Chapter - VI

THERMOELECTRIC POWER

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6.1 Introduction

The studies on thermoelectric power and d.c. electric conductivity give fundamental information of d.c conduction mechanism. The temperature variation of conductivity shows a maximum and reflects the changes in conduction mechanism that occur in ferroelectrics. Besides it yields information on the magnitudes of conductivity. On the other hand, studies on thermoelectric power reveal the role of different types of carriers that govern the electrical conductivity and help to decide whether the conduction is due to thermally activaed hopping or not. It is also possible from this data to compute temperature variation of the Fermi-level and explain the possible forms of conduction from the impurity concentration content of the samples.

Novik et al (1) measured thermoelectric effect in lithium metaniobate. Handerk et al (2) reported temperature dependence of the seebeck coefficient for potassium niobates of monocrystals. Yanovskii (3) measured temperature dependence of the thermoelectric power of the $KNbO_3$ crystal doped with impurities. Sroka and Wobel (4) reported the type of conductivity and the activation energy of the current carriers

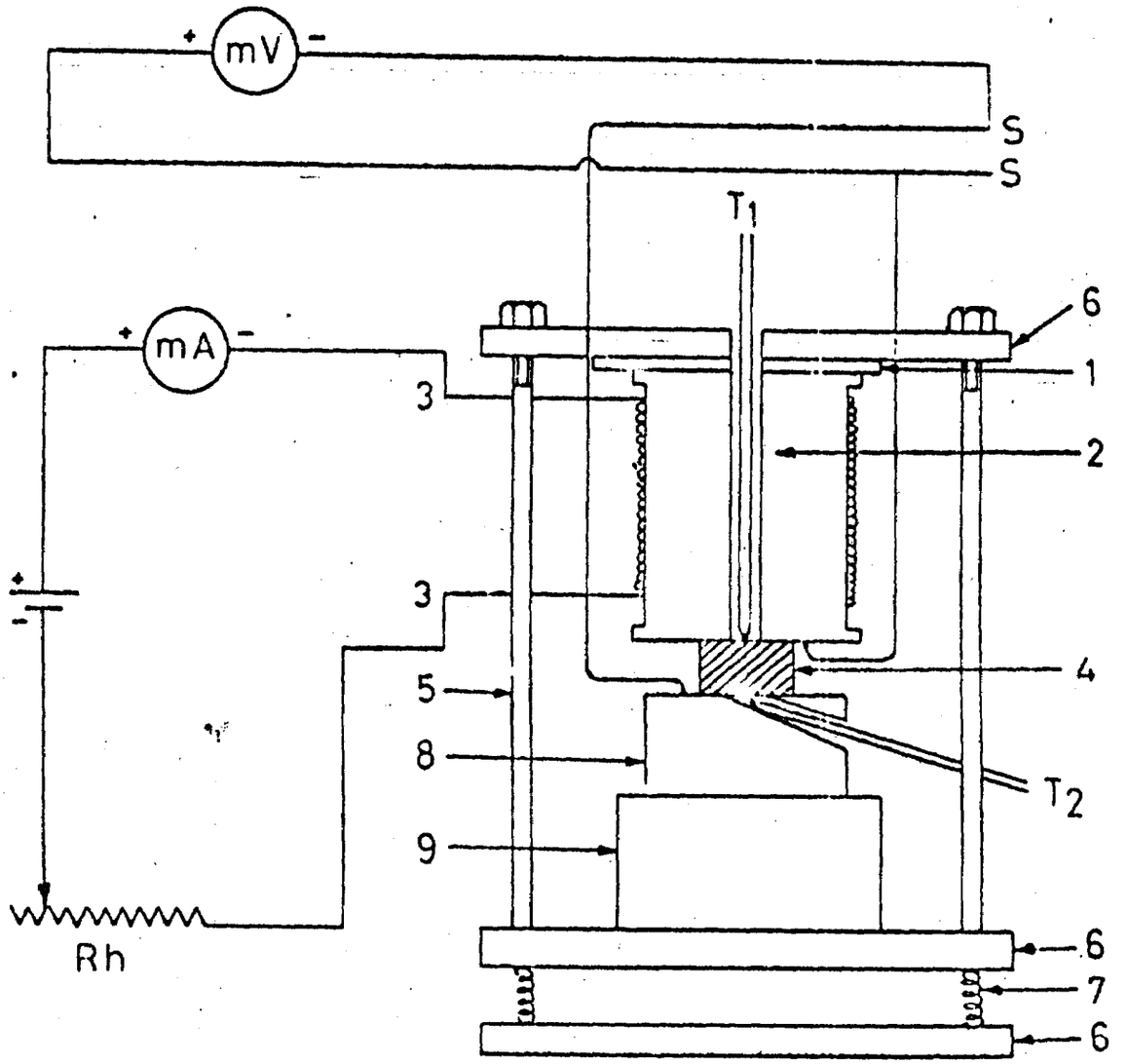
in $BaTiO_3$. Jesse (5) observed the seebeck effect in α-Nb_2O_5 . Saburi (6) studied the thermoelectric emf. variation with temperature in doped $BaTiO_3$.

6.2 Experimental

The experimental set up used in the present investigation for the study of the thermoelectric emf. by potassium niobate and the ferroelectric systems $K(Ni_x\ Fe_y\ Nb_z)O_3$, is schematically shown in Fig.6.1. The experimental set-up consists of a typical sample holder which is made of two cylindrical metal electrodes, an electrically heated furnace, a millivolt meter (Philips-P.P 9004 X) for measurement of voltage across the sample and a digtal multimeter.

6.3 Thermoelectric emf. of $KNbO_3$ and $K(Ni_x\ Fe_y\ Nb_z)O_3$ system :

The sintered pellet of above specified compositions was placed in between the two cylindrical metal electrods. By passing A.C. current through axillary heating coil the temperature difference across the pellet was maintained constant at about 25°C. The arrangement of pellet between electrodes was placed in the furnace. The measurements were carried out at different temperatures. The voltages data was next used to calculate thermoelectric power. The temperature variation of thermoelectric power for $KNbO_3$, $K(Ni_{0.02}\ Fe_{0.02}\ Nb_{0.96})O_3$, $K(Ni_{0.05}\ Fe_{0.05}\ Nb_{0.90})O_3$,



[1-Mion sheet; 2,8-Hard metal electrods, 3-Sub heater leads; 4-Sample pellet; 5-Metal rod; 6-Metal plates; 7-Spring; 9-Metal block; T_1 T_2 - Thermocuples; S- Silver wires welded at Ag electrods.]

Fig. 6·1 - Experimental set-up for the measurement of thermoelectric power.

$K(Ni_{0.10}\ Fe_{0.10}\ Nb_{0.80})O_3$ and $K(Ni_{0.15}\ Fe_{0.15}\ Nb_{0.70})O_3$ is shown in Fig.6.2 to 6.6.

6.4 Results and Discussion

Fig.6.2 to 6.6 show temperature variation of seebeck coefficient α for the potassium niobate and for the system $K(Ni_x\ Fe_y\ Nb_z)O_3$. The following observations have been made from the data of the Fig.6.2 to 6.6.

(1) For potassium niobate the seebeck coefficient is negative indicating that the majority carriers are electrons i.e. the material is an n-type semiconductor which is quite consistent with the report of Srivastava et al (7). It should be noted that in $KNbO_3$ at $498^{\circ}k$ there occurs a transition between two ferroelectric phases, whereas at $685^{\circ}k$ there occurs a transition from a ferroelectric phase to a paraelectric phase. This result is also found to be consistance with the report by Handerek et al (8). The Table 6.1. lists the temperature at which the seebeck cofficoent changes in its sign i.e. to be regarded as a the transition temperature.

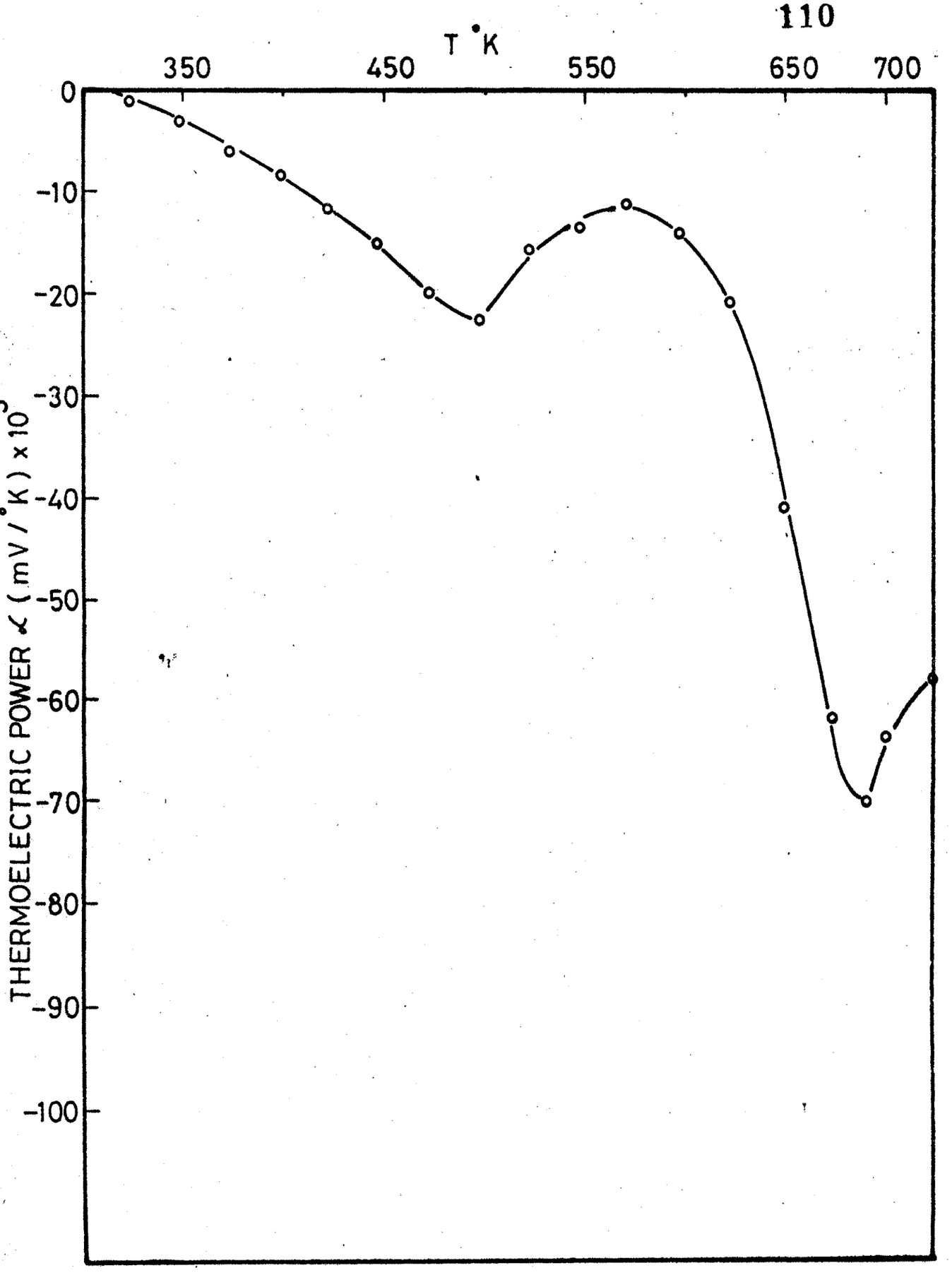


Fig. 6·2: THE VARIATION OF THERMOELECTRIC POWER WITH TEMPERATURE IN $KNbO_3$.

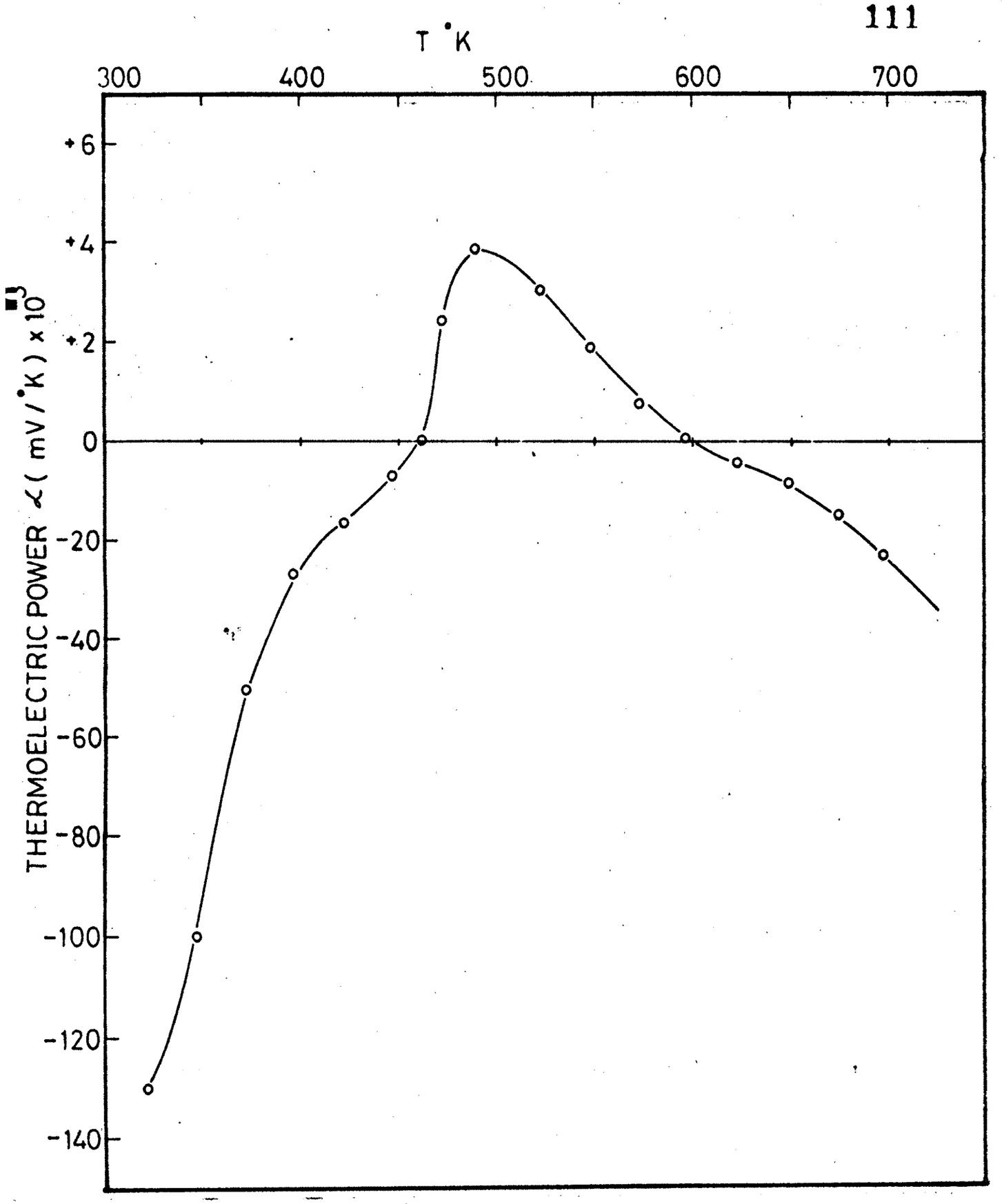


Fig. 6·3: THE VARIATION OF THERMOELECTRIC POWER WITH TEMPERATURE IN K $(Ni_{0.02}Fe_{0.02}Nb_{0.96})O_3$.

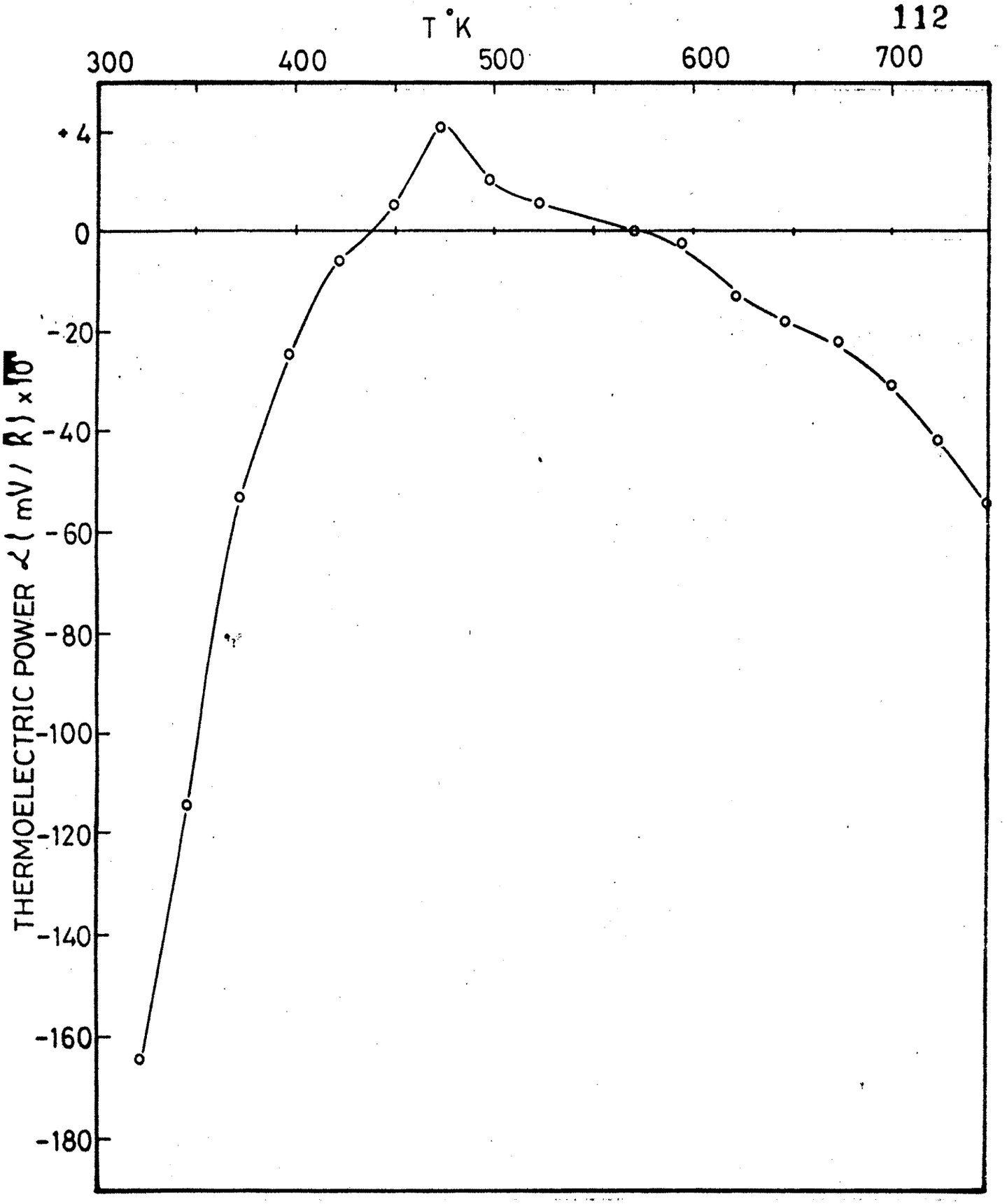


Fig. 6·4: THE VARIATION OF THERMOELECTRIC POWER WITH TEMPERATURE IN K ($Ni_{0.05}$ $Fe_{0.05}$ $Nb_{0.90}$) O_3 .

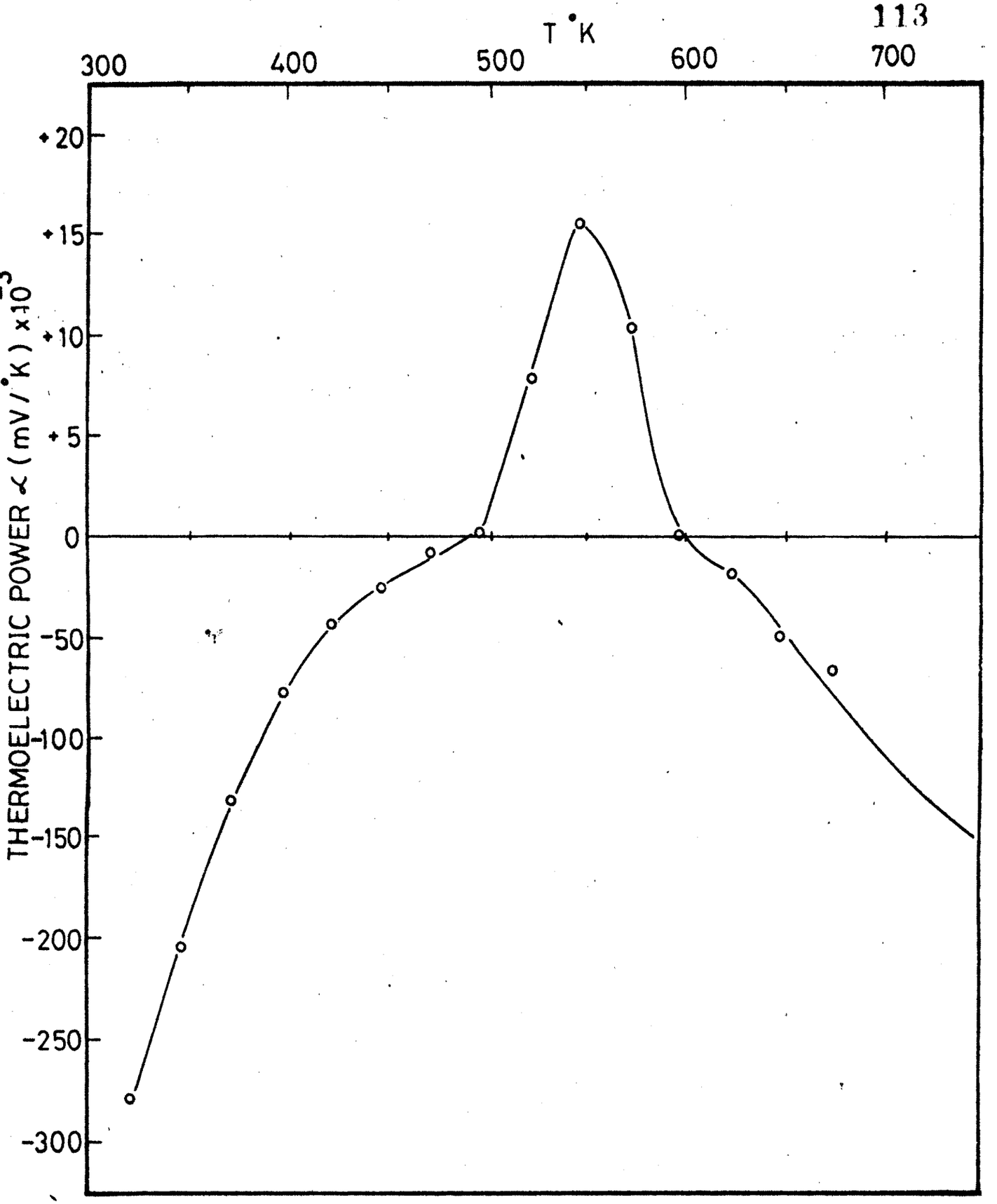


Fig.6·5: THE VARIATION OF THERMOELECTRIC POWER WITH TEMPERATURE IN K ($Ni_{0.10}Fe_{0.10}Nb_{0.80})O_3$.

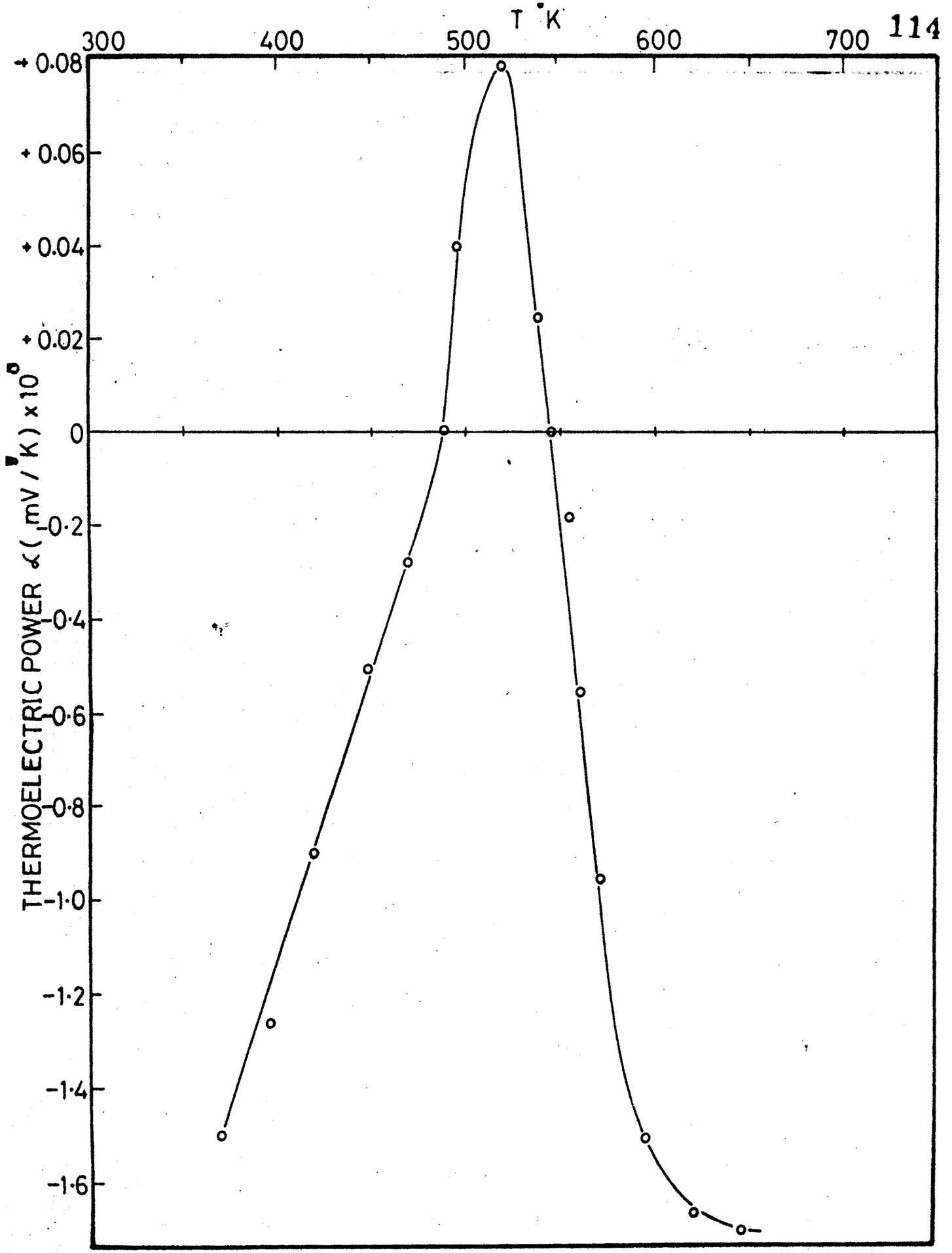


Fig.6·6: THE VARIATION OF THERMOELECTRIC POWER WITH TEMPERATURE IN $K(Ni_{0.15}Fe_{0.15}Nb_{0.70})O_3$.

6.1 Transition and Peak Temperatures

Sample	Transition temperature		Peak temperature	
(1) $KNbO_3$	-		498°k	685°k
(2) $K(Ni_{0.01}\ Fe_{0.01}\ Nb_{.98})O_3$	460°k	598°k	485°k	
(3) $K(Ni_{0.05}\ Fe_{0.05}\ Nb_{0.90})O_3$	435°k	573°k	473°k	
(4) $K(Ni_{0.1}\ Fe_{0.10}\ Nb_{.80})O_3$	498°k	598°k	548°k	
(5) $K(Ni_{0.15}\ Fe_{0.15}\ Nb_{0.70})O_3$	498°k	548°k	523°k	

Thus it is seen that with the addition of impurities in the system the transition temperature decreases.

Above the transition temperature the samples exhibit a p-type of semiconducting behaviour, except for the ferroelectric $KNbO_3$, which has only a negative value of α.

(2) Peaks of α-values are observed during the n-type conduction and p-type conduction. These peak temperature data is also listed in Table 6.1. It is seen that as the impurities concentration increases the value of the peak temperature decreases.

The fact that α-varies with temperature and shows peak occurrence indicates that the changes in charge carrier concentration reflects the significant role of these on the nature of conductivity temperature variation. Below the peak temperature it can be safely assumed that the conduction is

the sum of two types of conductivities.

i.e. $$\sigma = \sigma_n + \sigma_i \qquad (6.1)$$

Where σ_n is the free electric conductivity σ_i is the impurity conductivity and σ the total conductivity.

According to Bosman and Crevecour (9) and Dutt et al (10) the following expression is valid for a description of in thermoelectric-power;

$$\alpha = -\frac{k}{e}\left[\frac{\sigma_n}{\sigma}\left(\frac{E_F}{KT} + A\right) + \frac{\sigma_i}{\sigma}\left(\frac{E_D - E_F}{KT}\right)\right] \qquad (6.2)$$

Where E_F is the Fermi-level, A-term is related to the kinetic energy of free electrons, E_D-energy of donor with respect to transport level. From the theory of, partly compensated semiconductors it is known that at low temperature the mixed conduction occurs, where the electrons are supposedly the majority charge carriers. We have,

$$E_F = E_D + KT \ln\left(\frac{N_D - N_A}{N_A}\right) \qquad (6.3)$$

Where $N_D > N_A > 0$, N_A and N_D are the concentration of acceptor and donors respectively. At $T = 0$, $E_F = E_D$ as the temperature increases $E_F > E_D$ i.e. $F_F - E_D$ is positive. The first term in equation (6.3) dominates as long as $\sigma_i < \sigma < 1$ when the temperature is increased the thermoelectric power first increases with increasing temperature. However, as soon as σ_i becomes comparable with σ_n the first term in

equation (6.3) decreases while the second term increases positively. This explains why the peak in α-T variation occurs in the negative region of the ordinates.

For the samples which exhibit the peaks subsequent to transition from n to p-type, the following explanation usually offered is found to hold good. Below the peak temperature the conduction due to impurity conduction (σ_i) and free hole conduction (σ_p) add up to

$$\sigma = \sigma_p + \sigma_i. \tag{6.4}$$

The expression for α-T variation will then be

$$\alpha = -\frac{k}{e}\left[\frac{\sigma_p}{\sigma}\left(\frac{E_F}{KT} + A\right) + \frac{\sigma_i}{\sigma}\left(\frac{E_F - E_A}{KT}\right)\right] \tag{6.5}$$

The Fermi level is given by

$$E_F = E_A + KT \ln\left(\frac{N_A - N_D}{N_D}\right) \tag{6.6}$$

At T = 0, $E_F = E_A$ with increasing temperature $E_F - F_A$ becomes negative. Thus as long as $\sigma_i/\sigma << 1$. The first term in equation (6.5) governs the α-T variation i.e., α increases initially with decreasing T. When σ_i becomes comparable to σ_p the first term in equation (6.5) decreases while the second term increases lowering the value of α. This explains occurrence of a peak in α-T variation in the positive region.

In the region where conduction is by one type of carriers only say by holes, then α and E_F are related by

$$E_F = e\alpha T - AKT \qquad (6.7)$$

It is thus concluded significantly, in the present work, that these samples of $K(Ni_X\ Fe_Y\ Nb_Z)O_3$ (X=Y=0.02, 0.05, 0.10, .15) which show negative values of α upto transition temperature have more donor centres in comparison with the acceptor. At a certain temperature $\alpha = 0$. Basically α is created due to difference in the mobility of carriers or their densities. The fact that α becomes zero suggests that at the temperature of transition, whatever difference exists, either in the mobilities or the density of carriers, reduces to zero.

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