# A Study of the Optical and Electrical Properties of Spray Pyrolysis $CuAl_{1-x}Fe_xS_2$ Thin Films

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## *Abstract*

$CuAl_{1-x}Fe_xS_2$ thin films have been prepared using the chemical spray pyrolysis technique with substrate temperature ($T_s$) at 593˚K for which x varies from 0 to1. The optical absorption at room temperature is studied for the different Fe concentrations**.** The electrical resistance is measured in the temperature range (300-400)˚K for different x values.

The absorption optical spectra show two electronic transitions. The first is due mainly to the iron presence, which is around 2.55 eV, and is concentration independent. The second is concentration dependent changing from 3.35 eV for x=0 to 3.65 eV for x=1. The introduction of iron atoms into the ternary compound $CuAlS_2$ has a drastic effect on the electrical properties: The amorphous samples go through a transition from semiconductor behavior to a semi-metallic one for x as low as 0.1.

## *Introduction*

Single crystals of non-magnetic semiconductors such as $CuAlS_2$ and $CuGaS_2$ have shown an optical band gap located around 3.4 and 2.5eV respectively [1-5]. On the other hand, the analogous $CuFeS_2$ is an antiferromagnetic semiconductor with a band-to-band transition around 3.7eV [6-8]. Some authors have been working on the effect of introducing the magnetic Fe-ion on the properties of the first two compounds [9-12]. These have been expected to pave the way to understand the role played by these magnetic ions in such compounds even as far as the full replacement of Al or Ga by Fe as in the $CuFeS_2$ compound. Beside its prominent role in the magnetic properties, the iron; as a transition element; has been found to play an important role in the optical and electrical properties.

Experimentally, single crystals of $CuAl_{1-x}Fe_xS_2$ and $CuGa_{1-x}Fe_xS_2$ systems are grown by means of chemical transport reaction [7,13,14]. The magnetic susceptibility, optical reflection and electrical conductivity of these systems have been measured as a function of the magnetic ion concentration. It has been found from the optical investigations on these systems that the introduction of Fe-ions makes intense charge-transfer absorption with peaks around 1.3 and 1.9eV. Also, the intrusion of the iron-ions makes these semiconductors opaque. These results are supported by theoretical calculations by Kambra [15]. On the other hand; there is an abrupt change in the character of the electrical conductivity by such an ion replacement [7]. The conductivity changes from a semiconductor behavior to a metallic one. This change appears around the critical x-values x ~ 0.1 [7]. These (optical and electrical) properties changes are attributed to the roleplayed by the Fe-3d electrons. The mechanism is divided between the delocalization of these electrons and/or their hybridization with the Cu-p electrons in the presence of S-ions [7,14]

In the present work, thin films of $CuAl_{1-x}Fe_xS_2$ have been prepared by the chemical spray pyrolysis technique. The optical and electrical properties of the sprayed $CuAl_{1-x}Fe_xS_2$ thin films (for x-values varied from 0-1) have been investigated. To our knowledge this technique has not been tried before for such compounds.The results obtained are correlated with previous works and discussed in relation to the band model.

## ***Experimental Technique***

For $CuAlS_2$ thin films, three separate 0.048M solutions of $Cu(NO_3)_2.3H_2O$, $Al(NO_3)_3.9H_2O$, and thiourea $CS(NH_2)_2$ are prepared in tri-distilled water. Appropriate amounts of the three solutions are mixed together to obtain a final solution with Cu:Al:S ratio proportional to 1:1:2. The $CuFeS_2$ thin films are prepared following the same procedure with Fe replaces Al. The different $CuAl_{1-x}Fe_xS_2$ films are prepared with the x value varying from zero to one. The x-value is the factor determining the Al:Fe ratio in the Aluminum solution fraction. The obtained solution is immediately sprayed onto a temperature controlled glass substrate. Compressed air is used as the carrier gas. The substrate is heated and kept at the required temperature for 20 min prior to the spraying. The spraying was carried out on and off periodically (10 seconds on and 20 seconds off). This procedure gives enough time for the solution droplets to evaporate and the compound to settle down and results in well adherent films. The amounts of the mixed solutions used (40cc), substrate temperature ($T_s$=593˚K), spraying rate, (10cc/min) are unchanged throughout the investigation for the different x values. The experimental set-up for the deposition has been described elsewhere [16].

The thin films obtained are clear, changing in color from green (for $CuAlS_2$) to brown-red (for $CuFeS_2$) as x increases from (0-1). The addition of iron renders the film opaque. The films have good adhesion to the substrate and exhibit smooth surfaces free from pinholes. The thickness of the prepared thin films are of the order of ~0.5μm. The undoped $CuAlS_2$ thin film shows some polycrystalline, while the Fe-doped ones are amorphous [17].

Optical absorbance measurements are carried out using a Pye-Unicom SP-800 UV/VIS Double beam spectrophotometer. It covers the range from 200-800 nm. Optical measurements are carried out at room temperature. The resistivity is measured using the gap method in the temperature range of (300-400)˚K. Hot-probe method shows that $CuAlS_2$ thin films have n-type character, while $CuAl_{1-x}Fe_xS_2$ thin films show p-type character.

## ***Results and Discussion***

The optical absorption coefficient $\alpha$ is calculated from the absorption spectra of the thin films as a function of photon energy ($h\nu$) as shown in Fig (1). The value of $\alpha$ is found to be of the order of $10^4$ $cm^{-1}$ ($>10^3$ $cm^{-1}$) indicating the presence of direct band-to-band transition [18]. The nature of the transition involved can be established on the basis of the dependence of the absorption coefficient ($\alpha$) on photon energy ($h\upsilon$). For allowed direct transition, $\alpha$ is related to the energy gap, $E_g$ by the relation [19,20].

$$\alpha h\upsilon = \alpha_o (h\nu - E_g)^{1/2}$$

where $\alpha_o$ is a constant and $E_g$ is the energy gap in the optical direct band to band transition. The value of which is determined by plotting $(\alpha h\upsilon)^2$ as a function of photon energy ($h\upsilon$) as shown in Fig(1) for different x-values. Extrapolating of the straight lines to $(\alpha h\upsilon)^2=0$ gives the allowed band gap transitions. From Fig.(1), we have an interesting situation. First, the $CuAlS_2$ thin films have an allowed band-to-band transition with an allowed energy gap equal to ~3.35eV (compared with 3.4eV [3]). This transition persists with the introduction of iron and depends on its concentration. The dependence is shown in the insert in Fig.(1). As can be seen, we have an increase in the gap by increasing the iron concentration. This may be explained by the delocalization of the Cu-3p states as a sequence of its hybridization with the $Fe^{+3}$ 3d states. Consequently, the upper level of the valence band would go down, to some limit, as the iron concentration goes up. Second, the introduction of iron into the compound is accompanied by the presence of a second smaller gap of ~2.55eV. The value of the second gap is independent of the iron concentration introduced. It is worth mentioning that for $CuAlS_2$ thin film there is an indirect gap transition of $E^i_g$=1.8eV [9,17]. Our investigation does not cover this range. As for the conductivity measurements, the values of log ($\sigma$) versus 1/T for $CuAl_{1-x}Fe_xS_2$ films are calculated for different x-value and shown in Fig.(2). Some comments on Fig.(2) seem in order. The curve of the $CuAlS_2$ thin films exhibits a semiconductor behavior up to ~380˚K. The activation energy ($E_a$) is determined by using the Arrhenius relation [21]: $\sigma = \sigma_o \exp(-E_a/KT)$. Where K is the Boltzman constant, and other terms have their usual meanings. $E_a$ is found to be in the order of 42meV. This value is comparable with the 30meV obtained by other workers [22]. The conductivity in this semiconductor phase can be attributed by impurity states near the bottom of the conduction band. This explains the donor character mentioned above. For temperatures above 380˚K, the

conductivity decreases with increasing the temperature. The donor's electrons at this temperature gain enough energy to be captured by the acceptor's ions or holes. The presence of these acceptors is due again to the presence of impurities. The net result is a decrease in the number of carriers.

On replacing Al by Fe, the situation is altered completely. The d-electrons of $Fe^{3+}$ atoms will build up an inter-band gap. This band is not fully occupied. It can overlap the valance band. Hence, it plays the role of a conduction band. The behavior is a metallic one, though the value of the resistivity is in the semiconductor region. The situation is like an acceptor-doped semiconductor.In Fig.(2), the curves for the $CuAl_{1-x}Fe_xS_2$ thin films are drawn after normalizing the values to coincide with x=0 at room temperature. The room temperature resistivity (ρ) versus the change of the iron concentration (i.e. x-values) is shown in Fig.(3). One gets the same behavior for the different temperatures as can be concluded from Fig.(2). The figure shows that there will be a transition in the property from a semiconductor behavior to a metallic one on the replacing of Al by Fe. Sato and co-workers [7] have found a similar effect in single crystals. They established the transition at x ~0.12. In our case the transition is apparently for x<0.1. The dependence of the resistivity (ρ) on iron concentration, as shown in Fig.(3), is in favor of the idea that the conduction is carried out by the $Fe^{3+}$ 3d-electrons as they form an inter-gap band.

## ***Conclusion***

In this study, the optical and electrical properties of $CuAl_{1-x}Fe_xS_2$ system, (thin films prepared by spray pyrolysis method) have been measured as a function of magnetic ion concentration, for x-values varied from (0-1) at substrate temperature of (593 + 10)˚K. The direct allowed band-to-band transition was found to vary from 3.35eV to 3.65eV for $CuAlS_2$ to $CuFeS_2$ thin films, respectively. The introduction of iron atoms into the $CuAlS_2$ compound means the introduction of an inter-band gap consisting of $Fe^{3+}$ 3d (or a mixed ones). This band plays the role of a conduction band. This band is partially filled, and overlaps partially with the valence band. Increasing the number of iron atoms will increase the number of the 3d electron, and consequently, increasing the width of the band or the filling of the existing band. In other words, increasing the iron percentage will change the character of the inter-band. Consequently, this would result in the conductivity values. By increasing temperature, scattering increases, mean free path decreases and resistivity increases. Hence, the conductivity is reduced, this is due to electron-phonon interaction effect. The inter-band gap will disappear with the disappearance of iron atoms. The overlapping will disappear. In this case we have a true semiconductor.

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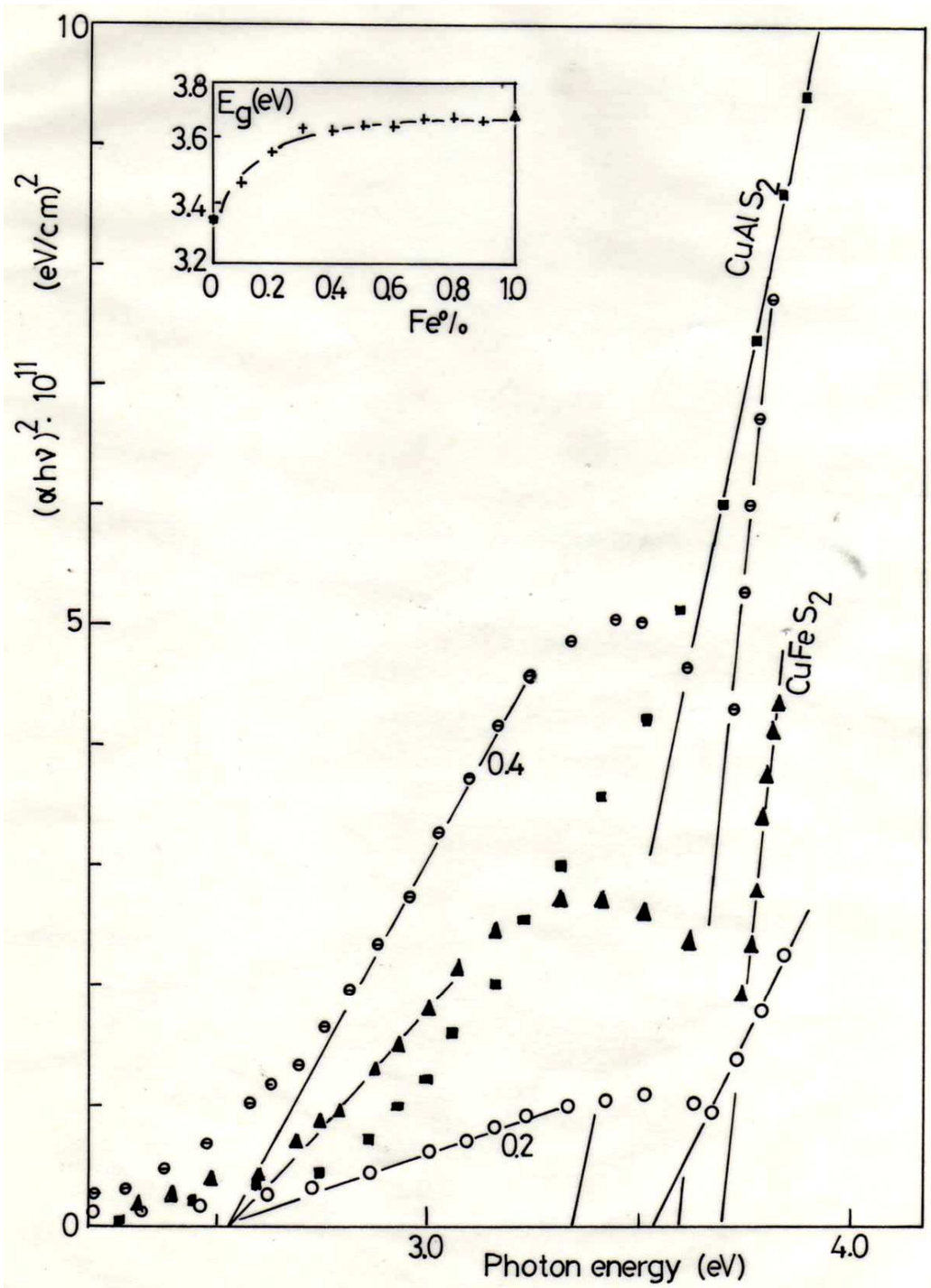


Fig.(1): The plot of $(\alpha h\nu)^2$ versus $(h\nu)$ for $CuAl_{1-x}Fe_xS_2$ thin films prepared at $T_s$=593°K for different x values. The insert is the band-to-band transition as a function of x values.

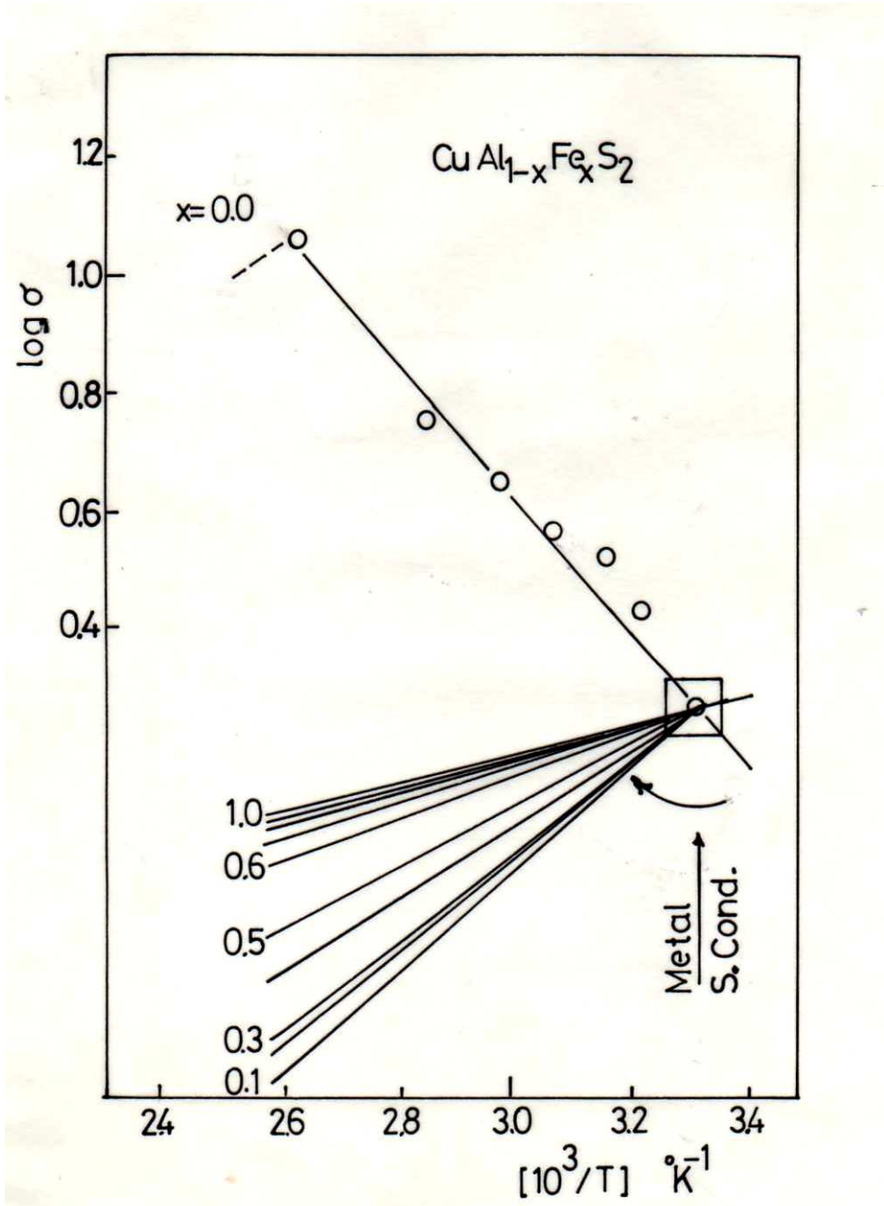


Fig.(2): The variation of conductivity log(σ) as a function of (1/T) for $CuAl_{1-x}Fe_xS_2$ system at x varied from (0-1). The mini-square is normalized to the room temperature value.

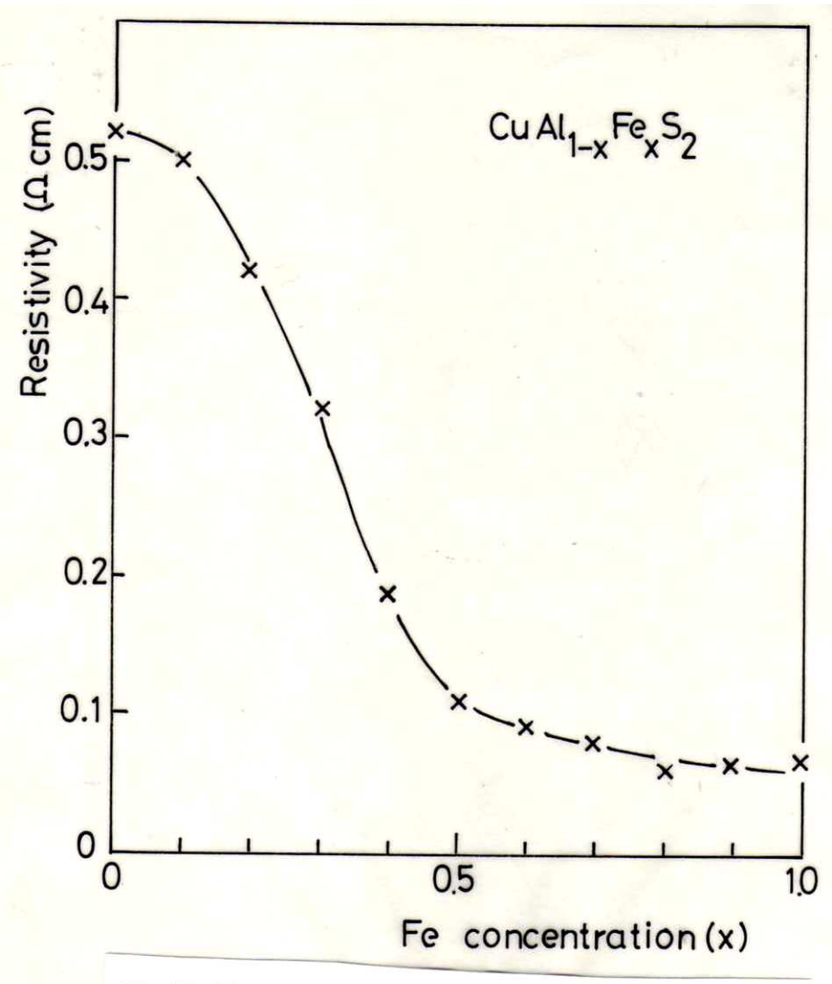


Fig.(3): The variation of room temperature resistivity ($\rho$) as a function of x-for $CuAl_{1-x}Fe_xS_2$ thin films.

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**المستخلص**

تم في هذا البحث تحضير اغشيه رقميه لـ $CuAl_{1-x}Fe_xS_2$ بطريقه الرش الكيميائي الحراري وبدرجه ( 593 ) كلفن ولقيم x من 0 الى 1 .
تم دراسه خواص الامتصاصيه الضوئيه وبدرجه حراره الغرفه ولمختلف قيم x كما تم حساب المقاومه الكهربائيه ضمن درجه الحراره ( 400 - 300 ) كلفن ولمختلف قيم x .
من دراسه طيف الامتصاصيه اتضح وجود انتقالات الكترونيه اثنين ، الاول يعود لوجود الحديد ويكون بحدود 2.55 ev ولا يعتمد على تركيز الحديد . اما الانتقال الثاني فيكون معتمد على تركيز الحديد ويتغير ضمن المدى 3.35 ev عند x=0 الى 3.65 ev عند x=1 .