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Evaluation of Activation Energy from the Ionic Thermocurrent Spectrum

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An attempt is made to give a method for the determination of the activation energy of a monoenergetic ITC band. In the method described only the values of two characteristic temperatures of the ITC band are needed: the former T_M corresponding to the peak of the ITC band and the latter T_L ($< T_M$) a low temperature for which the value of the ionic thermocurrent is $I = I(T_M)/e^3$.

Es wird versucht, eine Methode zur Bestimmung der Aktivierungsenergie eines monoenergetischen ITC Bandes, zu geben. Bei der hier beschriebenen Methode sind nur die Werte zweier charakteristischer Temperaturen des ITC Bandes notwendig: die erste (T_M), die dem höchsten Wert des ITC Bandes entspricht und die zweite T_L ($< T_M$), die eine niedrige Temperatur ist, bei der der ionische Thermostrom den Wert $I = I(T_M)/e^3$ hat.

1. Introduction

The mechanism involved in the reorientation of impurity–vacancy (I–V) dipoles in a crystalline lattice is ascertained through dielectric relaxation studies. Out of various experimental techniques employed for this purpose, ionic thermocurrent (ITC) measurement [1] is preferred over the others particularly because of its convenience, sensitivity, and accuracy.

ITC, also known as thermally stimulated depolarization current (TSDC) measurement [2], has contributed substantially to a better understanding of the role of the dipolar imperfections.

In ITC measurements [1], the sample is polarized by applying an electric field (E_p) at some suitable polarization temperature (T_p) for a time long compared to the relaxation time at T_p. With the electric field still on, the sample is rapidly cooled down to a fairly low temperature, the relaxation time is practically infinite, and the polarized dipoles are frozen-in in the crystalline lattice. The sample is then heated at a linear rate b, and the resulting depolarization current is recorded with the help of an electrometer. The depolarization current (I) observed in ITC measurements is similar to a thermoluminescence glow curve with a monomolecular kinetics which is expressed as [1]

$$I(T) = \frac{Q}{\tau_0} \exp\left(- \frac{E}{kT}\right) \exp\left[- \frac{1}{b\tau_0} \int_{T_0}^{T} \exp\left(- \frac{E}{kT'}\right) dT'\right], \tag{1}$$

where T_0 is the temperature at which the depolarization current starts to appear, τ_0 is the pre-exponential factor, E the activation energy for the orientation of I–V dipoles, and k the Boltzmann constant. Q in (1) represents the total charge released in ITC measurements which depends on such polarization. The maximum depolariza-

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tion thermocurrent I_M appears at a temperature T_M according to

$$T_M = \left(\frac{bE\tau_M}{k}\right)^{1/2},\tag{2}$$

where τ_M is the relaxation time at T_M. The temperature dependence of the relaxation time (τ) is given by the Arrhenius relation

$$\tau = \tau_0 \exp (E/kT).\tag{3}$$

2. Methods to Evaluate the Relaxation Parameters

We shall describe some classical methods for the determination of the relaxation parameters.

In (1) the first exponential dominates in the low-temperature range of the ITC spectrum and is responsible for the initial increase of the current, whereas the second exponential dominates in the high-temperature range and is responsible for slowing down the current rise. Thus, the initial rise of the current will be controlled through the equation

$$I = \frac{Q}{\tau_0} \exp (-E/kT) .\tag{4}$$

Equation (4) has been estimated [3, 4] to be valid with a satisfactory approximation in the temperature range between T_0 and $T^*(T^* > T_0)$, where T^* is that temperature for which $I(T^*) = I_M/10$.

Equation (4) can further be rearranged as

$$\ln I(T) = \ln \left(\frac{Q}{\tau_0}\right) - \frac{E}{kT}.\tag{5}$$

Thus, $\ln I$ plotted against $1/T$ should give a straight line. The slope in turn gives the value of E. Evaluation of E following (5) is known as initial rise method. In this method, the dielectric relaxation parameters are determined essentially from that part of the ITC spectrum where the uncertainty in the background current is important. Thus, this method is not that accurate, but serves as a convenient procedure for roughly estimating the activation energy.

The BFG method has the advantage of using the data of the whole ITC curve as

$$\tau(T) = \frac{\int\limits_{t}^{\infty} I(t)\, dt}{I(T)} .\tag{6}$$

For recording the depolarization current (I), the sample is heated at a linear heating rate b according to the scheme

$$T = T_0 + bt .\tag{7}$$

With the help of (6) and (7) one gets

$$\tau(T) = \frac{\dfrac{1}{b} \int\limits_{t}^{\infty} I(t)\, dt}{I(T)} .\tag{8}$$

Obviously, τ at different temperatures can be evaluated by graphical integration either of the whole ITC curve using (6) when I is plotted as a function of t, or of the whole ITC spectrum using (8) when I is plotted as a function of T. τ thus evaluated with the help of (8) gives the values of E and τ_0 in conjunction with (3). A straight line plot of $\ln \tau$ against $1/T$ is commonly referred to as BFG plot.

Another method for the determination of the parameters E and τ_0 is to minimize the difference between the experimental and theoretical normalized curves,

$$\varepsilon = \frac{\sum_{i=1}^{n} (I_{i,\exp} - I_{i,\mathrm{th}})^2}{n}, \tag{9}$$

where n is the number of experimental measurements. In both cases the theoretical curve for the best fitting is calculated. Finally, other methods have also been proposed [5, 6].

3. Suggestion for the Determination of the Parameter E

The integral appearing in (1) cannot be solved. Replacing E/kT by x, one can develop [7]

$$\int_{T_0}^{T} \exp\left(-E/kT\right) \mathrm{d}T = -\frac{E}{k} \int_{T_0}^{T} \frac{\exp\left(-x\right)}{x^2} \mathrm{d}x =$$

$$= -\frac{E}{k}\left[-\frac{\exp\left(-x\right)}{x^2}\left(1 - \frac{2!}{x} + \frac{3!}{x^2} - \frac{4!}{x^3} + \ldots\right)\right]. \tag{10}$$

If we call

$$F(x) = 1 - \frac{2!}{x} + \frac{3!}{x^2} - \frac{4!}{x^3} + \ldots, \tag{11}$$

then (10) becomes

$$\int_{T_0}^{T} \exp\left(-\frac{E}{kT}\right) \mathrm{d}T = \frac{E}{k} \frac{\exp\left(-x\right)}{x^2} F(x). \tag{12}$$

With the help of (12) and (3) one can rearrange (11) as

$$I(T) = \frac{Q}{t} \exp\left[-\frac{1}{b\tau_0}\frac{kT^2}{E} \exp\left(-\frac{E}{kT}\right) F(x)\right].$$

The maximum depolarization thermocurrent I_{M} can thus be expressed as

$$I_{\mathrm{M}} = \frac{Q}{\tau_{\mathrm{M}}} \exp\left[-\frac{kT_{\mathrm{M}}^2}{bE\tau_{\mathrm{M}}} F(x_{\mathrm{M}})\right], \tag{14}$$

where $x_{\mathrm{M}} = E/kT_{\mathrm{M}}$ and τ_{M} is the relaxation time at T_{M}, which in conjunction with (2) yields

$$I(T_{\mathrm{M}}) = \frac{Q}{\tau_{\mathrm{M}}} \exp\left[-F(x_{\mathrm{M}})\right] = \frac{Q}{\tau_0} \exp\left[-x_{\mathrm{M}} - F(x_{\mathrm{M}})\right]. \tag{15}$$

We denote arbitrarily a low temperature T_L ($T_L < T_M$) such that

$$I(T_L) = I(T_M) \exp(-3) .$$ (16)

The selection of temperature T_L was made so, that the corresponding value $I(T_L)$ can be defined by (4) i.e.

$$I(T_L) = \frac{Q}{\tau_0} \exp(-x_L) ,$$ (17)

where $x_L = E/kT_L$.

By combining (15) and (16) one gets

$$x_L = x_M + 3 + F(x_M) .$$ (18)

Thus, if (18) is used, one finally gets to the following relation for energy E:

$$E = \frac{kT_M T_L[3 + F(x_M)]}{T_M - T_L} .$$ (19)

The majority of the systems that produce monoenergetic ITC bands are characterized by values of the quantity x_M ranging between 25 and 40 [6]. For these values of x_M,

Table 1
Values of the activation energy in various systems

system	reported E (eV)	calculated after (20) E (eV)	ref.
$NaCl:Eu^{+2}$	0.58 ± 0.01	0.58	[8]
$NaI:Ca^{+2}$	0.594 ± 0.005	0.59	[9]
$NaBr:Eu^{+2}$	0.33 ± 0.02	0.35	[8]
$NaF:Ca^{+2}$	0.86 ± 0.02	0.85	[10]
$:Mg^{+2a})$	0.83 ± 0.01	0.83	[11]
$KI:Eu^{+2}$	0.46 ± 0.02	0.47	[8]
$:Se^{-2b})$	0.62	0.63	[12]
$KBr:Eu^{+2}$	0.54 ± 0.01	0.56	[8]
$:NCS^-$	0.108	0.11	[13]
$KCl:NCS^-$	0.137	0.14	[13]
$LiF:Co^{+2}$	0.59	0.58	[14]
$:Mg^{+2}$	0.64	0.65	[15]
$LiH:Ca^{+2c})$	0.42 ± 0.01	0.42	[16]
$LiH:Mg^{+2c})$	0.38 ± 0.01	0.39	[16]
$CaF_2:Gd^{+3}$	0.377	0.38	[17]
$:Ho^{+3c})$	0.38 ± 0.01	0.38	[3]
$:Ho^{+3d})$	0.63 ± 0.01	0.63	[3]
$SrF_2:Na^+$	0.473	0.48	[18]
$:Ce^{+3}$	0.48	0.47	[19]
$AgCl:Pb^{+2}$	0.333	0.34	[20]

[a]) The band that is responsible for the reorientation of nnn dipoles after the clearing technique.
[b]) Concerns the a-band.
[c]) nn dipoles.
[d]) nnn dipoles.

the function $F(x_M)$ takes values between 0.928 and 0.953 [6]. Thus, one may estimate a constant mean value for $F(x) = 0.94$. Then, (19) can be simplified to the following expression:

$$E = \frac{3.94\, kT_L T_M}{T_M - T_L}.$$

(20)

In (20) Boltzmann's constant has the value $k = 1/11609$ eV/K.

Finally, we took into account a set of ITC bands from various systems and we applied (20) in order to determine the value of the activation energy E. The results of the determination of E on the basis of (20) as well as the results that have been reported can be compared in Table 1.

The error in the calculation of the activation energy on the basis of (20) is mainly due to the inaccuracy of determination of the temperatures T_M and T_L from the ITC band. It has been estimated that if the error in the determination of the above temperatures is within ± 1 K, then the corresponding error in the calculation of E is $\pm 3\%$. As far as the approximating value of the function $F(x_M) \approx 0.94$ is concerned, its effect on the calculation of E is negligible.

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