IC/89/75
INTERNAL REPORT
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International Atomic Energy Agency
and
United Nations Educational Scientific and Cultural Organization
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

THERMODYNAMIC STUDIES ON THE FERROELECTRIC PHASE TRANSITION IN NEUTRON IRRADIATED $(Li_x K_{1-x})_2SO_4$ CRYSTALS AT HIGH TEMPERATURE *

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MIRAMARE – TRIESTE
May 1989

ABSTRACT :

Thermodynamic studies of $(Li_xK_{1-x})_2SO_4$, LKS, mixed crystals have been made in the concentration range (x=0.1,0.2, ..., x=0.5). The thermal behavior has been investigated by differential thermal analysis, DTA, and differential scanning calorimeter, DSC, in the vicinity of high temperature phases. Also, the effect of the mixed neutron field of fast and thermal neutrons (10% of the reactor neutron pile is fast neutrons) on the thermal properties of mixed crystals was studied. The results showed a change in the transition temperature Tc, as well as the value of specific heat Cp at transition temperature, due to the change of stoichiometric ratio and radiation doses. The change of enthalpy and entropy of mixed crystals have been estimated numerically. The obtained small values of $\Delta S/R$ is characteristic of incommensurate phase transition as previously confirmed by the results of neutron diffraction technique.

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1. INTRODUCTION

In the last few years ferroelastic phase transition has been the subject of a considerable number of theoretical and experimental studies[1-2]. Crystals with the general formula $A'A''BX_4$ in several cases exhibit phase transformation associated with the onset of spontaneous strain in low[3-4] and high temperature phases[5]. Lithium potassium sulphate, $LiKSO_4$, crystal is pyroelectric[6] with a hexagonal symmetry at room temperature. The system corresponds to the space group $P6_3$ and there are two molecules in the hexagonal unit cell. Extensive studies on the physical properties of $LiKSO_4$ in various temperature ranges have been reported[7-10].

No thermodynamic data for $(Li_xK_{1-x})_2SO_4$, (x=0.1,...,0.5) irradiated with neutron pile have been reported in literatures.

The aim of this work is to show the defects induced by neutron pile irradiation and the corresponding changes which are produced in the thermodynamic properties in the vicinity of high phase transitions of $(Li_xK_{1-x})_2SO_4$ crystals. Such results will be compared with those due to fast neutrons only.

2. EXPERIMENTAL

2.1- Sample Preparation :

Clear, colourless single crystals of $(Li_xK_{1-x})_2SO_4$

were grown isothermally at 315 K from aqueous solution containing the initial salts at different adapted stoichiometric ratios.

2.2- Neutrons Irradiation Technique :

Samples were irradiated with neutrons using a special kind of polyethylene capsule known as Lazy Susan. Neutrons are produced from Triga Mark III, Berkeley research reactor, with steady state power 1000 KW. The neutron fluxes are determined by the activation of natural gold foils (1.2 cm diameter, 0.01 cm thickness). The resulting activity from $^{197}Au(n,\gamma)\ ^{198}Au$ reaction was measured and analysed by using Ge (Li) gamma detector and pulse height analyzer connected to PDP 11/34 based data acquisition system. A normalization factor due to the degradation of the neutron flux through the samples during the irradiation process was considered. Crystals are irradiated to a flux $\phi = 4x10^{12}\ n.cm^{-2}.S^{-1}$ through different time intervals from 2 minutes up to 10 minutes.

2.3- Thermal Measurements :

The thermal behavior of irradiated mixed crystals was studied in the temperature range 300-970 K by applying the following techniques :

a) The specific heat under constant pressure, Cp, was determined using a differential scanning calorimetry (DSC) technique, where a Heraeus DSC cell was connected to Heraeus DTA

500 thermal analyzer. Measurements were achieved by applying the base line method[11]. Lidded Pans of aluminium were used to eliminate the sloping of the base line. A Pt 100 thermocouple was used as a temperature sensor, while a heating rate of 2 degree/min was applied.

b) For differential thermal analysis, the sample was contained in a glass tube in the standard DTA cell connected to the DTA 500 analyzer. The temperature sensor used was NiCrNi and the heating rate applied 5 degree/min.

c) Thermogravimetric (TG) measurements were performed on a Heraeus. TG 500 thermobalance with a Pt-Rh-Pt temperature sensor, and the heating rate used was 10 degree/min. Dry nitrogen was allowed to flow at rate 15 ml/min, while the flow rate of cooling water was 10 l/h.

3. RESULTS AND DISCUSSION

$LiKSO_4$ crystals exhibit two structural phase transitions at 715 K and 960 K as shown in Fig. (1-a) which are in good agreement with the published values[12-13]. But with the change of stoichiometric ratio of such crystal according to the formula $(Li_xK_{1-x})_2SO_4$, where x=0.1,0.2,0.3, and 0.4, it is observed that the anomaly in the temperature dependence of specific heat, Cp, at the first phase transition disappeared. While in the second transition, Tc shows a decrease in its value

with the decrease lithium content as presented in Fig. (1-b). Moreover, the value of specific heat, Cp, at transition shows a maximum at x=0.3 (Fig. (1-b)). This behavior may be attributed to the enhancement of the phonon lattice vibrations due to the difference in cationic ratio $Li^+:K^+$ and phononic scattering.

As a result of the neutron irradiation of $(Li_xK_{1-x})_2SO_4$ crystals, where x=0.1,0.2,0.3 and 0.4, radioisotope ^{42}K is detected by means of the γ-spectrometer while the other radioisotopes are not detected either due to their short half-lives or very small yields. Fig. (2) represents the γ-spectrum of the activated crystal and Table (1) shows the possible produced radioisotopes with their decay products and the number of induced defects due to fast and thermal neutron fluence. $(Li_xK_{1-x})_2SO_4$ crystals are irradiated to neutron pile of different integrated flux ϕt doses, ranging from 4.8×10^{14} to 2.4×10^{15} $n.cm^{-2}$.

As an example the variation of the temperature dependence of specific heat, Cp, of $Li_{0.4}$ $K_{1.6}$ SO_4 crystal under the action of neutron fluence is presented in Fig. (3). It is observed that the anomaly in the first high temperature phase appears again showing an endo-thermic behavior. In general, the values of specific heat, Cp, for irradiated samples increase the result of irradiation[14]. From Fig (3) one can conclude that the dependence of Cp on the neutron integrated flux ϕt shows a decrease to a minimum at neutron fluence $\Phi t = 1.92 \times 10^{15}$ $n.cm^{-2}$ and increases to 1200 $J.K^{-1}$ $mole^{-1}$ at $\phi t=2.4\times10^{15}$ $n.cm^{-2}$. This behavior may be attributed to the decomposition induced by irradiation, as well as the generation of new species(15).

The three-dimensional diagram (temperature-concentration-specific heat), for the system under consideration in the whole range of concentration (x = 0.1, 0.2, 0.3, 0.4) irradiated with neutrons of fluence 1.92×10^{15} $n.cm^{-2}$, is presented in Fig. (4). As one can see (16), the further increase of x results in disappearance of the second high temperature phase besides the increase in the value of specific heat Cp at the first high temperature phase for the same neutron fluence.

Furthermore, the changes in enthalpy ΔH and entropy ΔS of $Li_{0.6}K_{1.4}SO_4$ crystal are plotted versus the neutron fluence Φt as shown in Fig. (5). It is clear from Fig. (5) that ΔH and ΔS increase as a function of the increase of the fluence. The non linearity in the ΔH and ΔS depends on the interactions of defects induced by neutrons irradiation.

ACKNOWLEDGMENTS

The authors are much indebted to Prof. Dr. B. Hilczer, Visiting Professor at the Physics Department, Alexandria University, from the Institute of Molecular Physics, Polish Academy of Sciences, for her valuable comments and cooperation. They are also grateful to Professor S.G. Prussin, the members of the activation group of the Nuclear Engineering Department, California University, Berkley, California, for their valuable help in the course of irradiation and the Institute of Graduate Studies and Research for their cooperation. One of the authors (M.E.K.) would like to thank Professor Abdus Salam, the International Atomic Energy Agency and UNESCO for hospitality at the International Centre for Theoretical Physics Trieste.

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Table 1

Nuclide (Abundance)	Reaction	Product nucleus	Decay product	No of*) defects	No of +) defects
^{7}Li (92.48%)	(n, γ)	^{8}Li	^{8}Be	$2.8x10^{3}$	688
^{18}O (0.204%)	(n, γ)	^{19}O	^{19}F	$7.6x10^{-10}$	223
^{32}S (95.018%)	(n, γ)	^{33}S			
^{34}S (4.125%)	(n, γ)	^{35}S	^{35}Cl	$8.1x10^{-4}$	26
^{36}S (0.017%)	(n, γ)	^{37}S	^{37}Cl	$9.5x10^{-4}$	
^{39}K	(n, γ)	^{40}K	^{40}Ca ^{40}Ar	0.046	
(93.08%)	(n, P)	^{39}Ar	^{39}K	$1.46x10^{-5}$	
^{41}K (6.91%)	(n, γ)	^{42}K	^{42}Ca	0.015	32

*) For thermal neutrons per unit fluence per gram.

+) For fast neutrons per unit fluence per gram

FIGURE CAPTIONS

Fig (1-a): Temperature dependence of Cp for $(Li_xK_{1-x})_2SO_4$ crystals for (x=0.1,..,0.5)

Fig (1-b): The variation of Tc and Cp as a function of stiochiometric ratio.

Fig (2) : γ-Spectrum of irradiated $Li_{0.2}K_{1.8}SO_4$ for 10 minutes.

Fig (3) : Variation of Cp of $Li_{0.4}K_{1.6}SO_4$ crystal versus temperature for different neutron fluences.

Fig (4) : Temperature dependence of Cp for $(Li_xK_{1-x})_2SO_4$ crystals irradiated with neutron fluence 1.92 x 10^{15} cm^{-2}.

Fig (5) : Variation of the changes of enthalpy and entropy for $Li_{0.6}K_{1.4}SO_4$ crystal as a function of neutron fluence.

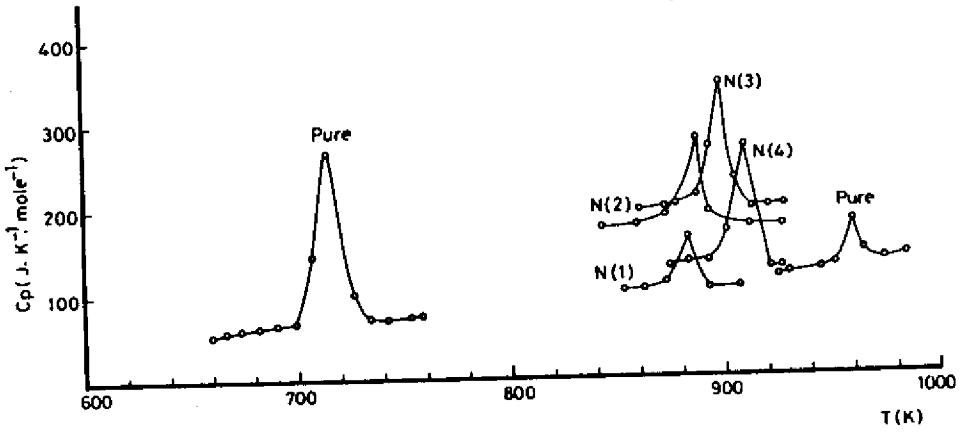


Fig. (1a)

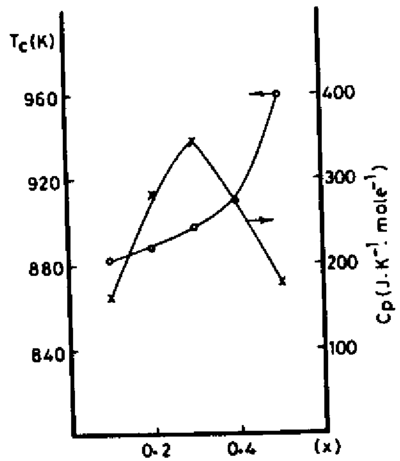


Fig. (1b)

N (1) : $Li_{0.2}K_{1.8}SO_4$

N (2) : $Li_{0.4}K_{1.6}SO_4$

N (3) : $Li_{0.6}K_{1.4}SO_4$

N (4) : $Li_{0.8}K_{1.2}SO_4$

Pure $LiKSO_4$

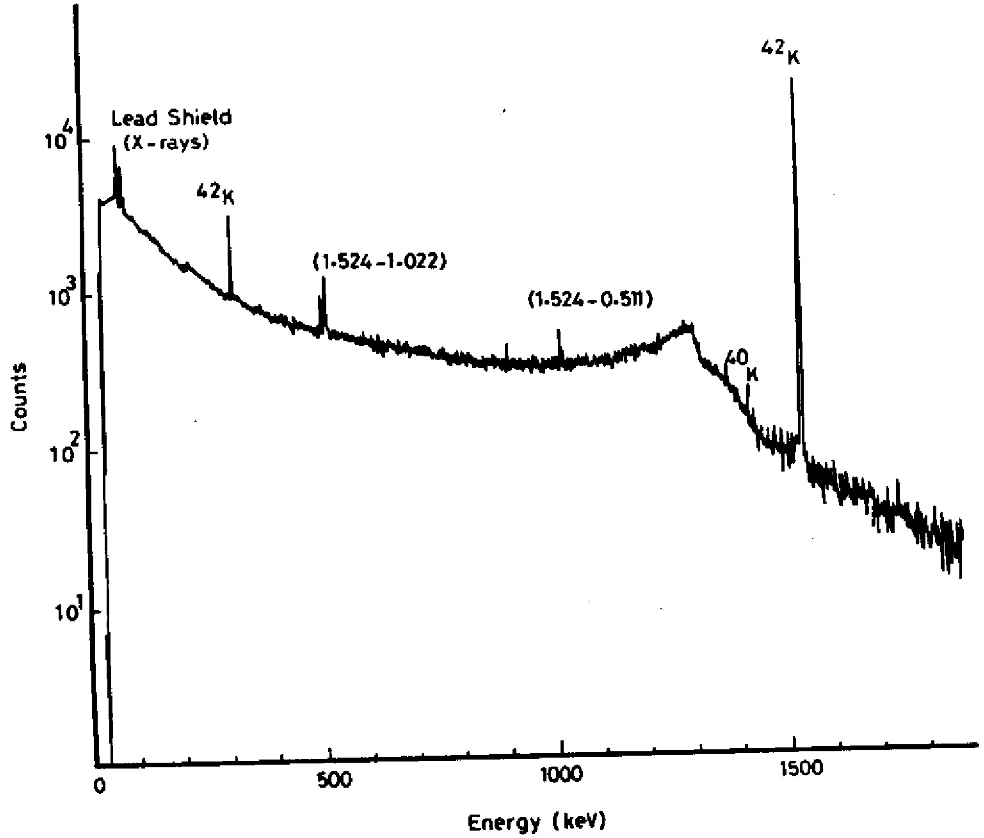


Fig. (2)

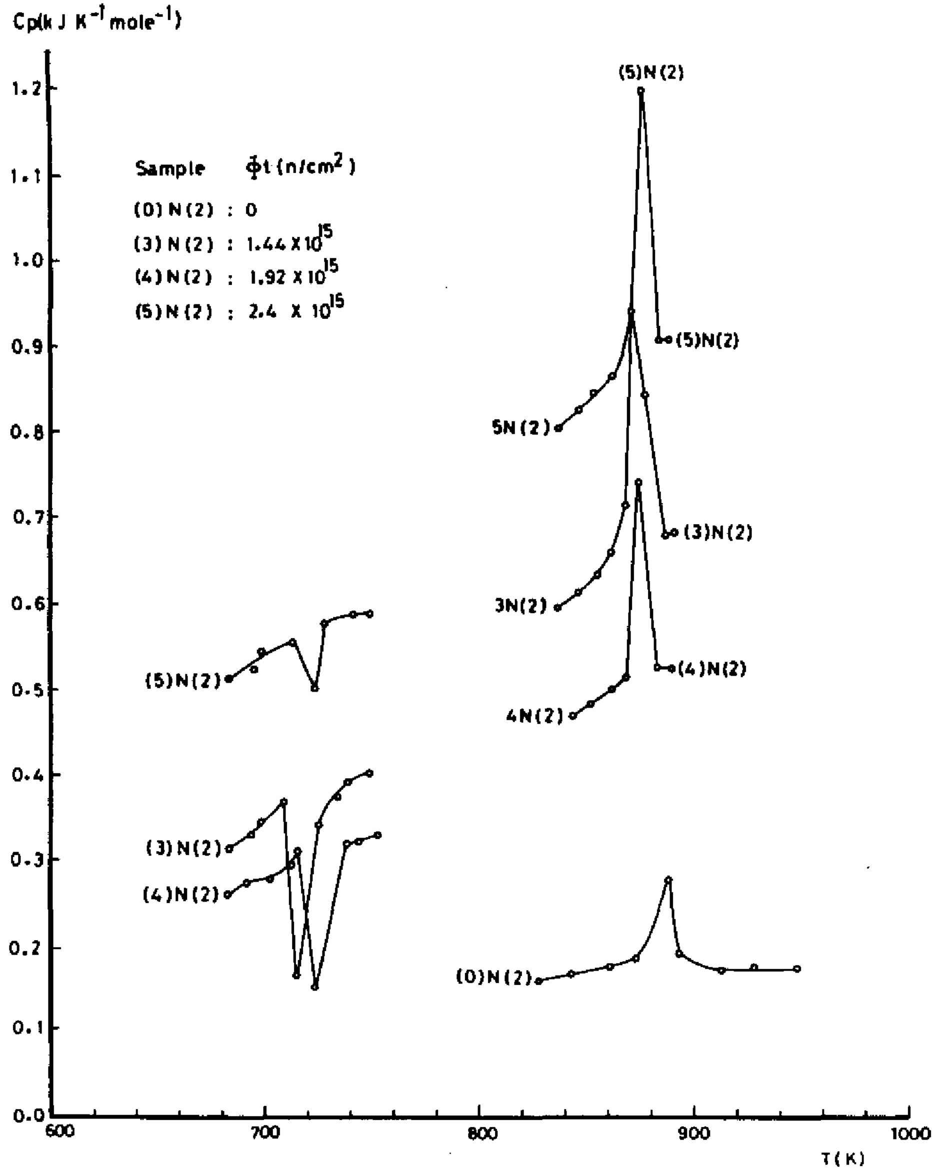
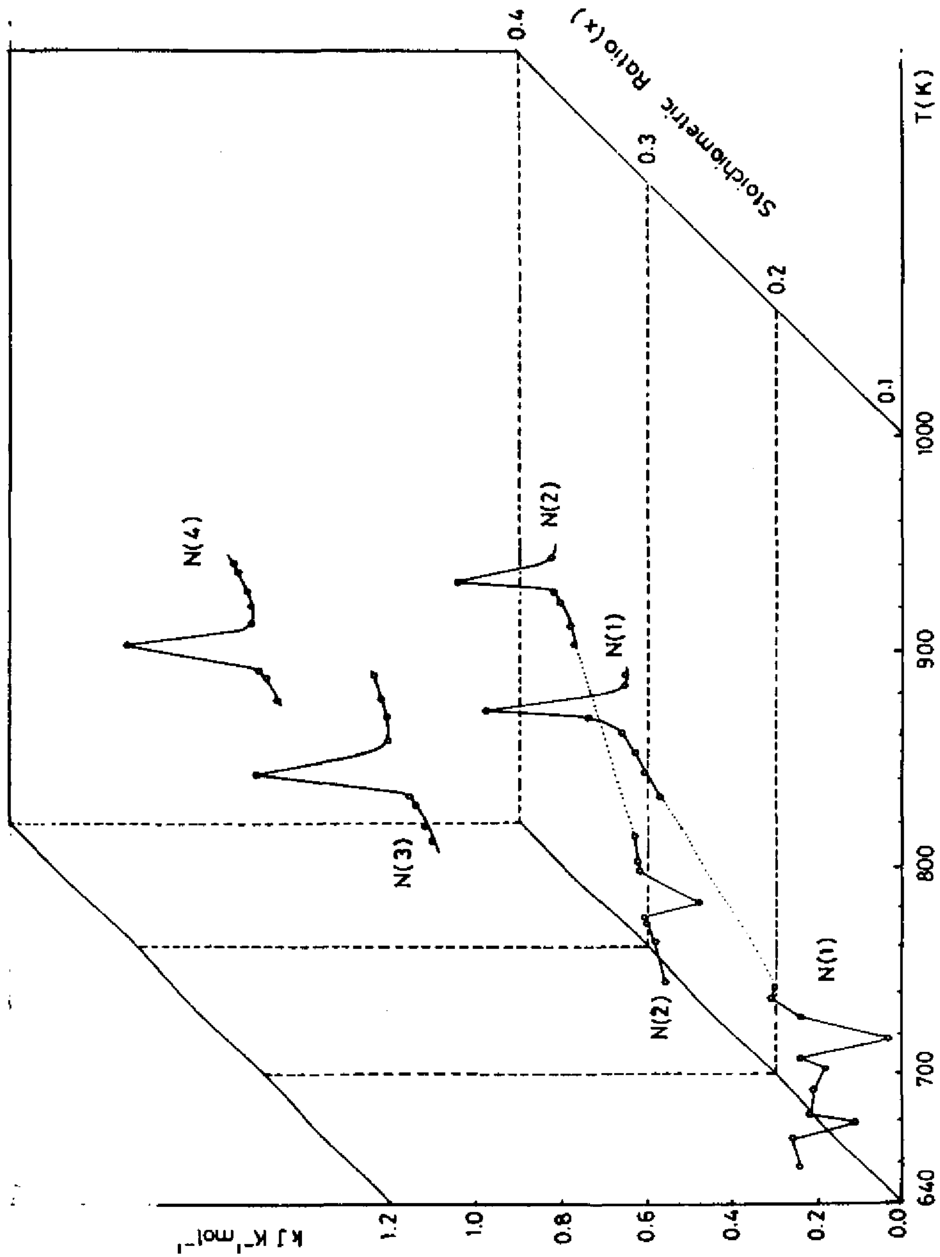

Cp(kJ K-1 mole-1)
Sample   ϕt (n/cm2)
(0) N(2) : 0
(3) N(2) : 1.44 X 10^15
(4) N(2) : 1.92 X 10^15
(5) N(2) : 2.4 X 10^15
(5)N(2)
5N(2)
3N(2)
(3)N(2)
4N(2)
(4)N(2)
(0)N(2)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
600
700
800
900
1000
T(K)

Fig.(3)


T(K)
Stoichiometric Ratio (x)
0.1
0.2
0.3
0.4
640
700
800
900
1000
N(1)
N(2)
N(3)
N(4)
kJ K-1 mol-1
0.0
0.2
0.4
0.6
0.8
1.0
1.2

Fig(4)

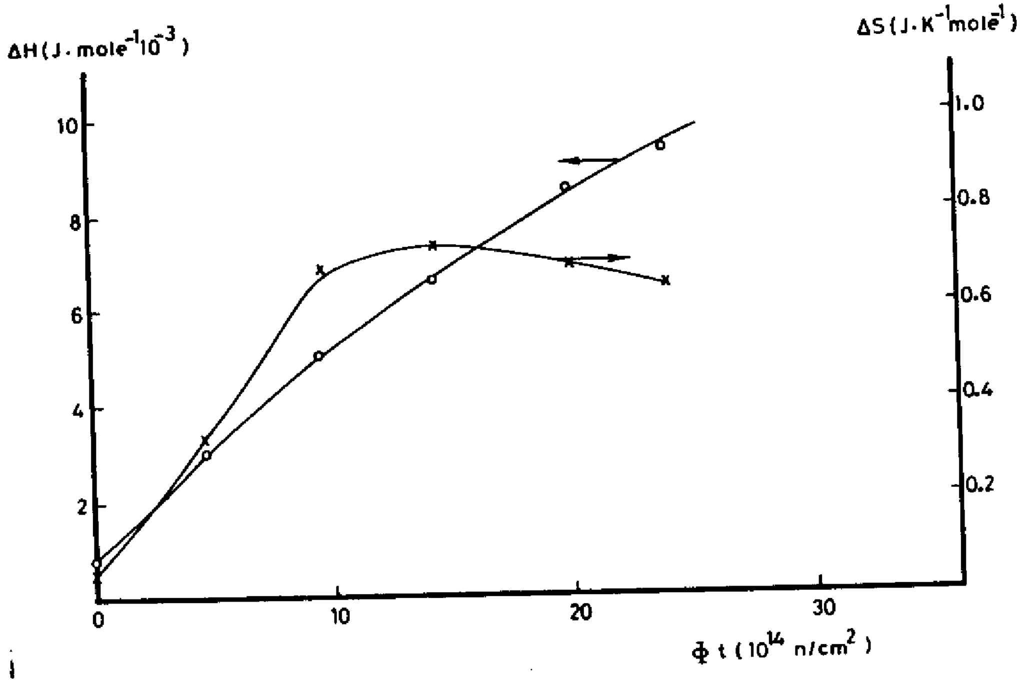

ΔH (J . mole^{-1} 10^{-3})
ΔS (J . K^{-1} mole^{-1})
10
8
6
4
2
1.0
0.8
0.6
0.4
0.2
0
10
20
30
Φ t (10^{14} n/cm^2)

Fig. (5)