# Critical behavior of the thermoelectric power of binary composite materials

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An analysis is made of a composite material formed from two components with different electrical and thermal conductivities. When the ratio of the electrical conductivities of the components is high but the thermal conductivities are similar, the critical behavior of the thermoelectric power is governed by the critical behavior of a shunting effective resistance and has the same critical exponents. For large ratios of the thermal conductivities of the components there are "active points" of the thermoelectric power which make a large contribution to the effective Seebeck coefficient. This gives rise to $\alpha^{\text{eff}}(p) = \text{const}$ for $p < p_c$ ($p$ is the concentration of the conducting component 1 and $p_c$ is the threshold concentration at which an infinite cluster is formed) and to a new critical exponent, which cannot be reduced to conductivity when $p > p_c$: $\alpha^{\text{eff}}(p) \propto (p - p_c)^{-k} + \alpha_1$, where $k = 2.0 \pm 0.1$.

The high degree of interest which percolation theory is attracting is due to the fact that the site and bond problems are the simplest models which can be used to study first-order phase transitions.[1] The problem most thoroughly investigated is the conductivity of a random network of resistances, which makes it possible not only to calculate the critical exponents of the electrical conductivity for a metal-insulator transition [$p > p_c^*$ (Ref. 2), where $p$ is the concentration of the conducting component 1 and $p_c$ is the threshold concentration at which an infinite cluster is formed] and for a metal—"ideal metal" transition [$p < p_c$ (Ref. 3)], but also to estimate the limits of validity of the theory of an effective medium for a two-component random mixture of materials with different electrical conductivities.

The corresponding problem in the case of the thermoelectric power has been investigated much less thoroughly. Straley[4] analyzed the matrix equation for the entropy flux and the current density, and came to the conclusion that the problem of determination of thermoelectric properties of composite materials reduces to that of finding the electrical conductivity. The matrix equation was solved postulating continuity of the normal component of the entropy flux across a boundary between two media, which is valid only in the case of equal thermal conductivities of the components, so that Straley's conclusions are valid only in such a case. Halpern[5] developed further the Straley method[4] and obtained an equation relating the electrical conductivity, thermal conductivity, and thermoelectric power, which is valid in the critical interval when the ratios of the electrical conductivities and thermal conductivities of the components are different, demonstrating that the critical exponents of the electrical conductivity and thermoelectric power are identical.

A formula for calculating the effective Seebeck coefficient was obtained in Refs. 6 and 7 on the assumption that the temperature field of an external source does not change under the action of the thermoelectric current in a sample and which is valid for any ratios of the electrical conductivities and thermal conductivities of the components. The effective Seebeck coefficient is defined in this formula in terms of the effective Peltier coefficient found by summing the Peltier heat evolved at the interface between the components during the flow of an electric current through a sample:

$$\alpha^{\text{eff}}(p) = (\alpha_2 - \alpha_1) \int_S j_n(S) T(S) \, dS [U \sigma^{\text{eff}}(p) (T_1 - T_2) L]^{-1} + \alpha_1, \tag{1}$$

where $j_n(S)$ is the projection of the current density along the normal $\mathbf{n}$ to the interface $S$ between the components, deduced solving the equation $\nabla[\sigma(r) \nabla U] = 0$ with the boundary conditions $U = U|_{x=0} - U|_{x=L}$. Although Eq. (1) is valid for any temperature distribution in a sample, in the simplest case the temperature $T(S)$ on the interface $S$ can be obtained by solving the same equation but replacing the local electrical conductivity $\sigma(r)$ with the local thermal conductivity $\varkappa(r)$ and using the contact boundary conditions $T_{x=0} = T_1$, $T_{x=L} = T_2$, where $\alpha_1$ and $\alpha_2$ are the Seebeck coefficients of the components 1 and 2, $\sigma^{\text{eff}}(p)$ is the effective electrical conductivity, and $L$ is the length of the sample. Therefore, in the simplest case the problem reduces to the solution of a system of Kirchhoff equations for the electrical conductivities and thermal conductivities, which converge rapidly when iteration methods are used on a computer, and this is followed by calculation of the integral in Eq. (1). This method was used in Refs. 6 and 7 to calculate the effective Seebeck coefficients and to compare the results obtained from the effective medium theory.

The critical behavior of the thermoelectric power was studied in Ref. 8 in a model experiment employing a system of glass beads some of which were covered with silver. When the concentration of metallized beads was altered, the effective Seebeck coefficient was found to be independent of the composition in the range $p > p_c$ [$\alpha^{\text{eff}}(p) = \text{const}$]. The experiments results showed that $\alpha^{\text{eff}}(p) \propto (p - p_c)^h$, where $h = 0$, which disagreed with the results of Refs. 5-7. In the model experiment the ratio of the thermal conductivities of the components was large, but this case was not studied in Ref. 7, so that we shall consider it below. After solving the prob-

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lem we shall return to a discussion of the experimental results.

It was shown in Refs. 9 and 10 that on approach to the threshold from either side ($p \to p_c \pm 0$) almost all the Joule heat is evolved at "hot spots" representing narrow bottlenecks or bridges between finite clusters of the component 1 when $p > p_c$ and thin spacers of the component 2 in the same places when $p < p_c$. The main change in the electrical conductivity in the critical interval is governed by the number of such hot spots and by their contribution to the Joule heat. The closer to the threshold, the smaller is the number of such hot spots and the greater their contribution, so that at the threshold only one hot spot remains in a finite volume and almost all the Joule heat is evolved there. This is not predicted for the thermoelectric power[10] and the extension of the above results to this power will be made below.

We shall introduce the concept of the contribution $q$ to the Peltier coefficient representing the Peltier heat evolved as a result of passage through a unit area of the surface $S$ of a current element $J_n(S)$ per unit time:

$$q = (\alpha_2 - \alpha_1) j_n(S) T(S). \qquad (2)$$

The parts of the surface in which the Peltier heat is evolved or absorbed are also responsible for the transformation of the thermal into the electrical energy during the passage of a thermoelectric current. We shall use the term "active points of the thermoelectric power" for those parts of the surface $S$ where the contributions $q$ are large. In order to understand how the active points of the thermoelectric power affect the effective Seebeck coefficient and how they disappear at $\varkappa_1 \approx \varkappa_2$, we must consider two limiting cases of similar or very different thermal conductivities of the components.

1) *Similar thermal conductivities of the components*: $\varkappa_1 \approx \varkappa_2$. We shall assume that the contributions to the thermoelectric power are negative, since the current flows into a cluster made of the component 1 and positive when it flows out. Therefore, approximately half the surface $S$ reduces the thermoelectric power, whereas the other half enhances this power. The calculations indicate that the contributions may differ by many orders of magnitude. For example, the regions parallel to the field are characterized by $j_n(S) = 0$ and $q = 0$ and are analogous to "dead ends" in the electrical conductivity problem. At these hot spots the high current densities make the positive and negative contributions large, but they are similar in the absolute sense since the temperature is distributed uniformly throughout the sample and the resultant contribution is small. This results in the absence of the active points of the thermoelectric power and the role of the component 1 reduces entirely to shunting. This property is reflected in the Halpern formula[5]:

$$\alpha^{\text{eff}}(p) = (\alpha_2 - \alpha_1)\left(\frac{\varkappa^{\text{eff}}(p)}{\sigma^{\text{eff}}(p)} - \frac{\varkappa_1}{\sigma_1}\right)\left(\frac{\varkappa_2}{\sigma_2} - \frac{\varkappa_1}{\sigma_1}\right)^{-1} + \alpha_1, \qquad (3)$$

from which it follows that if $\varkappa_1 \approx \varkappa_2$, then the relative effective Seebeck coefficient is proportional to the difference between the effective resistance of the component 1 since $\alpha^{\text{eff}}(p) - \alpha_1$ tends to zero when the component 2 disappears. A check of the formula (3) was made by computer calculations and the left- and right-hand parts of the formula were determined independently: $\sigma^{\text{eff}}(p)$ and $\varkappa^{\text{eff}}(p)$ from the Kirchhoff system of equations and $\alpha^{\text{eff}}(p)$ was found from Eq. (1). An increase in the number of iterations and of the computer time reduced the relative error in the calculation of these functions from 0.5 to 0.005% and the overall error in Eq. (3) did not exceed the errors in the quantities occurring in it. The formula (3) becomes indeterminate for $\sigma_1/\sigma_2$ close to $\varkappa_1/\varkappa_2$, since the denominator and the numerator both tend to zero. This gives us grounds for assuming that, outside the interdeterminacy interval in the case when the distribution of the temperature field in a sample can be calculated from a system of the Kirchhoff equations, Eq. (3) becomes a consequence of Eq. (1) and is similar to the Dykhne relationship[11] between the effective electrical conductivity and the Hall coefficient. It should be pointed out that whereas the Dykhne relationship is valid only in the two-dimensional space, which is due to the sensitivity of the Hall effect to spatial dimensions (see Fig. 2 in Ref. 12), Eq. (3) is valid in the case of two-dimensional and three-dimensional spaces, since the thermoelectric power exhibits no fundamental features that might be associated with the dimensions of space. It readily follows from Eq. (3) that if $\varkappa_1 \approx \varkappa_2$, then

$$p \to p_c + 0, \quad \alpha^{\text{eff}}(p) \propto (p - p_c)^{-g_1}, \quad g_1 = t_1, \qquad (4)$$

$$p \to p_c - 0, \quad \alpha^{\text{eff}}(p) \propto (p_c - p)^{g_2}, \quad g_2 = t_2, \qquad (5)$$

where $t_1$ and $t_2$ are the critical exponents of the effective electrical conductivity below and above the threshold.

Moreover, it follows from formula (3) that $\alpha^{\text{eff}}(p)$ increases on increase in $\varkappa_1/\varkappa_2$ and decreases on increase in $\sigma_1/\sigma_2$ (compare curves 1 and 2 in Fig. 1).

2) *Large ratio of the thermal conductivities of the components*. When the thermal conductivity ratio becomes large so that $\varkappa_1/\varkappa_2 \to \infty$, the interfaces between the components become isothermal, and those interfaces which touch the contact area assume the contact temperatures. Finite clusters which are separated spatially from contacts do not affect the magnitude of the thermoelectric power because $\alpha^{\text{eff}}(p)$ is independent of the composition until the isothermal clusters from the opposite contacts are joined and this occurs at the

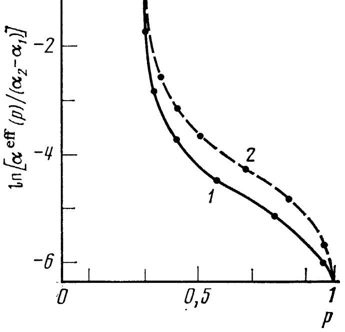

FIG. 1. Effective Seebeck coefficient $\alpha^{\text{eff}}(p)$ calculated for: 1) $\sigma_1/\sigma_2 = 10^5$, $\varkappa_1/\varkappa_2 = 1.001$; 2) $\sigma_1/\sigma_2 = \varkappa_1/\varkappa_2 = 10^5$.

threshold. The value of $\alpha^{\rm eff}(p)$ is independent also of the ratio $\sigma_1/\sigma_2$. This follows from the fact that the difference between the potentials at any points on isothermal surfaces with contact temperatures $T_1$ and $T_2$ is the same, $(\alpha_2-\alpha_1)(T_1-T_2)$, and there is no shunting of any kind. In the range $p<p_c$ the effective Seebeck coefficient assumes the maximum possible value $\alpha^{\rm eff}(p)=\alpha_2$, which is evidence of the absence of shunting (see curve 2 in Fig. 1). When the external circuit is closed across a load, the thermoelectric current measured in the critical range has the highest density at the hot spots, but now not only are the contributions to the positive and negative parts of the thermoelectric power large, but their differences are also large since the temperature gradient is high. We shall call these the active points of the thermoelectric power. If we can assume for the rest of the surface $S$ that $\alpha_1=\alpha_2=0$, then $\alpha^{\rm eff}(p)$ changes only slightly.

When the concentration of one of the components is above the threshold, two processes occur simultaneously: electrical and thermal percolation. A system of isothermal clusters is rapidly broken up in the critical interval, the temperature of an infinite cluster tends to a linear function, and curves 1 and 2 in Fig. 1 approach one another. The greatest difference between them occurs in the critical interval where a new critical exponent now applies:

$$p\to p_c+0,\quad \alpha^{\rm eff}(p)\sim(p-p_c)^{-k},\quad k=2.0\pm0.1, \tag{6}$$

and can be related to the exponents of the correlation radius of an infinite cluster[13] and of the electrical conductivity. The relationship can be obtained by selecting the value of $\varepsilon$ close to unity and finding the lower limit of the integral $c(\varepsilon)$ from

$$\varepsilon\alpha^{\rm eff}(p)=\int\limits_{c(\varepsilon)}^{\infty} q\Phi(q)\,dq, \tag{7}$$

where $\Phi(q)$ is the density of the probability of the distribution of thermoelectric power contributions. We shall use $N_\alpha(p, \sigma_1/\sigma_2, \varkappa_1/\varkappa_2, \varepsilon)$ to denote that fraction of the surface $S$ which contributes $\varepsilon\alpha^{\rm eff}(p)$ to the effective Seebeck coefficient:

$$N_\alpha\left(p,\frac{\sigma_1}{\sigma_2},\frac{\varkappa_1}{\varkappa_2},\varepsilon\right)=L^3\int\limits_{c(\varepsilon)}^{\infty}\Phi(q)\,dq. \tag{8}$$

Near the threshold we go to the limit as $p\to p_c\pm0$, $\sigma_1/\sigma_2\to\infty$, $\varkappa_1/\varkappa_2\to\infty$, and $\varepsilon\to1$:

$$\lim N_\alpha(p,\ \sigma_1/\sigma_2,\ \varkappa_1/\varkappa_2,\ \varepsilon)=0. \tag{9}$$

The limit of $\varepsilon$ is taken last. The fraction of the surface on which the Seebeck coefficient reaches the fraction $\varepsilon\alpha^{\rm eff}(p)$ of its value tends to zero on approach to the threshold. The procedure of going to the limit can be justified numerically by graphs demonstrating that the function $N_\alpha(p, \sigma_1/\sigma_2, \varkappa_1/\varkappa_2, \varepsilon)$ approaches zero for each of the arguments, as is shown in Figs. 1, 2, and 3 of Ref. 10 for the electrical conductivity and the Hall coefficient. For reasons of space, Fig. 2 demonstrates only the case $N_\alpha(\varepsilon)$.

The active points of the thermoelectric power can be represented by the average contribution to this power:

$$\lim_{p\to p_c\pm0,\varepsilon\to1}\langle\alpha(p,\varepsilon)\rangle\infty(p-p_c)^{-m},$$

by analogy with the procedure for the hot spots of the Joule heat $W_{\rm eff}(p)$:

$$\lim_{p\to p_c\pm0,\varepsilon\to1}\langle w(p,\varepsilon)\rangle\infty(p-p_c)^{-l}.$$

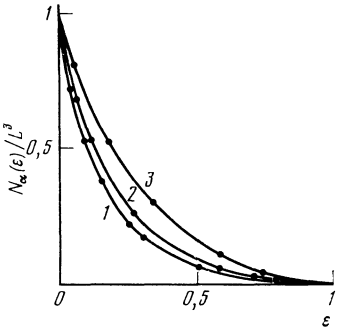

FIG. 2. Fraction $N_\alpha(\varepsilon)$ of the surface between the components responsible for the fraction $\varepsilon\alpha^{\rm eff}(p)$ of the effective Seebeck coefficient, plotted as a function of $\varepsilon$ and calculated for the following concentrations: 1) $p=0.3$; 2) 0.34; 3) $p=0.5$. The calculations were carried out on the assumption that $\sigma_1/\sigma_2=\varkappa_1/\varkappa_2=10^5$.

It readily follows from Eq. (9) that

$$k=d\nu-m, \tag{10}$$

where $\nu$ is the exponent of the correlation radius of an infinite cluster; $\alpha^{\rm eff}(p)\propto N_\alpha(p,\varepsilon)<\alpha(p,\varepsilon)>$; $N_\alpha(p,\varepsilon)\propto(p-p_c)^n$; $n=d\nu$; $d$ is the number of spatial dimensions. If we use $t=d\nu-l$ (Ref. 9), we find that $k=t+l-m$.

The model experiment of Ref. 8 did not yield Eq. (6) because the dependence of the thermoelectric power on the composition for materials with such a difference between the electrical conductivities of the components should be manifested only very close to the threshold where the conductivity of a sample is sensitive to the conductivity of glass. It is, however, not possible to attain experimentally such a close approach to the threshold. The experimental conditions for $p>p_c$ correspond to the metal-insulator model, which can be used to study the critical behavior of the electrical conductivity and the Hall effect. The thermoelectric power found using this model is the trivial expression $\alpha^{\rm eff}(p)=\text{const}$, which follows from Eq. (1) when $j_n(S)=0$ and is associated with the fact that the thermoelectric power appears when the current through the surface $S$ between the components is $j_n(S)\neq0$, and both components should conduct ($\sigma_2\neq0$). It is impossible to study the critical behavior of the thermoelectric power beginning from the ratio[9] $\sigma_1/\sigma_2\geqslant10^5$.

It therefore follows that the active points of the thermoelectric power together with the hot spots of the conductivity and the active points of the Hall *emf* provide a unified picture of a phase transition in disordered composite systems and allow us to draw the conclusion that other transport coefficients which are affected significantly by percolation problems in systems of this kind also have singularities at the threshold.

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