Eco-Friendly Alternative Refrigeration Systems

1. Magnetic and Thermoelectric Refrigeration

S S Verma

Refrigeration applications at the domestic, commercial and industrial levels are becoming an integral part of the present day living. The demand and supply of refrigeration systems is increasing day by day with the changing lifestyle. The existing compressor-based refrigeration (i.e., mechanical refrigeration) system has reached the maximum level of innovation. For the last few decades, there has not been any significant increase in the efficiency (i.e., coefficient of performance, COP) of the system. Moreover, with the increasing awareness of environmental degradation, the production, use and disposal of ChloroFluoro Carbons (CFCs) and HydroChloroFluoroCarbons (HCFCs) as refrigerants in mechanical refrigeration system has become a subject of great concern. However, such systems are being developed using more ecofriendly refrigerants viz., air, CO_2, NH_3, etc. Besides, efforts are being directed to develop other types of refrigeration technologies e.g., magnetic refrigeration, thermoelectric refrigeration (discussed in Part 1) and thermoacoustic refrigeration (discussed in Part 2), which will be more *ecofriendly, cost effective, efficient, simple in design, convenient and reliable.*

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Introduction

A device that transfers heat from a cold body to a warm body with the aid of an external energy source is called a refrigerator and use of natural refrigeration in day to day life is as old as the human race. The invention of Joule–Thomson's cooling effect (i.e., when a fluid is allowed to expand through a nozzle, it gets cooled) and its combination with compression gave rise to mechanical refrigeration/vapour compression refrigeration technology. This system of refrigeration technology is shown in

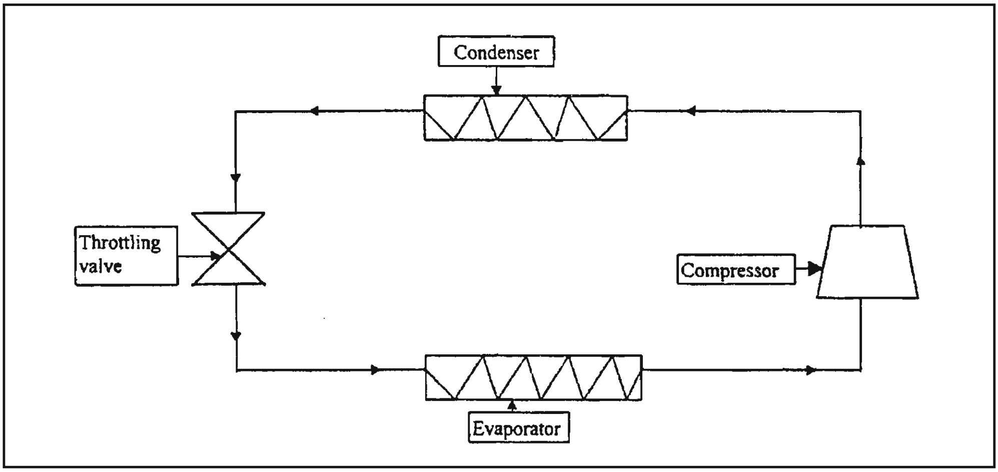

Figure 1. Schematic diagram showing the mechanical refrigeration system.

Figure 1. In such a refrigerator, the low-temperature (evaporator) reservoir is the cold body (which is located inside the refrigerator) and from where the stored substances get cooled and the high-temperature reservoir (condenser) is the hot body from where heat is given off to the surroundings in which the unit is housed. To extract heat from the stored substances and reject it to the surroundings, work has to be done. This is accomplished using a refrigerant and a mechanical compressor.

The demand and supply of refrigeration systems is growing rapidly. The fluids (i.e., refrigerants) used in refrigeration systems nearly a century ago such as, air, CO_2, NH_3 were more or less eco-friendly. But the quest of scientists and engineers for fluids with better thermo-physical and chemical properties led to the development of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). This gave a big boost to the mechanical refrigeration industry in terms of reduced cost, increased efficiency, higher reliability, etc. However, the development of equipment/auxiliaries of a mechanical refrigeration system (*Figure* 1), e.g., compressor, evaporator, condenser, throttling valve have attained a level of optimality in terms of increased coefficient of performance (COP) of the system and there is little new development in these since a long time. Presently most of the efforts are towards design of systems with variable capacity, a better appearance and cost effectiveness than efficiency.

With growing environmental hazards, public awareness towards a sustainable development is increasing now. One of the serious threats to the environment is the stratospheric ozone layer depletion. The stratospheric ozone layer plays a beneficial role by absorbing most of the biologically damaging ultraviolet sunlight called UV-B coming towards the Earth. Ozone also plays a key role in the temperature regulation of the Earth's atmosphere. Recent investigations have shown that human-made chemicals are responsible for the observed depletion of ozone layer. The ozone depleting compounds (i.e., CFCs and HCFCs) contain reactive gaseous atoms of chlorine or bromine. Although, the CFC and HCFC molecules are heavier than the molecules of air, the atmospheric air-circulation takes these compounds to the stratosphere over a period of time. Halon (i.e., chlorine and bromine) molecules of CFCs and HCFCs react very rapidly with ozone via their oxide formation and thus decrease the concentration of stratospheric ozone.

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Besides, the phenomenon of trapping of reflected short wavelength radiation from the surface of earth in the troposphere by various types of atmospheric constituents gives rise to the increase in the Earth's surface temperature known as greenhouse effect. Thus Earth retains heat and its progressive warming is taking place. Increase of Earth's surface temperature by a few degrees is expected to produce many unwanted environmental effects. The presence of CFCs and HCFCs in the troposphere region also plays a significant role in the greenhouse effect. Thus, in the present environmentally conscious age, it has been pointed out [1] that production, leakage, disposal, etc. of CFCs and HCFCs refrigerants has an adverse effect on our environment by contributing towards ozone layer depletion and greenhouse effect.

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Thus, due to slow improvement of efficiency and concern for the environment, efforts are now being directed to develop eco-friendly alternative refrigeration systems. In this regard, some alternatives are – magnetic refrigeration, which uses magnetocaloric effect, thermoelectric refrigeration which uses

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Peltier's effect and thermoacoustic refrigeration. In Part 1, a brief introduction is given to the principles involved in the first two eco-friendly alternate refrigeration systems along with the latest developments in respective technologies.

Magnetic Refrigeration

Principle and Thermodynamics of Technology

Magnetic refrigeration is based on the magnetocaloric effect – the ability of some materials to become hot when magnetized and to cool when removed from the magnetic field. The reversible change of temperature is achieved through the change of magnetization of a ferromagnetic or paramagnetic material. Thermodynamic theory shows that, for an adiabatic change of field ΔH, the change of temperature ΔT is given by [2],

$$(\Delta T/\Delta H) = -(T/C_{H})\,(\delta M/\delta T)_{H,}$$

where C_H is the specific heat per unit volume at constant H, and M is the magnetization. Except in antiferromagnets, $(\delta M/dT)_H$ is negative and an adiabatic decrease in H causes T to drop. This is the basis of the Giauque–Debye adiabatic demagnetization of paramagnetic salts, a technique that has achieved extremely low temperatures. Adiabatic demagnetization has been employed since 1933 to produce temperatures below those readily obtainable by using only liquid helium (i.e., below 1K).

Basics of Refrigeration System

Gadolinium has a favourable magnetocaloric coefficient.

The magnetic refrigerator based on magnetocaloric effect [3] is shown in *Figure* 2. It has two rotating cylinders containing powdered gadolinium – a dense, gray, rare earth metal and a superconducting magnet. Gadolinium has a favourable magnetocaloric coefficient. Each atom of gadolinium has seven unpaired electrons in an intermediate shell, which gives the element a strong magnetic moment. This type of refrigerator is reported to work at near-room temperature to produce substantial amounts of cooling power. At a fixed temperature, the entropy of a magnetic system gets lowered as the spins align with

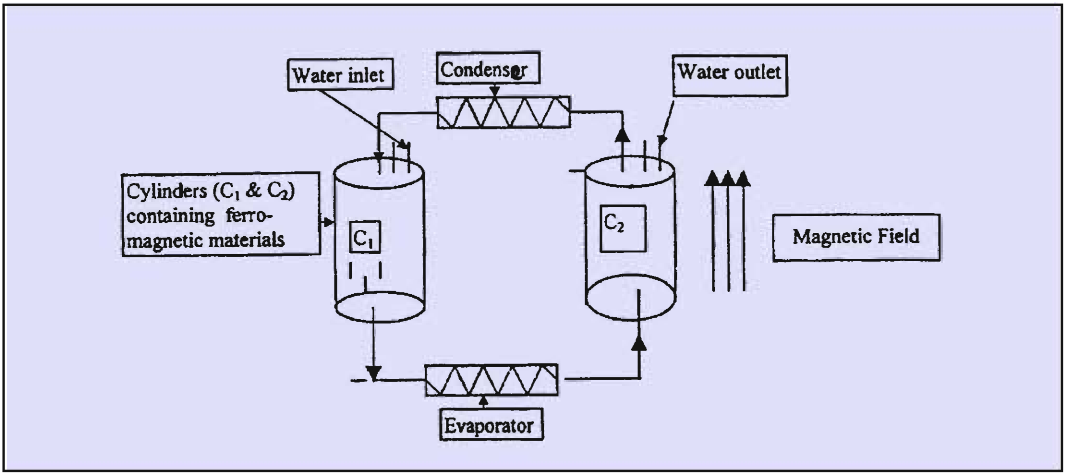

Figure 2. Schematic diagram showing the magnetic refrigerator.

an applied magnetic field. When a ferromagnetic material, such as gadolinium, is placed in a magnetic field, the magnetic moments of its atoms become aligned, making the material more ordered. But, the amount of entropy in the magnet must be conserved, so the atoms vibrate more rapidly, raising the material temperature. Conversely, when gadolinium is taken out of the magnetic field, the material cools. This magnetocaloric effect typically produces a temperature drop of 0.5-2K for a field change of 1 Tesla at room temperatures.

The two cylinders containing gadolinium metal can be made to rotate through the magnetic field and arrangements should be made such that, water is pumped into one of the cylinders of gadolinium immediately after it moves out of the magnetic field. The water cools as it flows through the porous bed of demagnetized gadolinium, and then through a heat exchanger. Next, the water passes through the cylinder of gadolinium that is inside the magnetic field. This stream of water heats up and flows through another exchanger, providing ample refrigeration power by continually heating one exchanger and cooling the other. After a preset time interval, the two cylinders of gadolinium compound switch places, and the flow of water is reversed. Besides, antifreeze can be added to the water to allow the machine to cool below zero degrees Celsius.

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Technological Developments

This type of refrigeration system will prove remarkably efficient because very little energy is lost during the magnetic warming and cooling. The experimental prototype system based on this principle has run at 30% efficiency of the Carnot limit, which is comparable with the efficiency of most household units. It is expected that a larger magnetic refrigeration system can be built, which could operate at 70% of the limit, making it competitive with the best industrial-scale refrigerators. Recently synthesized class of gadolinium alloys – mixed with silicon and germanium – exhibited an even greater magneto-caloric effect. The only major obstacle to the development of magnetic refrigerators is the cost of the superconducting magnet. Hence, if the magnetocaloric effect can be sufficiently enhanced, the device may run efficiently even with a weaker field generated by a permanent magnet. Moreover, with the help of recent developments and future prospects in superconducting magnetic materials (for use in superconducting magnets) as well as the materials exhibiting high level of magnetocaloric coefficient, a magnetic refrigerator for households with enough temperature change may be possible in future.

In the United States, the department of energy (DoE) [4] is also exploring the possible use of magnetic refrigeration in automobile air-conditioner systems. An automobile air-conditioner system based on magnetic refrigeration (shown in *Figure* 3) would run on the electrical power generated by the alternator, thereby reducing the load on the power train and making the car more fuel-efficient. As the refrigeration system will also work using only a part of the power produced to drive the vehicle so no extra consumption of fuel is required. In *Figure* 3 'rotation' indicates to and fro movement of the magnetocaloric wheel inside the magnets with the help of axle (i.e., drive). However, the challenge

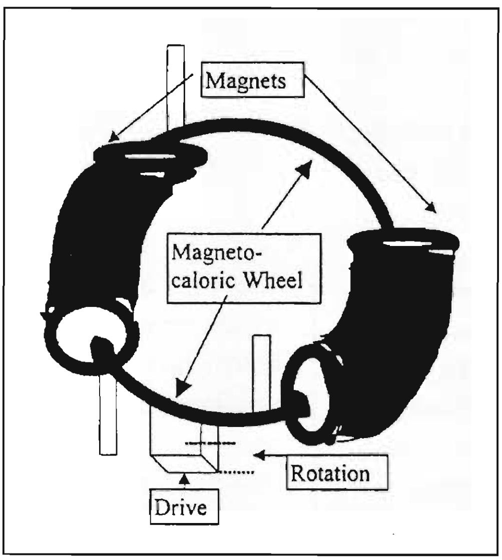

Figure 3. Schematic diagram of a magnetic refrigeration system for an automobile air-conditioner.

lies in the development of an air-conditioning system that is light, inexpensive and efficient. The technology ideally lends itself to be used in electric cars, and the cooling process can also be reversed to heat the vehicle.

Thermoelectric Refrigeration

Principle of Technology

In 1823, Seebeck discovered that a voltage drop appears across a junction (i.e., a combination of two dissimilar metals) that has a temperature gradient. This effect is known as *Seebeck effect.* This effect was the basis for thermocouples and for thermoelectric power generation. The reverse of the Seebeck effect i.e., when a voltage drop is maintained across two junctions of the sample, one end gets heated up and the other gets cooled, was given by Peltier and known as *Peltier effect.* Here it is worth mentioning that Peltier effect is totally different from Joule effect of heating. Joule effect is irreversible whereas Peltier effect is reversible and the direction of current reverses the effect from cooling to heating and vice-versa. In 1838 Henrich Lenz showed that when a drop of water was placed on the junction of metal wires made up of bismuth and antimony and current was passed through the junction, the water drop froze; on reversing the current the ice melted. Thus thermoelectric refrigeration was achieved in the first phase of his experiments. Thermoelectric cooling module given in *Figure* 4 shows a single coupled configuration. The labels P (+ve) and N (–ve) refer to the sign of the charge carriers in each leg. The black portions in the *Figure* 4 indicate the junction with the respective electrodes (i.e., cathode and anode). Refrigeration (or the cooling effect) is achieved

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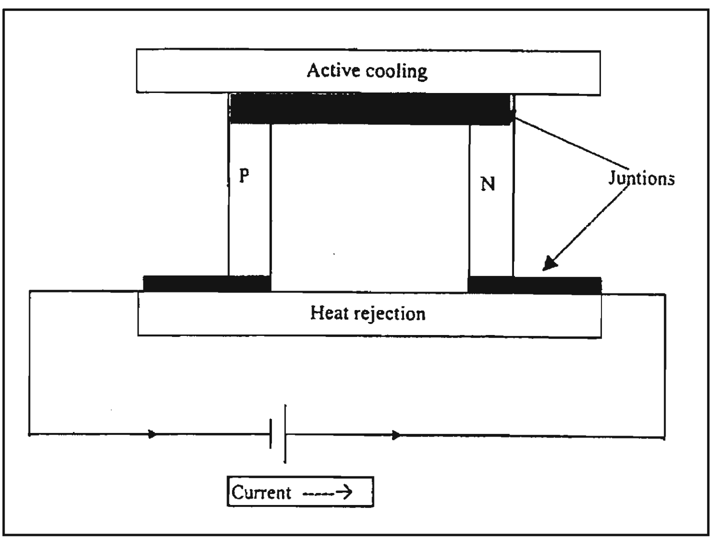
Figure 4. Schematic diagram of a thermoelectric refrigeration system.



in the device because electrons carry heat, and 'hot' electrons can be forced away from the cold end of the device by the battery.

Technological Developments

The thermoelectric effect is of very small magnitude with ordinary metals. But late in the 1950s it was found that doped semiconductors had much larger Peltier coefficients. Abram Ioffe, for the first time suggested the possibility of a thermoelectric home refrigerator using semiconductors. Virtually every known semiconductor, semi-metal and alloy was evaluated for its thermoelectric properties and Bi_2Te_3/Sb_2Te_3 alloys were found to be the best materials at room temperature. However, only moderate amount of cooling was produced with the help of these thermoelectric materials giving poor efficiencies as compared to compressor-based refrigerators [5,6].

As a result, thermoelectric refrigeration technology was limited to its applications in which reliability or convenience is more important than economy. Thermoelectric refrigeration is being used in surgery for cooling the instrument used for extracting the crystalline lens out of the eye. After the operation has been performed, the lens is replaced in the eye with the aid of the same instrument. The instrument consists of a junction of two different semiconductors cooled by passing a current such that low temperatures are produced whereby the crystalline lens, upon contact, sticks to the instrument. A reversal of the current frees the lens. With the development of more suitable semiconductors, today thermoelectric coolers can be powered by a car battery for portable beverages storage, or by a power supply to provide active cooling for a computer's central processing unit or for an infrared detector. Moreover, temperatures as low as 160K can be reached with multistage coolers obtained by combining single stage coolers. The development of superior thermoelectric materials [5-7] in the form of new complex materials such as $Bi_2Te_3/Sb_2Te_3/Bi_2Se_3/PbTe/SnTe/GeTe/CeS$ alloys; $LaFe_3CoSb_{12}$, $CeFe_3CoSb_{12}$, $CoSb_3$,$La_{0.9}Fe_3CoSb_{12}$, $Ce_{0.9}Fe_3CoSb_{12}$ rattling semiconductors; $IrSb_3$, $CoAs_3$, $RhSb_3$ broad-

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band semiconductors; GaAs/AlAs multiple quantum wells and understanding the theoretical background make this option quite attractive.

Basic Thermodynamics

The basic thermodynamics of thermoelectric devices was worked out in mid-1800s by Lord Kelvin, who gave the mathematical relationship between heat and electrical currents in a conducting isotropic solid as $J = \sigma(E - S\Delta T)$ and $Q = (\sigma TS)E - \kappa\Delta T$, where J is the electrical current density, σ is the electrical conductivity, E is the electric field, S is the Seebeck coefficient, T is the temperature, Q is the heat current density (i.e., current density as a function of temperature) and κ is the thermal conductivity. Only S causes any conceptual difficulty. It is the average entropy per charge carrier divided by the electron charge. These equations are solved to get the expression for the efficiency of an idealised thermoelectric device. The efficiency of a thermoelectric solid is found to depend on the material properties through the dimensionless parameter ZT, where $Z = S^2/\kappa\rho$ and $\rho = 1/\sigma$. Z is called the figure of merit and has units of inverse temperature; ZT is often referred to as the dimensionless figure of merit. For thermoelectric refrigerator the coefficient of performance is $(\gamma T_c - T_h)/[(T_h - T_c)(1 + \gamma)]$. Here, T_c and T_h are the temperatures of the cold and hot ends respectively, and $\gamma = (1 + ZT)^{1/2}$ varies with the average temperature T. For $ZT >> 1$, Carnot efficiency is obtained, but materials currently used in thermoelectric devices have ZT values between 0.4 and 1.3.

All materials used at present are heavily doped semiconductors and their figure of merit ZT is a function of carrier concentration. It is found that metals are poor thermoelectric materials due to their large electronic contribution to thermal conductivity. The largest value for ZT is obtained midway between two extremes (metal or insulator) at a carrier concentration of about $10^{19}/\text{cm}^3$. For optimum performance, the energy gap of the semiconductor must be at least 10 times kT_{max}, where T_{max} is the

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maximum operating temperature. Otherwise simultaneous excitation of intrinsic electrons and holes lower *S* and *ZT*. Investigations show that maximum value of *ZT* for many materials is near 1. However, theoretically there is no fundamental limit to *ZT*, and values upto 2 to 4 may be possible and a value of 3 will make thermoelectric home refrigerators competitive to the existing mechanical refrigerating systems.

Development of Materials

The four different approaches to the development of new superior thermoelectric materials are:

i) binary and ternary covalently bonded semiconductors
ii) semiconductors with *'rattling'* atoms or molecules
iii) correlated metals or semiconductors and
iv) super lattices.

The latest developments in these materials are as follows:

i) Bi_2Te_3 /Sb_2Te_3/Bi_2Se_3 alloys with $ZT = 0.9$ are being used in today's state-of-the-art Peltier refrigerators. Further investigations suggest compounds made from elements found in the lower right corner of the periodic table – group IIIB to VIB.

ii) The maximum thermoelectric efficiency is achieved when the lattice contribution to the flow of heat is as low as possible. It is proposed that the ultimate thermoelectric material should conduct electricity like a crystal but conduct heat like a glass. And this can be obtained from a material having crystal structure containing weakly bound atoms or molecules that 'rattle' within an atomic cage. This class of materials with required characteristics of good thermoelectric material is the filled skutterudite antimenides. Compounds with such character having formula RM_4X_{12}, where X is phosphorus, arsenic or antimony; M is iron, ruthenium or osmium; and R is lanthanum, cerium, prasodymium, or neodymium have been developed. The values for *ZT* at elevated temperatures for these materials are comparable to the best values reported for any material. Thus, the data provide strong support for the hypoth-

Suggested Reading

[1] B K Sharma and H Kaur, *Air Pollution*, First edition, Goel Publishing House, Meerut (India), 1993-94.

[2] Magnetocaloric effect and adiabatic demagnetisation, *McGraw-Hill Encyclopedia of Science and Technology*, 8th edition, USA, 1997.

[3] Mark Alpert, A cool idea, *Scientific American*, p. 44, May 1998.

[4] *ASHRAE Journal*, p.8, January 1999.

[5] G Mahan, B Sales and J Sharp, Thermoelectric materials: new approach to an old problem, *Physics Today*, pp. 42-47, March 1997.

[6] D G Fink and D Christiansen, Electronics Engineer's HandBook (Coolers) 2nd edition, McGraw-Hill, USA, pp.11-85, 1986.

[7] G D Rai, Thermoelectric materials, *Non-conventional Sources of Energy*, 3rd edition, Khanna Publishers, New Delhi, pp. 720.

esis that compounds with rattling guest atoms may be superior thermoelectrics.

iii) Many rare earth inter-metallic compounds (usually containing cerium or ytterbium) in which the energy level is near the fermi energy were investigated. Theoretical support showed that the best electronic structure for thermoelectric material is a delta function in the transport distribution centered about 2-3 KT from the fermi energy. Unusual correlated semiconductors may represent a closer approximation of the ideal electronic structure. For viability, the Seebeck coefficient must be $>156\ \mu V/K$. Presently, $CePd_3$ a correlated alloy has the highest Seebeck coefficient of $115\ \mu V/K$ at 125 K.

iv) Semiconductor quantum wells are supposed to have a larger value of ZT. It has been shown theoretically and experimentally that ZT for a single quantum well increases as the wellwidth decreases. A refrigerator may need many quantum wells. However, main benefit of the multiple quantum wells is thermal, not electrical.

Conclusion

The ecofriendly alternate refrigeration technologies described in this article are still in the stage of infancy. But there is a strong support of the principles used in these technologies. Moreover, rapid developments are taking place in various fields of science and technology. Therefore, scientists and technologists are confident that the ecofriendly, reliable, simple and convenient technologies of refrigeration described in this article will be used for domestic and commercial purposes in the near future. Although at present these technologies look very ecofriendly, same as mechanical refrigeration systems were before the development of CFCs and HCFCs as refrigerants, further developmental efforts should always be checked from the environmental point of view before they are implemented.

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