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LETTER TO THE EDITOR

Thermoelectric Power for Carriers in Localized States: A Generalization of Heikes and Chaikin–Beni Formulae

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An extension of the well-known Heikes and Chaikin–Beni formulae is proposed for the expression of the thermoelectric power for carriers occupying localized states. The derivation is based on the same approximations as those previously used. It is emphasized that the use of any of these formulae is far from being straightforward, but requires a careful evaluation of the relevant parameters.

It is generally assumed that for localized particles diffusing due to a hopping process, in the high temperature limit, the thermoelectric power is given by the entropy per carrier

$$\alpha = -\frac{1}{|e|}\frac{\delta S}{\delta n}, \qquad [1]$$

where e is the electron charge and S is the configurational entropy. Then the problem reverts to a simple calculation of the number Ω of configurations in the most probable state and to apply the usual Boltzmann formula:

$$S = k \ln \Omega + \text{const.}$$

For carriers in nondegenerate states and forbidden double occupancy of a single site, Ω is given by

$$\Omega = \frac{N!}{(N-n)!\,n!}.$$

Using Stirling's formula leads to the well-known Heikes formula

$$\alpha = -\frac{k}{|e|}\ln\frac{1-c}{c},$$

with $c = n/N$, where n is the number of electrons and N is the number of available sites.

However, Chaikin and Beni (CB) have pointed out that if carriers are electrons having a spin $S = \frac{1}{2}$, one must take into account a $\beta_e = 2$ spin degeneracy. For n electrons, the number of configurations is therefore multiplied by 2^n and formula [2] must be changed to reflect the CB formula:

$$\alpha = -\frac{k}{|e|}\ln\left(2\frac{1-c}{c}\right). \qquad [2]$$

We may note that the CB formula can also be expressed as a function of the hole concentration. Assuming a hole concentration $c_h = p/N$, we have $c_h = 1 - c$ and

$$\alpha = +\frac{k}{|e|}\ln\left(\frac{1}{2}\frac{1-c_h}{c_h}\right). \qquad [3]$$

We immediately see that this equation differs from the "symmetric" one of the CB formula, sometimes used for holes:

$$\alpha = +\frac{k}{|e|}\ln\left(2\frac{1-c_h}{c_h}\right). \qquad [4]$$

Actually, Eq. [4] corresponds to twofold-degenerate holes distributed over a network of nondegenerate electrons. For instance, Eq. [3] should apply to *low spin* ($S = 0$) Cu^{3+} holes in a network of ($S = \frac{1}{2}$) Cu^{2+} ions, whereas Eq. [4] is relevant to O^- ($2p^5$) holes distributed among oxides ($S = 0$) O^{2-} ions.

Actually, derivation of a formula more general than the CB equation—i.e., corresponding to a system of n electrons with a degeneracy factor β_e and p holes ($p = N - n$) with a degeneracy factor β_h—is straightforward.

Starting with Eq. [1] and the Boltzmann formula and using Stirling's approximation, one finds

$$\alpha = -\frac{k}{|e|}\ln\left(\frac{\beta_e}{\beta_h}\frac{1-c}{c}\right) = +\frac{k}{|e|}\ln\left(\frac{\beta_h}{\beta_e}\frac{1-c_h}{c_h}\right).$$

Therefore, for a system containing a mixed valent cation $M^{n+}/M^{(n+1)+}$, where the spin values of M^{n+} is S_n and the spin value of $M^{(n+1)}$ is S_{n+1}, we have

$$\alpha = -\frac{k}{|e|}\ln\left(\beta\frac{1-c}{c}\right) = +\frac{k}{|e|}\ln\left(\frac{1}{\beta}\frac{1-c_h}{c_h}\right), \quad [5]$$

where

$$\beta = \frac{2S_n + 1}{2S_{n+1} + 1}. \quad [6]$$

However, in the presence of a magnetic ordering or if an external magnetic field is applied, which would remove the spin degeneracy, Eq. [6], of course, no longer holds; in this case, $\beta = 1$ and the Heikes formula is expected to hold. These very simple considerations might better explain why many interpretations worked out with the Heikes formula ($\beta = 1$)– gave good agreement with experiment. This simply means that the ratio β_e/β_h was close to unity.

In conclusion, I would like to emphasize that the application of CB or Heikes formulae is not as straightfoward as it looks at first glance; besides the problem of choosing the right β value, there remains that of evaluating the values of the number of available sites (N) and that of carriers, taking into account the possibility of trapping, polaron formation, and various types of interactions!

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REFERENCES

1. P. M. Chaikin and G. Beni, *Phys. Rev. B* **13,** 647 (1976).