. This absorption tends to disappear in the annealed samples. The analysis of the experimental points of the as-grown samples

indicates that this absorption can be described by the relation /9/

$$\alpha_R \approx \frac{A_R}{h\nu} (h\nu - E_g + E_A)^{1/2} \quad (2)$$

corresponding to an acceptor-to-conduction band transition, where  $E_A$  is the acceptor ionization energy and  $A_R$  is a constant nearly independent of the photon energy. The extrapolation of the curve to  $\alpha_R = 0$  yields  $E_A = (0.14 \pm 0.01)$  eV and the coefficient  $A_R$ , as determined from the slope of the curve is  $513.2 \text{ cm}^{-1} \text{ eV}^{1/2}$ . The acceptor concentration  $N_A$  related to this level can be estimated from the value of  $A_R$  by the relation /9/

$$A_R = \frac{512 \pi e^2 \hbar P^2}{n_o c m_o} \left( \frac{m_c}{m_v E_A} \right)^{3/2} N_A,$$

where  $n_o$  is the refractive index,  $c$  is the vacuum velocity of light,  $m_c$  and  $m_v$  are the conduction and the valence band effective masses, and  $P^2$  is a transition matrix element. For CuInS<sub>2</sub>, with  $m_c = 0.16 m_o$  and  $m_v = 1.3 m_o$  /1/,  $P^2 = 10 \text{ eV}$  /9/, and  $n_o = 2.79$  /10/ we obtain  $N_A \approx 2 \times 10^{16} \text{ cm}^{-3}$ .

It is interesting to note that the same acceptor ionization energy,  $E_A = 0.14 \text{ eV}$ , can be obtained by using the expression /11/

$$E_A = E_{Ao} + \beta N_A^{1/3} \quad (3)$$

together with the hydrogenic model approximation

$$E_{A_0} = 13.6 (m_v/m_0) / \epsilon_0^2 \text{ (eV)}. \quad (4)$$

Here,  $E_{A_0}$  is the acceptor ionization energy at the dilute limit of the acceptor concentration;  $\beta \approx 2.4 \times 10^{-8}$  eV cm is a proportionality constant; and for the present case,  $\epsilon_0 = 11$  /1/, is the static dielectric constant.

It is possible to speculate on the origin of the acceptor state in our p-CuInS<sub>2</sub> crystals. We exclude the possibility of an S interstitial acceptor level, since the residual absorption tends to disappear after annealing in an S atmosphere (see curve B), it can be concluded that the level observed in this note is probably due to the Cu vacancy, because copper participates only weakly in the covalent band and Cu vacancies are more probable than In vacancies in CuInS<sub>2</sub>. This is consistent with the decrease of the residual absorption observed after annealing in vacuum, since the annealing tends to reduce the copper vacancies in the crystal by the migration of copper from interstitial to lattice sites.

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