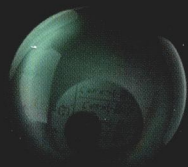
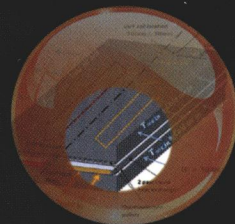
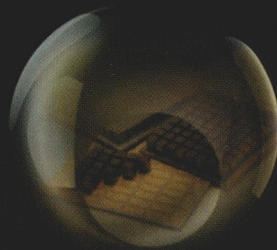
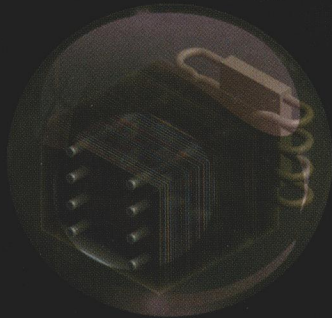
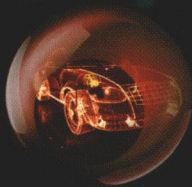


# Thermoelectrics

Design and Materials



HoSung Lee

WILEY

# THERMOELECTRICS

## DESIGN AND MATERIALS

**HoSung Lee**

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**WILEY**

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# THERMOELECTRICS



*For Young-Ae and Yujin*



# Preface

This book is written as a senior undergraduate or first-year graduate textbook. Thermoelectrics is a study of the energy conversion between thermal energy and electrical energy in solid state matters. Thermoelectrics is an emerging field with comprehensive applications such as exhaust waste heat recovery, solar energy conversion, automotive air conditioner, deep-space exploration, electronic control and cooling, and medical instrumentation. Thermoelectrics involves multiple interdisciplinary fields: physics, chemistry, electronics, material sciences, nanotechnology, and mechanical engineering. Much of the theories and materials are still under development, mostly on the materials but minimally on the design. The author has taught the thermoelectrics courses in the past years with a mind that a textbook is necessary to put a spur on the development. However, the author experienced considerable difficulties, partly because of the need to make a selection from the existing material and partly because the customary exposition of many topics to be included does not possess the necessary physical clarity. It is realized that the author's own treatment still has many defects, which are desirable to correct in future editions. The author has an open mind and appreciation for any comments and defects that may be found in the book. Typically, design and materials are separate fields, but in thermoelectrics, the two fields are interrelated particularly when the size is small and the variation of temperature is large. Hence, this book includes the design and materials for future vigorous engagement.

This book consists of two parts: design (Chapters 1 through 8) and materials (Chapters 9 through 16). The design covers the theoretical formulation, optimal design, experimental verification, modeling, and applications. The materials cover the physics of thermoelectrics for electrons and phonons, experimental verification, modeling, nanostructures, and thermoelectric materials. Each part can be suggestably used for a semester period (usually an introductory session for the subtle phenomena of thermoelectrics is given in the beginning of class) or two parts in a semester period by skimming some topics when students or readers are familiar with the topics. The author put significant effort into managing the contents in Part I with a fundamental heat transfer course as prerequisite and the contents in Part II with an introductory material science course. The author also attempted to provide detailed derivation of formulas so students or readers can have a conviction on studying thermoelectrics, as well as to provide detailed calculations, so that they can even build their own mathematical programs. Hence, many exercise problems at the end of chapter ask students or readers to provide Mathcad programs for the problem solutions.

I would like to acknowledge the suggestions and help provided by undergraduate and graduate students through classes and research projects. Special thanks are given to Dr. Alaa Attar, who is now professor at King AbdulAziz University, Saudi Arabia, for his help in measurements and computations. I am also indebted to Professor Emeritus Herman Merte Jr. for his lifetime inspiration on the preparation of the book. I am very grateful to Professor Emeritus Stanley L. Rajnak, who read the manuscript and made many useful comments.

HO SUNG LEE  
KALAMAZOO, MICHIGAN





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# 1

## Introduction

### 1.1 Introduction

Thermoelectrics is literally associated with thermal and electrical phenomena. Thermoelectric processes can directly convert thermal energy into electrical energy or vice versa. A *thermocouple* uses the electrical potential (electromotive force) generated between two dissimilar wires to measure temperature. Basically, there are two devices: thermoelectric generators and thermoelectric coolers. These devices have no moving parts and require no maintenance. Thermoelectric generators have great potential for waste heat recovery from power plants and automotive vehicles. Such devices can also provide reliable power in remote areas such as in deep space and mountaintop telecommunication sites. Thermoelectric coolers provide refrigeration and temperature control in electronic packages and medical instruments. The science of thermoelectrics has become increasingly important with numerous applications. Since thermoelectricity was discovered in the early nineteenth century, there has not been much improvement in efficiency or materials until the recent development of *nanotechnology*, which has led to a remarkable improvement in performance. It is, thus, very important to understand the fundamentals of thermoelectrics for the development and the thermal design. We start with a brief history of thermoelectricity.

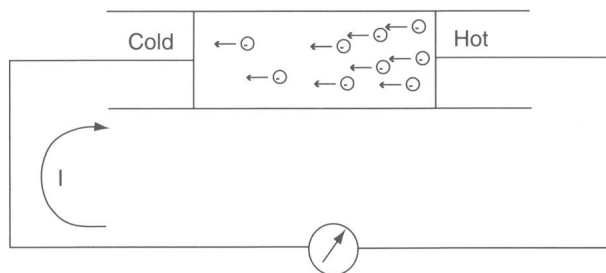
In 1821, *Thomas J. Seebeck* discovered that an electromotive force or a potential difference could be produced by a circuit made from two dissimilar wires when one of the junctions was heated. This is called the *Seebeck effect*.

Thirteen years later, in 1834, *Jean Peltier* discovered the reverse process—that the passage of an electric current through a thermocouple produces heating or cooling depending on its direction. This is called the *Peltier effect*. Although these two effects were demonstrated to exist, it was very difficult to measure each effect as a property of the material because the Seebeck effect is always associated with two dissimilar wires and the Peltier effect is always followed by the additional Joule heating that is heat generation due to the electrical resistance to the passage of a current. Joule heating was discovered in 1841 by James P. Joule.

In 1854, *William Thomson* (later *Lord Kelvin*) discovered that if a temperature difference exists between any two points of a current-carrying conductor, heat is either liberated or absorbed depending on the direction of current and material, which is in addition to the *Peltier heating*. This is called the *Thomson effect*. He also studied the relationships between these three effects thermodynamically, showing that the electrical Seebeck effect results from a combination of the thermal Peltier and Thomson effects. Although the Thomson effect itself is small compared with the other two, it leads to a very important and useful relationship, which is called the *Kelvin relationship*.

The mechanisms of thermoelectricity were not understood well until the discovery of electrons at the end of the nineteenth century. Now it is known that solar energy, an electric field, or thermal energy can liberate some electrons from their atomic binding, even at room temperature, moving them (from the valence band to the conduction band of a conductor) where the electrons are free to move. This is the reason why we have electrostatics everywhere. However, when a temperature difference across a conductor is applied as shown in Figure 1.1, the hot region of the conductor produces more free electrons, and diffusion of these electrons (charge carriers including holes) naturally



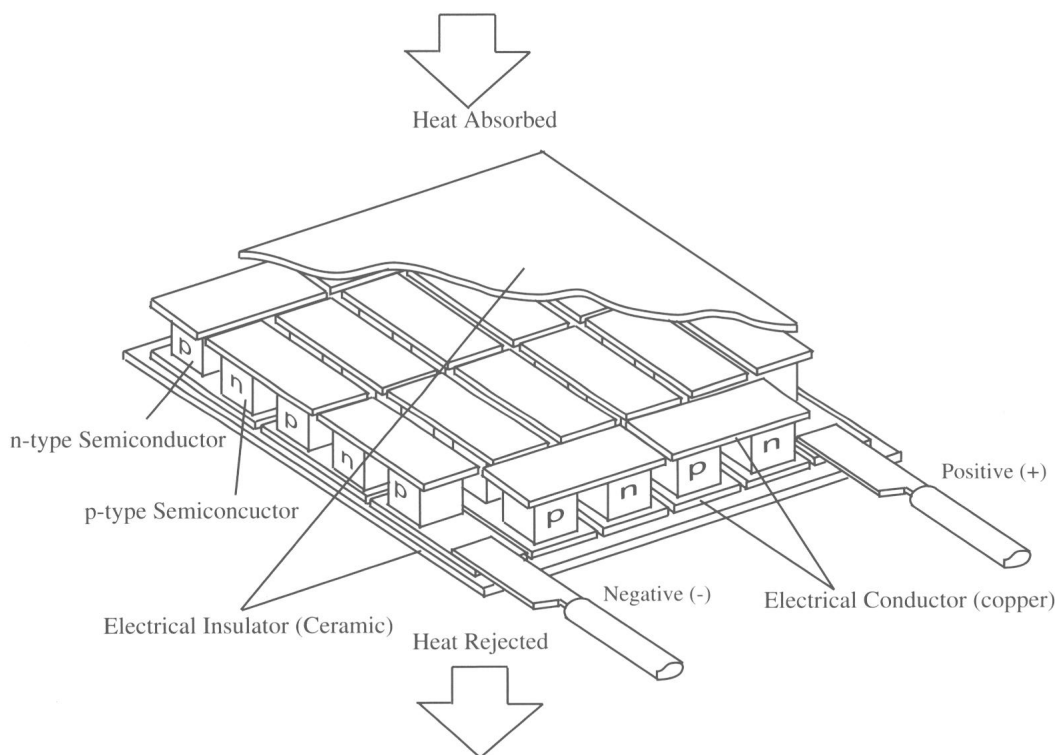


**Figure 1.1** Electron concentrations in a thermoelectric material

occurs from the hot region to the cold region. On the other hand, the electron distribution provokes an electric field, which also causes the electrons to move from the hot region to the cold region via the Coulomb forces. Hence, an electromotive force (*emf*) is generated in a way that an electric current flows against the temperature gradient. As mentioned, the reverse is also true. If a current is applied to the conductor, electrons move and interestingly carry thermal energy. Therefore, a heat flow occurs in the opposite direction of the current, which is also shown in Figure 1.1.

In many applications, a number of thermocouples, each of which consists of p-type and n-type semiconductor elements, are connected electrically in series and thermally in parallel by sandwiching them between two high-thermal conductivity but low-electrical conductivity ceramic plates to form a module, which is shown in Figure 1.2.

Consider two wires made from different metals joined at both ends, as shown in Figure 1.3, forming a close circuit. Ordinarily, nothing will happen. However, when one of the junctions is heated, something interesting happens. Current flows continuously in the circuit. this is the *Seebeck effect*. The circuit that incorporates both thermal and



**Figure 1.2** Cutaway of a typical thermoelectric module