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Unified thermopower in the variable range hopping regime

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Abstract

Since nearly 4 decades, various theoretical behaviours have been found for the thermopower in the variable range hopping regime. In 1969, Cutler and Mott have predicted a linear variation with temperature T of the thermopower: S = const.T. In the seventies, it has been found by Zvyagin, Overhof and Mott that S = const.T(1/2). In 1986, Triberis and Friedman have found S = const.T(-1/4) . But there is up to now no theoretical formulation of the thermopower when this one is T-independent. By choosing a specific distribution for the density of states, we show in this paper that all behaviours above can be unified in a unique thermopower formula. We find in addition with this formula, a T-independent expression given by: S=(L/xi)(k/e), in which xi is the wave function decay length and L is a characteristic length, depending on the form of the density of states.

Key words: Hopping conduction, Thermopower, Electric properties, Conductivity, Percolation

1 Introduction

Mott's paper1 [1] of 1969 has played a key role in the construction of the important theoretical edifice [2]-[9] on which is rested our understanding of the hopping conduction mechanism. The electric properties of various disordered systems and amorphous semiconductors have been explained [10] during more than 3 decades by using Mott's variable range hopping (VRH) theory. Such a theory is still extensively used today in varied fields, to investigate the mechanism of charge transport for example as well in correlated electron systems [11] as in biological systems as DNA [12].

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However, the study in the VRH regime of some thermoelectric properties such as the thermopower have been somewhat neglected. It seems indeed, that this one is ill adapted in its present form to support the experimental measurements of the Seebeck coefficient carried out on different VRH systems. A simple illustration of this is its persistent disobedience during more than 3 decades, to the predicted theoretical laws [4]-[8], observed in most amorphous semiconductors [6], [8], [13]-[17].

Because of new environmental problems, the field of the thermoelectric power generation has attracted recently a major interest in materials with high thermoelectric properties [18]. In this context, the explanation of the experimental behaviour of the VRH thermopower remains still problematic since there is not yet a clear theory that explains some TEP behaviours when conduction is by variable range hopping, as the divergent one observed at low temperature in ref [19] or the temperature independent one, reported by the authors of ref [20].

Such a theoretical insufficiency of the TEP is attributed in this work to the fragility of the original hypothesis concerning the nature of the density of states (DOS), with which the evaluation of the Seebeck coefficient has been made. By reconsidering the hypothesis of the "slow linear variation of the DOS" near Fermi level on which most of the VRH theories of the TEP are rested [4]-[8], we investigate by using the percolation theory both conductivity and thermoelectric power when the DOS takes the asymmetric generalized form:

$$N(E) = N(E_F) + g(E) \tag{1}$$

where N(E_F) is a finite density of states at Fermi level E_F and g(E) represents the asymmetrical part of N(E):

$$g(-E) = -g(E) \tag{2}$$

This choice of g(E), is motivated by the following reason: by using the concept of the random network of conductances [2],[3],[6], we can expect to find Mott $T^{-1/4}$ conductivity again since the number of conductances that belong to the critical path [3],[6], generated by N(E) of eq.(1 -2)would be quasi similar to the one generated by a constant DOS [2]. If so, we can expect to obtain different thermopower classes that correspond to the Mott $T^{-1/4}$ conductivity, rather than the unique an insufficient formula obtained by the classic VRH theories.

2 Percolation method for the VRH problem

It has been shown by using the percolation theory [2]-[7], that the conduction problem between localised states is equivalent to the conduction problem through a random network of conductances. Each conductance σ_{ij} defined by:

$$\sigma_{ij} = \exp\{-\frac{2r_{ij}}{\xi} - \frac{|E_i| + |E_j| + |E_i - E_j|}{2kT}\} \tag{3}$$

links two sites located at energies E_i and E_j, separated in space by the distance r_{ij}. In eq.(3), k is the Boltzmann constant, T is the temperature and ξ is the decay length of the wave function.

To solve a conduction-percolation problem, two critical conditions must be satisfied: the first concerns the number $m(E_i)$ of incoming conductances (or bonds) to a site located at energy E_i and positioned at the center of a sphere of radius r_{ij} :

$$m(E_i) = \frac{4\pi}{3} \int r_{ij}^3 N(E_j) dE_j \tag{4}$$

When averaged by a weighting probability function, $m(E_i)$ must reach the critical concentration c of conductances per site, solicited for conduction within an active energy layer Δ, given by (percolation criterion):

$$c = \frac{\int_{-\Delta}^{\Delta} m^2(E_i) N(E_i) dE_i}{\int_{-\Delta}^{\Delta} m(E_i) N(E_i) dE_i} \tag{5}$$

The second critical condition concerns the nature of conductances that are solicited for conduction. To be an efficient conductor, each conductance σ_{ij} must be larger than a critical conductance given by:

$$\sigma_c = \exp\{-\frac{\Delta}{kT}\} \tag{6}$$

Physically, when these two critical conditions are satisfied, it appears a continuous (critical) path of conductances, joining one side of the VRH system to the other. The problem of the random network is said solved only when σ_c is identified, and this occurs when eq. (5) is solved with respect to Δ.

3 Conductivity of the asymmetric DOS

We show now that our prediction to find again Mott $T^{-1/4}$ conductivity for the DOS given by eq.(1, 2) is true. We take for this a generalized asymmetric DOS form given by:

$$N(E) = N(E_F) + s_q.E^q = N(E_F)\left[1 + \nu_q.E^q\right] \tag{7}$$

In this equation s_q is a positive constant, the energy E is measured from the Fermi level E_F=0 and q is a real number so that g(E) obeys eq.(2). Typical values of q can be q=1, 3, 5, etc, or q=1/3, 1/5, 1/7 or 5/3, 5/7 etc.

Let start our conductivity computation by evaluating the number $m(E_i)$, when $\sigma_{ij}>\sigma_c$. For E_i >0 eq.(4) yields:

$$m(E_i) = \frac{4\pi}{3}\left(\frac{\xi}{2kT}\right)^3 \left[I_1 + I_2 + I_3\right] \tag{8}$$

where the I_1, I_2 and I_3 integrals are given by:

$I_1 = \int_0^{E_i}(\Delta - E_i)^3 N(E_j)dE_j$

$I_2 = \int_{E_i}^{\Delta}(\Delta - E_j)^3 N(E_j)dE_j$

$I_3 = \int_{-\Delta+E_i}^{0}(\Delta - E_i + E_j)^3 N(E_j)dE_j$

By inserting the DOS of eq.(7) in I_1, I_2 and I_3 and by putting x=E_i/Δ, a new dimensionless energy variable, eq.(8) yields after an extremely laborious calculation:

$$m(x,q) = m_0(x) + \mu(x,q) \tag{9}$$

We have written in eq.(9) the number of conductances attached to the site of energy E_i as the sum of two terms: $m_0(x)$ represents the number of conductances resulting from the symmetrical part $N(E_F)$ of the density of states and $\mu(x,q)$ is the number of conductances resulting from the asymmetrical part of N(E):

$$m_0(x) = \frac{M_0}{2}(1+x)(1-x)^3 \tag{10}$$

$$\mu(x,q) = M_0\frac{\Delta^q}{E_0^q}\frac{6\Gamma(q+1)}{\Gamma(q+5)}f(x,q) \tag{11}$$

Here -E_0 is an energy below E_F (see Fig.1), solution of the equation N(E) = 0; $\Gamma(z)$ is the gamma function of z and the parameters M_0 and $f(x,q)$ are given by the following expressions:

$M_0 = \frac{4\pi}{3}\left(\frac{\xi}{2kT}\right)^3 \Delta^4 N(E_F)$

$f(x,q) = 1 - A_q.x^{q+2} + B_q.x^{q+3} - C_q.x^{q+4} - (1-x)^{q+4}$

where we have: $A_q = (q^2+7q+12)/2$; $B_q = q^2+6q+8$; $C_q = (q^2+5q+6)/2$

We are now ready to solve our percolation-conductivity problem by replacing eq.(7) and eq.(9) in eq.(5):

$$c = \frac{\int_{-1}^{1} \left[m_0^2(x) + 2m_0(x)\mu(x,q).\nu_q.x^q + \mu^2(x,q)\right] dx}{\int_{-1}^{1} \left[m_0(x) + \mu(x,q).\nu_q.x^q\right] dx} \tag{12}$$

In eq.(12) we have omitted to write the asymmetrical functions since their integrations cancel over positive and negative energies.

Before tackling the tedious resolution of this equation, may be it would be advantageous to examine and compare first the terms of each integrand. If we place ourselves in the situation shown in fig.1, where the temperature of the VRH system is such as the active energy layer $\Delta < E_0$, it becomes then apparent that we can neglect in eq.(12) all terms containing the $\mu(x,q)$ number since the surface delimited by these terms is negligible in comparison with the one corresponding to $m_0^2(x)$ when q$\geq$ 1/3 (see Fig.2).

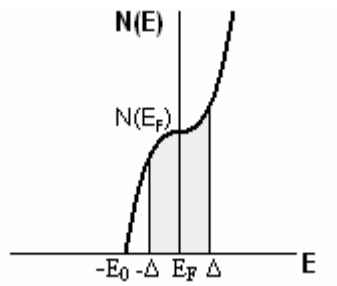

Fig. 1. Density of states representation with an active energy layer $\Delta < E_0$.

In such a situation, eq.(12) becomes quasi similar to the one found in [3] for a constant DOS:

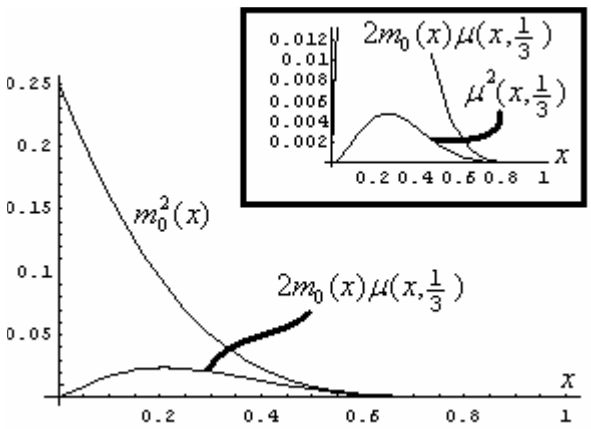

Fig. 2. Representation of two integrand terms of eq.(12) in unit of M_0^2 for q=1/3. The inset figure shows how much $\mu^2(x,q)$ in eq.(12) is small.

$$c = \frac{\int_{-1}^{1} m_0^2(x)dx}{\int_{-1}^{1} m_0(x)dx} \tag{13}$$

Integrating eq.(13) and taking as in [3] c = 1.7, we obtain:

$$\frac{\Delta}{kT} = \left(\frac{T_0}{T}\right)^{\frac{1}{4}} \tag{14}$$

where $T_0^{1/4} = 1.8/(k.N(E_F).\xi^3)^{1/4}$.The numerical value 1.8 of $T_0^{1/4}$ is similar to the one found earlier by Pollak in [3]. Consequently, equations (6) and (14) show that Mott $T^{-1/4}$ conductivity is valid with a very good approximation for any DOS of eq.(7), when q$\geq$ 1/3.

In the limit q$\rightarrow$0 (step like DOS at E_F), we lose the approximation that gave eq.(13) since $m_0^2(x)$ and $2m_0(x)\mu(x,0)$ become comparable. The re-evaluation of eq.(12) in this case yields:

$$c \approx \frac{\int_{-1}^{1} \left[m_0^2(x) + 2m_0(x)\mu(x,0).\nu_0\right] dx}{\int_{-1}^{1} \left[m_0(x) + \mu(x,0).\nu_0\right] dx} \tag{15}$$

$$= \frac{4\pi}{3}\frac{85}{252}\left(\frac{\xi}{2kT}\right)^3 .N(E_F).\Delta^4$$

Here again the conductivity follows Mott law: $\sigma = \exp\{-(T_0/T)^{-1/4}\}$ in which the new numerical constant of $T_0^{-1/4}$ takes the value: 1.76. Such a negligible change of $T_0^{-1/4}$ is of course indetectable during any experimental mesurement, implying the validity of eq.(14) for any q.

4 The unified thermopower

To compute the Seebeck coefficient S, we make use of the formula:

$$S = \frac{k}{e}\frac{\Pi}{kT} \tag{16}$$

here e is the electronic charge and Π is the Peltier heat. Equation 16 is one of the classical Kelvin relations of thermoelectricity. For metals it gives [21]:

$$S = \frac{\pi^2}{3}\frac{k}{e}kT\left[\frac{\partial \ln \sigma(E)}{\partial E}\right]_{E=E_F} \tag{17}$$

In the variable range hopping regime, Π may be interpreted [5] as the mean energy of any site that belongs to the continuous critical path of conductances. We can then write it under the form:

$$\Pi = \frac{\int E.N(E).p(E)dE}{\int N(E).p(E)dE} \tag{18}$$

The Peltier heat in this expression appears as an energy E, weighted the by a probability factor p(E) that is assumed proportional to the number m(E) of conductances attached to a site located at energy E. Inserting equations (7) and (9) in eq.(18) we obtain:

$$\Pi = \frac{\int \left[N(E_F).E.\mu(E,q) + s_q.m_0(E).E^{q+1}\right] dE}{\int \left[N(E_F).m_0(E) + s_q.E^q.\mu(E,q)\right] dE} \tag{19}$$

In this expression, we have omitted again to write the asymmetrical factors of E since their integrations cancel over positive and negative energies. For q$\geq$ 1/3 we can also neglect the second denominator term since the active layer of states solicited for the conduction process must verify eqs (1) and (2), in which case we have $s_q.E^q < N(E_F)$. Integrating and inserting the Peltier heat of eq.(19) in the thermopower expression of eq.(16), we obtain:

$$S = F(q)\frac{k}{e}\frac{\Delta^{q+1}}{kT}\left[\frac{d\ln N(E)}{dE^q}\right]_{E=E_F} \tag{20}$$

where $F(q) = 60\left[\Gamma(q+1)/\Gamma(q+7)\right](q+1)(q+4)$. Replacing the active layer energy Δ by its expression of eq.(14), we find that the T dependence of the variable range hopping thermopower is a class given by:

$$S = F(q)\frac{k}{e}k^q T_0^{\frac{q+1}{4}} T^{\frac{3q-1}{4}}\left[\frac{d\ln N(E)}{dE^q}\right]_{E=E_F} \tag{21}$$

In the case of a linear asymmetry of density of states (q = 1), the classical variable range hopping thermopower formula [4-6] is recovered:

$$S = F(1)\frac{k}{e}k\left(T_0 T\right)^{\frac{1}{2}}\left[\frac{d\ln N(E)}{dE}\right]_{E=E_F} \tag{22}$$

with the exact numerical factor found in [5]: F(1) $=\frac{5}{42}$.

In the limit q$\rightarrow\infty$ (constant DOS near Ef), we have S=0 since F(∞)=0. This is in agreement with all thermopower theories indicating that S=0 when the density of states is symmetric with respect to Fermi level.

Eq.(21) is in fact an unified formulation of the thermopower corresponding to Mott conductivity since it includes according to q, the following thermopower class/behaviors:

4.1 Integer metallic class

It is a class obtained from eq.(21) for any odd integer q. S$\sim T^{1/2}$ (q= 1) is only one element of this class.

4.2 Fractional metallic class

It is a class obtained from eq.(21) for any fractional q>1/3, satisfying eqs.(1 and 2). We find in this class for q=5/3, the first VRH thermopower, predicted in 1969 by Cutler and Mott [22].

4.3 Semiconductor class

It is a class obtained from eq.(21) for any fractional) with 0<q<1/3. If q tends to zero as 1/p, where p is an infinite odd number (step like DOS at E_F), we find , the thermopower due to small polarons found earlier by Triberis and Friedman [23] for constant DOS band above E_F.

4.4 The constant thermopower

The pivotal value q=1/3, delimits the metallic and semiconductor classes. Its thermopower is T-independent and is given by:

$$S = F(\frac{1}{3})\frac{k}{e}\,(kT_0)^{\frac{1}{3}}\left[\frac{d\ln N(E)}{dE^{1/3}}\right]_{E=E_F} \tag{23}$$

Putting in this expression $\left[d\ln N(E)/dE^{1/3}\right]_{E_F} = 1/E_0^{1/3}$ and replacing T_0 by its expression of eq.(14), we obtain a T-independent formula of the thermopower:

$$S = \beta\frac{L}{\xi}\frac{k}{e} \tag{24}$$

where β is a numerical factor of order 1 and :

$$L = \left(\frac{1}{N(E_F).E_0}\right)^{\frac{1}{3}} \tag{25}$$

is a characteristic length defined by the nature of the DOS. In amorphous semiconductors where a constant thermopower of magnitude $\approx 100\mu VK^{-1}$can be observed [14], we expect a length of order ξ for L.

5 Conclusion

We have shown in this work that the thermopower in the VRH regime may have according to the DOS shape of eq.(7) 3 different behaviours: it can have a metallic behaviour if q>1/3, it can have a semiconductor behaviour if 0<q<1/3, or it can be T-independent if q=1/3.

References

[1] N.F. Mott, Phil. Mag. **19**, 835 (1969)

[2] V. Ambegaokar, B.I. Halperin, and S. Langer, Phys.Rev. **B 4**, 2612 (1971)

[3] M. Pollak, Journ. Non-cryst. Sol. **11**, 1 (1972)

[4] I.P. Zvyagin, phys. stat. sol. (b) **58**, 443 (1973)

[5] I.P. Zvyagin in *Hopping transport in solids,* eds. M. Pollak and B. I. Shklovskii, (North Holland, Amsterdam, 1991), p.143

[6] H. Overhof, phys. stat. sol. (b) **67**, 709 (1975)

[7] M. Pollak, and L. Friedman, *Localization and Metal-Insulator Transitions* Vol.2 Eds. H. Fritzsche and D. Adler, (Plenum Press, New-York, 1985), p.347

[8] P. Nagels, M. Rotti, and R. Gevers, Journ. Non-cryst. Sol. **59-60**, 65 (1983)

[9] D. Janaa and J. Fort: Physica B **344**, 62 (2004)

[10] N.F. Mott and E.A. Davis, *Electronic Processes in Non-Crystalline Materials, 2nd Ed.* (Clarendon Press, Oxford 1979)

[11] A. A. Taskin and Yoichi Ando: Phys. Rev. Lett. **95**, 176603 (2005)

[12] Z. G. Yu and X. Song, Phys. Rev. Lett. **86,** 6018 (2001)

[13] W. Beyer, and J. Stuke, *Proceedings of the 5th Int. Conf. on Am. and Liquid Semiconductors*, Eds. Stuke, J. and Brenig, (Taylor and Francis, London, 1974) p.251

[14] A. J. Lewis, Phys. Rev. B **13**, 2565 (1976)

[15] G. Sherwood, M.A. Howson and G. J. Morgan; J. Phys.: Condens. Matter **3,** 9395 (1991)

[16] T. Kawahara, S. Tamura, H. Inai, Y. Okamoto, and J. Morimoto: J. Mater. Res., Vol. **14,** No. 4, (1999)

[17] S. Nakamae, D. Colson, A. Forget, I. Legros, J.F. Marucco, C. Ayache and M. Ocio, Phys. Rev. B **63,** 092407 (2001)

[18] A. A. Taskin, A. N. Lavrov, and Yoichi Ando; Phys. Rev. B **73,** 121101(R) (2006)

[19] G. S. Nolas, M. Beekman, and R. W. Ertenberg: J. Appl. Phys. **100,** 036101 (2006)

[20] J. J. Neumeier and H. Terashita Phys. Rev. B **70,** 214435 (2004)

[21] J.M. Ziman, *Principles of the theory of solids*, (University Press, Cambridge 1972)

[22] Cutler, M. and Mott, N. F., Phys. Rev. **181,** 1336 (1969).

[23] G. P. Triberis and L. R. Friedman, Journ. Non-cryst. Sol. **79,** 29 (1986).