COMMENTS ON THE ASYMMETRY OF THE IONIC THERMOCURRENT BAND

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Summary

In a monoenergetic ionic thermocurrent (ITC) band, the area S_1 of the part of the band to the left of the peak (for $T < T_M$) and the area S_2 to the right of the peak (for $T > T_M$) have a ratio $a = S_1/S_2$ that is related to the quantity $x = E/kT_M$, where E is the activation energy and T_M is the temperature corresponding to the peak. In this paper the function $a(x)$ is found and an approximating expression is formed with the method of computer fitting.

The mechanism involved in the reorientation of impurity–vacancy (I–V) dipoles in a crystalline lattice is ascertained through dielectric relaxation studies. Among the 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.

For simple non-interacting dipoles involving a single relaxation mechanism, a single ITC peak is obtained. In ITC measurements the sample is polarized by applying an electric field (E_p) at some suitable polarization temperature (T_p) for a long time 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 at which the electric field is switched off. At such a 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 ionic thermocurrent is recorded with the help of an electrometer.

Under these conditions the time dependence of the polarization $P(t)$ can be described with first-order monoenergetic equations:

$$\frac{\mathrm{d}P(t)}{\mathrm{d}t} = -\frac{P(t)}{\tau} \tag{1}$$

where τ is a temperature parameter, i.e. $\tau = \tau(T)$ is the relaxation time for the I–V dipoles. We may represent the temperature variation of τ by the Arrhenius-type equation

$$\tau(T) = \tau_0 \exp(E/kT) \tag{2}$$

where τ_0^{-1} is the characteristic frequency factor for a vacancy jump from one lattice site to another for orientation of the I–V dipole and is independent of temperature; E is the activation energy.

Equation (1) is a differential equation, the isothermal solution of which is

$$P(t) = P(0) \exp(-t/\tau) \tag{3}$$

where $P(0)$ is the "frozen-in" polarization at $t = 0$.

Assuming a linearly increasing temperature, starting from a low value T_0 at which ITC begins to appear, at a rate b (i.e. $T = T_0 + bt$), the non-isothermal solution of eqn. (1) is

$$P(t) = P(T_0) \exp\left(-\int_0^t \frac{\mathrm{d}t}{\tau(T)}\right) \tag{4}$$

Taking into account eqn. (2)

$$P(T) = P(T_0) \exp\left[-\frac{1}{b\tau_0} \int_{T_0}^T \exp\left(-\frac{E}{kT'}\right)\mathrm{d}T'\right] \tag{5}$$

The corresponding expression for the polarization at $T = T_\mathrm{M}$, where the ionic thermocurrent attains its greatest value, is given by:

$$P(T_\mathrm{M}) = P(T_0) \exp\left[-\frac{1}{b\tau_0} \int_{T_0}^{T_\mathrm{M}} \exp\left(-\frac{E}{kT}\right)\mathrm{d}T\right] \tag{6}$$

The integral appearing in eqn. (6) cannot be solved without approximation. After replacing (E/kT_M) by x, the integral can be expressed [3] as:

$$\int_{T_0}^{T_\mathrm{M}} \exp\left(-\frac{E}{kT}\right)\mathrm{d}T = \int_0^{T_\mathrm{M}} \exp\left(-\frac{E}{kT}\right)\mathrm{d}T = -\frac{E}{k}\int \frac{e^{-x}}{x^2}\,\mathrm{d}x$$

$$= \frac{E}{k}\left[\frac{e^{-x}}{x^2}\left(1 - \frac{2!}{x} + \frac{3!}{x^2} - \frac{4!}{x^3} + \frac{5!}{x^4} - \cdots\right)\right] \tag{7}$$

For a temperature T_M we have:

$$T_M = (bE\tau_M/k)^{1/2} \tag{8}$$

where τ_M is the relaxation time at T_M. By substituting the quantity x in eqn. (8) we have:

$$\frac{1}{x^2} = \frac{k}{E} b\tau_0\, e^x \quad \text{or} \quad \frac{e^{-x}}{x^2} = \frac{kb\tau_0}{E} \tag{9}$$

Combining eqns. (6), (7) and (9) we have:

$$P(T_M) = P(T_0)\, \exp\left[-\left(1 - \frac{2!}{x} + \frac{3!}{x^2} - \frac{4!}{x^3} + \frac{5!}{x^4} - \cdots \right) \right] \tag{10}$$

It is known that the polarization decay is proportional to the integral $\int_T^{T_T} I(T)\, dT$, which is equivalent to the shaded area of the ITC band from temperature T to T_T in Fig. 1.

If we define

$$S_2 = \int_{T_M}^{T_T} I(T)\mathrm{d}T, \qquad S_{\text{tot}} = \int_{T_0}^{T_T} I(T)\mathrm{d}T \quad \text{and} \quad S_1 = S_{\text{tot}} - S_2$$

then the ratio $a = S_1/S_2$ characterizes the asymmetry of an ITC band (Fig. 2).

On the basis of the above, the ratio a must be

$$a = \frac{S_1}{S_2} = \frac{P(T_0) - P(T_M)}{P(T_M)} = \frac{P(T_0)}{P(T_M)} - 1$$

and finally, taking into account eqn. (10) we conclude:

Fig. 1. The shaded area in the ITC band is proportional to the polarization decay $P(T)$.

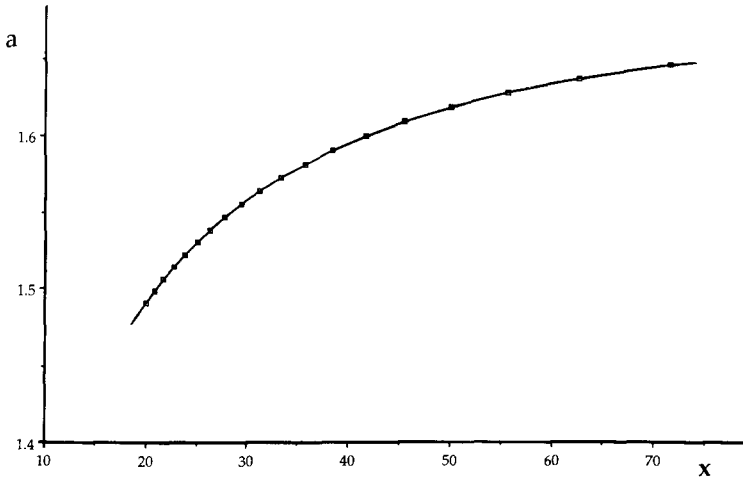Fig. 2. The ratio of the shaded areas S_1 and S_2 is used to describe the asymmetry of the ITC band.

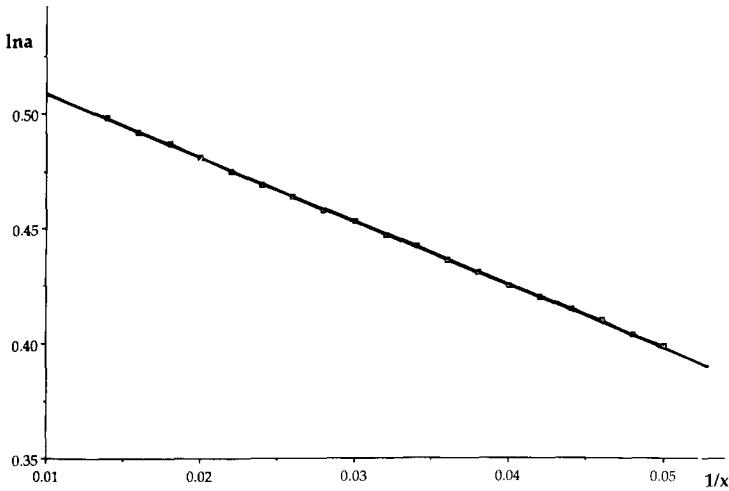Fig. 3. The ratio $a = S_1/S_2$ as a function of the quantity $x = E/kT_M$.

Fig. 4. Plot of computer fitting using the least-squares method applied to values of ln a versus 1/x.

$$a = \exp\left(1 - \frac{2!}{x} + \frac{3!}{x^2} - \frac{4!}{x^3} + \frac{5!}{x^4} - ...\right) - 1$$

$$= \exp\left\{\sum_{n=0}^{\infty}(-1)^n(n+1)!x^{-n}\right\} - 1 \tag{11}$$

Using eqn. (11) the value of a was calculated for various values of the quan-

TABLE 1

Values of the ratio a given through eqns. (11) and (13) for various values of x

x	a eqn. (11)[a]	a eqn. (13)
20	1.491	1.490
25	1.530	1.531
30	1.558	1.560
35	1.579	1.581
40	1.595	1.596
45	1.607	1.608
50	1.618	1.618
55	1.626	1.626
60	1.633	1.633
65	1.639	1.639
70	1.644	1.644

[a]Terms up to 6th order were used.

tity x ($20 \leqslant x \leqslant 70$) (because it is between these limits that the values of x may fluctuate). According to the diagram $a = f(x)$ (Fig. 3) a small but obvious dependence of a on the quantity x was observed. For values of x between 20 and 70 the ratio a takes on values between 1.49 and 1.65 respectively.

On the other hand, in the diagram $\ln a = f(1/x)$, it is observed that the graph approximates a straight line with a correlation factor $R = 1$ (Fig. 4). More precisely, with the least-squares method it was found that

$$\ln a = 0.536 - 2.75/x \tag{12}$$

Thus, eqn. (11) may take the following approximate, simple expression:

$$a = 1.71 \exp(-2.75/x) \tag{13}$$

It should be noted that the factor 1.71 in eqn. (13) approximates the value $e - 1$ (1.718) because for very large values of x, if we ignore the terms of first order and greater in eqn. (11) we shall get $a \approx e - 1$.

Finally, in Table 1 the values of a calculated by eqns. (11) and (13) are compared for various values of x.

References

1   C. Bucci, R. Fieschi and G. Guidi, Phys. Rev., 148 (1966) 816.
2   J. van Turnhout, in: G.M. Sessler (Ed.), Electrets, (Topics in Applied Physics, Vol. 33), Springer, Berlin, 1979, Chap. 3, p. 81.
3   J. Vanderschueren and J. Gasiot, in: P. Bräunlich (Ed.), Thermally Stimulated Relaxation in Solids, (Topics in Applied Physics, Vol. 37), Springer, Berlin, 1979, Chap. 3, p. 149.