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Optical-absorption spectrum near the exciton band edge in $CuGaS_2$ at 5 K

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The absorption spectrum of $CuGaS_2$ near the fundamental absorption edge measured at 5 K has been analyzed taking into account both the discrete and continuum excitons. It has been shown that a transition from an acceptor level, originated by copper vacancies, to the conduction band occurs in this spectral region. It has been shown that the experimental slope of the optical-absorption curves, the strength of excitons, and the binding energies of excitons and acceptors are well accounted for by existing theoretical models.

I. INTRODUCTION

Among the large number of ternary chalcopyrite semiconductors, $CuGaS_2$ is of considerable interest because it has a direct band gap of about 2.5 eV at room temperature which makes this compound a promising material for green-light-emitting devices.[1] The fundamental absorption edge of this compound at low temperatures,[2–9] as well as a function of both temperature[5,7,10] and pressure,[11,12] has been reported in the literature. It is also well established that excitons play an important role in determining the optical properties of $CuGaS_2$ at low temperatures. Tell and Kasper[2] have studied the optical absorption and reflectivity of this compound at 2 K, and have determined its most relevant free-exciton parameter by using the two-oscillator model. On the other hand, Kobayashi, Tsuboi, and Kanelo[3] have analyzed the absorption spectrum of $CuGaS_2$ above 77 K, and they found this model inapplicable in the temperature range between liquid nitrogen and 300 K. They suggest that the absorption spectra can be adjusted by assuming that the absorption band of the lowest-energy exciton, as obtained from the two-oscillator model, is superposed on the absorption tail governed by Urbach's rule. After these earlier works most of the published data at low temperatures concerning free-excitonic transitions were obtained from the luminescence spectra, and very few have been reported on the absorption coefficient α of this compound. However, except for the characteristic transition energies, not much qualitative information about the free excitons or about impurity states can be deduced in general from these measurements. This is because the interpretation of the luminescence peaks is in most cases limited by the presence of several unknown recombination processes. For these reasons a more realistic theoretical analysis of this problem considering, for example, Elliot's[13] or Toyozawa's[14] exciton models for the optical cross sections, is of considerable interest in order to obtain more complete information about the optical properties of free excitons in $CuGaS_2$. On the other hand, in the case of a typical direct-gap semiconductor, the absorption coefficient near the fundamental absorption edge is usually in the range 10^4–10^6 cm^{-1}, which corresponds to an effective penetration depth of about 0.1 μm. Thus the experimental values of α represent the properties of the perturbed surface layer, and no information about the bulk properties of the sample can be obtained from such measurements. Hence neither the Elliot nor Toyozawa models can be compared with experiment for such semiconductors. The situation is different in the I-III-VI_2 chalcopyrite semiconductors where, according to the optical selection rules, the A exciton transition is weakly allowed when **E**, the electric vector of incident light, is normal to the **c** axis. In this case α is only about 10^2 cm^{-1}, and experimental data obtained using samples of about 100 μm in thickness can be compared with theoretical models. Hence in the present paper the optical-absorption spectra near the lowest-energy gap of $CuGaS_2$ at 5 K are analyzed, taking into account both the discrete and continuum excitons. It is shown that the experimental curves, strengths, and binding energies of free excitons in this compound are well accounted for by the existing models. Also, an additional absorption feature, observed as a shoulder near the lower-energy end of the spectrum and attributed to a transition between the conduction band and a defect acceptor level, has been analyzed. From the data, the binding energy of such a level and its defect concentration have been obtained.

II. CRYSTAL GROWTH AND EXPERIMENTAL DETAILS

The crystals used in this work were prepared by the chemical vapor deposition method, as has been described elsewhere.[15] All samples obtained were green in color and showed p-type conductivity. X-ray analysis from Debye-Scherrer powder photographs indicates the presence of a single phase having the chalcopyrite structure with lattice parameters $a=5.347$ Å and $c=10.474$ Å.

Samples were mechanically polished by diamond powder of variable grain size. Later they were etched in a 1:1:1 solution of H_2O:HNO_3:HCl for about 10 s, and then they were washed with distilled water.

Optical measurements at 5 K were made in an exchange-gas helium cryostat. The sample was held with dabs of silicon grass in order to minimize strains. The transmittance ($T=I/I_0$), obtained with polarized light ($\mathbf{E}\perp\mathbf{c}$) from a tungsten lamp, was recorded by means of a simple Jobin-Yvon monochromator yielding a linear dispersion of 12 Å/mm in the first order. This corresponds to a spectral resolution of about 0.2 meV with a slit width of 0.035 mm. The transmitted radiation was detected by a cooled GaAs photomultiplier whose signal was processed with routine lock-in techniques. The absorption coefficient was obtained by the expression

$$T-T_{\min}=[(1-R)^2e^{-\alpha d}]/[1-R^2e^{-\alpha d})], \qquad (1)$$

where d is the thickness of the sample, and R the reflectivity. It can be obtained from the refractive index n and the extinction coefficient k by the relation

$$R=[(n-1)^2+k^2]/[(n+1)^2+k^2]. \tag{2}$$

Although no values of extinction coefficient near the exciton band-edge region have been reported for CuGaS$_2$, it is expected that $k\approx 0$ in this energy range as observed in other ternary chalcopyrite compounds.[16,17] For this reason, the reflectivity was determined by means of the expression $R\approx[(n-1)/(n+1)]^2$. For the calculations, values of n as a function of wavelength reported by Boyd, Kasper, and McFee[18] at 100 K were used.

The values of T in Eq. (1) have been corrected by subtracting a nearly constant apparent transmittance $T_{\min}$ induced by diffuse straight light. In the present case the value of $T_{\min}$, which can be measured in the high-energy range of the spectra, was about 3×10^{-4}.

The thickness of the sample was calculated from the first-order interference pattern obtained at room temperature by means of the well-known relation $2nd=k\lambda$. A typical value of d thus determined was $d=90$ μm.

III. THEORETICAL CONSIDERATIONS

A. Fundamental absorption edge

In perfect semiconducting crystals the optical-absorption spectra near the fundamental absorption edge are expected to consist of a series of sharp lines within the band gap. These lines correspond to various quantum states of the relative motion of the electron-hole pair due to the Coulomb attraction between them.

For the simple case of two parabolic bands, a series of lines is predicted at energies[13]

$$E_n=E_g-R^\star/n, \quad n=1,2,3,\ldots\ . \tag{3}$$

Here E_g is the energy gap and R^* the effective rydberg of the exciton. The intensity of the lines decreases as n^{-3} with increasing n. As the fundamental absorption edge is approached, the infinite number of lines will overlap, so that it may be considered as a continuum. The total absorption coefficient, including both the discrete and continuum contributions, is given by[14]

$$\alpha(h\nu)=A[2R^\star[\delta(h\nu-E_n)/n^3]+\mu(h\nu-E_g)/(1-\exp \times\{-2\pi[R^\star/(h\nu-E_g)]\}^{1/2})], \tag{4}$$

where A is a constant nearly independent of energy, $\delta(h\nu-E_n)$ is the Dirac delta function, and $\mu(h\nu-E_g)$ the unit-step function.

In the actual crystal the spectrum may be expected to differ from the model because lattice vibrations and crystal defects broaden the excitonic levels and smear out the band edge. Thus, in order to obtain realistic curves which can be compared with absorption data, it is necessary to convolute Eq. (4) with Lorentzian or Gaussian functions depending on the strength of the exciton-phonon coupling. This is determined quantitatively by the dimensionless coupling constant g defined as[14]

$$g=Vm^*E_d^2/h^3Mv, \tag{5}$$

where M and V are the volume and mass of the unit cell, v is the sound velocity, and E_d is the deformation-potential constant.

In the limit of weak exciton-phonon coupling (i.e., $g\ll 1$) the absorption line shape can be obtained by convoluting $\alpha(h\nu)$ with the Lorentzian function: $\Gamma\pi[(h\nu)^2+\Gamma^2]^{-1}$. In this case, the absorption coefficient is given by[14]

$$\alpha(h\nu)=A\left\{\sum_n (R^\star/n^3)[\Gamma_n/2+b(h\nu-E_n)]/[(\Gamma_n)^2+(h\nu-E_n)^2]+C\{\pi/2+\tan^{-1}[(h\nu-E_g)/(\Gamma_n/2)]\}\right\}, \tag{6}$$

where Γ_n and Γ_c are the half width at half maximum of the Lorentzian, and the width of the continuum excitons, respectively. For calculation, the parameter is assumed to follow a dependence of the form[19]

$$\Gamma_n=\Gamma_c-(\Gamma_c-\Gamma_1)/n^2. \tag{7}$$

Also, b is an asymmetry parameter introduced to describe the interaction between the exciton levels and the continuum.

B. Optical transitions between a defect level and a band

Residual absorption observed near the fundamental absorption edge at energies below the exciton absorption is probably related to transitions between shallow acceptor or donor levels and the bands. These transitions occur at a photon energy which is given by $h\nu\geqslant E_g-E_i$, where E_i is the binding energy of the impurity. Unlike the exciton absorption which occurs between the well-defined edge of the valence band and a discrete level, the transition between a defect level and the band involves the whole band of levels. Hence such a transition should manifest itself as a shoulder in the absorption spectra having a threshold lower than the energy gap by an amount of E_i.[14]

Assuming, in the case of a direct-gap semiconductor with parabolic bands, that the defect states are shallow, discrete, and nonoverlapping, the absorption coefficient for the acceptor-state-to-conduction-band transition is given by[20]

$$\alpha(h\nu)=B(h\nu+E_A-E_g)^{1/2}(m_e/m_0)^{3/2}/h\nu[1+m_e(h\nu+E_A-E_g)/m_hE_A]^4, \tag{8}$$

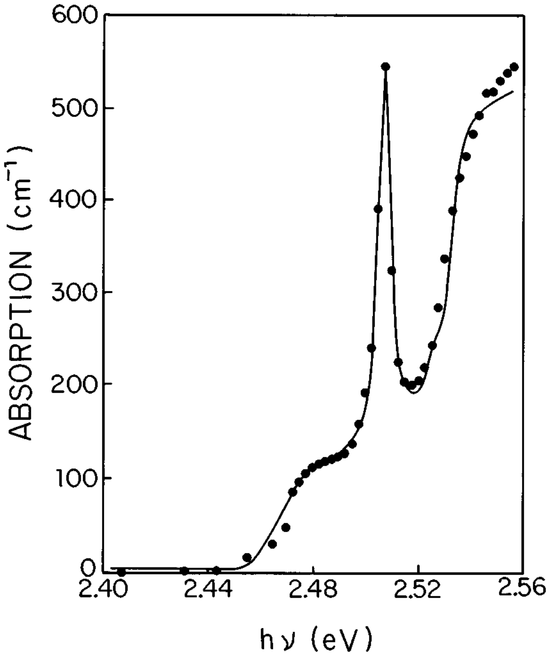

FIG. 1. Absorption spectrum of $CuGaS_2$ at 5 K. Dotted curves are present experimental data. The theoretical absorption curve obtained from Eqs. (6) and (8) with parameters given in Table I is represented as a solid line.

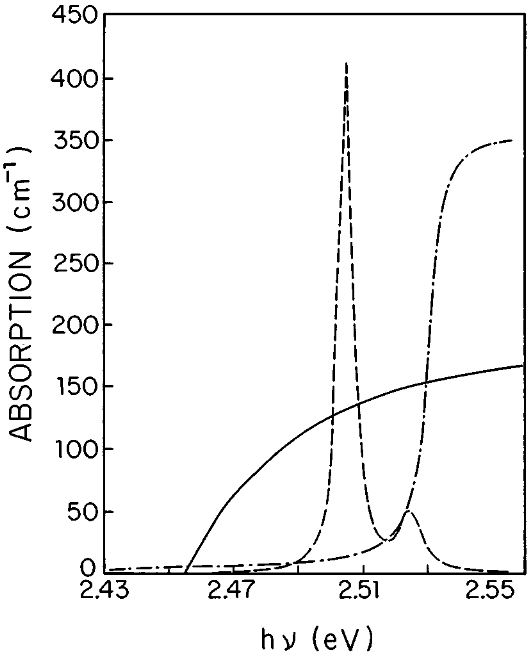

FIG. 2. Theoretical discrete and continuum exciton contributions and also the acceptor-state-to-conduction-band transition for $CuGaS_2$ at 5 K, shown separately as dashed, dash-dotted, and solid curves, respectively.

where E_A is the binding energy of the acceptor level, m_e is the electron effective mass, m_h is the density of states of holes, and B is a constant, again nearly independent of energy, expressed as

$$B=512\pi e h\nu\langle P\rangle^2(N_A-P_A)/ncm_0^2(m_hE_A/m_0)^{3/2}, \quad (9)$$

where c is the vacuum velocity of light, N_A-P_A the number of unfilled acceptors, and $\langle P\rangle^2$ the average interband matrix element of the momentum operator which can be estimated by the f-sum rule for the electron effective mass as

$$(m_0/m_e)-1=(4/m_0)\langle P\rangle^2\{2/(E_g)+[1/(E_g+\Delta E)]\}. \quad (10)$$

Here ΔE is the spin-orbit splitting of the valence band at $\mathbf{k}=\mathbf{0}$. Expressions (6) and (8), as will be discussed below, were used to adjust the absorption data of $CuGaS_2$ at 5 K.

IV. EXPERIMENTAL RESULTS

The absorption spectrum of $CuGaS_2$ at 5 K is shown as a dotted curve in Fig. 1. The A-excitonic peak is clearly evident at about 2.51 eV. In addition, a shoulder is observed between about 2.45 and 2.49 eV. Because of the p-type character of this material this shoulder is probably due to an optical transition from a shallow acceptor level to the conduction band associated with the presence of intrinsic defects in $CuGaS_2$, similar to that observed in $CuInSe_2$ (Ref. 21) and $CuInS_2$ (Ref. 22).

The analysis of the experimental points shows that the absorption spectrum follows an energy dependence which is in agreement with Eqs. (6) and (8). This is consistent with the value $g=0.02$, obtained from Eq. (5) taking $m^*=0.12m_0$, estimated by means of the expression $1/m^*=1/m_e+1/m_h$, and $E_d\approx 6$ eV for $CuGaS_2$ (Refs. 6 and 23), indicating that the exciton-lattice coupling is very weak.

Thus, by adjusting these equations to the experimental values of α, with E_g, R_0^*, E_A, A, B, b, and Γ_c as variable parameters, and using the half width at half maximum of the $n=1$ exciton peak, as obtained directly from Fig. 1, and $m_e=0.14$, $m_h=0.69m_0$ for $CuGaS_2$ (Refs. 5 and 24), a good fit, as shown in Fig. 1 by the solid line, was obtained with the values given in Table I.

It can be observed, however, that near the higher-energy end of the spectrum ($h\nu \geqslant 2.55$ eV) the slope of the theoretical curve is smaller than the experimental one. This disagreement is probably due to the contributions of two effects not taken into account in the calculation: (i) a nonparabolicity which tends to increase the hole effective mass and also the absorption coefficient as the **k** vector increases, and (ii) the absorption of B and C excitons whose maximum is about 2.62 eV (Ref. 2). There is probably some indication of these in this spectral region.

For illustrative purposes, in Fig. 2 we plot separately the

TABLE I. Parameters obtained by adjusting the absorption spectrum shown in Fig. 1.

E_g (eV)	R^* (meV)	A (eV cm^{-1})	C (eV^{-1})	b	Γ_c (meV)	B (eV$^{1/2}$ cm^{-1})	E_A (meV)	N_A (cm^{-1})
2.530	25.5	450	6.00	0.028	6.0	1.16×10^6	89	4.0×10^{16}

theoretical curves related to the acceptor-level-to-band transition, and the discrete and continuum excitonic contributions. Our value of E_g in Table I is in complete agreement with that obtained at 2 K by using the two-oscillator model.[2] Also, a value of 2.53 eV was obtained by Tell, Shay, and Kasper[4] at 2 K from their analysis of the luminescence spectra.

The value of the exciton rydberg is also in agreement with $R^*=29$ meV obtained in Ref. 2. This can be also estimated by means of the hydrogenic approximation using the expression

$$R^*=m^*e^4/2h^2\varepsilon^2, \tag{11}$$

where m^* is the effective mass of the exciton, ϵ a constant whose exact value depends on the angular frequency of the exciton in the orbit $\omega=R^*/h$, and the frequency ω_{TO} of the transversely polarized optical phonons. If $\omega \ll \omega_{\mathrm{TO}}$ the static dielectric constant ϵ_0 should be used; whereas for $\omega \gg \omega_{\mathrm{TO}}$ it should be the high-frequency dielectric constant ϵ_∞.

With the value of R^* from Table I, we obtain $\omega=3.9\times10^{13}$ s^{-1}. On the other hand, the highest value of the transversely polarized optical phonons in $\mathrm{CuGaS_2}$ determined from Raman scattering[25] is $\omega_{\mathrm{TO}}=6.9\times10^{13}$ s^{-1}. Since these two frequencies are of the same order of magnitude, a value of ϵ lying between $\epsilon_{0\perp}$ and $\epsilon_{\infty\perp}$, which are 8.9 and 7.6, respectively, for this compound,[26] could be expected in the present case. Thus, the value $\epsilon=7.9$ obtained from Eq. (11) by using $R^*=25.5$ meV and $m^*=0.12m_0$ is consistent with the above-mentioned considerations.

Our damping constant for the ground exciton state (full width at half maximum of the peak) is slightly larger than $\Gamma_1=2$ meV obtained in Ref. 2. This difference can be attributed to the fact, as pointed out by Tell and Kasper,[2] that the polishing of the surfaces broadens the exciton peak, increasing the damping constant as observed in this case.

The oscillator strength is given by

$$f_{cv}=\alpha_0 n_g/16\pi^2(RR^*)^{1/2}(m^*/m_0)^{3/2}, \tag{12}$$

where α_0 and n_g are the absorption coefficient and the refractive index at the energy gap, respectively, and R is the hydrogen rydberg. Thus we find $f_{cv}\approx0.02$, in good agreement with that obtained in Ref. 6, which is 0.01, and is smaller than those obtained for zinc-blende II-VI semiconductors where f_{cv} is two orders of magnitude higher (e.g., $f_{cv}\cong1.8$ in ZnS).[27] This is consistent with the above-mentioned fact that the A excitonic transition is weakly allowed in chalcopyrite compounds when $E\perp c$.

In the case of the acceptor-level-to-conduction-band-transition, it has been pointed out[24] that such levels, observed in $\mathrm{CuGaS_2}$ from electrical properties, show a decrease in binding energy when increasing in the acceptor concentration. This variation is given by

$$E_A=E_{A0}-\beta N_A^{1/3}, \tag{13}$$

where β is a proportionality constant which was estimated to be 2.4×10^{-8} cm^{-1} for this compound,[24] and E_{A0}, the binding energy in the dilute limit of acceptor concentration, can be estimated by using the hydrogenic model,

$$E_{A0}=13.6(m_h/m_0)/\epsilon^2, \tag{14}$$

in units of eV. In this expression, as in the case of exciton binding energies, the value ϵ lies between the static dielectric constant and the optical dielectric value, depending on the relation between the angular frequency of the hole in the orbit ω and the frequency of the transverse-optical-polarized phonons ω_{T0}.

In the case of $\mathrm{CuGaS_2}$, using the value $E_A=0.089$ eV obtained from the fit of the absorption spectrum, we obtain $\omega=1.0\times10^{14}$ s^{-1}, which is of the same order as $\omega_{\mathrm{TO}}=7.5\times10^{13}$ s^{-1}. This indicates that a value lying between $\epsilon_{0\perp}$ and $\epsilon_{\infty\perp}$ should be used in the calculations. Thus, using the above-calculated values of $\epsilon_0=7.9$ and $N_A=4.0\times10^{18}$ cm^{-3}, we obtain $E_A=0.15$ eV from Eqs. (13) and (14). This is slightly larger than the observed value. However, by using the static dielectric constant $\epsilon_0=8.6$, we obtain $E=0.089$ eV, in complete agreement with the value obtained from the optical-absorption curve. This indicates that ϵ_0 is a better choice in order to estimate the binding energies of shallow levels in $\mathrm{CuGaS_2}$.

As regards the origin of this level, it must be intrinsic because our samples were not intentionally doped. The chemistry of intrinsic defects in ternary compounds has been discussed by several authors, and it has been suggested that it is dominated mainly by an acceptor-donor majority defect pair.[28] The conditions for the existence of such a pair are determined by deviations from the molecularity and the valence stoichiometry, Δm and Δs, respectively. For $\mathrm{CuGaS_2}$, these parameters are defined as[28]

$$\Delta m=[\mathrm{Cu}]/[\mathrm{Ga}]-1, \tag{15}$$

$$\Delta s=2[\mathrm{S}]/([\mathrm{Cu}]+3[\mathrm{Ga}])-1, \tag{16}$$

where [Cu], [Ga], and [S] represent the total concentration of Cu, Ga, and S atoms in the sample.

From a study of the ternary phase relations of $\mathrm{Cu_{1-x}Ga_{1+x/3}S_2}$ (where $0<x<0.13$) chalcopyrite crystals,[29] it is shown that although the green variety of $\mathrm{CuGaS_2}$ is very nearly stoichiometric (i.e., $x\approx0$) it is slightly rich in Ga (i.e., $[\mathrm{Cu}]/[\mathrm{Ga}]<1$]). This is partly because a fine dispersion of $\mathrm{Cu_2S}$, as observed by a scanning electron microscope, precipitates in the stoichiometric composition region. Thus, from Eqs. (15) and (16), we estimate $\Delta m<0$ and $\Delta s\approx0$ in the present samples. This gives, according to Ref. 28, three possible majority defect acceptor-donor pairs, respectively, which may be present in the material: copper vacancies (V_{Cu}) and gallium on copper sites ($\mathrm{Ga_{Cu}}$), V_{Cu} and sulfur vacancies (V_{S}), and V_{Cu} and gallium interstitial (Ga_i).

Since in all these cases the copper vacancy appears as the common acceptor, we conclude that it is the predominant active acceptor in $\mathrm{CuGaS_2}$ and, hence, that the level observed at about 90 meV from the top of the valence band is due to this intrinsic defect. Tell and Kasper[2] have also interpreted that the shallow level observed in $\mathrm{CuGaS_2}$ is due to V_{Cu}. The corresponding donor pair binding energy, estimated from Eq. (14) but using $m_e=0.14m_0$, is $E_D\approx20$ meV. These results are consistent with the value $E_A+E_D\approx120$ meV deduced from the donor-acceptor pair luminescence peak at 2.41 eV. This is the dominant photoluminescence (PL) peak in Ga-rich crystals of $\mathrm{CuGaS_2}$ at 4.2 K, especially in S-deficient crystals.[8] This apparently indicates that this donor is either V_{S} or $\mathrm{Ga_{Cu}}$.

V. CONCLUSIONS

The absorption spectrum of $CuGaS_2$ near the fundamental absorption edge at 5 K has been measured and analyzed using current theoretical models. It has been found that the transition from defect levels to the conduction band can be associated with the presence of copper vacancies. Band-to-band excitonic transitions have been analyzed by taking into account both the discrete and continuum contributions to the absorption coefficient, and it has been shown that experimental shapes of the absorption curves, strengths of excitons, and binding energies of excitons and acceptors are well accounted for by the existing theoretical models.

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