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LETTER TO THE EDITOR

Internal field-assisted thermally activated hopping and tunnelling in insulators and composite materials

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Abstract. A description of transport hopping processes at the Fermi surface in insulators is presented in which the role of internal fields is emphasized. Taking account of these fields up to the quadrupole term, we find that the conductivity σ at low applied fields obeys a $\ln(\sigma/\sigma_0) \approx -(T_0/T)^{\beta}$ law, with β varying from 1/2 to 1/4 as the temperature is raised. Typical orders of magnitude $L \approx 10^5$ V cm^{-1}, $Q \approx 100$ A^2 and $d \approx 3\sqrt{Q}$ for the field, the quadrupole moment and the dipole length respectively can be obtained from experimental data in the $\beta = 1/2$ and $\beta = 1/4$ regimes.

The existence of internal fields of order of magnitude 10^4–10^5 V cm^1 has been previously suggested to explain the broadening of optical and spin resonance lines [1] in insulators. Subsequent work on Poole–Frenkel systems indicated the need to account for such fields in order to arrive at a consistent explanation of transport data; the obtained values of the fields agreed with those obtained by optical means [2]. Later on, a theoretical argument based on a diffusion equation was advanced [3] indicating the need for the introduction of an internal field in transport processes. Around coulombic centres, such a field superimposes upon the Coulomb field producing a barrier at zero applied external field, and hence in the ohmic region, which the carriers can overcome either assisted by the temperature or by tunnelling at low temperatures. It allowed an explanation of deviations from the classical Poole–Frenkel characteristics, especially at low fields [2].

In this paper the internal field idea is proposed for disordered insulators in which transport occurs at the Fermi level. Examples are insulators of Mott's type and Coulomb gap Efros–Shklowskii type, and granular metals in the dielectric regime. We suggest that internal fields result either from the fluctuation of the charge among the sites while maintaining electrical neutrality (Mott's case), or from coulombic fields due to the charging of sites (Coulomb-gap case) or grains during electron hops. Taking account of contributions to the local fields up to the quadrupole term we are able to give a unified picture of hopping mechanisms as an internal field-assisted conduction. We obtain an estimate of such fields which indicates an almost universal value.

The charge transport in a disordered system can be studied with the Fokker–Planck equation in the Smoluchowski limit for the distribution function f [3]:

$$\partial f/\partial t = (kT\mu/e)\mathrm{div}\left[\mathrm{e}^{-U/kT}\,\mathrm{grad}\left(f\,\mathrm{e}^{U/kT}\right)\right] \tag{1}$$

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where μ is the mobility, and $U(\boldsymbol{r})$ the potential energy of a carrier, including the contribution of the field of the actual charges distributed in the system and in general also the contribution of the applied electric field. Under steady-state conditions the left-hand side vanishes, so we have

$$\mathrm{e}^{-U/kT}\mathrm{grad}\left(f\mathrm{e}^{U/kT}\right) = \boldsymbol{A} \qquad (\mathrm{div}\boldsymbol{A} = 0). \tag{2}$$

On neglecting the solenoid vector $\boldsymbol{A}$, the solution is $f = C\mathrm{e}^{-U/kT}$. In general, however, the solution turns out to be of the form

$$f = C\mathrm{e}^{-(U+\delta U)/kT} \tag{3}$$

where the quantity $\delta U(\boldsymbol{r})$ defines corrections to $U(\boldsymbol{r})$ which can be interpreted as the potential energy due to an internal field $\boldsymbol{L} = -\mathrm{grad}\delta U/e$. This field satisfies the equation, according to (1) and (2)

$$\mathrm{div}\boldsymbol{L} = (\boldsymbol{A}/f)\mathrm{grad}(U + \delta U) = \left(e\boldsymbol{L}\cdot\mathrm{grad}U - (eL)^2\right)/kT. \tag{4}$$

In general, $\delta U(\boldsymbol{r})$ is a random function whose origin is (excluding the applied field) the Coulomb interactions of carriers with the actual charges in the system. According to (4), the field $\boldsymbol{L}$ will be solenoidal when $\mathrm{grad}(U + \delta U) = 0$, i.e. $\boldsymbol{L} = -\mathrm{grad}U/e$, but in general $\mathrm{div}\boldsymbol{L} \neq 0$, indicating from Gauss' law a polarization charge. The conductivity of the system can be evaluated through the relation

$$\sigma = fne\mu f\,P(\xi)\,\mathrm{d}\xi \tag{5}$$

where n is the carrier density. Since the local field corrections fluctuate in space, an average over all conducting paths is performed, with an assumed probability density distribution $P(\xi)$ of the paths or equivalently of the internal field L. In the presence of random disorder, a distribution of the form $P(\xi) = k\mathrm{e}^{-2\alpha\xi}$, where α is a constant, can usually be applied. The resultant integration can hardly be performed exactly. Asymptotic expansions of (5) can be obtained via an approximate scheme, i.e. a saddle-point method, looking at stationary points of $fP(\xi)$. If r_s represents such a point we can assume then $\sigma \approx f(r_s)P(r_s)$, for constant n and μ [2–4]. When the distribution $P(\xi)$ is exponential and f is given by (3), stationarity leads to the condition for r_s

$$\Delta(U + \delta U) = -2\alpha kT. \tag{6}$$

We note that, in general, this condition leads, according to equation (4), to $\mathrm{div}\boldsymbol{L} \neq 0$, i.e. to a polarization charge.

The internal field corrections have been previously discussed [2, 3] in Poole–Frenkel systems. We review such a case to introduce the results of the other insulators where conduction occurs at the Fermi surface.

In this case the transport process is determined by the ionization of randomly distributed centres [2]. In the classical study of this effect, it is assumed that the relevant potential energy in (1) is due to the coulombic field experienced by carriers near the centre left charged in the ionization process, ignoring the effect of the surrounding centres (single-centre approximation). On the other hand, the internal field arises just from all these other surrounding centres. If centres are located at random positions $\boldsymbol{R}_i$, for carrier distances r close to a given centre considered at $R = 0$, the potential energy of a carrier can be expanded in the form ($r \ll R_i$)

$$U + \delta U = -\frac{e^2}{4\pi\epsilon_0 r} - (\boldsymbol{E} + \boldsymbol{L})\cdot\boldsymbol{r} + \ldots \qquad \boldsymbol{L} = \Sigma\left(e/4\pi\epsilon_0 R_i^2\right)\hat{\boldsymbol{R}}_i \tag{7}$$

where $\hat{\boldsymbol{R}}_i$ denotes the unit vector of $\boldsymbol{R}_i$.

Assuming that emission occurs above the barrier given by equation (7) along the applied field direction and that the local field is parallel to E, taking $P(r) = k =$ constant (random centre distribution), we find that r_s is determined by the maximum of the barrier, i.e. $\Delta(U + \delta U) = 0$, according to equation (6) and we thus obtain

$$\sigma \approx f\left(r_{barr}\right) = \sigma_0 \mathrm{e}^{\beta\sqrt{(E+L)}/kT} \qquad \left(\beta = e\sqrt{e}/4\pi\epsilon_0\right). \tag{8}$$

In this case the internal field L is solenoidal around the top of the barrier, as follows from equation (4), implying absence of polarization charge.

Despite the particular configuration of the fields E and L, equation (8) has been shown to be a notable improvement of the original Poole–Frenkel result (corresponding to $L = 0$) and more extensive analysis including realistic configurations [2, 3] has further shown the relevance of the internal field corrections.

The order of magnitude of the internal field here is $L \approx e/4\pi\epsilon_0 r_{barr}^2$, independent of temperature.

Variable-range hopping at low applied fields (where the internal field effects are dominant) is considered, assuming the usual approximation of hopping between a pair of centres [4]. The relevant contributions to the potential energy $U(\boldsymbol{r})$ in equation (1) is a short-range $U_0(\boldsymbol{r})$ produced by disorder, responsible for carrier localization in space, to which internal local field corrections add, whose origin may be traced back to coulombic forces on carriers from the localized charge on the sites. This charge may be assumed to be confined to a region of dimension d much smaller than the distance r (evaluated from the initial site) of the carriers at the final hopping sites, so that at sufficiently large distances $r \gg d$ we can assume the expansion in multipoles, at applied field $E \to 0$ (in CGS units as usual):

$$U + \delta U = U_0 + \left(e^2/r + ep/r^2 + e^2Q/r^3 + \ldots\right)/\epsilon \tag{9}$$

where in parenthesis the internal field corrections are evidenced. Here, ϵ is a relative dielectric constant, e is the charge of a site and p and Q are dipole and quadrupole moments respectively. Tunneling from one localized state to another can be accounted for by a probability distribution of the form $P = k\mathrm{e}^{-2\alpha r}$, where α is the envelope of the wavefunctions [4]. Using equation (6) to find r_s as a function of temperature and substituting in the saddle-point result $\sigma = \sigma_0 f(r_s) P(r_s)$ we find

$$\ln\left(\sigma/\sigma_0\right) = -f(y, \lambda) = -2\alpha(3Q)^{1/2}\left[1/y + ((4/3)y^3 + 2\lambda y^2 + 4y)/x\right] \tag{10a}$$

$$y^4 + \lambda y^3 + y^2 - x/4 = 0. \tag{10b}$$

We have used dimensionless inverse distance $y = (3Q)^{1/2}/r_s$ and temperature $x = T/T_x$ with $T_x = e^2/24k\alpha Q$, the latter being the transition temperature of the crossover between the Coulomb-gap and Mott's regimes [5], and where $\lambda = 2p/q(3Q)^{1/2}$ is the ratio between the dipole length p/q and the quadrupole length $(3Q)^{1/2}$. In the absence of the dipole term, i.e. $\lambda = 0$, y obeys a biquadratic equation with coefficients independent of the system, i.e. it has a universal behaviour. In this case we get the result of Aharony *et al* [5], corresponding to $f(y, 0) = Af(x)$ where $A = (8/3)\alpha(6Q)^{1/2}$ and

$$f(x) = \frac{1 + [(1+x)^{1/2} - 1]/x}{[(1+x)^{1/2} - 1]^{1/2}}$$

a universal function of T/T_x.

As first shown by Aharony *et al*, such a universal behaviour holds for the general case in which the potential energy is a sum of terms proportional to $1/r$ and $1/r^3$, irrespective of their physical meaning. The limit forms of $f(x)$ for $T \ll T_x$ and for $T \gg T_x$ [5] lead to

$\ln(\sigma/\sigma_0) = -(T_0/T)^\beta$ with $\beta = 1/2$ at $T \ll T_x$ and $\beta = 1/4$ at $T \gg T_x$, which reproduce the Coulomb gap results of Efros–Shklowskii at low T and Mott at high T [5–7]. With our parametrization of the potential energy, equation (9) we find that $T_0' = 8e^2\alpha/\epsilon k$ as $T \ll T_x$ and $T_0 = (3/2)(8/3)^4\alpha^3 Q/k$ as $T \gg T_x$. We deduce that these two limit cases correspond to the dominance of the charge term (low T) or the quadrupole term (high T) in the multipole expansion. The quadrupole term of the internal field provides in a natural way a direct physical meaning of the potential energy term $\approx 1/r^3$, usually attributed to an average energy spacing $\Delta E = (1/N_F r^3)$ of the levels of the localized states, with N_F a density of states at the Fermi level [6]. Similar conclusions can be obtained in two dimensions. In such a case the quadrupole term is of the form e^2Q/r^2 so that there is a universal behaviour with $\beta = 1/2$ at low T and $\beta = 1/3$ at high T with similar expressions for the parameters T_x, T_0' and T_0.

When the dipole term is non-zero, the equation obeyed by y has a solution which depends on λ, i.e. universality is lost, and f has to be solved numerically in general. In figure 1 and figure 2 we report $f(y(x), \lambda)$ resulting from such a numerical analysis for various values of λ, together with the universal case λ_0 of Aharony *et al* [5]. We find that, despite the lack of universality, for not too large values $\lambda < 3$ the curves can be made to superimpose with great accuracy (figure 3) to the universal curve by a suitable rescaling of T_x, corresponding to an increase of T_x as compared to the universal case.

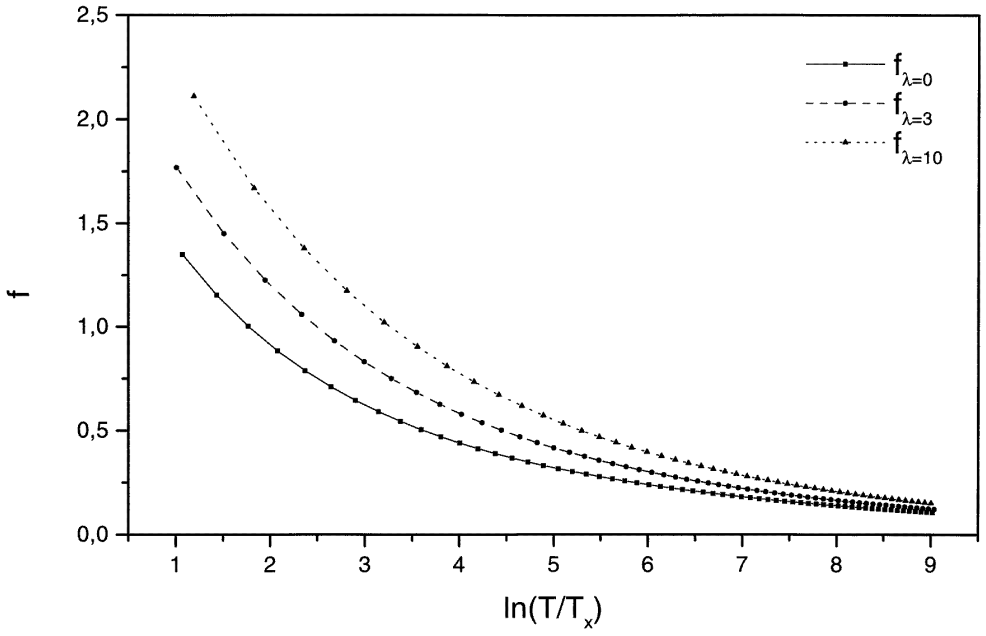

Figure 1. $f = f(y(x), \lambda)/[(8/3)\alpha\sqrt{6}Q]$ as a function of reduced temperature $x = T/T_x$ for various values of λ. $f_\lambda = 0$ refers to the case of [5].

Granular metals in the dielectric regime show insulating behaviour attributed to transport occurring through hopping of Fermi carriers between metallic grains dispersed in a dielectric matrix of width s between the grains [8]. The local field arises here from the charging of the grains during the hopping process. If r is the position of a carrier located close to the surface of grains such that $r \approx d$, d being the radius of grains, one has for the total potential

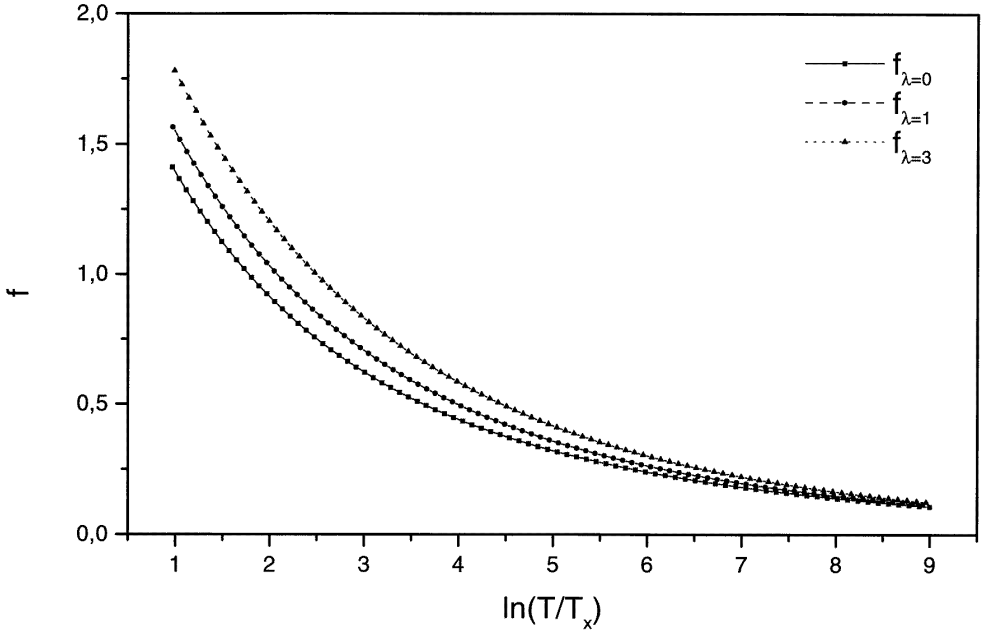

Figure 2. Same as in figure 1 or $\lambda < 3$.

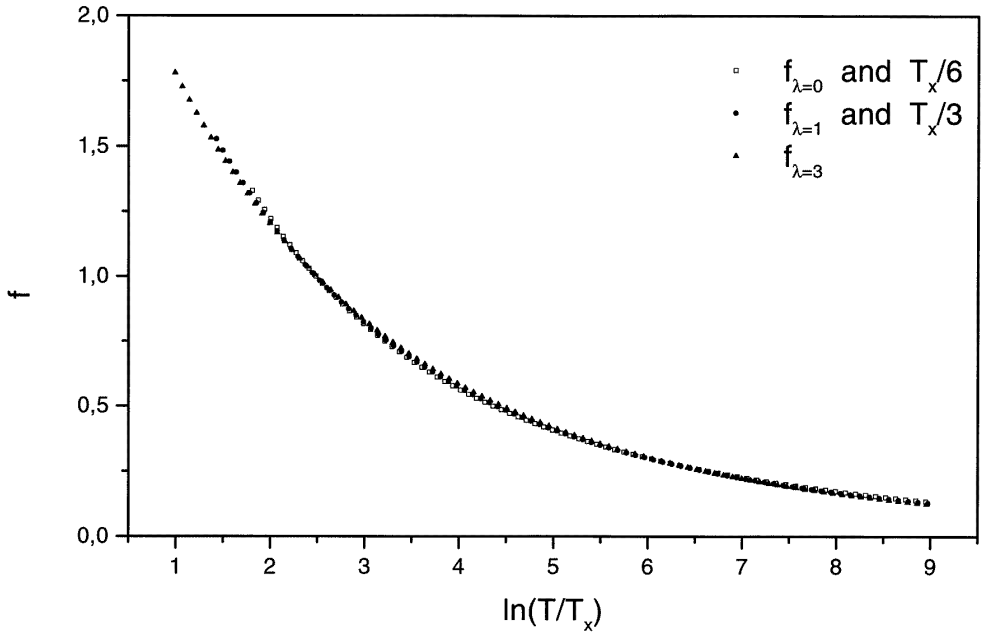

Figure 3. Same as figure 1, showing the effect of changing the scaling temperature.

energy

$$U + \delta U = e^2/4\pi\epsilon_0\epsilon r - e^2/4\pi\epsilon_0\epsilon(r+s). \tag{11}$$

The two terms represent the charging energy, occurring at the grain left charged. The two variables r and s are stochastic in nature. They can be connected through a relation $s/r = A =$ constant [8] from requirements of uniform internal composition. The charging energy can thus be rewritten in the form $e^2A/4\pi\epsilon_0\epsilon r(A+1)$. On using the probability of the form $P = k\mathrm{e}^{-2\chi r}$, χ being a suitable tunnelling factor [8], and the saddle-point procedure to maximize the emission probability one finds at the barrier point

$$\sigma = \sigma_0 \mathrm{e}^{-(T_0/T)^{1/2}} \tag{12}$$

where $T_0 = 2\chi e^2 A/\pi\epsilon_0\epsilon(A+1)k$.

The internal field is of the order of magnitude $L \approx e/4\pi\epsilon_0\epsilon d^2 A$ and is in general not solenoidal, due to a polarization charge between grains.

In general the simple assumption $s/r =$ constant may be relaxed on making more realistic assumptions on the probability of the grain dimension. In such cases, calculations predict [9–11] also temperature dependences of the form (12) with the exponent 1/4. The Coulomb term alone may prove to be a poor description of the internal field at the grain surface, and more terms arising from dipole and quadrupole contributions may be investigated.

Here too, crossover mechanisms may be expected. However, the distribution of the charge on the grains has different physical origin than the charge present on sites during hopping processes, the latter being related to the localization of the wavefunctions. Thus, the behaviour of the conductivity of granular systems may differ quantitatively, although not qualitatively, from the one in hopping systems [5].

Transport experiments in various systems can be parametrized by means of the internal field model and thus allow a determination of these fields. For Poole–Frenkel systems L can be deduced [3] either by fitting the I–V characteristics at large V or from the activation energy in the Arrhenius plots at low fields, which depends on L, according to equation (8). For hopping systems, one can determine the internal field from a knowledge of α, using its saddle-point value $L \approx 2\alpha kT/e$, at a given T. α can also be deduced from the reported T_0' values at $T < T_x$ in the Efros–Sklowskii regime [4]. The quadrupole moment Q can be obtained from the T_0 values in the Mott's regime as $T > T_x$ (with α known). From experiments in which a crossover regime is evidenced deduction of α and Q can be done simultaneously, by fitting the data through equations (10*a*) and (10*b*), either by using a universal parametrization as done in [5] (in this case the parameters are α and Q), or on allowing a dipole contribution as in this work (parameters are α, Q, p). For granular metals L can be inferred in a similar manner from the T_0 values of the conductivity law (12) or from knowledge of the dimension d of grains and the ratio d/s [8–11].

Results of conductivity studies reported in the literature refer to n-type Ge, n-type Si, the III–V compounds GaAs and InP and granular metal alloys [4], superconductors in the insulating phase [12–15] and systems close to a metal–insulator transition [4] also including Si:As [16], granulated Sn–Ge and Ag–Ge films [17], crystalline Ge with a high concentration of defects [18] and superconductors at the metallic border [19–21]. These studies indicate a $\ln(\sigma/\sigma_0) = -(T_0/T)^{\beta}$ law with the exponent changing from $\beta = 1/4$ to $\beta = 1/2$ as the temperature is lowered and the composition is varied. A crossover in temperature between the $\beta = 1/4$ and $\beta = 1/2$ regimes has been reported in insulating compensated n-type CdSe samples [22], CdTe doped semiconducting samples [23] (see also [5]) and in non-compensated Si:As [24]. Aharony *et al* [5] have shown that these data (referring in

particular to [22]) can be described by the universal function $f(x)$ with a proper scaling temperature T_x and a suitable choice of the parameter A.

Using our parametrization of T_0', T_0, T_x and A, all such results can be used to deduce information on the values of the parameters α, Q and p. In table 1 a summary of an analysis of this kind is reported for representative systems in which either exponent 1/2 or 1/4 is observed. It includes some exhibiting strong ($T_0 \approx 10^6$–10^7 K), moderate ($T_0 \approx 10^4$–10^5 K) and weak (vicinity of a metal–insulator transition) insulating character. In the insulating state, using typical values $\alpha^{-1} \approx 10$ A ($\alpha \approx 10^7$ cm^{-1}), $T_0 \approx 10^5$ K and $\epsilon \approx 10$, we find that the internal field $L = 2\alpha kT/e$ has the order of magnitude $L \approx 10^5$ V cm^{-1} at $T = 100$ K and the quadrupole moment $Q = kT_0\epsilon/[(3/2)(8/3)^4\alpha^3 e^2]$ as typical order of magnitude $Q \approx 100$ A^2. For the harder insulator, the increase of T_0 may be compensated by even a small decrease of α (note the cubic dependence of Q on α) and so the quadrupole may remain of the same order of magnitude. Close to a metal–insulator transition, the decrease of T_0 (vanishing at the transition) may be compensated by the increase of the localization length α^{-1} and the dielectric constant ϵ (both diverging at the transition, typical values being $\alpha^{-1} \approx 30$ A and $\epsilon \approx 100$ in weakly insulating samples [19]) and Q may remain of the same order of magnitude or increase. On the other hand, a definite monotonic decrease of L may be expected on approaching the transition to the metallic state, due to a progressive decrease of α.

Table 1. Orders of magnitude of the internal field evaluated at $T = 100$ K and of the quadrupole moment for representative materials, as obtained in this work.

Material	T_0 value (K)	β	Internal field ($\times 10^4$ V cm^{-1})	Quadrupole moment (A^2)
CdF_2:Gd [3]			1	—
SiO films [3]			5	—
Ge:Sb [4]	2×10^4	1/4	10	100
Ge:As [4]	210	1/2	1	—
Si:P [4]	2.2×10^6	1/4	10	100
Si.P [4]	10^3	1/2	1	—
n-InP [4]	8×10^4	1/4	10	100
a-$(Al_2O_3)_{1-x}W_x$ [4]	10^2		10	—
LaSrCuLiO [13]	7×10^6	1/4	10	100
BaKBiO [21]	1.8×10^6	1/4	10	100
$La_{2-x}Sr_xCuO_4$ [19]	645	1/4	1	100
	74	1/2	1	—
Si:As [16]	10^3	1/4	1	100
Ag:Ge [17]	25		1	100

Table 2. Comparison between the parametrization (α^{-1}, Q, $d = p/e$) of the data for the most insulating samples of [22] by means of the function $f(y(x), \lambda)$ with $T_x' = 6T_x$ (see text) of the present work, and the function $f(y(x), 0)$ with scaling temperature T_x of [5] ($\epsilon = 100$, $A = 8.03$, $T_x = 18.1 \times 10^{-3}$ K).

$-\ln(\sigma/\sigma_0)$	α^{-1} (A)	$\sqrt{Q}$ (A)	d (A)
$f(y(x), \lambda)$	441	520	$\approx 3\sqrt{Q}$
$f(y(x), 0)$	2650	3160	0

In table 2 we report the results for the parameters α, Q and p for systems exhibiting a crossover [22] with a comparison of values obtained with the universal parametrization of [5]. The results suggest that the same experimental data [2] or similar data [23, 24] may be consistent with a dipole contribution to the internal field, of length comparable to the quadrupole length $\sqrt{Q}$. The evaluated order of magnitude of this field $L = 2\alpha kT/e$ turns out to be $L \approx 10^4$ V cm^{-1}.

In conclusion, it can be said that there is evidence from both theoretical and experimental points of view of internal fields in insulators. In systems having centres of coulombic nature the field are temperature independent. In hopping systems they are (linearly) temperature dependent as a result of optimal hopping range between the localized sites.

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