



Original Research Article

CONVERTERS AND MATERIALS FOR EFFECTIVE GENERATION OF ELECTRIC ENERGY

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ABSTRACT

An overview of the development directions of Seebeck and Nernst thermoelectric converters was conducted. An analysis of the physical mechanisms of the Seebeck and Nernst effects in various materials was carried out, and the efficiency of thermoelectric converters based on them was considered. It is shown that nanocomposite nanodisperse structures and nanoscale powders and multilayer nanofilms are currently the most promising material for the development of thermoelectric sources of electrical energy based on them.

Keywords: Seebeck and Nernst effects, thermoelectric converters, nanocomposite materials

INTRODUCTION:

The problem of increasing the efficiency of existing energy sources, the search and development of new methods for energy production is one of the most actual tasks in the energy industry. Now, the most widely used is electrical energy. On an industrial level, electrical energy is obtained by nuclear, thermal, wind and hydroelectric power stations. The production of electricity by solar modules, which are considered the most ecologically clean sources of energy, is developing at a rapid pace. However, solar energy has drawbacks, the reason for which is the rather large area of solar power plants and the rather strong dependence of their efficiency on illumination and the geographical latitude and climate of their location. One of the promising methods for obtaining of ecologically clean electrical energy is generation using the Seebeck and Nernst thermoelectric effects. These effects describe the appearance of an electric field in materials when a temperature gradient occurs in them. Thermoelectric converters of this type can use natural heat sources or waste heat from industrial production. The advantage of energy sources that would be built on these principles is that Seebeck and Nernst thermoelectric converters do not contain moving details, these converters are reliable, fast-acting, silent, thermally stable and have very large lifetime values. Discovered in 1821, the Seebeck effect describes the appearance of an electric potential difference in the contact of two dissimilar conductors, or at the ends of a non-uniformly heated conductor whose contacts are at different temperatures. The reason for the contact potential difference is the difference in the chemical potentials of the contacting materials. The volumetric potential difference is due to the dependence of the concentration of conduction electrons on the temperature of conductor.

The bulk Seebeck effect is dominant at a sufficiently high value of the temperature difference ΔT at the ends of the conductor. Thermoelectric conversion coefficients of semiconductors are much higher than similar coefficients for metals, so experimental samples of thermocouples were created on the basis of semiconductors.

Discovered in 1886, the Nernst thermoelectric effect describes the phenomenon of the appearance of electric voltage in a non-uniformly heated conductor in magnetic field. The Nernst electric field is directed perpendicular to the temperature gradient and the magnetic field gradient, and its magnitude is proportional to the magnetic field strength. If the material of the conductor has spontaneous magnetization, then in addition to the normal Nernst effect, an anomalous Nernst effect may occur in it, which, as a rule, significantly exceeds the value of the normal Nernst effect.

The scheme of generation of electric field at the expense of thermoelectric effects Seebeck and Nernst is shown on the Figures 1.

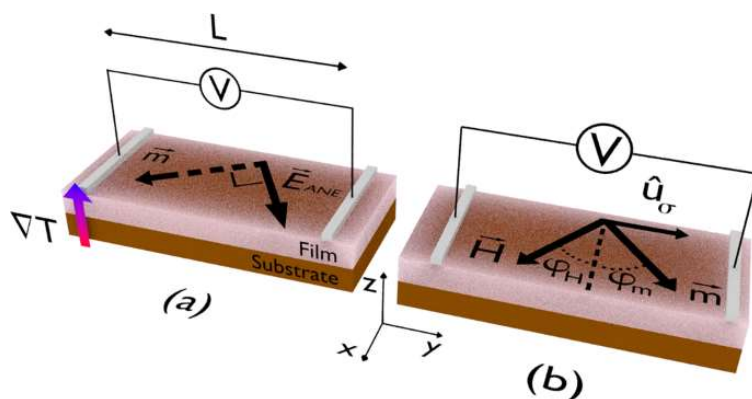


Рис. 1. The scheme of generation of electric field at the expense of thermoelectric effects Seebeck (a) and Nernst (b) is shown on the Figure 1.

Thermoelectric Seebeck and Nernst effects have been most widely studied in single crystal materials. In polycrystalline and composite nanostructured materials, they have been studied much less and almost not studied in amorphous materials. Therefore, today the field of use of Seebeck and Nernst thermoelectric converters is narrow, which is due to the low coefficients of direct conversion of heat into electrical energy, as well as the high cost of single-crystal materials. However, the latest results of laboratory research show that the transition to composite nanostructured film and nanopowder materials will make it possible to develop effective thermoelectric converters based on the Seebeck and Nernst effects, which can find their place in environmentally friendly energy.

Thermoelectric Seebeck and Nernst effects

Current thermoelectric power systems designed for applications on different scales mostly use Seebeck effect. Their power output ranges from microwatts to several kilowatts in commercial applications. The most efficient materials for thermoelectric generation are semiconductors with large Seebeck coefficient, and low thermal conductivity. The highest values of Seebeck coefficients (S) are registered in semiconductor single crystals ($\text{Pb}_{0.3}\text{Ge}_{0.7}\text{Se}_{0.9}$ - $S=1570 \mu\text{V/K}$). Semiconductor thermoelectric module consists of serially connected junctions of p-type and n-type materials and their best energy conversion efficiency achieves 12% according to recent work [1]. In metals, the concentration of conduction electrons depends very small on temperature, and the values of the Seebeck coefficients are not much smaller (Ni - $S=-15 \mu\text{V/K}$, Bi -

$S = -72 \mu\text{V/K}$). Good results in the production of thermoelectric energy sources have been obtained using rare earth metals, but they are also expensive.

The efficiency of electric field generation in the material due to the Seebeck effect is characterized by the value of the thermoelectric factor ZT [2].

$$ZT = S^2 \sigma / \chi, \quad S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{2/3}, \quad (1)$$

Here σ and χ are the specific electrical conductivity and specific thermal conductivity, S are the values of the Seebeck coefficient, k_B is the Boltzmann constant, h is the Planck constant, e and m^* are the charge and effective mass of the electron, and T is the temperature. The possibility of practical use of the Seebeck effect strongly depends on the material.

High values of $ZT \sim 1$ are obtained in materials such as alkali metal oxides, barium-cobalt oxide. The most promising material from the point of view of practical using in thermoelectric converters today are nanostructured materials and multilayer nanocomposite films in which they are obtained [3] obtained high values of ZT and high values of the Seebeck coefficient $S \approx 200 \mu\text{V/K}$. Higher values of the Seebeck coefficient are obtained in nanocomposite heterogeneous films and nanopowder materials. Thus, in multilayer PbTe/PbSe (10/10 nm) films, the absolute value of the Seebeck coefficient increases significantly when additional inhomogeneities are introduced into the film structure and reaches values of $|S| = 600 \mu\text{V/K}$. And in MnO_2 nanopowders, record high values of the Seebeck coefficient were obtained, where this coefficient reaches the value of $S \approx 20\,000 \mu\text{V/K}$ [4]. In the magnetic metal/nonmagnetic nanofilm composite structures, in which there is a strong spin-orbit interaction, in contrast to the classical longitudinal Seebeck effect, the transverse spin Seebeck effect can be observed. In such structures, by changing the direction of the magnetic moment of the magnetic metal, the magnitude and sign of the Seebeck electric field can be changed [5].

Summarizing the review, it can be said that the Seebeck effect was mainly studied in single-crystalline materials. It was poorly studied in nanostructured and non-composite materials and practically not studied in amorphous materials, although these materials have a lower thermal conductivity compared to crystalline materials, and there are promising to create thermoelectric Seebeck converters. Therefore, the transition to composite nanostructured and amorphous materials will allow the development of effective thermoelectric converters based on the Seebeck effect, which can be used in ecologically clean energy generation. Although the Nernst effect, unlike the Seebeck thermoelectric effect, is realized in a magnetic field, it is nevertheless more promising for practical use. Firstly, the Nernst effect makes it possible to create energy converters from a heat source of various shapes. Secondly, the heat reservoir in the Nernst effect device can be installed separately from the electrical unit. Thirdly, unlike devices based on the Seebeck effect, it uses only one and not two different p -materials and n -materials. The crucial difference between these effects is that the Nernst effect is a transverse effect, while the Seebeck effect is longitudinal. This difference does not affect the design features of thermoconverters based on them, but gives advantages to Nernst thermoconverters. The temperature difference in both devices creates an electromotive force and an electric current J_c . In Seebeck thermoconverters, the thermal current caused by such a useful current J_c flows in the same direction as the temperature gradient from the hot to the cold side.

Therefore, this thermal current transfers heat, and thus reduces the efficiency of the heat exchanger. In Nernst thermoconverters, J_c causes a thermal current from the cold side to the hot side, which increases

the efficiency of their operation. The calculated value of the maximum efficiency $\xi_{\max}$ [6] for both devices as a function of the Q is shown in Figure 2, where the Q for the Nernst effect is defined as:

$$Z_{ANE}T = \frac{N_0^2 \sigma_y H_z^2 T}{\chi_{xx}}, \quad (2)$$

here N_0 is the Nernst coefficient σ and χ - specific electrical conductivity and specific thermal conductivity, T - temperature.

If the material of the conductor has spontaneous magnetization, then in addition to the normal Nernst effect, an anomalous Nernst effect may occur in it, which is due to the action of the internal magnetic field. The magnitude of the total electric field E (Figure 1), which arises in a nonuniformly heated magnetic conductor under the action of the magnetic field H , is described as

$$\vec{E} = \vec{E}_{NNE} + \vec{E}_{ANE} = N_0[\vec{H} \times \nabla \vec{T}] + N_s \mu_0[\vec{M}_s \times \nabla \vec{T}], \quad (3)$$

here E_{NE} , E_{ANE} , N_0 , N_s , μ_0 and M_s refer to the normal Nernst electric field vector, the anomalous Nernst electric field vector, the Nernst coefficient, the anomalous Nernst coefficient, the vacuum permeability, and the magnetization vector, respectively

The anomalous Nernst effect (ANE), one of the thermoelectric effects in a magnetic materials, has recently attracted increasing interest due to its potential to generate electrical energy. The normal Nernst effect is proportional to H , and a sufficient magnetic field is required for thermoelectric conversion. Among the materials, a significant Nernst effect was observed in multilayer structures of Pt/Fe, Au/Fe, and Cu/Fe, in the magnetic semiconductor $Ga_{1-x}Mn_xAs$ ANE is spontaneous at zero field and, in principle, is proportional to the saturation magnetization. Therefore, when using magnetic materials with large values of the vector of anomalous Nernst coefficient Q_s and the vector of magnetization M_s , it is possible to obtain the electric field vector E of Nernst without an external magnetic field. However, in most of the registered efficiencies of thermoelectric conversion with ANE are small, which complicates its practical application. Therefore, the search for new materials with high values of anomalous Nernst coefficient is one of the most important, and most recent scientific works are devoted to this.

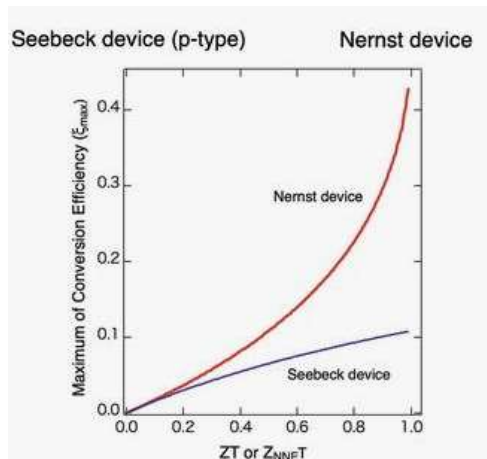


Fig. 2. The dependence of the efficiency of thermoelectric voltage generation on the parameters ZT and $Z_{NNE}T$ for the Seebeck effect and the Nernst effect.

Latter experimental and theoretical studies have shown that the ANE originates from a fictitious field (Berry curvature) in the momentum space in magnets and can be particularly enhanced when the Weyl points are tuned to be close to the Fermi energy [7-9]. The gigantic magnitudes of this effect in Heisler alloys can be easily predicted by calculating the electronic structure based on the presence of Weyl points, which serve as a kind of Berry curvature concentrators. This topological feature is responsible for the gigantic magnitudes of Nernst and Hall effects in Heisler alloys. Due to the features of the electronic structure, in particular, the significant value of Berry curvature, giant values of Nernst effects can be observed in antiferromagnets [10]. Results of stude show that the concentration of the Berry phase in an antiferromagnet can significantly increase the ANE. However, ANE in antiferromagnets is still largely unstudied, partly because ANE was thought not to exist. Although a joint research team from the Max Planck Institute for Chemical Physics of Solids in Dresden discovered a large anomalous Nernst effect. They obtained an ANE in YbMnBi₂ of 6 mV/K, a record value for antiferromagnets, close to the ANE value in the best ferromagnets. The high value of ANE is explained by the influence of crystal topology, high spin-orbit coupling and complex and uncompensated magnetic structure of YbMnBi₂. The skewed spin structure in YbMnBi₂ breaks the time-reversal symmetry and provides a non-zero Berry curvature. At the same time, the large spin-orbit coupling of the heavy element bismuth contributes to the creation of a large external contribution. It shows a way to obtain high ANE values in some antiferromagnets with non-collinear spin structure and large spin-orbit coupling. The enhancement of ANE is explained by the effect of interfacial strain on the Seebeck coefficient, which is almost negligible. This opens avenues for search and provides the prospect of obtaining a significant increase in ANE.

An interesting method for obtaining of high ANE values was shown experimentally in the Co₂MnGa alloy [11]. Anomalous Nernst effect beyond the magnetization scaling relation in the ferromagnetic Heusler compound Co₂MnGa. A large anomalous Nernst coefficient of 4.9 $\mu\text{V/K}$ is achieved for a polycrystalline Co₂MnGa/AlN multilayer film deposited on an amorphous substrate, which is higher than 3.8 $\mu\text{V/K}$ for a polycrystalline Co₂MnGa single-layer film.

In La_{0.5}Sr_{0.5}CoO₃, the Nerst thermomagnetic transformation coefficient at a temperature below the Curie temperature reaches values of 0.21 $\mu\text{V/K}$ at 180 K for H = 50 kOe [12]. In Co₂MnGa nanopowders, even higher values of the thermomagnetic Nerst transformation coefficient of ~6.0 $\mu\text{V/K}$ were obtained. In amorphous magnetic materials, the anomalous Nerst effect has practically not been studied. It shows that the study of the Nerst effect in polycrystalline nanodisperse and amorphous magnetic materials has not only a scientific novelty, but also a good prospect of practical using in the construction of efficient and thermoelectric electric field sources.

Conclusion

Seebeck and Nerst thermoelectric converters have high temperature and time stability, do not contain moving parts, are reliable, fast and silent. In addition, sources of electrical energy of this type of energy can use natural sources of heat or waste heat of industrial production. All this confirms the prospect of their practical use. But in order to solve this problem, it is necessary to carry out a set of experimental technological works aimed at developing technologies for obtaining heat-sensitive elements with high values of the Seebeck and Nerst coefficients. It is clear that it is desirable to use inexpensive materials in thermoelectric converters, and their manufacturing technology should also be inexpensive and based on modern production methods using 3D printers.

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