4.8 Optical absorption spectra

4.8.1 FeS_2

The forbidden gap energy is one of the most important parameters to describe physical properties in semiconductors. Since FeS_2 has been assumed to be a Wilson type semiconductor, there has been a number of studies to determine the energy gap from optical studies. Values of optical gap deviates from author to author and also from sample to sample. Since the material is strongly absorbing that most of the data were determined by measuring the photoconductivity (PC) spectrum. Fukui and coworkers (76) measured the PC spectrum on a sample of natural pyrite and obtained the value of 0.9 eV as the optical gap. Horita and colleagues (77) also reported PC spectra on several specimens of natural pyrite. Number of PC peaks appeared in their spectra which differ from sample to sample. The dominant PC peak was observed around 0.95 eV. The spectrum of k (extinction coefficient)(Fig. 24) deduced from Kramers-Kronig analyses of reflectivity data locates a well-defined optical gap at 0.92 eV.

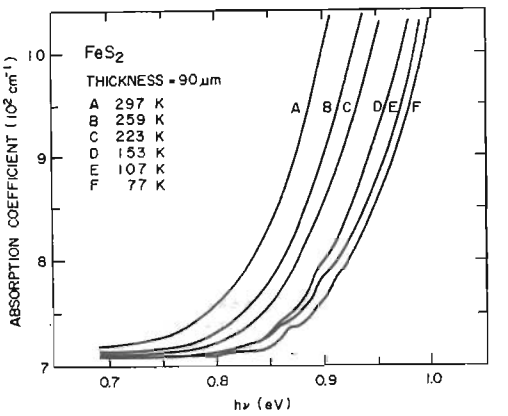

Fig. 42 Absorption spectra in natural crystals of FeS_2 at several temperatures. (from Kou and Seehra, (42)) →

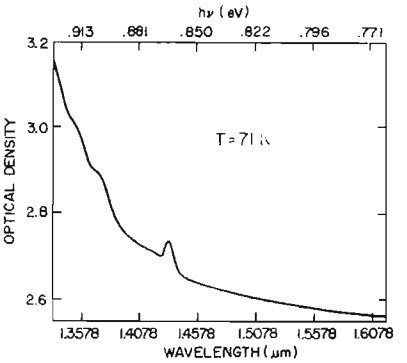

Fig. 43 Fine structure in the absorption edge of FeS_2 at 71 K. (from Kou and Seehra, (78))

Direct measurements of absorption spectrum on a bulk sample of natural pyrite were carried out by Kou and Seehra (78) and by Schlegel and Wachter(57). In Fig. 42 are shown the absorption spectra of natural pyrites at several temperatures between 40 and 298 K measured by Kou and Seehra. At low temperatures some of the samples exhibited several fine-structures superposed on the absorption edge spectra as shown in Fig. 43. They attribute these structures to excitons, although detailed analyses were not given. They made $(\alpha h\nu)^{1/2}$ vs. $h\nu$ plot for 0.7 to 1.0 eV region and determined indirect gap as 0.756 - 0.78 eV at room temperature. They discussed the temperature dependence of energy gap by using the Varshini's equation,

$$E_g(T) = E_g(0) - \alpha T^2/(T + \theta), \qquad (6)$$

where $\theta=\Theta_D$. They obtained $\alpha=-6.4\times10^{-4}$ eV/K and $\theta=-1395$K from the fit to the experiment. These

values were qualitatively similar to the observations in diamond and 6HSiC.

In their next paper Seehra and Seehra(79) discussed the temperature dependence by

$$E_g(T) = E_g(0) + aT + bT^2 \qquad (7)$$

and obtained $E_g(0)=0.835$, $a=4.0\times10^{-5}$ eV/K and $b=-7.4\times10^{-7}$ eV/K^2 by a fit. They associated aT^2 term with the electron-phonon interaction and the bT term primarily with lattice dilatation. Although experimental data fit to both equations they recommended the latter fit because of a better physical picture.

Above mentioned treatments by Seehra are based on the assumption that optical processes of FeS_2 are the same as in the ordinary semiconductors. Is that definitely true? It seems to me there are some problems in that interpretation. As has been discussed in earlier sections top of the valence band, i.e. t_{2g} states, has considerably localized character. In addition, the bottom of the conduction band also consists of narrow d band and broad p* bands as will be discussed in section 5. Then, band edges may be far from those of ordinary semiconductors. The linearity in the $(\alpha h\nu)^{1/2}$ vs $h\nu$ plot is not necessarily an evidence for indirect transition. Even amorphous silicon obeys this plot as has been pointed out by Tauc (81). There may exist a considerable amount of disorder at the bottom of conduction bands in natural samples, which may provide a similar situation to the amorphous material.
There is a possibility to assign the fine structures observed in the absorption spectra to the multiplets associated with t_{2g} -> e_g transitions such as $^3T_1$, $^3T_2$ and $^1T_1$. Analysis on such view point is strongly required as a future problem.

Thin FeS_2 films have been prepared on fused silica substrates by the present author using close spacing CVD technique as described in section 3.
Two types of absorption spectra were observed as illustrated in Fig. 44. Both types of films showed pyrite phase in X-ray diffraction. Curve (a) agreed well with absorption spectrum obtained by Kramers-Kronig analysis of reflectivity spectrum (see Fig. 45(a)) and can be considered intrinsic, while curve (b) may be related to some kind of defect state located in the middle of the gap.
Since the quality of the FeS_2 film was not in satisfactory situation no conclusion can be deduced on whether the band gap is of ordinary semiconductors or not. More effort should be done to obtain films of better quality.

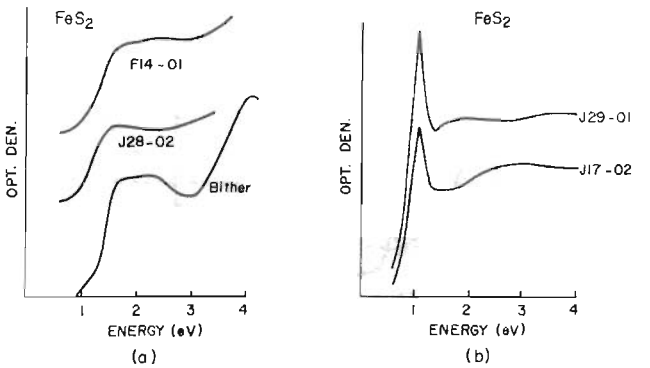

Fig. 44 Two types of absorption spectra observed in thin film samples of FeS_2.(Sato)

4.8.2 CoS_2

Sato and Teranishi (59) measured the absorption spectra on CoS_2 films produced by close spacing CVD technique on fused silica substrates. In contrast to FeS_2 only one type of spectrum was observed. In Fig. 45(b) is shown an absorption spectrum of 300 Å thick sample by a dotted curve. Two broad peaks were observed at about 1.5 and 3.5 eV caused by interband transitions and the curve rises up from 0.8 eV dip toward low energies which may be caused by the intraband transitions. The spectral feature was very close to the curve obtained from reflectivity spectrum.

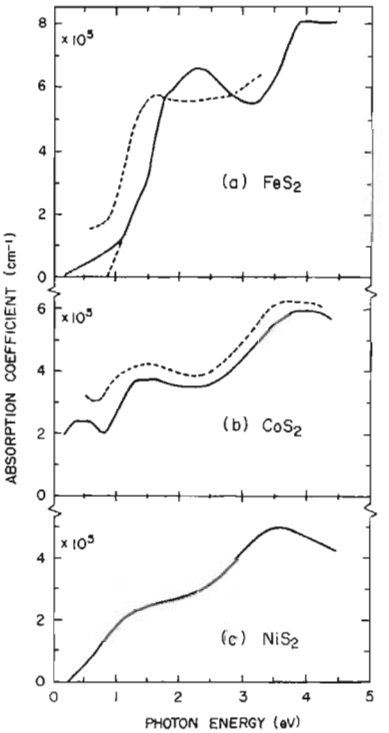

Fig. 45 Absorption spectra obtained from the Kramers-Kronig analysis of reflectivity specta in (a)FeS_2, (b)CoS_2 and (c)NiS_2.
(from Sato, (63))

4.8.3 NiS_2

Reflectivity data of NiS_2 reported by Bither et al. (30) were not reliable in the infrared region; according to his measurements reflectivity reaches as high as 60% at about 0.6 eV. Sato carefully remeasured the reflectivity of NiS_2 between 0.2 and 4.4 eV and found that reflectivity of NiS_2 does by no means get such a high value as 60%. As seen in Fig. 45(c) deduced absorption spectrum show a well-defined absorption edge at 0.37 eV.

Direct measurement of absorption spectrum on the bulk sample of NiS_2 was performed by Kautz and coworkers (80). Their result is illustrated in Fig. 46, from which absorption edge is determined to be 0.265-0.3 eV, depending on the method of plotting. Temperature dependence of the energy gap was found to be linear with temperature coefficient -4×10^{-4} eV/K.

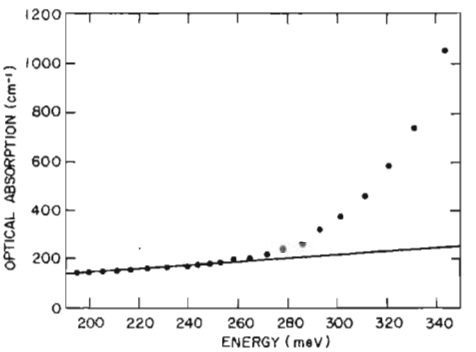

Fig 46 Optical absorption as a function of photon energy in NiS_2 at 295 K. Sample thickness is 58 μm.
(from Kautz et al.,(80))