Optical Reflectivity Spectrum of a $CuFeS_2$ Single Crystal

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Optical reflectivity spectra have been measured at room temperature on a single crystal of $CuFeS_2$ between 0.025 and 6 eV. The experimental results have been used to calculate the optical constants, the dielectric constant and the absorption coefficient. There have been found an absorption band with peaks at 1.0 and 2.1 eV and an absorption edge at approximately 3.2 eV. The band can be assigned to the charge-transfer transition from the valence band to the empty 3d states of Fe, and the edge can be attributed to the commencement of the band to band transition. A schematical energy level diagram for $CuFeS_2$ is given from the result.

§1. Introduction

The optical absorption edge of an antiferromagnetic semiconductor $CuFeS_2$ has been known to exist at approximately 0.5 eV.[1] This value is anomalously small compared with that of other chalcopyrite type semiconductors such as $CuAlS_2$ (3.4 eV)[2] and $CuGaS_2$ (2.5 eV).[3]

Based on absorption measurements of $CuAlS_2$: Fe and $CuGaS_2$: Fe and on molecular orbital calculations, we came to the conclusion that the absorption edge of $CuFeS_2$ is not the "band to band" edge in usual sense but is the foot of the "charge-transfer" absorption band associated with 3*d*-orbitals of Fe ions.[4,5] Absorption measurements on thin polycrystalline films of $CuFeS_2$ revealed that $CuFeS_2$ has a broad absorption band at 0.6–3.5 eV region similar to that of $CuAlS_2$: Fe and $CuGaS_2$: Fe as predicted by the previous work.[6]

The purpose of the present work is to get more accurate informations on the electronic structure of $CuFeS_2$ by means of the reflectivity measurement between 0.025 and 6 eV on single crystals of $CuFeS_2$.

The remainder of the paper consists of four sections; experimental techniques in §2, experimental results in §3, discussions in §4 and conclusions in §5.

§2. Experimental Techniques

Large single crystals of $CuFeS_2$ about 10 mm in diameter and a few cm in length were grown from melt by the Bridgman method. Specimens for measurements were cut from the boule into disk with thickness of approximately 2 mm and were polished mechanically by using alumina grinding powder, followed by sheets of lapping film (3M Inc.) of several grain size (9 μm, 3 μm, 1 μm, 0.3 μm). Polished samples were then rinsed in the ultrasonic water bath to get rid of the grinding powder.

The obtained surface showed a mirror-like golden luster which is characteristic of the chalcopyrite. The crystal orientation of the polished surface was determined by the X-ray Laue photography to be very close to (112) crystal plane.

Reflection measurements were performed using a Nikon P-250 monochromator with a specially designed double beam reflectance attachment as illustrated in Fig. 1. The principle of the measurement is as follows:—Light is split into two beams by BS; one is led to the sample, and the other to a reference mirror; two beams are chopped at different frequencies, by small-size rotating sectors (C_1, C_2); reflected beams are focused together onto the window of a light detector (D). The sample-channel signal (I_S) and the reference-channel signal (I_R) are separately amplified by lock-in amplifiers tuned to each frequency, and the ratio I_S/I_R is then taken by means of the feedback technique. The output data were punched on paper tape and processed by an off-line computor for further analysis; —correction of reflectivity of the reference mirror, data smoothing, Kramers-Kronig analysis.

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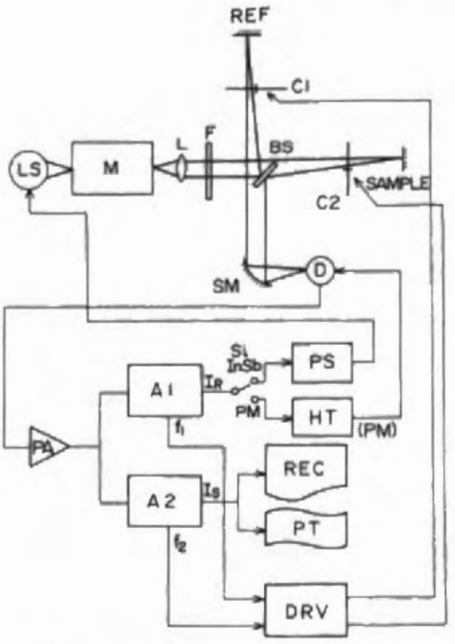

Fig. 1. A schematic diagram of the apparatus for reflectivity measurement. LS: Light Source (deutron or halogen-tungsten lamp), M: Monochromator (Nikon P-250; gratings with blaze wavelengths of 350, 750 and 2000 nm), L: Fused Silica lens, F: Glass-filters against higher order light, BS: Beam splitter (double faced mirror), C1 and C2: Light-chopper with rotating sector, SM: Spherical mirror, D: Light detector (Photomultiplier, Silicon photocell, or cooled InSb-photocell), PA: Preamplifier, A1, A2: Lock-in amplifiers, PS: Power supply for LS, HT: High-voltage supply for photomultiplier, REC: Chart recorder, PT: Perforated paper tape, DRV: Chopper driver.

Since the measurement covers fairly wide wavelength region (near u.v. to near i.r.), total region was devided into several sections and a suitable combination of optical elements were selected for every section, as listed in Table I.

To get i.r. data (2.5 μm to 50 μm) we employed a Hitachi 255 infrared spectrophotometer with a reflectance attachment (IRR-3).

Optical constants n and k measured at 632.8 nm by means of the ellipsometry have been used to calibrate the calculated values.

All measurements were performed at room temperature.

§3. Experimental Results

Optical reflectivity spectrum of the single crystal surface of $CuFeS_2$ between 0.025 and 6 eV measured at room temperature is shown in Fig. 2. The curve is a composition of reflectivity spectra for several spectral regions mentioned in the previous section.

The spectrum is characterized by a steep rise of R (reflectivity) below 0.2 eV, two peaks at 1 to 2 eV region and a strong dip around 3.2 eV. The yellowish color of this material is due to the strong dip of R at "blue" wavelength region.

Optical constants n and k were calculated by using the Kramers-Kronig relations,[7] with appropriate extrapolations for wavelengths beyond the region of measurement. Values of parameters for the anlysis were so determined that calculated values of n and k at 632.8 nm

Table I. Combinations of optical elements used in our measurement for the eight wavelength regions listed in the first column.

Region (nm)	Light source	Grating		Mirror coating	Detector	Filter
		Blaze (nm)	Grooves (G/mm)			
200– 400	D	300	600	Al	PM	—
250– 600	H-T	300	600	Al	PM	UV-35
400– 800	H-T	300	600	Ag	Si	UV-35/Y-50
550–1000	H-T	750	600	Ag	Si	Y-50
700–1300	H-T	750	600	Ag	Si	R-67
1000–1600	H-T	750	600	Ag	InSb	IRD-80A
1300–2000	H-T	2000	300	Ag	InSb	IRD-80A
1800–2600	H-T	2000	300	Ag	InSb	IRD-80A+G-54

D: Deutron lamp, H-T: Halogen-tungsten lamp, PM: Photo-multiplier (Hamamatsu R636), Si: Silicon-photocell (Hamamatsu S-875-66R), InSb: Cooled InSb-photocell (Hamamatsu P839S), Filters: (Toshiba glass filters), UV-35 (350 nm cut-off), Y-50 (500 nm cut-off), R-67 (670 nm cut-off), IRD-80A (900–4500 nm band-pass), G-54 (1000–4500 nm band-pass).

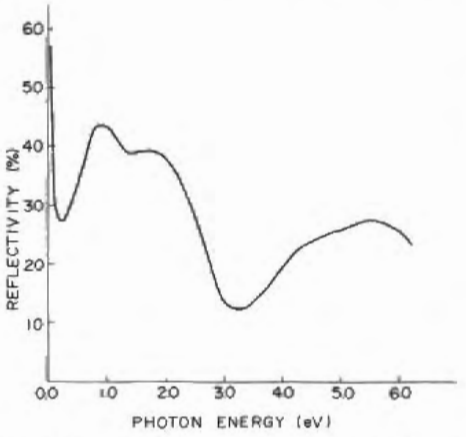

Fig. 2. The reflectivity spectrum of $CuFeS_2$ measured at room temperature.

fit those calibrated by means of the ellipsometry. In Fig. 3, spectra of n and k thus obtained are illustrated by a solid curve and a dotted curve, respectively.*

Optical absorption coefficient α was calculated from the k by the formula,

$$\alpha = \frac{4\pi k}{\lambda},$$

where λ is the wavelength. The absorption spectrum thus obtained is given in Fig. 4. The curve consists of a broad band between 0.6 and 3.2 eV and an absorption edge rising from approximately 3.2 eV. The broad band can be decomposed into two Gaussian components with centers at 1 eV (peak A) and 2.1 eV (peak B) as plotted by dotted curves in the same figure. By subtracting these two Gaussian curves from the original absorption spectrum the higher energy absorption edge (C) has been distinguished as shown by dashed curve.

Real and imaginary parts of the dielectric constant $\varepsilon = \varepsilon' + i\varepsilon''$ was also calculated from n and k and are shown in Fig. 5 together with the dielectric loss function $Im(-1/\varepsilon)$. It should be noted that ε' is negative for photon energies below 0.07 eV and for 2.0 to 2.5 eV.

In Fig. 6 is given a curve of n_{eff}, effective number of electrons per $CuFeS_2$ unit contributing to the optical transitions below the photon energy of consideration. The n_{eff} has been calculated by the following formula,

$$n_{eff}(\omega) = \frac{m}{2\pi^2 Ne^2} \int_0^{\omega} \omega' \varepsilon''(\omega')\, d\omega',$$

where N is a number of $CuFeS_2$ molecules per cm^3, m is the free electron mass and ε'' is the imaginary part of dielectric constant. It is noted that for usual semiconductors such as Si, n_{eff} saturates at a value of approximately 4 per atom; on the other hand for $CuFeS_2$, n_{eff} shows a plateau at nearly 0.25 electron per atom ($\sim$one electron per $CuFeS_2$) below 3 eV and rises again at higher energies, showing no

* Strictly speaking, optical constants n and k should be expressed in tensor form for $CuFeS_2$ which belongs to the tetragonal crystal system. However, since the tetragonality is rather small, we treat them, for simplicity, as scalar quantities in the present paper.

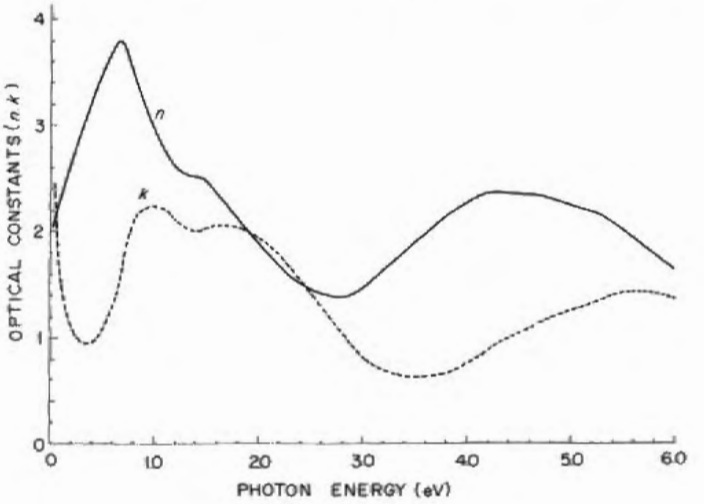

Fig. 3. The optical constants, n (solid curve) and k (dotted curve) of $CuFeS_2$ as calculated from the reflectivity spectrum.

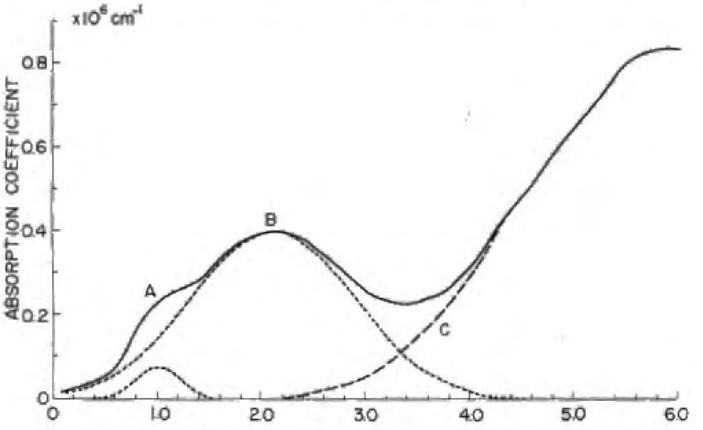

Fig. 4. The absorption spectrum of $CuFeS_2$ as calculated from k by using the formula $\alpha=2k\omega/c$ (solid curve). Two Gaussian curves (dotted curves) are fitted to reproduce peaks A and B. Dashed curve represents the absorption edge C.

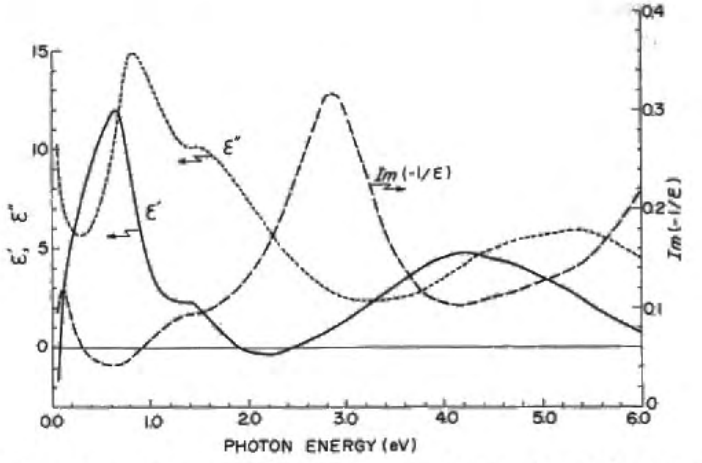

Fig. 5. The spectral dependence of the dielectric constant $\varepsilon=\varepsilon'+i\varepsilon''$ (left scale) and the dielectric loss function (right scale): solid curve—ε', dotted curve—ε'', dashed curve—loss function, $I_m(-1/\varepsilon)$.

saturation up to 6 eV.

§4. Discussions

In the first place, the absorption spectrum (Fig. 4) obtained by the present study is compared with that directly measured on polycrystalline film reported in ref. 6: Although the energy positions of two peaks A and B in two curves are very similar, the value of absorption coefficient of the present study is smaller by a factor of about 3 than the previous value for film. This difference may possibly be brought about from the ambiguity in evaluating the film thickness.

Secondly, the absorption curve is compared with that of $CuAlS_2$: Fe reported in ref. 4. We can find similar absorption peaks A and B in both curves; energy positions, half-widths and oscillator strengths of peaks A and B are listed in Table II for $CuFeS_2$ and $CuAl_{0.99}$

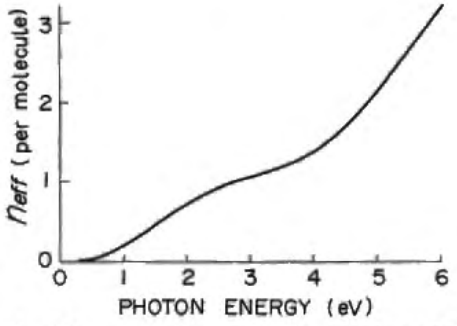

Fig. 6. The curve of n_{eff}, effective number of free electrons contributing to the optical constant up to the frequency of consideration.

Table II. Energy positions (E), half-widths (ΔE), and oscillator strengths (f) of peaks A and B for $CuFeS_2$ (present study) and $CuAlS_2$: Fe (ref. 4).

	Peak-A			Peak-B		
	E(eV)	ΔE(eV)	f	E(eV)	ΔE(eV)	f
$CuFeS_2$	1.0	0.5	7×10^{-3}	2.1	1.86	3.5×10^{-1}
$CuAl_{0.99}Fe_{0.01}S_2$	1.3	0.25	5×10^{-3}	1.9	0.8	0.9×10^{-1}

$Fe_{0.01}S_2$. The table shows that energy positions and oscillator strengths are very close between two cases, although the band widths of $CuFeS_2$ is about twice those of $CuAlS_2$: Fe. Therefore it is natural to assume that absorption peaks A and B of $CuFeS_2$ have the same origin as those of $CuAlS_2$: Fe; —the charge transfer from valence band to d-orbitals of Fe.

It has been known from previous works that although $3d$ states in $CuAl_{1-x}Fe_xS_2$ are sufficiently localized to be described in terms of the multiplet $^6A_1$ when x is much less than 0.1,[9] they are rather extended to form "$3d$-bands" due to hybridization with p-orbitals of anions when x exceeds 0.1.[10,11] This is consistent with the present result that band widths of peak A and B of $CuFeS_2$ is twice those of $CuAl_{0.99}Fe_{0.01}S_2$.

In the third place, it is seen in Fig. 3 that k increases steeply as the photon energy decreases below 0.4 eV. This increase is attributed to so-called Drude-tail which is caused by the plasma oscillation of the free electron gas. The plasma frequency ν_p can be estimated by the energy where ε' crosses zero from negative to positive in Fig. 5; $h\nu_p=0.07$ eV. It is well known that the charge concentration can be estimated by the formula,

$$N=\frac{\nu_p^2\pi m}{e^2}$$

where m is the free electron mass and e is the electronic charge. By applying $h\nu_p=0.07$ eV we obtain

$$N=3.46\times10^{18}\ \mathrm{cm}^{-3},$$

which is a reasonable value for synthetic $CuFeS_2$.

Next we discuss the curve of n_{eff} shown in Fig. 6. As stated in §3 n_{eff} does not saturate at a value of 4 per atom as seen in Si but has a plateau with a value of 0.25 per atom (1.0 per $CuFeS_2$ molecule) below 3 eV. Therefore the absorption band below 3 eV cannot be assigned to the usual "band to band" transition as seen in Si but can be assigned to a *transition* transferring one electron per molecule from the valence band to the empty "$3d$" band. A change of slope of n_{eff} curve which occurs around 3.2 eV may be interpreted as the biginning of the "band to band" transition of this material.

Finally, based on the experimental results of the present study and on the theoretical calculations by Kambara a schematic energy-level diagram for $CuFeS_2$ has been constructed and is shown in Fig. 7.

The composition of the atomic orbitals consisting each energy level determined by the theoretical study is also added in the figure.

The empty "$3d$"-band is located between valence and conduction band. The observed optical band gap of 0.5 eV corresponds to the

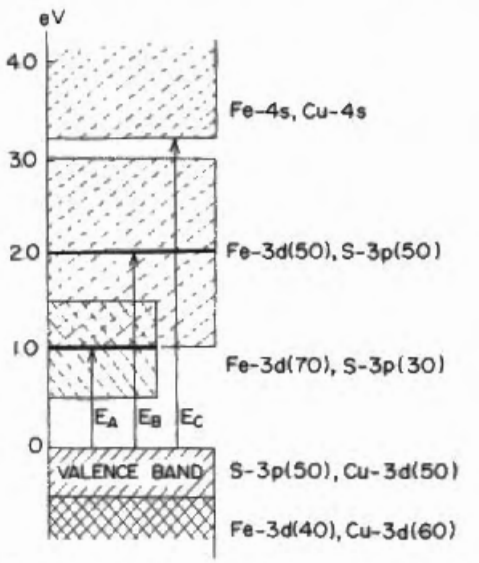

Fig. 7. A schematic energy-level diagram based on the optical properties of $CuFeS_2$. The leading constituent atomic orbitals and their composition ratio for each level obtained from the theoretical study[5] are also given in the right hand column.

energy separation between the "3*d*" band and the valence band. E_A, E_B are the energies associated with the maxima of the joint density of states between these bands. The bandwidth of the "3*d*" band cannot be unambiguously determined, since observed bandwidth is related to both "3*d*" and valence bands; so that the value shown in Fig. 7 may be regarded as the upper limit of the 3*d* bandwidth. The fact that photoconduction has been observed in the vicinity of the optical band gap indicates that the 3*d* band forms a conducting state.

The bottom of the 4*s*-conduction band is determined as 3.2 eV above the top of the valence band from the energy position where n_{eff} curve changes its slope. The theoretical calculation has given rather wrong values for the energy separation between valence and 4*s*-band; 6 eV. The discrepancy may possibly be caused by the crudeness of the theoretical calculation. The molecular orbital calculation for the atomic cluster cannot account for precise features of the extended states as it lacks considerations of the periodic boundary conditions.

Although the temperature of our study have been restricted to room temperature, we believe that most of the arguments discussed above on the electronic structures of $CuFeS_2$ is still valid for low temperature state: A preliminary measurement at liquid nitrogen temperature showed no marked shift nor measurable splitting of the spectra at least for visible wavelength region.

It is a future problem to examine the fine structure by means of low temperature studies or any kind of modulation spectroscopies, which would be effective for further understanding of the electronic structures of this material.

§5. Conclusions

In the present work the reflectivity spectrum measurements have been performed and the optical constants and the schematical energy-level diagram for $CuFeS_2$ have been deduced from the results. The absorption spectrum calculated from the optical constant essentially agrees with that measured directly for the thin polycrystalline film.

The position of the empty "3*d*" band has been determined by this work to locate in the gap between the valence and the 4*s*-conduction bands. The bandwidth of the "3*d*" band of $CuFeS_2$ has been found to be approximately twice that of $CuAl_{0.99}Fe_{0.01}S_2$ where 3*d* states are thought to be localized.

Since it has been known from our previous work[11] that a jump of R occurs when Fe-content in $CuAl_{1-x}Fe_xS_2$ is increased across the critical value of $x \sim 0.1$, at which content the resistivity and the effective magnetic moment show an abrupt change, it is desirable to measure reflectivity spectrum precisely for $CuAl_{1-x}Fe_xS_2$ samples with various content of iron in the vicinity of $x \sim 0.1$.

Acknowledgements

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References

1) C. H. L. Goodman and R. W. Douglas: Physica **20** (1954) 1107.
2) W. N. Honeyman: J. Phys. Chem. Solids **30** (1969) 1935.
3) B. Tell, J. L. Shay and H. M. Kasper: Phys. Rev. **B4** (1971) 2463.
4) T. Teranishi, K. Sato and K. Kondo: J. Phys. Soc. Jpn. **36** (1974) 1618.
5) T. Kambara: J. Phys. Soc. Jpn. **36** (1974) 1625.
6) K. Sato and T. Teranishi: J. Phys. Soc. Jpn. **40** (1976) 297.
7) F. Stern: Solid State Phys. **15** (1963) 327.
8) H. R. Philipp and H. Ehrenreich: Phys. Rev. **129** (1963) 1550.
9) K. Sato and T. Teranishi: J. Phys. Soc. Jpn. **37** (1974) 415.
10) T. Teranishi and K. Sato: J. Phys. (France) **36** (1975) C3, 149.
11) T. Teranishi and K. Sato: *Ternary Compounds* (1977) (Inst. Phys. Conf. Ser. No. 35) p. 59.