The polarization efficiency of the thermal sampling technique in thermally stimulated depolarization current measurements

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ABSTRACT

In this work, the polarization efficiency is examined for the technique of thermal sampling used in thermally stimulated depolarization current measurements, for the case where a very narrow temperature polarization window is used at the polarization temperature of T_p. It is found that this has appreciable values only along a straight line in the $E-\ln\tau_0$ plane. The selectivity of the method is expressed by the widths $\Delta E \approx 3kT_p$ and $\Delta\ln\tau_0 \approx 3$ of the distributions of the E and $\ln\tau_0$ values of the dipoles polarized by thermal sampling. A possible interpretation is also offered of the phenomenon known as compensation law, based on the selectivity characteristics of the thermal sampling technique examined in this work.

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1. Introduction

The method of thermal sampling, or fractional polarization, is used in TSDC measurements, in order to isolate peaks within narrow ranges of activation energies E and pre-exponential time constants τ_0, in samples where these parameters are distributed (see e.g. [1,2]). In the present work, an expression is derived for the effective fraction of dipoles polarized, as a function of the distributed parameters E and τ_0. The selectivity of the method is also determined, showing the range of E and τ_0 values in the dipoles polarized by a thermal sampling run. Based on the theoretical results for the selectivity of the method, a possible interpretation will be offered of the experimentally observed effect known as "compensation law". This interpretation reinforces the opinion that the effect is due to the measurement technique rather than to the molecular structure of the materials studied.

2. The polarization efficiency during the thermal sampling procedure

We consider a single relaxation mechanism, characterized by activation energy E and pre-exponential time constant τ_0. The relaxation time for this mechanism at an absolute temperature T is given by the Arrhenius expression

$$\tau(T) = \tau_0 \exp\left(\frac{E}{kT}\right), \tag{1}$$

where k is Boltzmann's constant. If a sample is being polarized in an electric field of intensity F, its polarization density at time t, $P(t)$, satisfies the Debye equation (see e.g. [3,4])

$$\frac{dP}{dt} = \frac{P_e - P}{\tau}, \tag{2}$$

with

$$P_e = \frac{\gamma\kappa F p^2 N}{kT}, \tag{3}$$

where γ is a geometrical factor, equal to 1/3 for free rotating dipoles, κF is the local electric field at the position of the dipoles, p is the dipole moment of the dipoles and N their concentration. P_e is the *equilibrium polarization density* and is the value reached with field F at temperature T after a very long time.

If the polarization density is initially equal to zero, at time t it will be, according to Eq. (2),

$$P(t) = \exp\left(-\int_0^t \frac{dt}{\tau}\right)\int_0^t \frac{P_e}{\tau}\exp\left(\int_0^t \frac{dt}{\tau}\right)dt. \tag{4}$$

Eq. (4) can be integrated if $T(t)$ and $F(t)$ are given.

We will assume a constant cooling rate $-dT/dt = q$, and that a constant electric field is applied at $t = 0$, when the temperature is T_0. We define $\alpha \equiv E/kq\tau_0$, and change the variable to $\varepsilon = E/kT$,

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which at $T = T_0$ has the value of $\varepsilon_0 = E/kT_0$. Then, for as long as the field F is applied

$$\int_0^t \frac{dt}{\tau} = \alpha \int_{\varepsilon_0}^{\varepsilon} \frac{e^{-\varepsilon}}{\varepsilon^2} d\varepsilon = \alpha \int_{\varepsilon_0}^{\infty} \frac{e^{-\varepsilon}}{\varepsilon^2} d\varepsilon - \alpha \int_{\varepsilon}^{\infty} \frac{e^{-\varepsilon}}{\varepsilon^2} d\varepsilon = \alpha \left[\frac{E_2(\varepsilon_0)}{\varepsilon_0} - \frac{E_2(\varepsilon)}{\varepsilon} \right],$$ (5)

in terms of the *second exponential integral*, a transcendental function defined by (see e.g. [5])

$$E_2(\varepsilon) \equiv \varepsilon \int_{\varepsilon}^{\infty} \frac{e^{-z}}{z^2} dz.$$ (6)

A rational approximation for this function, which is widely used in this work, is [5,6]

$$e^{\varepsilon} E_2(\varepsilon) = \frac{0.99997\varepsilon + 3.03962}{\varepsilon^2 + 5.03637\varepsilon + 4.19160} + \Delta(\varepsilon),$$ (7)

where $|\Delta(\varepsilon)| < 10^{-7}$ for $\varepsilon \geq 10$.

Using Eq. (5) in Eq. (4), the latter becomes

$$P(\varepsilon) = \frac{\gamma\kappa Fp^2 N}{kq\tau_0} \exp\left[\frac{\alpha}{\varepsilon} E_2(\varepsilon)\right] \int_{\varepsilon_0}^{\varepsilon} \frac{d\varepsilon}{\varepsilon} \exp\left[-\varepsilon - \frac{\alpha}{\varepsilon} E_2(\varepsilon)\right].$$ (8)

This expression can be used for particular cooling schemes [7].

If the sample is cooled down to very low temperatures, the exponential outside the integral in Eq. (8), which does not depend on the electric field, becomes unity, and

$$P(\varepsilon) = \frac{\gamma\kappa Fp^2 N}{kq\tau_0} \int_{\varepsilon_0}^{\varepsilon} \frac{d\varepsilon}{\varepsilon} \exp\left[-\varepsilon - \frac{\alpha}{\varepsilon} E_2(\varepsilon)\right].$$ (9)

In thermal sampling, if the field is applied at $t = t_1 = 0$, when the temperature of the sample is T_{p1}, corresponding to $\varepsilon_{p1} = E/kT_{p1}$, and removed at $t = t_2$, when the temperature of the sample is T_{p2}, corresponding to $\varepsilon_{p2} = E/kT_{p2}$ (Fig. 1), the integration in Eq. (9) must be between ε_{p1} and ε_{p2}, and the final polarization density is

$$P_0 = \frac{\gamma\kappa Fp^2 N}{kq\tau_0} \int_{\varepsilon_{p1}}^{\varepsilon_{p2}} \frac{d\varepsilon}{\varepsilon} \exp\left[-\varepsilon - \frac{\alpha}{\varepsilon} E_2(\varepsilon)\right].$$ (10)

We can express the *polarization efficiency* [8], defined as the effective fraction of dipoles which have been polarized,

$$\eta \equiv \frac{P_0}{pN},$$ (11)

as

$$\eta = \frac{\gamma\kappa Fp}{kq\tau_0} \int_{\varepsilon_{p1}}^{\varepsilon_{p2}} \frac{d\varepsilon}{\varepsilon} \exp\left[-\varepsilon - \frac{\alpha}{\varepsilon} E_2(\varepsilon)\right],$$ (12)

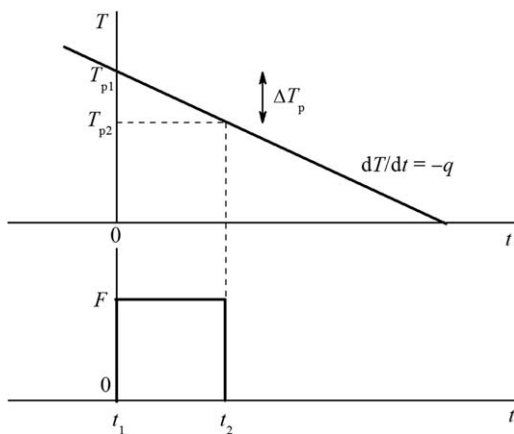**Fig. 1.** The mode of variation of the temperature T and the polarizing electric field F with time t, commonly used in the technique of thermal sampling.

which we may write explicitly as

$$\eta = \frac{\gamma\kappa Fp}{kq\tau_0} \int_{T_{p2}}^{T_{p1}} \frac{dT}{T} \exp\left[-\frac{E}{kT} - \frac{T}{q\tau_0} E_2\left(\frac{E}{kT}\right)\right].$$ (13)

We will limit our arguments to the case of a very narrow *polarization window* $\Delta T_p = T_{p1} - T_{p2}$. In this case, we can take $T_{p1} \approx T_{p2} = T_p$ and the integrand in Eq. (13) remains approximately constant, having its value at T_p. In the limit of a *delta-function polarization window*, the polarization window is narrowed while the strength of the electric field is increased, so that the product $F\Delta T_p$ remains constant. Eq. (13) can now be written as

$$\eta = \frac{\gamma\kappa Fp}{kq\tau_0} \frac{\Delta T_p}{T_p} \exp\left[-\frac{E}{kT_p} - \frac{T_p}{q\tau_0} E_2\left(\frac{E}{kT_p}\right)\right].$$ (14)

For a given narrow polarization window ΔT_p around T_p, the polarization efficiency η gives the effective fraction of dipoles having activation energy E and pre-exponential time constant τ_0, which have been polarized.

3. Numerical study of the polarization efficiency function

The polarization efficiency (14) can be expressed as

$$\eta = \frac{\gamma\kappa Fp}{k} \frac{\Delta T_p}{T_p^2} h,$$ (15)

where the *reduced polarization efficiency* h is a function of the dimensionless variables

$$\varepsilon_p \equiv \frac{E}{kT_p} \quad \text{and} \quad \lambda \equiv \frac{T_p}{q\tau_0},$$ (16)

defined as

$$h \equiv \lambda \exp[-\varepsilon_p - \lambda E_2(\varepsilon_p)].$$ (17)

For a given temperature of polarization T_p, the function h depends on the activation energy E and the pre-exponential time constant τ_0 of the polarized dipoles, through the corresponding variables ε_p and λ.

Fig. 2a shows plots of h as a function of $\ln \lambda$, for various values of ε_p. Asymmetrical bell-shaped peaks are seen, whose widths appear to be fairly constant, and whose heights appear to have a linear dependence on both ε_p and the values of $\ln \lambda_m$ at which their maxima occur. These indications can be verified by calculation, as shown in Figs. 2b–d.

Fig. 2b shows the linear dependence between the value ε_{pm} of ε_p at which h has maximum value and the value $\ln \lambda_m$ of $\ln \lambda$ at which this maximum occurs. The linearity is expressed by the equation $\ln \lambda_m = 2.39(6) + 1.033(2)\varepsilon_{pm}$, $(r = 0.99995)$. The number in parentheses gives the standard deviation of the number preceding the parentheses at the accuracy of the corresponding last figures [e.g. 2.39(6) stands for 2.39 ± 0.06]. The value of r given is the coefficient of correlation, showing how good the fit is to a straight line.

Fig. 2c shows the linear relationship between the maximum value h_m of h, and the value of ε_{pm} at which the maximum appears. The straight line fitted to this is given by $h_m = 0.686(3) + 0.3687(1)\varepsilon_{pm}$, $(r = 1.00000)$.

Fig. 2d shows the linear relationship between the maximum value h_m of h, and the value $\ln \lambda_m$ of $\ln \lambda$ at which the maximum appears. The straight line fitted to this is given by $h_m = -0.165(20) + 0.3570(5) \ln \lambda_m$, $(r = 0.99996)$.

A three-dimensional plot of h as a function of $\ln \lambda$ is given in Fig. 3 for various values of ε_p. It is seen that h has appreciable values only along and near a straight line on the $\varepsilon_p - \ln \lambda$ plane. The narrowness of this "ridge" shows the selectivity of the thermal sampling technique, a topic which will be examined below.
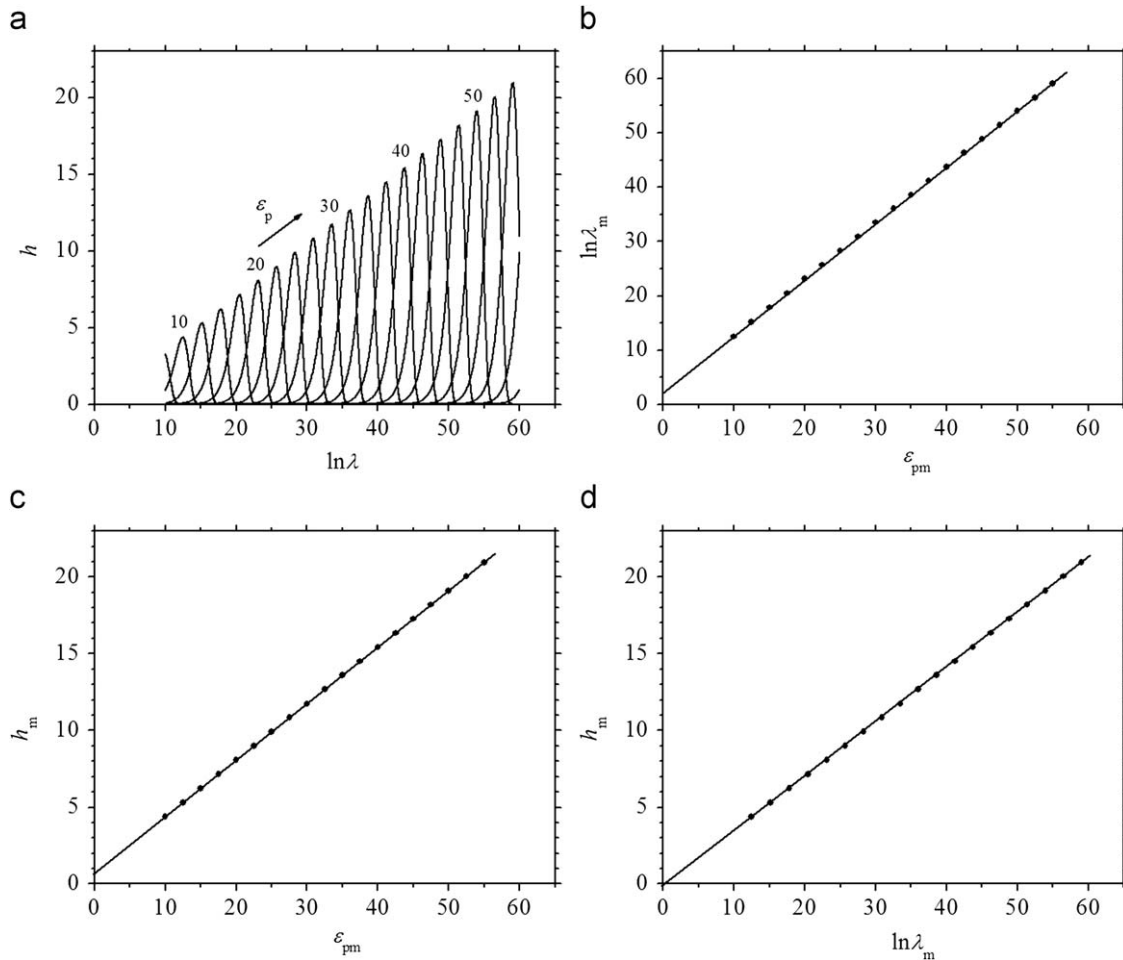
Fig. 2. (a) The dependence on $\ln \lambda$ of the polarization efficiency, as expressed by h, for various values of ε_p. (b) The values $\ln \lambda_m$ of $\ln \lambda$, for which h is maximum for a given ε_p equal to ε_{pm}, and the linear relationship between $\ln \lambda_m$ and ε_{pm}. (c) The linear relationship between the maximum value h_m of h, and the value of ε_{pm} at which the maximum appears. (d) The linear relationship between the maximum value h_m of h, and the value $\ln \lambda_m$ of $\ln \lambda$ at which the maximum appears.
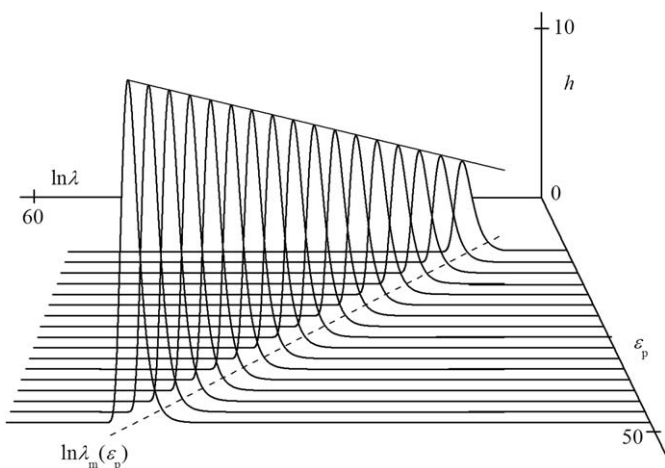

Fig. 3. Three-dimensional plot of the dependence on $\ln \lambda$ of the polarization efficiency, as expressed by h, for various values of ε_p. The sections of the h surface with the planes of constant ε_p produce the peaks shown.

Fig. 4a shows plots of h as a function of ε_p, for various values of λ. Similar linear relationships are seen to exist, as in the case of Fig. 2a.

Fig. 4b shows the values ε_{pm} of ε_p for which h is maximum for a given $\ln \lambda$, and the linear relationship between ε_{pm} and $\ln \lambda$. The

straight line fitted to this is given by $\varepsilon_{pm} = -2.04(6) + 0.960(2) \ln \lambda$, ($r = 0.99993$).

Fig. 4c shows the linear relationship between the maximum value h_m of h, and the value of $\ln \lambda$ at which the maximum appears. The straight line fitted to this is given by $h_m = -0.09(2) + 0.3545(6) \ln \lambda$, ($r = 0.99995$).

Fig. 4d shows the linear relationship between the maximum value h_m of h, and the value ε_{pm} of ε_p at which the maximum appears. The straight line fitted to this is given by $h_m = 0.664(4) + 0.3692(1)\varepsilon_{pm}$, ($r = 1.00000$).

Finally, a three-dimensional plot of h as a function of ε, for various values of λ is given in Fig. 5. Again, the selectivity of the thermal sampling technique is obvious.

4. The selectivity in $\ln \tau_0$ values, of the thermal sampling technique

Let us concentrate on a particular value of activation energy, E', and examine how η varies with τ_0. To find the maximum value of η for this particular energy, we examine

$$\frac{\partial \eta}{\partial \tau_0} = \frac{\gamma \kappa F p}{kq} \frac{\Delta T_p}{T_p} \left[-\frac{1}{\tau_0^2} + \frac{T_p}{q\tau_0^3} E_2\left(\frac{E'}{kT_p}\right) \right] \exp\left[-\frac{E'}{kT_p} - \frac{T_p}{q\tau_0} E_2\left(\frac{E'}{kT_p}\right) \right].$$
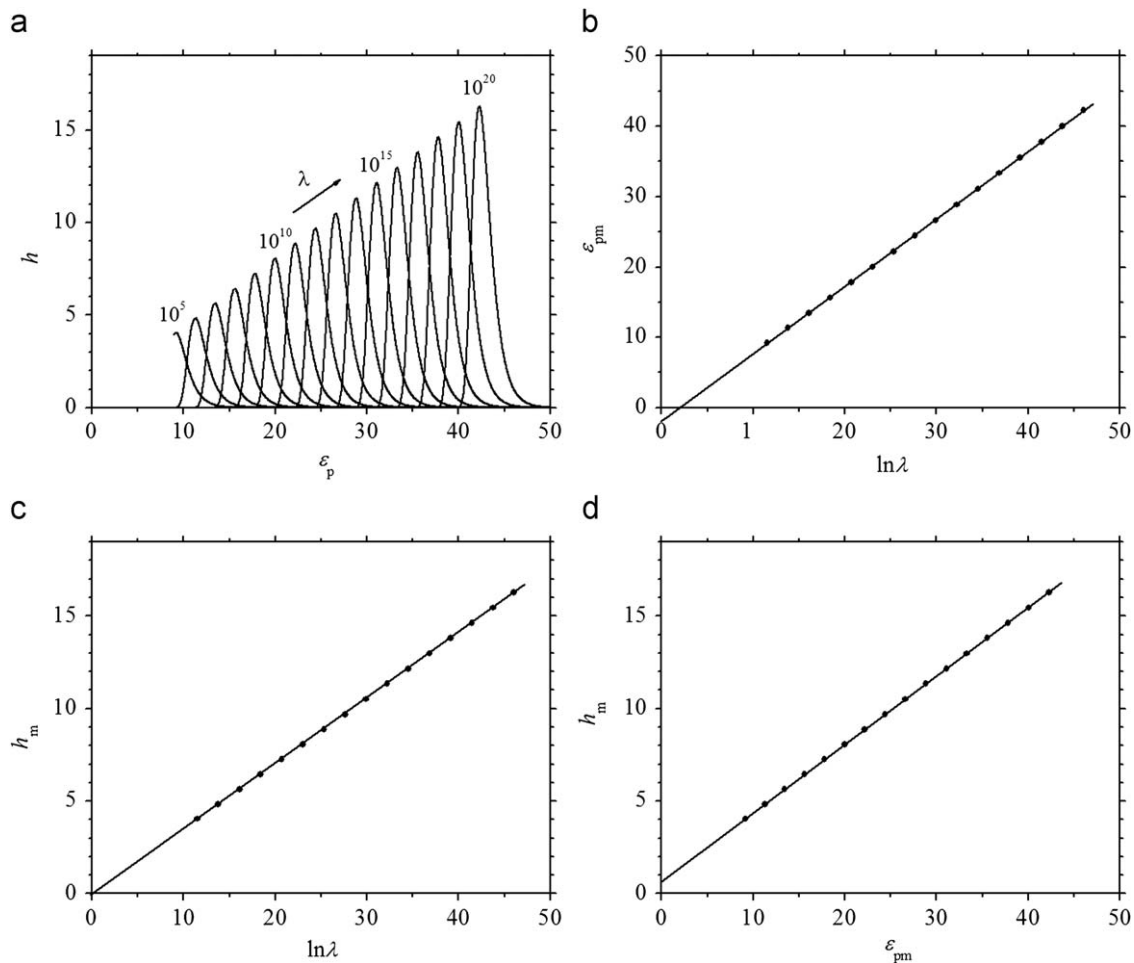
$$(18)$$

Fig. 4. (a) The dependence of the polarization efficiency, as expressed by h, on ε_p, for various values of λ. (b) The values ε_{pm} of ε_p, for which h is maximum for a given $\ln \lambda$, and the linear relationship between ε_{pm} and $\ln \lambda$. (c) The linear relationship between the maximum value h_m of h, and the value of $\ln \lambda$ at which the maximum appears. (d) The linear relationship between the maximum value h_m of h, and the value ε_{pm} of ε_p at which the maximum appears.
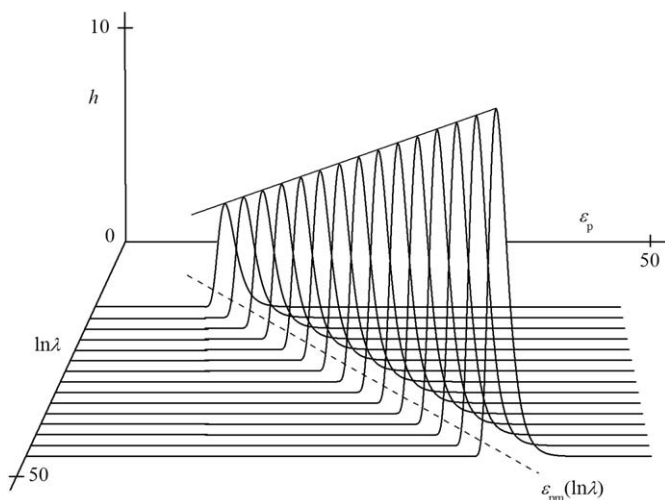

Fig. 5. Three-dimensional plot of the dependence on ε_p of the polarization efficiency, as expressed by h, for various values of λ. The sections of the h surface with the planes of constant $\ln \lambda$ produce the peaks shown.

Given a value of E', for maximum η there must be a value of τ_0, equal to τ_{0m}, for which $\partial \eta / \partial \tau_0 = 0$. From Eq. (18) it follows that

$$E_2\left(\frac{E'}{kT_p}\right) = \frac{q\tau_{0m}}{T_p}. \tag{19}$$

The function η becomes

$$\eta(E', \tau_0) = \frac{\gamma \kappa F p}{kq\tau_0} \frac{\Delta T_p}{T_p} \exp\left[-\frac{E'}{kT_p} - \frac{\tau_{0m}}{\tau_0}\right]. \tag{20}$$

This curve is shown in Fig. 6.

According to Eq. (20), $\eta(E', \tau_0)$ has a maximum value

$$\eta_{0\tau} = \eta(E', \tau_{0m}) = \frac{\gamma \kappa F p}{ekq\tau_{0m}} \frac{\Delta T_p}{T_p} \exp\left(-\frac{E'}{kT_p}\right). \tag{21}$$

Using Eq. (19)

$$\eta_{0\tau} = \frac{\gamma \kappa F p}{ek} \frac{\Delta T_p}{T_p^2} \frac{e^{-E'/kT_p}}{E_2(E'/kT_p)}. \tag{22}$$

This is an exact expression. It can be greatly simplified by using the approximation [5]

$$(\varepsilon + 2)e^\varepsilon E_2(\varepsilon) \approx 1. \tag{23}$$

The unity on the right-hand side is actually 1.0124 for $\varepsilon = 10$, 1.0038 for $\varepsilon = 20$ and 1.0002 for $\varepsilon = 100$. Eq. (23) becomes exact as $\varepsilon \to \infty$. Using Eq. (23) in Eq. (22)

$$\eta_{0\tau} = \frac{\gamma \kappa F p}{ek} \frac{\Delta T_p}{T_p^2} \left(2 + \frac{E'}{kT_p}\right), \tag{24}$$

showing that there is a linear relationship between $\eta_{0\tau}$ and E', to a very good approximation. The linear relationship in Fig. 2c gave the factor $(1.002/e)[1.861 + (E'/kT_p)]$ instead of $(1/e)[2 + (E'/kT_p)]$
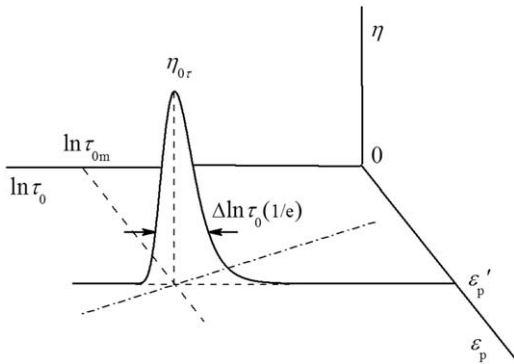
Fig. 6. The variation of η with $\ln \tau_0$, for a given value of $\varepsilon_p' = E'/kT_p$, for dipoles polarized at a temperature of T_p by the thermal sampling technique.

in Eq. (24). This is considered to be a good agreement, within the limitations of the approximation (23).

Dividing Eq. (20) by Eq. (21) we obtain the exact equation

$$\eta(E', \tau_0) = \eta_{0\tau} e \left(\frac{\tau_{0m}}{\tau_0} \right) \exp\left(-\frac{\tau_{0m}}{\tau_0} \right). \tag{25}$$

The width of the distribution of τ_0 values can be found using Eq. (25). The solutions of

$$\frac{\eta(E', \tau_0)}{\eta_{0\tau}} = \frac{1}{e} \tag{26}$$

are found, by numerical methods, to be

$$\tau_{01}\left(\frac{1}{e}\right) = \frac{\tau_{0m}}{3.1462} \quad \text{and} \quad \tau_{02}\left(\frac{1}{e}\right) = \frac{\tau_{0m}}{0.15859}. \tag{27}$$

These give the values of τ_0 at which $\eta(E', \tau_0)$ falls to a fraction of $1/e$ of its maximum value. The polarization procedure selects mechanisms which, *independently of E'*, have values within a factor of

$$\frac{\tau_{02}\left(\frac{1}{e}\right)}{\tau_{01}\left(\frac{1}{e}\right)} = \frac{3.1462}{0.15859} = 19.84 \tag{28}$$

or, to a good approximation, a factor of 20. The differences in the natural logarithms are

$$\ln \tau_{01}\left(\frac{1}{e}\right) - \ln \tau_{0m} = -1.1462 \quad \text{and} \quad \ln \tau_{02}\left(\frac{1}{e}\right) - \ln \tau_{0m} = 1.8414. \tag{29}$$

The corresponding range of the natural logarithms of the values of τ_0 selected is

$$\Delta \ln \tau_0 \left(\frac{1}{e}\right) = \ln \tau_{02}\left(\frac{1}{e}\right) - \ln \tau_{01}\left(\frac{1}{e}\right) = \ln 19.839 = 2.988, \tag{30}$$

or, to a good approximation

$$\Delta \ln \tau_0 \left(\frac{1}{e}\right) = 3. \tag{31}$$

$\Delta \ln \tau_0(1/e)$ is shown in Fig. 6.

If instead of the ratio $\eta(E', \tau_0)/\eta_{0\tau} = 1/e$ we use $\eta(E', \tau_0)/\eta_{0\tau} = 1/2$, we find

$$\tau_{01}\left(\frac{1}{2}\right) = \frac{\tau_{0m}}{2.6783} \quad \text{and} \quad \tau_{02}\left(\frac{1}{2}\right) = \frac{\tau_{0m}}{0.23196}, \tag{32}$$

$$\frac{\tau_{02}(\frac{1}{2})}{\tau_{01}(\frac{1}{2})} = 11.55, \tag{33}$$

$$\Delta \ln \tau_0(\tfrac{1}{2}) = \ln \tau_{02}(\tfrac{1}{2}) - \ln \tau_{01}(\tfrac{1}{2}) = 2.446, \tag{34}$$

or

$$\Delta \ln \tau_0(\tfrac{1}{2}) = 2.45. \tag{35}$$

This is the full width at half maximum (FWHM) of the distribution of the $\ln \tau_0$ values of the polarized mechanisms.

5. The selectivity in E values, of the thermal sampling technique

We now concentrate on a particular value of $\tau_0 = \tau_0'$ and examine the distribution of the values of the activation energy values E of the polarized mechanisms. To find the maximum value of η for this particular value of τ_0, we examine

$$\frac{\partial \eta}{\partial E} = \frac{\gamma \kappa Fp}{kq} \frac{\Delta T_p}{T_p} \left[-\frac{1}{kT_p} + \frac{T_p}{q\tau_0'} \frac{1}{kT_p} E_1\left(\frac{E}{kT_p}\right) \right] \exp\left[-\frac{E}{kT_p} - \frac{T_p}{q\tau_0'} E_2\left(\frac{E}{kT_p}\right) \right], \tag{36}$$

where [5]

$$E_1(\varepsilon) \equiv \int_\varepsilon^\infty \frac{e^{-z}}{z} \, dz, \tag{37}$$

is the *first exponential integral*, which has the properties

$$\frac{dE_2(\varepsilon)}{d\varepsilon} = -E_1(\varepsilon), \quad E_2(\varepsilon) = e^{-z} - \varepsilon E_1(\varepsilon), \quad (\varepsilon+1)e^\varepsilon E_1(\varepsilon) \approx 1. \tag{38}$$

The unity on the right-hand side of the third equation is actually 1.0072 for $\varepsilon = 10$, 1.0021 for $\varepsilon = 20$ and 1.0001 for $\varepsilon = 100$. Eq. (38) becomes exact as $\varepsilon \to \infty$.

Given a value of τ_0, for maximum η there must be a value of E, equal to E_m, for which $\partial \eta/\partial E = 0$. From Eq. (36) it follows that

$$E_1\left(\frac{E_m}{kT_p}\right) = \frac{q\tau_0'}{T_p}. \tag{39}$$

The function η becomes

$$\eta(E, \tau_0') = \frac{\gamma \kappa Fp}{kq\tau_0'} \frac{\Delta T_p}{T_p} \exp\left[-\frac{E}{kT_p} - \frac{T_p}{q\tau_0'} E_2\left(\frac{E}{kT_p}\right) \right]. \tag{40}$$

This curve is shown in Fig. 7.

According to Eq. (39), $\eta(E, \tau_0')$ has a maximum value

$$\eta_{0E} = \eta(E_m, \tau_0') = \frac{\gamma \kappa Fp}{k} \frac{\Delta T_p}{T_p^2} \frac{1}{E_1(E_m/kT_p)} \exp\left(-\frac{E_m}{kT_p} - \frac{E_2(E_m/kT_p)}{E_1(E_m/kT_p)} \right). \tag{41}$$

Using the second of Eq. (38)

$$\eta_{0E} = \frac{\gamma \kappa Fp}{k} \frac{\Delta T_p}{T_p^2} \frac{1}{E_1(E_m/kT_p)} \exp\left(-\frac{\exp(-E_m/kT_p)}{E_1(E_m/kT_p)} \right), \tag{42}$$

which is an exact relationship. Using the approximation $(\varepsilon+1)e^\varepsilon E_1(\varepsilon) \approx 1$ in Eq. (42) we obtain

$$\eta_{0E} = \frac{\gamma \kappa Fp}{ek} \frac{\Delta T_p}{T_p^2} \left(1 + \frac{E_m}{kT_p} \right), \tag{43}$$

showing that there is a linear relationship between η_{0E} and E_m/kT_p, to a good approximation. The linear relationship in Fig. 4d gave the factor $(1.004/e)[1.798 + (E_m/kT_p)]$ instead of $(1/e)[1 + (E_m/kT_p)]$ in Eq. (43). This is considered to be a good agreement, within the limitations in accuracy of the third of Eqs. (38).

The ratio of Eqs. (40) and (41) gives

$$\eta(E, \tau_0') = \eta_{0E} \exp\left[-\frac{E}{kT_p} + \frac{E_m}{kT_p} - \frac{E_2(E/kT_p) - E_2(E_m/kT_p)}{E_1(E_m/kT_p)} \right], \tag{44}$$

which, by use of the approximations $(\varepsilon+2)e^\varepsilon E_2(\varepsilon) \approx 1$ and $(\varepsilon+1)e^\varepsilon E_1(\varepsilon) \approx 1$, leads to

$$\eta(E, \tau_0') = \eta_{0E} \exp\left[1 - \varepsilon_p + \varepsilon_{pm} - \frac{(\varepsilon_{pm}+1)e^{\varepsilon_{pm}}}{(\varepsilon_p+2)e^{\varepsilon_p}} \right], \tag{45}$$
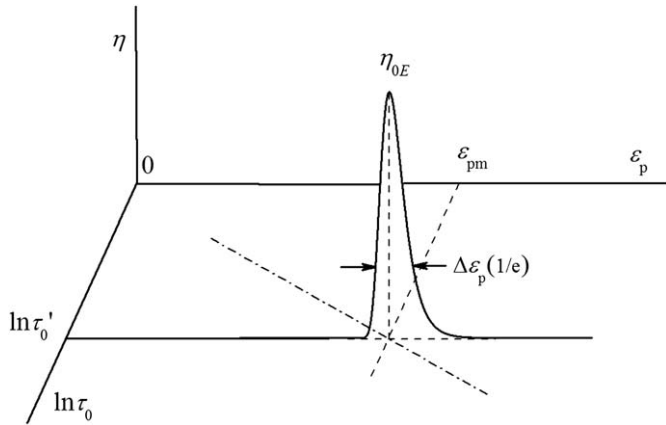
Fig. 7. The variation of η with ε_p, for a given value $\ln \tau_0'$ of $\ln \tau_0$, for dipoles polarized at a temperature of T_p by the thermal sampling technique.

where $\varepsilon_p = E/kT_p$ and $\varepsilon_{pm} = E_m/kT_p$. We define

$$\delta \equiv \varepsilon_p - \varepsilon_{pm}, \tag{46}$$

in terms of which

$$\eta(E, \tau_0') = \eta_{0E} \exp\left[1 - \delta - \frac{(\varepsilon_{pm}+1)}{(\varepsilon_{pm}+2+\delta)} e^{-\delta}\right]. \tag{47}$$

The term $(\varepsilon_{pm}+1)/(\varepsilon_{pm}+2+\delta)e^{-\delta}$ is important only for negative values of δ. In this case, and provided $|\delta|$ is small, we may put $(\varepsilon_{pm}+1)/(\varepsilon_{pm}+2+\delta) \approx 1$ and obtain

$$\eta(E, \tau_0') = \eta_{0E} \exp(1 - \delta - e^{-\delta}) \tag{48}$$

or

$$\eta(E, \tau_0') = \eta_{0E} \exp[1 + \varepsilon_{pm} - \varepsilon_p - e^{\varepsilon_{pm} - \varepsilon_p}]. \tag{49}$$

This equation is for $(\varepsilon_p - \varepsilon_{pm})$ what Eq. (25) is for $(\ln \tau_0 - \ln \tau_{0m})$.

The width of the distribution of E values can be found using Eq. (48). For

$$\frac{\eta(E, \tau_0')}{\eta_{0E}} = \frac{1}{e}, \tag{50}$$

the two solutions are

$$\delta_L\left(\frac{1}{e}\right) = -1.1462 \quad \text{and} \quad \delta_H\left(\frac{1}{e}\right) = 1.8414, \tag{51}$$

which correspond to

$$\varepsilon_{pL}\left(\frac{1}{e}\right) = \varepsilon_{pm} + \delta_L\left(\frac{1}{e}\right) = \varepsilon_{pm} - 1.1462 \quad \text{and}$$

$$\varepsilon_{pH}\left(\frac{1}{e}\right) = \varepsilon_{pm} + \delta_H\left(\frac{1}{e}\right) = \varepsilon_{pm} + 1.8414 \tag{52}$$

The range of ε values for the mechanisms polarized is

$$\Delta\varepsilon_p\left(\frac{1}{e}\right) = \varepsilon_{pH}\left(\frac{1}{e}\right) - \varepsilon_{pL}\left(\frac{1}{e}\right) = 2.988, \tag{53}$$

or, to a good approximation

$$\Delta\varepsilon_p\left(\frac{1}{e}\right) = 3, \tag{54}$$

independently of E'. This corresponds to an energy range

$$\Delta E\left(\frac{1}{e}\right) = 3kT_p. \tag{55}$$

$\Delta\varepsilon_p(1/e)$ is shown in Fig. 7.

If instead of the ratio $\eta(E, \tau_0')/\eta_{0E} = 1/e$ we use $\eta(E, \tau_0')/\eta_{0E} = 1/2$, we find

$$\delta_L(\tfrac{1}{2}) = -0.9852 \quad \text{and} \quad \delta_H(\tfrac{1}{2}) = 1.4612, \tag{56}$$

which correspond to

$$\varepsilon_{pL}(\tfrac{1}{2}) = \varepsilon_{pm} + \delta_L(\tfrac{1}{2}) = \varepsilon_{pm} - 0.9852 \quad \text{and}$$

$$\varepsilon pH(\tfrac{1}{2}) = \varepsilon_{pm} + \delta_{pH}(\tfrac{1}{2}) = \varepsilon_{pm} + 1.4612. \tag{57}$$

The range of ε values for the mechanisms polarized is

$$\Delta\varepsilon_p(\tfrac{1}{2}) = \varepsilon_{pH}(\tfrac{1}{2}) - \varepsilon_{pL}(\tfrac{1}{2}) = 2.446 \tag{58}$$

or

$$\Delta\varepsilon_p(\tfrac{1}{2}) = 2.45 \tag{59}$$

independently of E'. This corresponds to an energy range

$$\Delta E(\tfrac{1}{2}) = 2.45kT_p. \tag{60}$$

This is the full width at half maximum (FWHM) of the distribution of the E values of the polarized mechanisms.

We note the interesting facts that

$$\Delta\varepsilon_p\left(\frac{1}{e}\right) = \Delta \ln \tau_0\left(\frac{1}{e}\right) \approx 3 \quad \text{and} \quad \Delta\varepsilon_p\left(\frac{1}{2}\right) = \Delta \ln \tau_0\left(\frac{1}{2}\right) \approx 2.45. \tag{61}$$

6. The line $(-\ln \tau_0)$–E of maximum polarization efficiency for given q and T_p

The relationships established in Section 3 are in a sense universal, as they were derived from Eq. (17) which involves the dimensionless variables h, $\varepsilon_p = E/kT_p$ and $\lambda = T_p/q\tau_0$, and no other parameters. In examining η, it was found that the lines of maximum polarization efficiency, with respect to τ_0 or E, are given by conditions (19) and (39), respectively, as

$$E_2(\varepsilon_p) = \frac{q\tau_0}{T_p} \quad \text{and} \quad E_1(\varepsilon_p) = \frac{q\tau_0}{T_p}. \tag{62}$$

These give

$$-\ln \tau_0 = \ln q - \ln T_p - \ln E_2(\varepsilon_p) \quad \text{and} \quad -\ln \tau_0 = \ln q - \ln T_p - \ln E_1(\varepsilon_p). \tag{63}$$

The functions $-\ln E_1(\varepsilon)$ and $-\ln E_2(\varepsilon)$, when plotted as functions of ε, are seen to be, to a good approximation, straight lines that almost coincide (lower part of Fig. 8). For values of ε between 10 and 60, in steps of 1, the best linear fits are
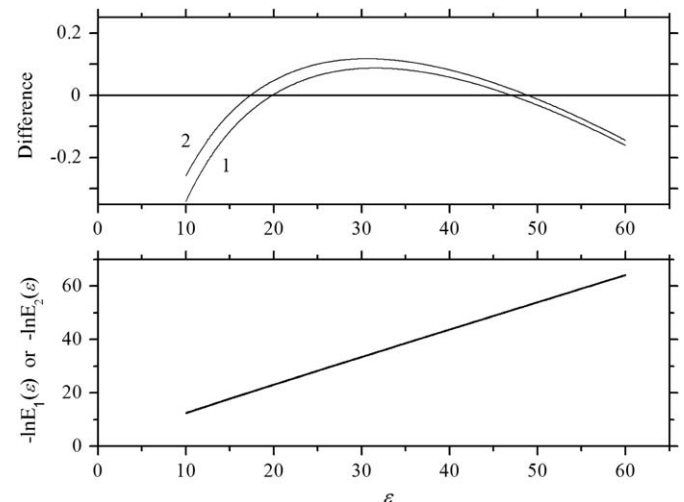

Fig. 8. The variation with ε of $-\ln E_1(\varepsilon)$ and $-\ln E_2(\varepsilon)$. Both functions are fitted very well by the straight line $2.42 + 1.031\varepsilon$ and are in fact indistinguishable in the lower figure. In the upper figure, lines 1 and 2 give, respectively, the differences between $-\ln E_1(\varepsilon)$ and $-\ln E_2(\varepsilon)$ and the values predicted by this linear approximation.

found to be

$$-\ln E_1(\varepsilon) = 2.389(11) + 1.0313(3)\varepsilon \ \text{ and } \ -\ln E_2(\varepsilon) = 2.457(11) + 1.0303(3)\varepsilon.$$
(64)

We take the straight line with coefficients the average values of those of these two equations, as representing both the functions $-\ln E_1(\varepsilon)$ and $-\ln E_2(\varepsilon)$:

$$-\ln E_1(\varepsilon) \approx -\ln E_2(\varepsilon) \approx 2.42 + 1.031\varepsilon.$$
(65)

The differences of the actual values of $-\ln E_1(\varepsilon)$ and $-\ln E_2(\varepsilon)$ from those predicted by Eq. (65) are shown by curves 1 and 2, respectively, in the upper part of Fig. 8. These differences drop from 2.5% at $\varepsilon = 10$, to 1% at $\varepsilon = 15$ and to much smaller values as ε increases.

Using these relationships in Eqs. (63), we obtain

$$-\ln \tau_0 = \ln q - \ln T_p + 2.42 + 1.031\varepsilon_p$$
(66)

and, substituting $\varepsilon_p = E/kT_p$ with $1/k = 11\,604.5\,\text{K/eV}$

$$-\ln \tau_0(s) = 2.42 + \ln q(\text{K/s}) - \ln T_p(\text{K}) + 12\,000\frac{E(\text{eV})}{T_p(\text{K})},$$
(67)

where the various quantities are expressed in the units shown in parentheses. Given the values of q and T_p used in thermal sampling, this equation gives the line on the E–$(-\ln \tau_0)$ plane along which the polarization efficiency is maximum. In Fig. 9, the lines corresponding to various values of T_p are shown, for $q = 0.1\,\text{K/s}$.

Also shown in Fig. 9, on the line for $T_p = 200\,\text{K}$, are the ranges of E and $\ln \tau_0$ of the polarized dipoles, as predicted by Eqs. (55) and (31), respectively. Fig. 10 shows this in more detail. For given polarization temperature T_p and cooling rate q, the polarization efficiency will be maximum along the straight line (thick line in the figure) given by Eq. (67). Around every point $(E, \ln \tau_0)$ of this line, the polarization efficiency has appreciable values in the ranges between $E - 1.15kT_p$ and $(E + 1.84kT_p)$ for energy E, and between $(-\ln \tau_0 - 1.15)$ and $(-\ln \tau_0 + 1.84)$ for $\ln \tau_0$ values. The region defined in this way lies between the dashed lines for E and the dotted lines for $\ln \tau_0$.

In a given sample, the dipoles which will be polarized will depend on the values of E and of $\ln \tau_0$ of the dipoles in the sample. Fig. 11 shows three such cases of samples which have dipoles with distributions of ranges of E and of $\ln \tau_0$ values. The cooling

Fig. 10. The ranges of values of E and of $\ln \tau_0$ for which the polarization efficiency has appreciable values lie between the dashed lines for E and the dotted lines for $\ln \tau_0$. These are defined, for a given point $(E, \ln \tau_0)$ on the line of maximum polarization efficiency corresponding to a polarization temperature T_p and cooling rate q, by the ranges between $(E - 1.15kT_p)$ and $(E + 1.84kT_p)$ for energy E, and between $(-\ln \tau_0 - 1.15)$ and $(-\ln \tau_0 + 1.84)$ for $\ln \tau_0$ values.
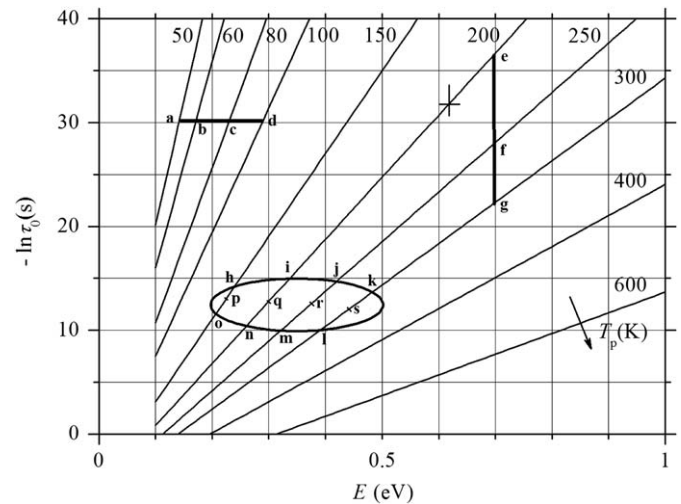
Fig. 11. The polarization of dipoles in three samples. One (abcd), in which the dipoles have a single value of $\ln \tau_0 = -30$ and a range of energies between about 0.14 and 0.29 eV. A second sample (efg), has dipoles of a single energy $E = 0.7\,\text{eV}$ and $\ln \tau_0$ values between -22 and -37. A third sample (hijklmno), has dipoles which are distributed both in energy E and $\ln \tau_0$ values, with a distribution which may be taken to be a two-dimensional Gaussian, indicated by the ellipse in the figure. The cooling rate in all cases shown was $-q = -0.1\,\text{K/s}$.

rate was taken to be $-q = -0.1\,\text{K/s}$. The dipoles which are polarized at a particular polarization temperatures T_p are determined by the section of the distribution by the line of maximum polarization efficiency corresponding to that T_p. It should be borne in mind that the polarization efficiency has appreciable values in a region around the lines of maximum. This region is indicated by a cross for a point on the $T_p = 200\,\text{K}$ line.

In the first sample (abcd), the dipoles have a single value of $\ln \tau_0 = -30$ and a range of energies between about 0.14 and 0.29 eV. The distribution is seen to be sampled for polarizing temperatures between 50 and 100 K.

The second sample (efg), has dipoles of a single energy $E = 0.7\,\text{eV}$ and $\ln \tau_0$ values between -22 and -37. This distribution is seen to be sampled for polarizing temperatures between 200 and 300 K.

In the third sample (hijklmno), the dipoles are distributed both in energy E and $\ln \tau_0$ values, with a distribution which may be taken to be a two-dimensional Gaussian, indicated by the ellipse in the figure. It is seen that at each of the sampling temperatures
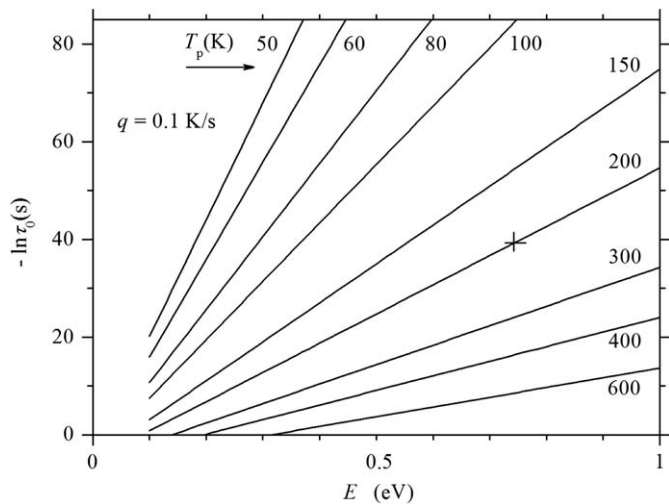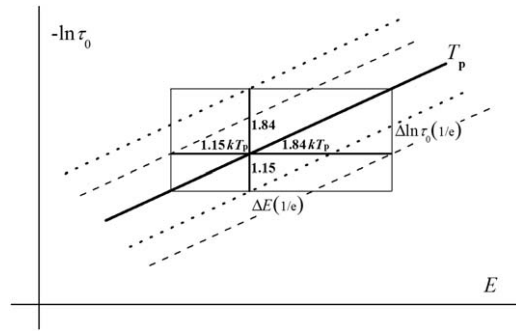

Fig. 9. The lines of polarization efficiency on the E–$(-\ln \tau_0)$ plane, for thermal sampling at a cooling rate of $-q = -0.1\,\text{K/s}$ and various polarization temperatures T_p. The crossed lines on the straight line for $T_p = 200\,\text{K}$, show the ranges of E and $\ln \tau_0$ of the polarized dipoles, as predicted by Eqs. (55) and (31), respectively.

150, 200, 250 and 300 K, dipoles within a range of both energies and $\ln \tau_0$ values are polarized. The mid-points of these ranges are marked, approximately, by the letters p, q, r and s in the figure. For $T_p = 300$ K, for example, the dipoles polarized have energies E between 0.39 and 0.48 eV, and $\ln \tau_0$ values between -10 and -13, the mid-point of these beings.

7. Thermal sampling and the compensation law

The selectivity of the thermal sampling technique could account, at least in certain cases, for the manifestation of the so-called "compensation law", i.e. a linear relationship between the measured values of E and the corresponding values of $\ln \tau_0$. This effect has been documented in the literature of TSDC for many years now [9–18]. The two main schools of thought offer explanations based on molecular structure considerations on one hand and on the effect being a result of the experimental technique used on the other. In all cases, the phenomenon depends on the existence in the sample studied of relaxation mechanisms having a distribution of E and $\ln \tau_0$ values. As an example, such a distribution is shown in Fig. 12 by the ellipse with axis the line abcde and center at the point O ($E = 0.2$ eV, $\ln \tau_0 = -25$). The ellipse denotes the points at which the distribution density falls to a value equal to, say, $e^{-1/2}$ times its maximum value at O. The lines of maximum polarization at the temperatures of T_p equal to 50, 60, 80, 100 and 150 K are shown, for a cooling rate of $-q = -0.1$ K/s.

The range of energies sampled at each temperature is approximately given by the sections of these straight lines lying inside the ellipse. The mean energies of the mechanisms sampled are given approximately by the points a, b, c, d and e, respectively. For a fairly symmetric distribution, these points will approximately lie on a straight line and this fact will lead to a manifestation of the so-called "compensation law". This would provide an explanation for the observation of the linear relation-

ship between the values of E and $\ln \tau_0$ measured for the peaks isolated by thermal sampling.

8. Conclusions

The TSDC polarization efficiency η was studied for the method of thermal sampling consisting of cooling the sample at a constant rate $-dT/dt = q$ and applying an electric field F for a time interval Δt, while the sample is cooled from the temperature of T_p to $T_p - \Delta T_p$. A delta-function polarization window was considered, with $\Delta T_p \rightarrow 0$ while the product $F\Delta T_p$ remains finite. The expression derived for η, Eq. (14), has maximum values with respect to E and $\ln \tau_0$ which approximately lie on a straight line in the $E-(-\ln \tau_0)$ plane, given by Eq. (67). The polarization efficiency is appreciable for values of E and $\ln \tau_0$ near the line of maxima, in the ranges between $(E-1.15kT_p)$ and $(E+1.84kT_p)$ for E, and between $(-\ln \tau_0 - 1.15)$ and $(-\ln \tau_0 + 1.84)$ for $\ln \tau_0$. The selectivity of the method, as expressed by the width of the η function at a point $(E, \ln \tau_0)$ in the directions of the E and $\ln \tau_0$ axes, is $\Delta E(1/e) \approx 3kT_p$ and $\Delta \ln \tau_0(1/e) \approx 3$. The effective fraction of dipoles polarized will depend on the product of $\eta(E, \tau_0)$ and the distribution function of the E and $\ln \tau_0$ values in the sample. The peaks isolated by the thermal sampling technique are far from being either monoenergetic or from corresponding to a single value of $\ln \tau_0$. In fact, those mechanisms present in the sample are isolated, which, on heating, will result in peaks at approximately the same peak temperature, and will appear as a single apparently pure peak.

The selectivity of the thermal sampling technique provides an explanation of the linear relationship observed between the values of E and $\ln \tau_0$ measured for the peaks isolated by this method, referred to in the literature as "the compensation law". Under certain circumstances, a fairly linear relationship arises, merely as a result of the method used and the distribution of the relaxation parameters in the sample. More work should be done along these lines, to test this claim, both experimentally and by computer simulation techniques.
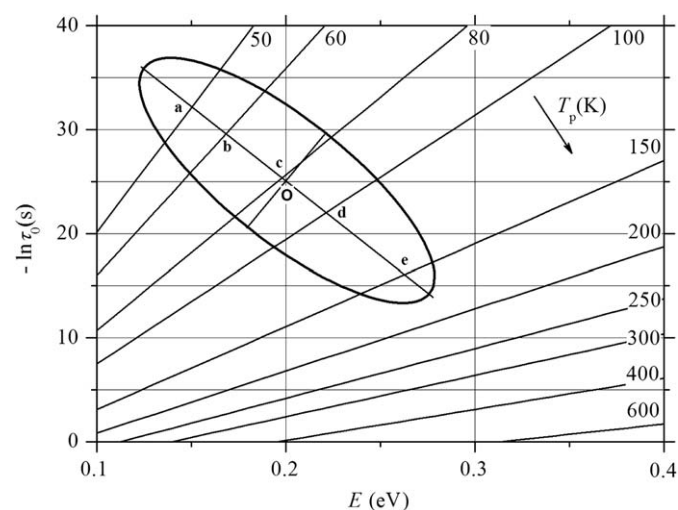
Fig. 12. The thermal sampling of a two-dimensional Gaussian distribution of both activation energy and pre-exponential factor. The axis of the distribution is along the line abcde and its center is at O ($E = 0.2$ eV, $\ln \tau_0 = -25$). The ellipse denotes the points at which the distribution density falls to a value equal to, say, $e^{-1/2}$ times its maximum value at O. The ranges of energies sampled at a cooling rate of $-q = -0.1$ K/s and for sampling temperatures T_p of 50, 60, 80, 100 and 150 K are approximately shown by the sections inside the ellipse, of the straight lines corresponding to sampling at these temperatures. The mean energies of the mechanisms sampled are given approximately by the points a, b, c, d and e, respectively. To the extent that these points lie on a straight line, we have a manifestation of the so-called "compensation law".

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