ON THE VARIABLE RANGE HOPPING THERMOPOWER IN AMORPHOUS MATERIALS

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Abstract: *By suggesting a simple density of localized states for amorphous materials and using the percolation method the analytical expression is obtained for describing qualitatively the observed variable-range hopping thermopower crossover from the Mott $T^{1/2}$-behaviour to the temperature-independent behaviour as the temperature increases. The crossover shows a profound manifestation of the Coulomb correlation along that observed in VRH conductivity crossover.*

1. Introduction

The Variable Range Hopping (VRH) conception was first introduced by Mott [1] with his famous $T^{-1/4}$-law for the temperature dependence of *dc* conductivity. Later, it was shown by Efros and Shklovskii (ES) [2] that the Coulomb correlation between localized electron states leads to an appearance of a depressed gap (Coulomb gap) in the density of states (DOS) at the Fermi level. The most observable manifestation of the Coulomb gap is that the temperature dependence of VRH conductivity should obey the ES law $\ln\sigma(T) \propto T^{-1/2}$, instead of the Mott law $\ln\sigma(T) \propto T^{-1/4}$ for three dimensional system.

Experimentally, both the Mott law and the ES-law have been observed in a great number of measurements for various materials [3]. Moreover, for some materials the low-temperature measurements show a smooth crossover in $\sigma(T)$ from the Mott $T^{-1/4}$-behaviour to the ES $T^{-1/2}$-behaviour or inversely as temperature decreases. Such a crossover is considered as an evidence of the role of the Coulomb correlation in VRH $\sigma(T)$ [4].

Thus the role of the Coulomb correlation effects in temperature dependence of VRH conductivity is well understood both experimentally and theoretically, while however much less is known about the role of this correlation in other transport properties, in particular, in the thermoelectric power (thermopower). The thermopower, as was originally noted by Mott [5], is very sensitive to the material parameters and may be expected to provide a good test for the principal ideas of the transport theory of disordered systems. However, the theoretical description of the thermopower data for amorphous materials encounters some difficulties. The reason, as pointed out by Overhof [6], is that an exact treatment is very tedious and can be carried out analytically only for the simplest form of DOS. Using Mott constant DOS and applying percolation method, Zvyagin [7] has obtained for the VRH thermopower the law $S(T) \propto T^{1/2}$. The same results were received by others [5, 6]. Burn and Chaikin [8] have pointed out that in contrast to a Mott model, the thermopower in the ES electron-electron interaction model should approach a non-zero constant as

$T \to 0$. There is a number of experimental reports of the VRH thermopower crossover from the Mott $T^{1/2}$-behaviour to the temperature-independent behaviour as the temperature decreases [9, 11]. However, in various amorphous materials the observed data match the inverse directions: the thermopower is almost constant at sufficient high temperature, but in the low temperature range it rapidly increases with increasing temperature [13-16].

To our knowledge, there is no adequate theoretical work has been made for description of such features.

In this paper, using an effective form of DOS for amorphous materials, we obtain the useful expression for describing Mott-ES crossover of VRH thermopower. The derived expression shows a profound manifestation of the Coulomb correlation along that observed in VRH conductivity. Besides, it is simple and easy to be used in comparison with experiments.

The outline of this work is as follows: In the second section, based on the percolation method the VRH thermopower is derived by using the DOS suggested for systems under study. The received result is discussed in the third section. It is shown that at low- and high- temperature limits our expression tends to the Mott- and ES behaviour, respectively. At an intermediate temperature range the present result describes the smooth crossover between these behaviours. The comparison with experiments is made at the end of third section. Finally, the conclusions are given in the fourth section.

2. VRH thermopower expression

The thermopower S is defined as [7]:

$$S = \Pi/eT, \tag{1}$$

where Π is the Peltier heat, e is the elementary charge. By linearizing the rate equation and applying the percolation method, Zvyagin shows that in the VRH regim the Peltier heat Π is equal to the hopping energy [9]. The VRH thermopower could be then found as:

$$S = \frac{1}{eT} \frac{\int EG(E)p(E)dE}{\int G(E)p(E)dE}, \tag{2}$$

where $G(E)$ is density of states, E is the one-particle energy, which is measured from the Fermi level and:

$$p(E) = \int d\mathbf{r} \int dE' G(E') \theta\Big(\eta_C - \frac{2r}{\xi} - \frac{|E| + |E'| + |E - E'|}{2k_B T}\Big). \tag{3}$$

Here θ is the Heaviside step function, η_C is the percolation threshold, ξ is the localization length and k_B is Boltzmann constant. The integration region is $|E| < \Delta = \eta_C k_B T$.

The expressions of Eqs. (2) and (3) show that the thermopower is entirely determined by the form of the DOS $G(E)$. From these expressions it is clear that, the symmetric part of the DOS does not contribute to the VRH thermopower and both the sign and the magnitude of thermopower are determined by an asymmetry (even if it is small) in the

contributions from sites above and below the Fermi level in the band $|E| < \Delta$. Assuming the DOS being a slowly varying function of energy we can neglect terms with higher derivatives in the expansion of the DOS and write it in the asymmetric form:

$$G(E) = G_a(E)\Big(1 + \gamma E\Big), \tag{4}$$

where $G_a(E)$ is symmetric part of the DOS, which does not give any contribution to the VRH thermopower [7]. The asymmetric correction that responds to the VRH thermopower is assumed to be small, i.e. it is assumed in Eq. (4) that $\gamma\in << 1$, where $\in$ is the optimum hopping energy. The factor γ, measuring an asymmetricalness of DOS, should be considered as a material parameter, which might even be negative [9].

To calculate VRH thermopower, we start from an assumption that for amorphous materials, the DOS near the Fermi level has the form [10]:

$$G_a(E) = G_0\Big(1 + \frac{E^2}{E_0^2}\Big), \tag{5}$$

where E_0 is adjustable parameter, which should be used in fitting theoretical results to experimental data. It is clear that the DOS of Eq. (5) tends to the Mott constant DOS in the limit of $|E| << E_0$ and to the ES Coulomb gap DOS $G(E) = (3/\pi)(\kappa/e^2)^3|E|^2$ in the opposite limit [2]. This form of DOS was previously suggested for describing the Mott-ES VRH conductivity crossover in amorphous materials [10]. The detail discussion of the chosen DOS of Eq. (5) is given in ref. [10]. We would like here mention only that the DOS (5) is widely accepted for amorphous materials [5].

The procedure of calculating the VRH thermopower consists of two steps: first we determine the threshold η_c, and then put it into Eq. (2) to evaluate $S(T)$. In order to evaluate $\eta_C(T)$, we use the standard Mott optimizing procedure [1], which is started with the hopping probability:

$$p = \nu_{ph}\exp(-2r/\xi - E/k_BT) = \nu_{ph}\exp(-\eta), \tag{6}$$

where ν_{ph} is an attempt frequency that cannot exceed the maximum phonon frequency. The energy E can be related to the hoping distance r by normalizing to unity the number of states in a given volume:

$$\frac{4}{3}\pi r^3\int_0^E G(E)dE = 1. \tag{7}$$

On the basis of the DOS Eq. (5), using Eq. (7) we already have:

$$r = \Big[\frac{4}{3}\pi G_0 E\Big(1 + \frac{E^2}{3E_0^2}\Big)\Big]^{-1/3} \tag{8}$$

Substituting r given by Eq. (8) into Eq. (6) and minimizing η we obtained following equations for determining $\eta_C(T)$:

$$\eta_C(T) = \frac{2r}{\xi} + x\frac{T_0}{T}, \tag{9}$$

$$x^{-4/3}(1 + x^2)(1 + \frac{x^2}{3})^{-4/3} = Q\Big(\beta_M\frac{T_0}{T_M}\Big)^{1/3}\frac{T_0}{T}, \tag{10}$$

$$\frac{2r}{\xi} = \frac{3}{Q}\Big(\beta_M\frac{T_0}{T_M}\Big)^{-1/3}\Big(x + \frac{x^2}{3}\Big)^{-1/3}, \tag{11}$$

where $x = E/E_0, T_0 = E_0/k_B, T_M = \beta_M/(k_B G_0 \xi^3), \beta_M \approx 18.1$ and $Q = (3/2)(4\pi/3)^{1/3}$.

These equations are very simple to solve numerically for determining η_C as a function of the temperature T. According to percolation theory, the VRH conductivity should behave as $\sigma(T) = \sigma_0 \exp[-\eta_C(T)]$. In the limiting case of $x \equiv E/E_0 >> 1$, from Eqs. (9)-(11) we already have $\eta_C = (T_M/T)^{1/4}$, which is exactly coincident with Mott $T^{-1/4}$-law. In the opposite limiting case of $x << 1$, we have $\eta_C = (T_{ES}/T)^{1/2}, T_{ES} = \beta_{ES}(e^2/k_B \kappa \xi), \beta_{ES} \approx 7.27$ and the ES $T^{-1/2}$-law.

Now, using the suggested DOS $G_a(E)$ of Eq. (5) the expressions of Eqs. (2) and (3) could be evaluated simply. To the terms linear in the small parameter $\gamma \in << 1$ the VRH thermopower obtained from Eqs. (2)-(3) is the following:

$$\frac{S}{S_0} = \eta_C^2 T_1 \frac{1/84 + (1/216)\eta_C^2 T_1^2 + (29/55440)\eta_C^4 T_1^4}{1/10 + (1/63)\eta_C^2 T_1^2 + (1/1080)\eta_C^4 T_1^4}, \tag{12}$$

where $T_1 = k_B T/E_0$ and $S_0 = \gamma E_0 k_B/e$.

Thus, to calculate S at a given temperature one has first to solve Eqs. (9) - (11) in getting η_C, and then, to put the obtained value of η_C into Eq. (12) for further calculating S.

3. Discussion

In the limiting case of $E << E_0$, the expressions (9)-(11) give $\eta_C = (T_M/T)^{1/4}$ and the expression (12) gives for VRH thermopower the $T^{1/2}$-law:

$$S(\text{Mott}) = \frac{5}{42}\gamma T_M T^{1/2} k_B^2/e. \tag{13}$$

In the opposite limit $E >> E_0$, when the DOS of Eq. (5) takes the form of the ES Coulomb gap, and therefore the expressions (9)-(11) give $\eta_C = (T_{ES}/T)^{1/2}$, we receive for the VRH thermopower following expression:

$$S(\text{ES}) = \frac{87}{159}\gamma T_{ES} k_B^2/e. \tag{14}$$

The expressions (13), (14) are agree qualitatively with those obtained by Burn and Chaikin [8], using the Mott constant DOS and the Coulomb gap DOS, respectively.

As an illustration, a solution of Eq. (12) is presented in Fig. 1 together with the limit expressions (13) and (14). Clearly, as can be seen from this figure, there exists smooth VRH thermopower crossover from the Mott $T^{1/2}$-behaviour of Eq. (13) to the temperature-independent behaviour of Eq. (14) as the temperature increases. Such a crossover is considered as a consequence of the electron-electron interaction [3]. One might expect that the thermopower and conductivity crossovers could be parallelly observed. The latter crossover is also shown in the inset, where the $\ln(\eta_c)$ is plotted vs $\ln(T)$. The slopes of the straight lines are equal $-\frac{1}{4}$ and $-\frac{1}{2}$ showing the Mott and ES limits, respectively. From Fig. 1 it is obviously that the crossover in the thermopower is even more clear than that in conductivity.

Experimentally, the thermopower measurements at low temperatures have been reported by many authors for a-Ge and a-Si [13-16]. Measuring various transport characters

of as-deposited a-Ge samples in a large temperature range, Lewis [14, 15] has observed the Mott $T^{-1/4}$-law and the more rapidly rise of the thermopower at lowest temperature, than that predicted by $T^{1/2}$ law. For most amorphous semiconductors [13-16], in the high temperature range, thermopower is almost constant, i.e. its temperature dependence is weaker than that given by $T^{1/2}$ law. We would like here emphasize that above mentioned features of thermopower behaviour could be qualitatively described in large temperature range by the curve in Fig. 1.

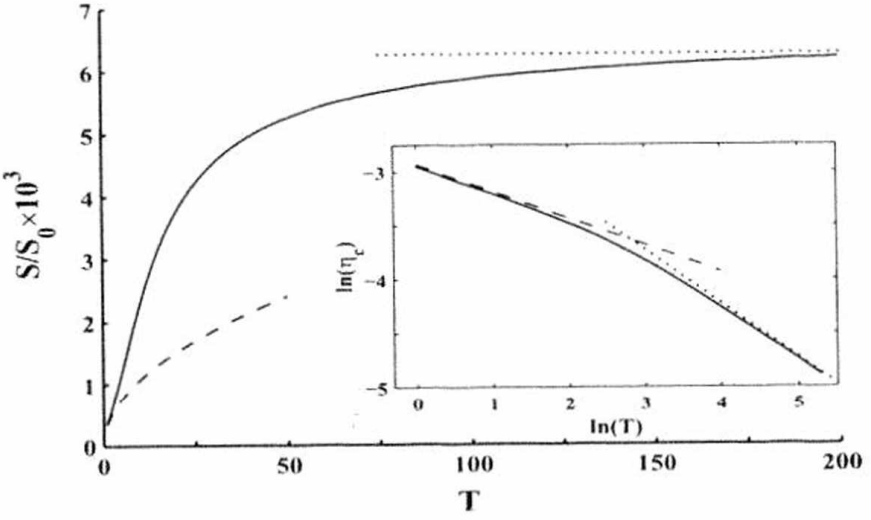

Figure 1. The numerical solution of expressions (9)-(12) (solid lines) is presented in together with the limits of Eqs. (13) (dashed line) and (14) (dots); $S_0 \equiv \gamma E_0 k_B/e$. The parameter used: $E_0 = 2.10^{-3}$.

Inset: $\ln(\eta_c)$ is plotted vs $\ln(T)$. The slopes of the straight lines are equal: -1/4 (dashed line) and -1/2 (dots).

We like to note that, there are still difficulties in quantitative comparison with experimentals [11]. There are some reasons: (i) the magnitude of thermopower is often so small that could even not dominate measurement errors; (ii) VRH thermopower is very sensitive to the conditions in preparing measurement samples (vacuum level, impurity content, deposition rate, substrate temperature ...). So, at the present stage the theory of the hopping thermopower can only be expected to provide a qualitative description of the experimental data [9].

4. Conclusion

Using suggested form of DOS (5) for amorphous materials and the standard Mott optimizing procedure we have obtained the exponent of the VRH conductivity as a function of the temperature. By applying percolation method we have received analytical expression for describing the dependence of VRH thermopower on temperature for amorphous materials. This expression shows the crossover in the temperature dependence of the thermopower from the Mott behaviour to the ES behaviour in parallel with the observed conductivity crossover. The obtained expression, on the one hand, is simple and easy to be used in comparison with experiments and, on the other hand, shows a profound manifestation of the Coulomb correlation.

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VỀ SUẤT NHIỆT ĐIỆN ĐỘNG Ở MIỀN DẪN NHẢY BƯỚC BIẾN ĐỔI TRONG VẬT LIỆU VÔ ĐỊNH HÌNH

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Bằng việc đề xuất một mật độ trạng thái đơn giản cho vật liệu vô định hình và sử dụng phương pháp lý thuyết thấm, đã tìm được biểu thức giải tích mô tả định tính sự chuyển của suất nhiệt điện động trong miền dẫn nhảy bước biến đổi (VRH thermopower) từ quy luật Mott $T^{1/2}$ đến quy luật ES không phụ thuộc nhiệt độ khi nhiệt độ tăng. Sự chuyển này cùng với sự chuyển Mott-ES đã được quan sát thực nghiệm đối với độ dẫn điện cho thấy rõ biểu hiện của tương quan Coulomb trong miền dẫn nhảy bước biến đổi.