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Optical absorption in iron pyrite (FeS_2)

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Optical absorption studies in thin (~ 100 μm) natural single crystals of iron pyrite (FeS_2) are reported in the energy range of 0.7–1 eV. The measurements were made at several temperatures between 20 and 297 K in two samples of different impurity level. In the low-resistivity sample, there is a pronounced absorption varying nearly as λ^2 (λ is the wavelength) for energies below the absorption edge. This is probably free-carrier absorption. In the high-resistivity sample, it is shown that the absorption band results from phonon-assisted indirect transitions between the valence and the conduction band. From this analysis, the energy of the participating phonon and the band-gap energy E_g are evaluated at different temperatures. It is found that $E_g = 0.835 - \alpha T^2/(1395 - T)$ with $\alpha = 6.5 \times 10^{-4}$ eV/K. At lower temperatures, three sharp peaks are superposed on the absorption curves. These peaks have been tentatively designated as transitions to exciton levels.

I. INTRODUCTION

In recent years there has been considerable interest in the electronic structure of transition-metal dichalcogenides, since they straddle the localization-itinerant regime for 3*d* electrons.[1-4] The materials MS_2 (M = Mn, Fe, Co, Ni, Cu, Zn) all have the pyrite structure. Although only one *d* electron is successively added as we go from Mn to Zn, the electronic and magnetic properties of these materials are quite different.[1-4]

The subject matter of this paper is the optical absorption in the material iron pyrite (FeS_2), the major sulfur-bearing mineral in coals. FeS_2 is a Van Vleck paramagnet[5] and a semiconductor.[6] In the literature there has been considerable controversy as to the correct value of the energy gap E_g for FeS_2. The values reported are: 1.2 eV by Marinace,[6] 1.12 eV by Sasaki,[7] 0.92 eV for synthetic crystals by Bither *et al.*,[8] and 0.73 eV by Horita and Suzuki.[9] The only optical absorption studies have been the recent report by Schlegel and Wachter,[10] who reported an energy gap of 0.95 ± 0.05 eV at room temperature. However, no detailed analysis of the absorption edge or its temperature dependence was reported. In this paper we report the first detailed study of the optical absorption in FeS_2. An analysis of the absorption curve suggests that the interband transitions in FeS_2 are indirect. The energy gap E_g is determined and its temperature dependence is measured for the first time. At lower temperatures, some additional peaks, superposed on the absorption curve, are observed, and these have been tentatively interpreted in terms of excitons. Details of these results are presented and discussed in this paper.

II. EXPERIMENTAL DETAILS

Measurements reported here were done on two natural single crystals of pyrite: a Peru n-type sample with room-temperature resistivity $\rho(RT) \simeq 90$ Ω cm (sample I) and a Spain n-type sample $\rho(RT) \simeq 9 \times 10^{-3}$ Ω cm (sample II). The samples were cut into thin slices with a diamond saw parallel to their prominent face (100). The faces were ground with successively finer grades of special silicon-carbide grinding paper to their final thickness of about 100 μm. The thickness and its uniformity for a sample was measured with a micrometer with 10-μm resolution.

The optical absorption measurements were made on a Cary Model 14, double-beam double monochromator which is an ultraviolet–visible–near-infrared recording spectrophotometer. The measurements were made at several temperatures between 30 K and room temperature. The specimens were mounted on a stainless-steel sample holder that fitted into a Dewar with optical windows. The temperatures were controlled with a heater wound near the sample and by controlling the flow of evaporating cryogenic fluids (helium and nitrogen). The temperatures were monitored with a copper-Constantan thermocouple. For higher optical density measurements, a filter with an optical density of 0.5, 1.0, 1.5, or 2.0 could be inserted into the reference channel during scanning.

It can be shown that if the optical thickness and spectral slit width are not too small, the radiation intensity transmitted by a plane parallel plate of thickness d and of absorption coefficient K is given by[11,12]

$$I_T/I_0 = (1-R)^2 \exp(-Kd)/1 - R^2 \exp(-2Kd)\,, \tag{1}$$

where R is the surface reflectivity of the sample and I_0 and I_T are, respectively, the incident and transmitted intensities. Equation (1) takes into account the effect of multiple reflections in the specimen. To evaluate K from Eq. (1), in general R must be shown. However, if R does not change appreciably in the frequency range of interest, and using the reasonable approximation that $R^2\exp(-2Kd) \ll 1$, one gets for the optical density $(D_0) = \log_{10}(I_0/I_T)$

$$D_0 = \log_{10} e Kd - 2\log_{10}(1-R)\,, \tag{2}$$

and therefore

$$K = \frac{(D_0)\times 2.303}{d} - \frac{4.606\log_{10}(1-R)}{d}\,. \tag{3}$$

According to the measurements of Schlegel and Wachter,[10] the value of R for FeS_2 at room temperature does not change by more than 2% in the energy range of our experiment (0.6–1.0 eV). A similar behavior is expected at lower temperature since the first peak in the reflectivity is at least 1 eV away,[10] and the changes in the energy levels in the temperature range of our experiments are less than 10%, as shown later. Consequently, the second term on the right-hand side of Eq. (3) is very slowly varying, and it has been treated as background. The absorption coefficient K due to the optical transitions can therefore be evaluated from the measured D_0 and the first term in Eq. (3).

III. EXPERIMENTAL RESULTS

The absorption coefficient as evaluated from Eq. (3) and the measured D_0 for sample I is shown as a function of energy in Figs. 1 and 2 for sample thicknesses of 90 and 150 μm, respectively. It is clear that there is a constant level of residual absorption at photon energies below the absorption edge, this level decreasing as the temperature of the specimen is lowered. Schlegel and Wachter[10] had also observed a residual absorption coefficient in excess of 10^3 cm^{-1} at 300 K in their study. In order to determine E_g, this constant level is subtracted out as described in detail in Sec. IV. As generally expected, the absorption edge shifts to higher energies (Figs. 1 and 2) as the temperature of the sample is lowered. At lower temperatures, three additional peaks are superposed on the absorption edge, a copy of a chart recording of which is shown in Fig. 3 for the 150-μm sample. For the 90-μm sample, only first of the two peaks are clearly resolved.

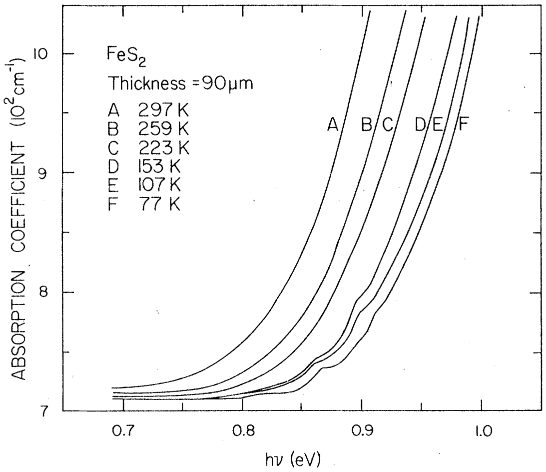

FIG. 1. Absorption coefficient vs photon energy for sample I (90 μm) at several temperatures. Note the peaks at lower temperatures.

For sample II, the absorption curves were obtained for the temperature range of 77–297 K. The data for 297 and 104 K are shown in Fig. 4. In contrast to the data in sample I, there is considerable energy-dependent absorption below the absorption edge. We believe that this extra absorption in this n-type material with very low resistivity $[\rho(RT) = 9\times 10^{-3}\ \Omega\,\mathrm{cm}]$ is due to free-carrier absorption, since it varies approximately as λ^2.[13,14] Due to experimental limitations, the absorption at still lower energies could not be measured. There are no indications of the extra peaks as observed in sample I.

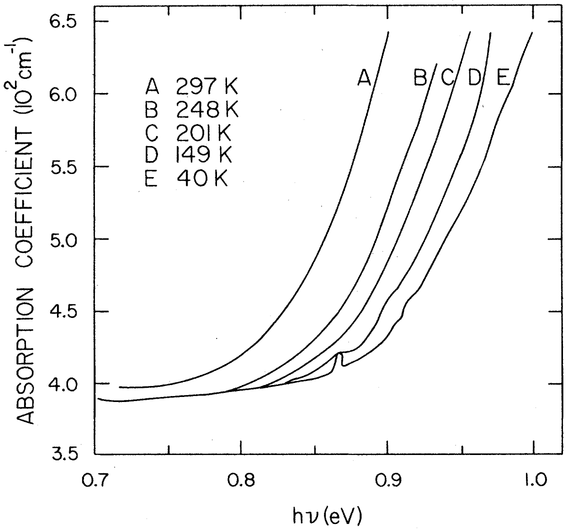

FIG. 2. Absorption coefficient vs photon energy for sample I (150 μm) at several temperatures.

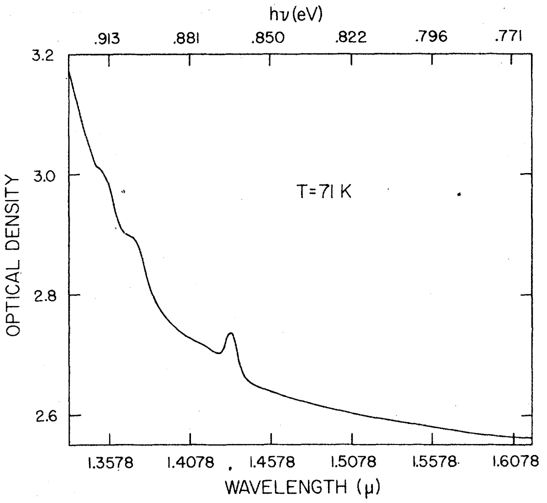

FIG. 3. Reproduction of the chart recording of the peaks for sample I (150 μm) at 71 K. Table II gives the position of these peaks at different temperatures.

IV. ANALYSIS

A major objective of this study was to determine the magnitude, the nature, and the temperature dependence of the semiconducting energy-band gap E_g for pyrite. To do so, a detailed analysis of the shape of the absorption edge needs to be carried out. The form of the absorption edge in semiconductors such as Ge and Si has been discussed by a number of investigators.[13-20] Our analysis will essentially follow the knowledge gained from these studies. In general, the absorption coefficient K is found proportional to $(h\nu - E_0)^n$, where $n=\frac{1}{2}$ for direct transitions, $n=\frac{3}{2}$ for direct "forbidden" transition, $n=2$ for indirect transition, and $n=3$ for indirect "forbidden" transitions. E_0 is closely related to the energy-band gap. The indirect transitions involve the absorption or emission of a phonon in order to conserve momentum. Thus, in indirect transitions, the top of the valence band and the bottom of the conduction band occur at different k (momentum) values in the Brillouin zone. From Figs. 1 and 2, it is quite evident that $n\neq\frac{1}{2}$. From Fig. 1, analysis of the data [K vs $(h\nu - E_0)^n$] yields $n\simeq 2.3$ if the tail on the absorption edge at the lower value of K is disregarded. This value of n is close to the theoretically predicted value of 2 for indirect transitions. A more complete analysis of the data, taking into account both the absorption and emission of phonons, is now given.

For indirect allowed transitions, the absorption coefficient K for a single-phonon process can be

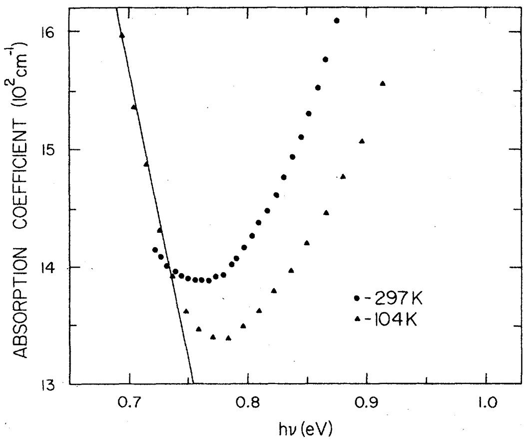

FIG. 4. Absorption coefficients vs photon energy for sample II (70 μm) at two temperatures. The solid line represents λ^2 contribution of the free-carriers.

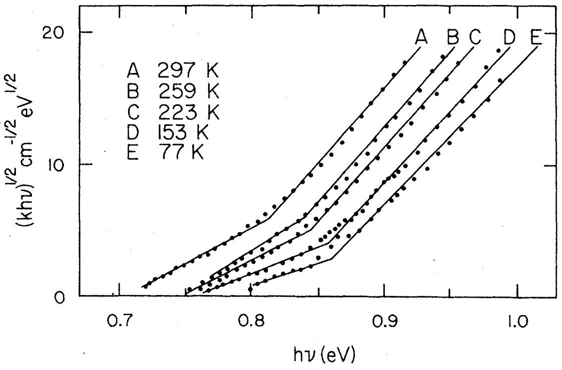

FIG. 5. $(Kh\nu)^{1/2}$ vs $h\nu$ for sample I (90 μm) at several representative temperatures. The solid circles are representative experimental points and the solid lines are fits to Eq. (4) with the parameters given in Table I.

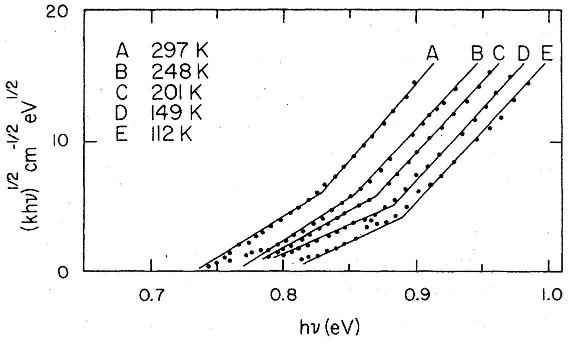

FIG. 6. $(Kh\nu)^{1/2}$ vs $h\nu$ for sample I (150 μm). The solid lines are fits to Eq. (4) with parameters in Table I. The solid circles are representative experimental points.

TABLE I. Parameters of Eq. (4) for sample I.

Thickness (μm)	T (K)	Energy gap E_g (T) (eV)	Phonon energy E_p (eV)	A ($\times 10^4$)	B ($\times 10^4$)
90	297	0.756	0.050	1.817	1.340
	259	0.784	0.041	2.105	1.006
	223	0.790	0.040	1.975	1.059
	153	0.798	0.046	4.408	1.201
	77	0.818	0.043	76.623	1.337
150	297	0.780	0.040	1.632	1.034
	248	0.803	0.040	2.337	0.925
	201	0.811	0.044	4.044	1.020
	149	0.820	0.050	10.173	1.341
	112	0.830	0.041	12.214	1.160
	80	0.834	0.046	201.725	1.113
	53	0.837	0.042	2363.5	0.919
	40	0.833	0.049	19889	1.510

expressed as

$$Kh\nu = \frac{A(h\nu - E_g + E_p)^2}{\exp(\theta_p/T) - 1} + \frac{B(h\nu - E_g - E_p)^2}{1 - \exp(-\theta_p/T)}, \quad (4)$$

where $h\nu$ is the energy of the incident photon, $E_p = k_B\theta_p$ is the energy of the phonon, E_g is the band gap, T is the absolute temperature, k_B is the Boltzmann constant, and A and B are constants.[12,14,17] The first term in Eq. (4) corresponds to absorption of a photon and a phonon, whereas the second term corresponds to absorption of a photon and emission of a phonon and contributes only for $h\nu > E_g + E_p$.

To evaluate A, B, E_g, and θ_p with the use of Eq. (4), first the background absorption, which in sample I is nearly independent of $h\nu$ (Figs. 1 and 2) is subtracted out. Since for $h\nu < E_g + E_p$, only the first term in Eq. (4) contributes, a plot of $(Kh\nu)^{1/2}$ vs $h\nu$ should yield a straight line with the square of the slope equal to $A/[\exp(\theta_p/T) - 1]$ and the intercept on the $h\nu$ axis equal to $E_g - E_p$. For $h\nu > E_g + E_p$, a similar plot after subtracting the extrapolated contribution from the first term yields $B/[1 - \exp(-\theta_p/T)]$ and $E_g + E_p$. Thus all the four constants are evaluated. Using this procedure, the data at different temperatures are fit to Eq. (4) and results are shown in Figs. 5 and 6. Here the solid lines are the fits to Eq. (4) with the evaluated parameters given in Table I. We estimate the relative accuracy of E_g determined this way to be within ± 0.02.[21] The fit at all temperatures is quite good, although at lower temperatures, where additional peaks are observed (Fig. 3), there is considerably more deviation from the solid lines as expected. A further test of our fitting procedure involving a single phonon and Eq. (4) is the energy E_p of the phonon. The reasonable constant value of E_p assures us that in the region of $h\nu$ investigated in this work, the single phonon makes the dominant contribution in assisting the interband indirect transition.

The temperature dependence of the energy gap E_g for the 150-μm sample I is shown in Fig. 7. Varshni[22] has suggested an empirical relation for the temperature dependence of the energy gap of semiconductor. This relation is

$$E_g(T) = E_g(0) - \alpha T^2/(\beta + T), \quad (5)$$

where $E_g(0)$ is the value of the E_g at $T = 0$ K and α and β are constants to be evaluated from the data.[23] The physical basis for the above relation is that for most semiconductors the dominant temperature dependence arises from the change in the widths of the energy bands due to the elec-

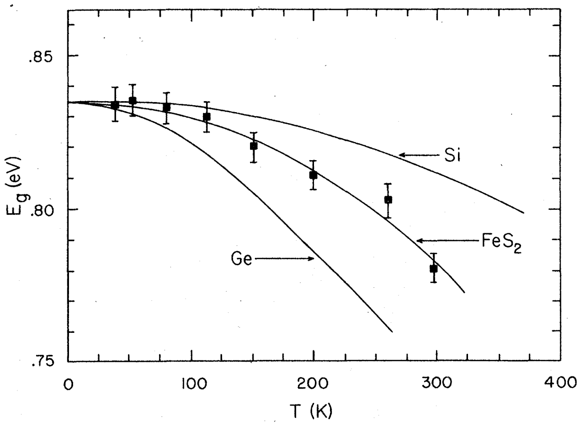

FIG. 7. Temperature dependence of E_g (energy gap) for the 150-μm sample I. The solid line for FeS_2 is Eq. (5) with parameters given in text. The relative variations of E_g for Si and Ge are also shown for comparison purposes.

tron-phonon interaction. This dependence varies as T^2 for $T \ll \theta_D$ (Debye temperature). An additional temperature dependence, usually weaker, is due to lattice dilation with temperature. The solid line in Fig. 7 is Eq. (5) with $E_g(0) = 0.835$ eV, $\alpha = -6.5 \times 10^{-4}$ eV/K, and $\beta = -1395$ K. Since in our region of interest, the denominator $\beta + T$ does not change appreciably, the decrease in energy gap varies approximately as T^2. This has important implications in determining $E_g(0)$ from the electrical resistivity measurements as discussed later. In Fig. 7, we have also shown the relative variations of E_g for Si and Ge for comparison purposes.[22]

Evaluation of E_g for sample II is more difficult because of the energy-dependent background. Assuming the λ^2 contribution of the background to be valid in the experimental range of energies (see Fig. 4), the resulting curve of $(Kh\nu)^{1/2}$ vs $h\nu$, after subtracting out the λ^2 contribution, yields essentially a single straight line. Thus it is not possible to determine E_g unambiguously. It is believed that the errors in the subtraction procedure are too large for small K values to allow us to determine E_g accurately. However, a comparison of the positions of the absorption edges of samples I and II at nearly the same temperatures shows that the absorption edge for sample II occurs at about 0.05 eV lower than that for sample I. Thus there is some evidence that the effective E_g for sample II is about 7% lower than that for sample I.

Now we examine the extra peaks of sample I, as shown in Fig. 3. The observed positions of these peaks at different temperatures for the 150-μm sample I are shown in Table II. The data for the 90-μm sample I is similar. If we assume that these are exciton peaks, then the separation of the first two peaks is given by[16]

$$E_{n2} - E_{n1} = (\mu e^4 / 2\hbar^2 \epsilon^2)(1 - \tfrac{1}{4}) , \qquad (6)$$

where μ is the effective mass of the exciton and ϵ is the dielectric constant. Using the values from Table II (say, at 40 K) and $\epsilon = 10.9$ for FeS_2,[24] we find that $\mu \simeq 0.45 m_e$. (We have used E_{n1} and E_{n2} since they can be measured to a greater accuracy than E_{n3}.) In view of the possibility that the hole is heavy,[2] μ would be close to the effective mass of electrons in FeS_2. This value of $0.45 m_e$ is quite reasonable, although we are not aware of any other independent measurement with which to compare our result. The calculated values of E_{n3} with $\mu = 0.45 m_e$ agree quite well with the observed values. It is noted that the sharp transitions of Fig. 3 could also result from transitions between valence-band and shallow donor levels. In this case, Eq. (6) is still valid, with μ now being the effective mass of the electron. A microprobe analysis of sample I (sample 2 of Ref. 5a) shows that the transition metals Cr–Zn of order 0.05 at.% are the major impurities. Therefore, at this time, it would be premature to try to assign these transitions to any one donor. However, there is one additional observation that tends to favor the transitions to be excitonic in origin. Since the peak for $n = 1$ is well resolved, the width of the peak can be measured at different temperatures. The fact that the width increases with increasing temperatures is consistent with a mobile exciton. From Eq. (6), binding energy E_e of the exciton is estimated to be 0.054 eV.

TABLE II. Positions of the exciton peaks for sample I (150 μm) at different temperatures.

T (K)	E_{n1} (eV)	E_{n2} (eV)	E_{n3} (eV)
24	0.867	0.906	0.917
40	0.866	0.905	0.917
53	0.866	0.905	0.917
80	0.866	0.904	0.914
112	0.865	0.903	0.915
149	0.861	0.901	
201	0.844		

V. DISCUSSION

As noted in Sec. I, a major objective of this work was to determine the nature, the magnitude, and the temperature dependence of the energy gap of FeS_2. The fact that our data can be described by an indirect transition suggests that the top of the valence band and the bottom of the conduction band in FeS_2 occur at different points in the Brillouin zone, somewhat similar to the situation in Ge and Si.[17, 18] The only known band-structure calculations of FeS_2 are the recent work by Khan.[25] Although this paper does not stress the point of indirect transitions, an examination of the energy bands show that the minimum in the conduction band occurs close to the M symmetry point $[(1, 1, 0)\pi/a]$ whereas the maximum in energy in the valence band occurs close to the Σ point $[(\xi, \xi, 0)\pi/2]$. Thus these band calculations are consistent with our observations. Additional details on the calculations on this point are certainly needed.

Another objective of this work is to determine the energy gap E_g. In Fig. 7, we have shown the temperature dependence of E_g, as determined from this study. It is evident that one must take into account the temperature at which E_g is determined. Perhaps the most careful electrical resistivity measurements to date are those of

Horita and Suzuki.[9] In these studies E_g is determined from $\log \rho$ vs $1/T$ plot in the 500–700 K range. Thus the lower value of 0.73 eV as determined by them is most likely due to the temperature dependence of E_g. If, for example, Eq. (5) is valid at 500 K, $E_g(T)$ at 500 K is calculated to be 0.18 eV lower than $E_g(0)$. (Horita and Suzuki have discussed in detail why earlier resistivity measurements might have yielded higher values of E_g, including the effects of possible non-Ohmic contacts.) As noted earlier, the only other optical absorption studies are by Schlegel and Wachter,[10] who determined $E_g = 0.95 \pm 0.05$ eV at 300 K. However, they have not presented any detailed analysis of the absorption edge, without which the determination of E_g is not straightforward in the case of indirect transitions. One cannot, also, discount the possibility that different samples do yield slightly different E_g, most probably due to different impurity concentrations. In our measurements on sample II (estimated $N_D \simeq 5 \times 10^{18}/\text{cm}^3$), E_g for the heavily doped sample is about 7% lower. A similar effect has been observed in Ge by Haas,[26] in which a Ge sample with a concentration of $N_D = 4.3 \times 10^{19}/\text{cm}^3$ had a band gap of 0.08 eV smaller than the band gap of pure Ge (0.74 eV). There is also the possibility of band-tailing effect as observed in NiS_2 (Ref. 27) when in the heavily doped semiconductor, the impurities themselves form a band, thereby decreasing the effective band gap.

Another possibility that would affect the absolute value of E_g determined from this work is the effect of excitons on the measured band gap, which was neglected in the analysis of the data in Figs. 5 and 6. Although the theory of excitons in indirect transition is filled with computational difficulties,[16] it would seem that E_g of Eq. (4) should be replaced by $E_g - E_e$. If this is so, then the value of the energy gap of 0.84 eV estimated for absolute zero (Fig. 7) is actually equal to $E_g - E_e$. This yields a band gap of 0.89 eV. Clearly, this does not affect the temperature dependence of E_g and any of the other major conclusions drawn from this study. Therefore, at the present state of knowledge, a more realistic estimate of $E_g(0) = 0.84^{+0.05}_{-0.02}$ eV.

VI. CONCLUDING REMARKS

In this work on FeS_2, the nature of the valence to conduction-band transitions, and the value of the energy gap and its temperature dependence have been determined. There is also a strong possibility that we have observed the transitions to exciton levels in FeS_2. This being the first such study in FeS_2, these results are quite significant. However, it is clearly desirable to carry out similar experiments on synthetic samples with controlled level of impurities, something which is impossible to do in natural samples. Unfortunately, samples of FeS_2 large enough for absorption studies are quite difficult to prepare. On the theoretical side, details of the band structure of the valence and conductive bands near the extrema are clearly needed for better interpretation of the data. It is hoped that this work would provide the necessary impetus for further studies along the lines suggested above.

ACKNOWLEDGMENTS

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[21] E_g values for the 90-μm sample are consistently lower by about 0.02 eV, the quoted uncertainty, compared to those for the 150-μ m sample at a given temperature. Since the nearly constant background has been subtracted out, this difference between the two samples is probably not related to any differences in the reflectivities. The uncertainties in the analysis are about 0.01 eV. The sample uniformities are not known to better than 10 μm. This might have a bearing on the systematic difference observed between the two samples.

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[23] Only the data for the 150-μm sample I is shown in Fig. 7, since E_g for this sample are available at more temperatures. Since there is a constant difference of 0.02 eV for E_g for the two samples at a given temperature, the constants α and β are unaffected.

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