Observable Variables in Thermoelectric Phenomena

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New transport equations for the thermoelectric phenomena have been deduced. All of the variables in this formulation are observable quantities. The limitations of the usual formulations, which work with nonobservable quantities, have been overcome. The electric potential can be measured by using auxiliary probes which connect the electronic conductor to a potentiometer. This observable electric potential depends on the nature of the probes but not on the room temperature where the potentiometer is placed. Also, we emphasize that absolute values for the thermoelectric power are in contradiction with the thermodynamic limitation of measuring electric potential differences in these systems. Therefore, the thermoelectric powers calculated either through the Thomson coefficient or in reference to a superconductor cannot be absolute quantities.

Introduction

Studies on thermoelectric phenomena have always taken into account that it is not possible to measure electric potential differences between points of different temperature.[1−3] This limitation has forced the use of nonobservable variables in order to describe the phenomena. This is evident when one analyzes the usual transport equations of thermoelectric phenomena in an electronic conductor[4−8]

$$j_s = -\left(\frac{\kappa}{T} + \sigma S^2\right)\nabla T + \sigma S \nabla\left(-\frac{\tilde{\mu}_e}{|e|}\right) \tag{1a}$$

$$j = \sigma S\, \nabla T - \sigma \nabla\left(-\frac{\tilde{\mu}_e}{|e|}\right) \tag{1b}$$

where j_s is the entropy flux density, j is the electric current density, T is temperature, $\tilde{\mu}_e$ is the electrochemical potential of electron, $|e|$ is the electron charge modulus, κ is the thermal conductivity, σ is the electrical conductivity, and S is the thermoelectric power, also named Seebeck coefficient. Table 1 shows the classification of quantities in eqs 1 between observable and nonobservable variables.

From the two thermodynamic forces of eqs 1, $\nabla(-\tilde{\mu}_e/|e|)$ and ∇T, only this latter is an observable quantity. This is the reason of the limited knowledge which provides these equations and to the nonobservable character of the thermoelectric power S. However, if we were able to find a transformation of $\nabla(-\tilde{\mu}_e/|e|)$ into an observable variable, the new transport equations would describe better the thermoelectric phenomena.

New Transport Equations

Recently, a procedure to transform nonobservable variables into observable quantities has been described.[9−14] This method has been developed for nonequilibrium electrolyte solutions with concentration gradients. Probes of reversible electrodes are used to convert the local true electric potential (TEP) ϕ into the observable electric potential (OEP) ψ. This electric potential is measured by a potentiometer at the electrode terminal. Using this variable, a new formulation has been built; only observable quantities appear in the resulting transport equations.

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TABLE 1: Observable and Nonobservable Variables

observable	nonobservable
∇T	
j	$\nabla(-\tilde{\mu}_e/|e|)$ when $\nabla T \neq 0$
$\nabla(-\tilde{\mu}_e/|e|$ when $\nabla T = 0)$	S
σ	j_s when $j \neq 0$
κ	j_s when $j = 0$
j_s when $j = 0$	

In the case of thermoelectric phenomena, the arrangement which defines and measures the OEP is shown in Figure 1a. A temperature gradient and an electric current are imposed in the electronic conductor X. Consider a point in this system at electric potential ϕ and temperature T. A probe of material R has its active end in equilibrium with that point; its terminal is at room temperature T_0 and connected to a potentiometer. Electric current is not permitted inside the probe. The electric potential of the terminal ψ is considered as the OEP of the chosen point. Therefore, the electric potential ψ is the OEP of the wire X observed with the probe R. The material R may or may not be the same as the wire X; in any case, the value of ψ will depend on probe material.

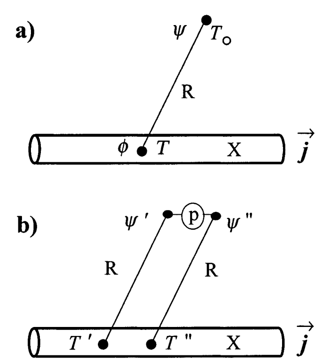

Figure 1. Sketch of the wire X with probe R. (a) The point considered is at temperature T, with TEP ϕ and OEP ψ. The OEP is the electric potential at the terminal of the probe. The probe terminals are always at room temperature T_0. (b) Arrangement for measuring OEP differences with the potentiometer p. The electric current j is passing through the conductor X; the electric current is zero in the probes.

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In order to insert the OEP in the transport equations, we need to deduce the relationship between the gradient of electron electrochemical potential and that of OEP. The arrangement for measuring OEP differences using two probes and a potentiometer is given in Figure 1b. The potentiometer and the two terminals have the same temperature T_0. The differential change $d\tilde{\mu}_e$ between two points which differ dT in temperature along the wire X may be decomposed in two terms

$$d\tilde{\mu}_e = (d\tilde{\mu}_e)_{pot} + (d\tilde{\mu}_e)_R \tag{2}$$

where $(d\tilde{\mu}_e)_{pot}$ is that term observed by the potentiometer and $(d\tilde{\mu}_e)_R$ is the total change of the electrochemical potential $\tilde{\mu}_e$ along the two probes R. These two quantities are

$$(d\tilde{\mu}_e)_{pot} = -|e|\, d\psi \tag{3a}$$

$$(d\tilde{\mu}_e)_R = -|e| S_R\, dT \tag{3b}$$

where S_R is the thermoelectric power of the probes R. Therefore

$$-d\tilde{\mu}_e = |e|\, d\psi + |e|\, S_R\, dT \tag{4}$$

and we obtain the equation

$$\nabla\left(-\frac{\tilde{\mu}_e}{|e|}\right) = \nabla\psi + S_R \nabla T \tag{5}$$

that applies to a point of the wire X with temperature T and temperature gradient ∇T. The thermoelectric power S_R is evaluated at temperature T. The room temperature T_0 does not enter in this expression.

Equation 5 can be inserted in eqs 1 to obtain

$$j_s + S_R j = -\left(\frac{\kappa}{T} + \sigma (S_{XR})^2\right)\nabla T + \sigma\, S_{XR}\, \nabla\psi \tag{6a}$$

$$j = \sigma\, S_{XR}\, \nabla T - \sigma\, \nabla\psi \tag{6b}$$

where $S_{XR} = S_X - S_R$ is the thermoelectric power of material X observed with probes R.

These transport equations have the advantage of using the gradient of the OEP. The two thermodynamic forces, ∇T and $\nabla\psi$, which drive the thermoelectric processes can be measured at any point of the system. Note that $j_s + S_R j$ is always an observable quantity, and therefore, the uncertainty involved in S_R, a nonobservable variable, is exactly compensated by the uncertainty in j_s. When the probes are of the same material as the system (R ≡ X), the transport equations simplify because $S_{XX} = 0$.

To evaluate the thermoelectric power S_{XR}, measurements of the OEP are needed. Conversely, the OEP profile in a system can be calculated from values of S_{XR}. Consider as an example the skutterudite $Tl_{0.1}Co_4Sb_{12}$,[15,16] with a linear temperature profile, from 200 K at $x = 0$ to 290 K at $x = 1$ m. The values of the electric current densities are −2000, −1000, 0, +1000, and +2000 A m^{-2}. Copper probes are used. The calculated OEP profiles are shown in Figure 2. The values of the transport coefficients S_{XR} and σ have been taken from ref 15.

Now, the OEP profile depends on the probe material. The skutterudite $Tl_{0.1}Co_4Sb_{12}$ may be studied either with copper probes, R≡Cu, or with skutterudite probes, R≡X. When the same linear temperature profile of Figure 2 is applied and the electric current density is −1000 A m^{-2}, we deduce two OEP profiles, as shown in Figure 3. The values of the transport coefficients S_{XR} and σ have been taken from ref 15.

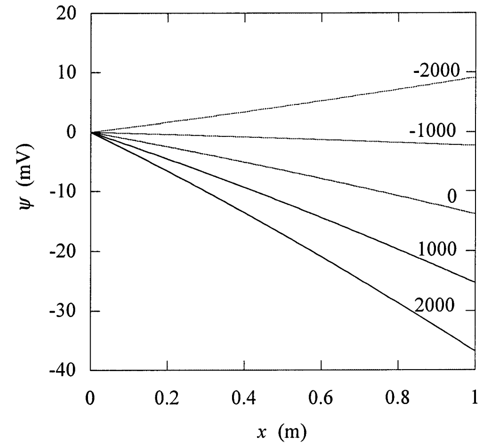

Figure 2. OEP profiles along a wire of skutterudite $Tl_{0.1}Co_4Sb_{12}$ studied with copper probes. A linear temperature profile is applied: 200 K at $x = 0$ to 290 K at $x = 1$ m. Electric current densities are −2000, −1000, 0, +1000, and +2000 A m^{-2}. The values of the transport coefficients S_{XR} and σ have been taken from ref 15.

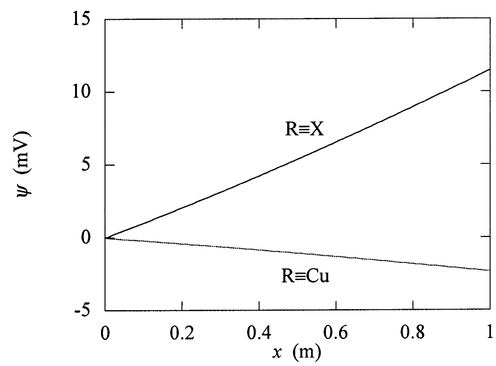

Figure 3. OEP profiles in a wire of skutterudite $Tl_{0.1}Co_4Sb_{12}$, studied with copper probes (R≡Cu) and with skutterudite probes (R≡X). The same linear temperature profile of Figure 2 is applied. The electric current density is −1000 A m^{-2}. The values of the transport coefficients S_{XR} and σ have been taken from ref 15.

However, as it is repeatedly assured, it is not possible to measure or calculate the profile for the TEP ϕ. The transformation $\psi \rightarrow \phi$

$$\nabla\phi = \nabla\psi + \left(\frac{(\partial\mu_e)/|e|}{\partial T} + S_R\right)\nabla T \tag{7}$$

where μ_e is the chemical potential of the electrons, may be deduced when the usual splitting

$$\tilde{\mu}_e = \mu_e - |e|\phi \tag{8}$$

is applied to eq 5. That transformation contains the nonobservable factor $[(\partial\mu_e)/|-e|\ \nabla T + S_R]$.

We have also assumed that the transport equations hold the Onsager reciprocity relations (ORR) between the cross coefficients. We can measure S_{XR} through eq 6b making $j = 0$ and through eq 6a by Peltier effect in a X−R junction when $j \neq 0$ and $\nabla T = 0$. The experimental results confirm the ORR.[17]

Absolute Thermoelectric Power?

Finally, we may discuss thoroughly the concept of absolute thermoelectric power. Nowadays, absolute values of thermoelectric powers are given in the literature.[7,18−19] Two plausible but arbitrary references are assumed: (i) the absolute Seebeck coefficient of any material is zero at zero Kelvin and (ii) the superconductor materials, devoid of thermoelectric properties, have a negligible absolute Seebeck coefficient.[7]

The first reference need to evaluate the Thomson's coefficient[20]

$$\tau = -T\frac{dS}{dT} \tag{9}$$

The measurement of the energy flux densities by applying opposite electric currents with the same temperature profile provides a way of evaluating the coefficient τ. With the values of $\tau(T)$ in the temperature interval (0, T), the absolute thermoelectric power $S(T)$ could be evaluated if the value of S at 0 K were known. In these days, the plausible reference $S(0) \equiv 0$ is assumed.

However, from the impossibility of measuring the gradient $\nabla\tilde{\mu}_e$ at any point of a material affected only by a nonzero gradient of temperature, the thermoelectric power

$$\nabla\left(-\frac{\tilde{\mu}_e}{|e|}\right) = S\nabla T \tag{10}$$

will never be an observable coefficient, at any temperature, including zero Kelvin. Two nonobservable variables are related with ∇T, measurable quantity. The recourse to a statement of the kind of the third law of thermodynamics, or to the thermoelectric properties of superconductor materials, will never be able to transform a nonobservable variable into an absolute variable.

Many experimental papers, having accepted absolute values for the Seebeck coefficient of the probes S_R, evaluate absolute thermoelectric powers of other materials S_X correcting the contribution of the leads. It is evident that this correction does not reach absolute thermoelectric powers.

Therefore, we may conclude that the thermoelectric studies of the materials finish when the relative Seebeck coefficient S_{XR} is measured. The efforts developed to provide absolute values will never reach the aim. Besides, Thomson coefficients are not easy to measure because of the smallness of the heat generated and the large temperature gradients required to give a measurable value.[7] This may be the reason for the discrepancies between the experimental output of a thermocouple and that calculated from absolute thermoelectric powers shown by Roberts et al.[20]

Conclusions

We have just transformed the nonobservable variable $\tilde{\mu}_e$ into an observable quantity, the OEP ψ. Now the local states in the electronic conductor are fixed by a pair of observable values (T,ψ). Several examples of the profiles of these variables in an electronic conductor have been given. New transport equations for the thermoelectric phenomena have been deduced; all of the variables in this formulation are observable quantities. Thus, the limitations of the usual formulations which work with nonobservable variables have been overcome.

The thermodynamic limitation of measuring electric potential differences when temperature is nonuniform excludes any possibility to obtain absolute values of thermoelectric power. The thermoelectric powers, calculated through the measurement of the Thomson coefficient, cannot thus be absolute quantities; these values depend on the arbitrary references assigned to the thermoelectric power at zero Kelvin. Only the relative Seebeck coefficient S_{XR} can be evaluated. The efforts developed to provide absolute values may get other results but never the main aim.

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