It has been known for more than 150 years that the transport of electric charge in conductors is accompanied by flow of heat/energy. In conducting materials there are three types of reversible effects that arise when both electric currents and temperature differences are present: the Seebeck effect, the Peltier effect, and the Thomson effect. These phenomena are known as thermoelectric effects, and they have been proven to be very fundamental for the advance of our understanding of the properties of metals and semiconductors. Studies of thermoelectric effects provide information about the electronic structure and the interactions between electrons and both phonons and impurities. In addition, they have significant applications to industrial technology such as energy conversion, power production, and refrigeration. Today a great variety of thermoelectric generators and thermoelectric infrared detector coolers exist.

The history of the Peltier effect started in 1834, when a French watchmaker and amateur scientist named Jean Charles Athanase Peltier discovered that when an electric current (I) is forced through a junction between two different materials, which are initially at uniform temperature, heat flows from one material to another. The amount of heat that is liberated (junction heats up) or absorbed (junction cools

down) per unit of time (Q) is proportional to the current. The coefficient of proportionality, Π , is called the Peltier coefficient, $Q = \prod I$, where the sign of Q (plus for heating and minus for cooling) depends on the direction of the current. The Peltier heating/cooling is a reversible phenemenon in the sense that it depends linearly on the current, and it should be distinguished from the irreversible Joule heating (quadratic dependence) that takes place in any single conductor. Namely, if heat is released when current flows from one conductor to the other conductor, then upon current reversion heat will be absorbed. The simple physical principle that describes all the thermoelectric effects is as follows: As electrons travel through the junction between the two different conductors, on average, they will either lose or gain energy, since their electronic states in these conductors have different energies. For example, if a temperature difference is maintained across the junction, in the absence of external flow of current, electrons will diffuse from the hot conductor to the cold one where they can find states of lower energy. Eventually, more electrons will be accumulated on the cold side of the junction, and this results in the appearance of a voltage difference (Seebeck effect).

Although the Peltier effect is usually the effect that takes place when two different materials are in contact, the Peltier coefficient II can be defined for each individual conductor and it is an intrinsic property of the conductors. The same is true for all other thermoelectric coefficients, and generally they are strongly temperature-dependent. However, it is difficult to measure II for individual conductor experimentally, and usually the Seebeck coefficient can be measured rather readily and accurately. In order to calculate II, the Kelvin relations can be employed. In 1857 Lord Kelvin, using equilibrium thermodynamics, derived two very simple equations that relate the three thermoelectric coefficients (Kelvin relations):

$$\Pi = TS^* \tag{1}$$

$$\mu_{\rm T} = T \frac{dS^*}{dT} \tag{2}$$

where S^* is the thermopower or Seebeck coefficient and μ_T is the Thomson coefficient. More rigorously, these relations follow from the theory of irreversible thermodynamics, as it was shown by Onsager almost a century later.

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The temperature dependence of Π can be easily estimated for metals, using the free-electron gas model. The Thomson coefficient has the meaning of specific transport heat capacity (1) per unit of electric charge. In metals, only a small fraction of conduction electrons contribute to transport, approximately $T/T_{\rm F}$, where $T_{\rm F}$ is the Fermi temperature of the electrons, typically of the order of 10^4 K, and we have $\mu_{\rm T} \simeq k_{\rm B}(T/eT_{\rm F})$. Kelvin's relations then immediately give us

$$\Pi \simeq \frac{k_{\rm B} T^2}{e T_{\rm F}} \tag{3}$$

It is worth mentioning the value of the ratio of the Boltzmann constant to the electric charge of the electron, $k_{\rm B}/e = 85.4 \ \mu V/K$, since it helps to understand the order of magnitude of the thermoelectric effects. The above estimate of the

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Peltier coefficient holds practically in most cases of pure nonmagnetic metals and can be derived using the kinetic theory of electrons in metals. Both the Peltier coefficient and the Seebeck coefficient in superconducting materials are equal to zero for temperatures below their critical temperature.

PELTIER EFFECT IN METALS AND SEMICONDUCTORS

The thermoelectric coefficients are defined in the context of linear response theory: The temperature gradient or the electric field induce small perturbations from the equilibrium state of the conductor so that the electric charge current and the heat current are linear functions of these gradients. The heat current density $J_{\rm h}$ is analogous to the electrical current density $J_{\rm e}$; but instead of measuring electric charge, it measures thermal energy being carried. The formal definitions are

$$\boldsymbol{J}_{\rm e} = \int \boldsymbol{e} \boldsymbol{v}(\boldsymbol{k}) f(\boldsymbol{k}) \, d\boldsymbol{k} \tag{4}$$

$$\boldsymbol{J}_{\rm h} = \int [\boldsymbol{\epsilon}(\boldsymbol{k}) - \boldsymbol{\mu}] \boldsymbol{v}(\boldsymbol{k}) f(\boldsymbol{k}) \, d\boldsymbol{k}$$
 (5)

where $\boldsymbol{v}(\boldsymbol{k})$ is the velocity of the electrons, μ is the temperature-dependent chemical potential, and $f(\mathbf{k})$ is the distribution function of the electrons. For metals that are in equilibrium, $f(\mathbf{k})$ is given by the Fermi–Dirac distribution function $f(\mathbf{k}) = (1 + \exp\{[\epsilon(\mathbf{k}) - \mu]/k_{\rm B}T\})^{-1}$. In addition, in the equilibrium state (i.e., absence of "external forces" such as electromagnetic fields or temperature differences) both current densities are zero. The dynamics of the electron transport is hidden in the distribution function since it carries information about the scattering of electrons by impurities or lattice vibrations. Usually it is determined by the solution of Boltzmann transport equation with appropriate boundary conditions. Upon linearization with respect to the electric field Eand temperature gradient ∇T , Eqs. (4) and (5) provide the mathematical connection between all the thermoelectric coefficients:

$$\boldsymbol{J}_{\rm e} = \sigma \left(\boldsymbol{E} - S^* \boldsymbol{\nabla} T \right) \tag{6}$$

$$\boldsymbol{J}_{\rm h} = \sigma \,\Pi \boldsymbol{E} - \kappa \boldsymbol{\nabla} T \tag{7}$$

where σ and κ are the electrical conductivity and the thermal conductivity, respectively.

For a degenerate metallic conductor, the Peltier coefficient is given by the celebrated Mott formula:

$$\Pi = \frac{\pi^2}{3e} \frac{(k_B T)^2}{\epsilon_{\rm F}} \left(\frac{\partial \ln \sigma(E)}{\partial \ln E} \right)_{E=\epsilon_{\rm F}}$$
(8)

where $\sigma(E)$ is the conductivity that would be found in a metal for electrons of average energy E, $\sigma(E) = e^2 n(E)v^2(E)\pi(E)$, and $\epsilon_{\rm F}$ is the Fermi energy. When the scattering of electrons is mainly due to impurities and is isotropic—as in dillute alloys—the mean free path l is constant. Consequently, the relaxation time is $\pi(E) = l/v(E) \propto E^{-1/2}$, since the average electron velocity v(E) is proportional to \sqrt{E} . The electron density of states for a free electron gas is $n(E) \propto \sqrt{E}$. As a result, Eq. (6), reads

$$\Pi = \frac{\pi^2}{3e} \frac{(k_{\rm B}T)^2}{\epsilon_{\rm F}} \tag{9}$$

In pure metals and for temperatures above a few degrees kelvin, the relaxation time is determined primarily by electron– phonon scattering. Approximately, $\tau(E) \propto E^{3/2}$ and

$$\Pi = \frac{\pi^2}{e} \frac{(k_{\rm B}T)^2}{\epsilon_{\rm F}} \tag{10}$$

The Peltier coefficient for metals is of the order of 50 μ V at room temperatures, and for a wide range of temperatures it is quadratic in temperature. Moreover, because of the smallness of the *degeneracy factor* $k_{\rm B}T/\epsilon_{\rm F}$, the thermoelectric effects in metals are very weak. This is not true in semiconductors, where this factor is absent.

For a semiconductor with relatively few conduction electrons that are characterized by the Boltzmann distribution, the Peltier coefficient has the following form (1):

$$\Pi = \frac{k_{\rm B}T}{e} \left(\frac{5}{2} + \frac{\partial \ln \tau(E)}{\partial \ln E} - \frac{\mu(T)}{k_{\rm B}T} \right) \tag{11}$$

where

$$\mu = k_{\rm B} T \ln \left(\frac{1}{2} N_{\rm c} \left(\frac{2\pi \hbar^2}{m^* k_{\rm B} T} \right)^{3/2} \right) \tag{12}$$

 m^* is the effective mass of the carriers in the semiconductor and N_c is the carrier concentration—the number of charge carriers per unit volume—which has a strong temperature dependence. Generally, the relaxation time can be written as

$$\tau(E) = g(T)E^s \tag{13}$$

where g(T) is a function of temperature only and s is a constant that depends on the type of scattering that is dominant. Usually s is in the range from -2 to 2 (2). Consequently, the second term in Eq. (11) is equal to s, whereas the last term is at least of the order of unity. From the above analysis, it is clear that the order of magnitude of the Peltier coefficient is of the order of 1 V, which is much higher than that of metals, and varies linearly with the temperature. The simplicity of the above expression for Π is restricted only to extrinsic semiconductors. When the carriers are holes (i.e., in *p*-type semiconductors), Π has opposite sign. For intrinsic semiconductors, where both type of carriers are present, the Peltier coefficient takes a more complicated form and its magnitude, generally, is smaller.

PELTIER REFRIGERATION

The most important applications of the Peltier effect lie in the possibility to create efficient cooling solid-state devices that can operate at room temperatures. The bare essentials of the operation of the Peltier cooler (or heater) are straightforward: Two different materials, usually a p-type and an n-type semiconductor, are brought in contact. Sometimes p and n refer to

the positive and negative thermoelements, respectively. Let $T_{\rm c}$ be the temperature of the junction which is in thermal equilibrium with a reservoir that we want to cool down. The other two ends remain at a temperature $T_{\rm h} > T_{\rm c}$ and are connected to a battery that produces an electric current I that passes through the junction. A diagram of this type of solid-state thermoelectric device is presented in Fig. 1. There are three types of processes (one reversible and two irreversible) that transfer thermal energy from the cold to the hot reservoir:

- The rate of Peltier heat absorption $Q_1 = \prod_{np} I$, which is determined by the Peltier coefficients of the two semiconductors $\prod_{np} = \prod_n \prod_p$ and the current I.
- The rate of heat generation $Q_2 = K\Delta T$, due to existence of a temperature difference between the two reservoirs $\Delta T = T_{\rm h} - T_{\rm c}$. It is characterized by the sum of the thermal conductances of the two semiconductors $K = K_n + K_p$.
- The rate of Joule heat production, which is delivered to each reservoir—that is, $Q_3 = (1/2)I^2R$, where R is the total resistance of the two semiconductors. The junction resistance is assumed to be negligible compared to the bulk resistances of the two thermoelements.

In order to evaluate the efficiency of the cooling device, one has to calculate the coefficient of performance, which is defined as the ratio of the rate of heat removed from the cold reservoir to the total electrical power supplied by the battery. Upon maximization with respect to the electric current (2), the coefficient of performance for the Peltier cooling unit is

$$\phi = \frac{T_{\rm c}}{T_{\rm h} - T_{\rm c}} \frac{\Omega - T_{\rm h}/T_{\rm c}}{\Omega + 1} \tag{14}$$

where $\Omega = \sqrt{1 + zT_A}$ and $T_A = (T_c + T_h)/2$ is the average temperature of the two reservoirs. The figure of merit *z* of the



coupled system is a function of the thermopowers, electrical conductivities (σ), and thermal conductivities (κ) of the two materials:

$$z = \left(\frac{S_{\rm pn}^*}{\sqrt{\kappa_{\rm n}/\sigma_{\rm n}} + \sqrt{\kappa_{\rm p}/\sigma_{\rm p}}}\right)^2 \tag{15}$$

The optimal value of the current is

$$I_{\rm opt} = \frac{S_{pn}^* \Delta T}{R(\Omega - 1)} \tag{16}$$

where $S_{pn}^* = S_p^* - S_n^*$ is the difference between the thermopowers of the two components. The maximum value of the coefficient of performance is limited by the Carnot cycle coefficient of performance $\phi_c = T_c/\Delta T$. The second factor in Eq. (14) is between zero and unity and describes the reduction of the efficiency due to irreversible processes of thermal conduction and Joule heat generation that occur in the device. The maximum temperature difference that the Peltier refrigerator can achieve is obtained by setting the optimal coefficient of performance, ϕ , equal to zero—that is, $\Omega = T_h/T_c$ —or

$$\Delta T_{\rm max} = \frac{zT_{\rm c}^2}{2} \tag{17}$$

To get a sense of the operation values of the parameters, say that the figure of merit is $z = 2 \times 10^{-3} \text{ K}^{-1}$, the hot reservoir is kept at approximately room temperature $T_{\rm h} = 300$ K, and the cold reservoir is kept at ice temperature, about $T_{\rm c} = 270$ K; then $\Omega = 1.253$, the efficiency is $\phi = 0.56$, and $\Delta T_{\rm max} = 73$ K.

A unique property exists in the thermoelectric devices that is based on the reversible nature of the effects. For example, the solid-state refrigerator can act as a heating device (heat pump) by reversing the direction of the current. The coefficient of performance for the heat pump $\phi_{\rm p}$ is equal to $\phi_{\rm p}$ = ϕ + 1, and it is greater than unity. The optimal values for the operation of the heating device are the same as for the cooling device. Also if the battery that provides the current is replaced by a resistance load $R_{\rm L}$ and we exchange the temperatures of the two reservoirs in Fig. 1, then upon heat deposition in the hot junction the device can act as a power generator (current is generated in the load, due to the Seebeck effect). However, depending on the type of operation, the design of the thermoelectric device has to be adjusted so that it provides the optimal performance. For a thermoelectric power generator it can be shown (2) that under optimal conditions of operation, the efficiency, defined as the ratio of the output electric power on the resistance load to the input heat at the hot junction is

$$\phi_{\rm g} = \frac{\Delta T}{T_{\rm h}} \frac{\Omega - 1}{\Omega + T_{\rm c}/T_{\rm h}} \tag{18}$$

(19)

The optimal resistance load is $R_L^{\text{opt}} = \Omega R$ and the output power is

$$P_{
m out} = rac{\Omega}{R} \left(rac{S_{pn}^* \Delta T}{\Omega+1}
ight)^2$$

Figure 1. Schematic of the solid-state refrigerator. Due to the Peltier effect the current drives heat out of the cold reservoir, which is in thermal equilibrium with the n-p junction, towards the dark region. The maximum temperature difference that can be achieved is given by Eq. (17). Upon current reversion, the inverse process takes place.

The above equations indicate that the figure of merit is the most fundamental quantity for thermoelectric refrigeration and provides us with a quality criterion for the selection of the materials to be used for thermoelectric devices. As a matter of convenience, the quantity that is most studied in the literature is the dimensionless figure of merit ZT, which is defined for an individual conductor as

$$ZT = \frac{\Pi^2}{TRK} = \frac{TS^{*2}}{RK}$$
(20)

To a good approximation, the total figure of merit can be taken to be the average of the two individuals figures of merit. It is evident from the above expressions that the efficiency of the Peltier cooler depends on the temperatures $T_{\rm c}$ and $T_{\rm h}$ (sometimes called the ambient temperature) and also on the transport properties of the materials through the figure of merit. It is also clear that the figure of merit should be as large as possible. This is actually the central problem in the thermoelectric refrigeration and, although some success has been attained in the past, is still an open problem. In order to obtain an effective Peltier cooler, the Seebeck coefficients of the two components should have opposite signs and should be large. Moreover, we need materials with high electrical conductivity and low thermal conductivity. Furthermore, the strong temperature dependence of the figure of merit, which usually peaks at some temperature and then decreases quickly, must be considered, since it is not easy to find good positive and negative thermoelements that have the same properties within the same temperature window.

A pair of thermoelectric materials usually performs well within some temperature range, as determined by Eq. (17), but might not fit our requirements. One way to resolve this problem is to design a multistage cooling unit or refrigeration cascade. At each stage the thermoelectric materials can achieve some fraction of the total temperature difference that is of interest. Thus, in order to get a large temperature difference, a variety of materials have to be chosen so that they operate optimally within some temperature window. The cascades have the form of pyramids of pairs of thermoelements that are electrically in series, and the hot junction of the first stage acts as a cold junction for the second stage, and so on. For multilayer refrigerating devices the heat cooling capacity of each layer is required to be larger than that of the previous stage since, at each level of operation, not only the amount of heat absorbed from the previous cold junction, but also the electrical power put into the preceding stage, has to be removed. Therefore, for each extra stage the number of Peltier elements has to be larger than that of the previous one. In a cascade type of arrangement, not only the attainable temperature differences are larger but also the coefficient of efficiency increases significantly. Therefore, cascades are certainly superior to single-stage thermoelectric devices. However, there are some technical limitations related to thermal isolation of each unit, and only two to three stages are used in practice.

Using metals as thermoelectric components is not preferable, in spite of the favorable small values of the ratio κ/σ : From the Wiedemann–Franz law we have where the Lorenz number is

$$L = \frac{\pi^2}{3} \left(\frac{k_{\rm B}}{e}\right)^2 \tag{22}$$

This is due to the fact that the Peltier effect in metals is very weak (as was shown in the previous section) at all temperatures, and, as a result, typical values of the figure of merit, ZT, for metals at room temperatures is approximately 0.05. The performance of a metal-based cooler is approximately 1% and has no practical value. Furthermore, the metals do not meet the requirements for efficient cooling at liquid nitrogen temperatures. For lower temperatures, the Peltier coefficient in metals can be increased substantially by adding certain magnetic impurities (e.g., iron) to pure metals. A rapid increase in the density of states at energies close to the Fermi level occurs, related to the Kondo effect. From the Mott formula, one then can see that this change in the density of states would increase the Peltier coefficient.

Semiconductors have more advantages than metals, since the Peltier coefficient is larger. Also, by varying the concentration of the impurities (doping) a further optimization of thermopower, electrical conductivity, and thermal conductivity is possible. This flexibility of carrier concentration adjustment made the semiconducting materials the most favorite among researchers for the past 50 years. Usually higher doped semiconductors are preferable, but the doping impurities that determine the carrier concentration must be so chosen, to maximize S^{*2}/R . However, highly doped semiconductors have large phonon thermal conductivity in addition to the electronic one. At room temperatures, typical values of ZT for semiconductors are near unity. The semiconducting compound Bi₂Te₃ and other solid solutions such as bismouth selenide or antimony telluride were extensively studied in the past (3) for thermoelectric refrigeration at room temperatures. They can provide a maximum temperature difference of the order of 40 K, and the efficiency is of the order of 10%. At cryogenic temperatures, the carriers in the semiconducting materials are frozen, which limits their potential use for refrigeration in this temperature range.

The performance of a Peltier refrigerator is much smaller than the one of conventional vapor-compression-type systems that are used for domestic refrigerators. The attainable cooling power is approximately 10 W, and there is a need for substantial improvement in the figure of merit of the Peltier thermomaterials. The use of reduced dimensionality systems was recently suggested (4) in order to increase the figure of merit of conventional bulk semiconducting thermoelectric materials which for the past 20 years seemed to reach their maximum potential performance. Based on the latest advances in nanolithography and fabrication technology, it is possible to confine electrons in a very narrow, one-dimensional region and thus create quantum wires or one-dimensional conductors. In such exotic systems, lattice thermal conductance appears to diminish due to increased phonon scattering from the surface. The results show a very drastic change in the figure of merit at room temperatures: for a bulk three-dimensional bismuthtelluride alloy ZT = 0.67, whereas for a wire with 5 Å diameter ZT = 14 (4).

For Peltier refrigeration at and below liquid-nitrogen temperatures (77 K), Bi–Sb alloys are promising candidates for the *n*-type material with individual figure of merit about $7 \times$

 10^{-3} K⁻¹ at 80 K. On the other hand, traditional *p*-type thermoelectric materials, like bismuth-antomony-tellurides, have low individual figure of merit and would significantly degrade the potential performance of solid-state refrigerators. That is, the total figure of merit is less than the figure of merit of the negative thermoelement. If we use a superconducting material in which the Seebeck coefficient is zero and the ratio of the thermal to electrical conductivity is significantly smaller than that of the semiconductor, the efficiency will be restored. The use of high- T_c superconductors like YBCO, with high critical current density, as a *p*-type material offers this alternative solution (5). A maximum temperature drop of 7 *K* with the hot junction at 78 K was reported recently (5).

In spite of their low cooling power, there are certain advantages that make Peltier refrigerators more desirable. For example, they have a smaller size, they use no refrigerant, and they lack moving mechanical parts. Also among their features are low weight, maintenance-free operation, and extreme silence, which make them of major interest for military applications. Another application is related to the property that it is very simple to control the rate of cooling by adjusting the current, while reversal of the current direction transforms the cooling device into a heater. This makes Peltier coolers/heaters very useful units for temperature control system. Adjusting the current within some range of values, heat can either be removed or added to one of the junctions that is in contact with the device whose temperature we want to be stabilized. In general, thermoelectric units can be part of miniature electronic and optoelectronic devices. For example, incorporation of a Peltier cooler/heater was suggested to stabilize the output wavelengths of a scanning laser diode with broad thermal scanning range (6).

As a final comment, it should be mentioned that the marathonian search for more exciting and exotic thermoelectric materials at room temperatures still continues (7).

PELTIER REFRIGERATION IN THE MILLIKELVIN TEMPERATURE RANGE

At very low temperatures—below a few hundred millikelvin—the coupling between electron and phonons in metals is very poor, and as a result the heat/energy flow between the phonon system (lattice) and the electron gas can be negligible. Therefore, electrons and phonons can be viewed as almost independent thermodynamic systems with well defined, but different temperatures. The energy transfer between lattice and electrons can be derived quantum mechanically by calculating the rate at which electrons exchange (absorb or emit) energy with phonons. The final result is calculated to be (8)

$$P_{\rm e-p} = \Sigma U (T^5 - T_{\rm L}^5)$$
(23)

where U is the volume of the metal. Σ differs from material to material, but it is a constant and in general depends on the strength of electron-phonon coupling. When the electronic temperature T is equal to lattice temperature $T_{\rm L}$, $P_{\rm e-p}$ vanishes at it should, since then electrons and phonons are in thermal equilibrium, and therefore there is no energy flow from one system to the other. Most notably, the minimum electronic temperature that can be achieved when some small incident Joule heat $P_{\rm ext}$ is deposited in the metal, possibly due to some external voltage source, is

$$T_{\rm min} = (P_{\rm ext} / \Sigma U)^{1/5} \tag{24}$$

Traditionally, in order to achieve such low temperatures, the metals are immersed into liquid helium, a rather indirect procedure because the lattice is cooled first. A novel technique was suggested recently (9) that exploits the thermal transport properties of a normal-metal-insulator-superconductor (NIS) tunnel junction, in order to decrease the electronic temperature of the metal (usually called normal metal because of the absence of superconductivity which can be suppressed by an applying magnetic field). The principle of the Peltier cooling in hydrid superconducting structures can be understood as follows. At zero temperature, electrons in the normal metal are distributed among the energy levels in a way that all levels with energy below the Fermi energy are occupied and all states with higher energy are empty. Namely, their distribution function is a step function. At very low temperatures the occupational probabilities of the energy states are determined by the Fermi-Dirac distribution function: approximately a step function with a thermal smearing of $k_{\rm B}T$ about the Fermi energy. The electrons lying in a strip of energy $k_{\rm B}T$ above the Fermi energy carry more energy than the rest. If we manage to extract only those electrons from the normal metal, then the smeared distribution function will be sharpened. Consequently the electronic temperature will be lowered. This effect can be achieved with the help of the adjacent superconductor, which possesses a gap in the excitation spectrum. When the biased voltage of the NIS tunnel junction is close to the superconducting gap Δ and the tunnel barrier between the normal metal and the superconductor is very strong, only the hot electrons of the normal metal can tunnel effectively to the superconductor, since for the rest there are no states available in the superconducting electrode. Figure 2 illustrates the highlights of refrigeration in an NIS junction. In this space-energy diagram, all energies are measured from the chemical potential of the superconductor. When the junction is biased about the superconducting gap, only electrons from the tail of the distribution of the normal metal can tunnel to the superconductor where they can find available empty states (shown by the arrow).



Figure 2. Energy-space diagram for the NIS junction. Biasing the junction at voltages about the superconducting gap, the highly excited electrons from the normal metal tunnel to the superconducting region where unoccupied electronic states are available. The horizontal arrow describes the tunneling process. (Based on Ref. 9.)

Mathematically, the heat transport through the NIS junction can be formulated along the lines of tunneling Hamiltonian theory. Under the condition that the tunneling probability through the barrier (insulating region) is small, then the heat current P out of the normal electrode and the electric current through the junction are

$$P(V) = \frac{1}{e^2 R_{\rm T}} \int_{-\infty}^{+\infty} dE N(E) (E - eV) [f(E - eV) - f(E)]$$
(25)

$$I(V) = \frac{1}{eR_{\rm T}} \int_{-\infty}^{+\infty} dE N(E) [f(E - eV) - f(E)]$$
(26)

where R_T is the resistance of the tunnel junction when both electrodes are in the normal state (9–11). It is assumed that the two electrodes (N and S) have the same temperature. f(E) denotes the equilibrium distribution function for the electrons:

$$f(E) = \frac{1}{1 + \exp(E/k_{\rm B}T)}$$
(27)

N(E) denotes the density of states in the superconducting region, given by the BCS theory

$$N(E) = \frac{|E|}{\sqrt{E^2 - \Delta^2}} \Theta(E^2 - \Delta^2)$$
(28)

and taken to be zero within the gap region.

Several properties can be deduced from Eq. (25) for the heat current. First of all, it is a symmetric function of the voltage, P(-V) = P(V); that is, the heat flows out of the normal metal regardless of the direction of the electric current. Second, it is inversely proportional to the resistance of the junction. Namely, the cooling power will be increased if the junction area or the conductivity of the insulating barrier is increased. One then would expect that when transmission probability through the contact between the normal metal and the superconductor increases, the cooling power will be magnified.

However, as was demonstrated (10), at larger transparencies coherent two-electron tunneling (Andreev reflection) begins to dominate the electron transport and suppresses the flow of heat from the N region to the S region. Andreev reflection is a special mechanism of transport in which a quasiparticle from the normal metal with energy below the superconducting gap combines with a Cooper pair from the superconducting electrode to produce a hole in the normal metal that travels in the opposite direction of the incident electron. It can be also visualized as a Cooper pair breaking that creates an electron and a hole that travel coherently in the normal metal. Andreev reflection process dominates the transport in microcontacts (NS interfaces), and as an imminent result from its existence, electrons with all energies, including those with energies below the superconducting energy gap, can tunnel to the S electrode. Thus, it limits the cooling power of the NIS junction. Moreover, the heat current exhibits a nonmonotonic dependence on the interface transparency: It increases at small transparencies and decreases at larger ones. The interplay between the single-electron tunneling process and the Andreev reflection type of transport determines the crossover value for the transmission probability

which maximizes the cooling power (10). At low temperatures the transition value of the transparency is proportional to the ratio $(k_{\rm B}T/\Delta)^{3/2}$.

Figure 3 shows the heat current as a function of the bias voltage for different temperatures calculated numerically using Eq. (25). The optimal value of the heat current is obtained for voltages about the gap $V \simeq \Delta/e$ and has a nonmonotonous behavior with respect to the temperature. When the applied voltage is less than the gap, heat is extracted from the normal metal and dissipated in the superconducting region through electron-phonon collisions, but for higher voltages P becomes negative and the normal metal is heated. The inset of Fig. 3 shows the heat current at the optimal bias voltages as a function of the temperature. The maximum value of the optimal heat current $P \simeq 0.06 \Delta^2 / e^2 R_{
m T}$ is reached at $k_{
m B}T \simeq 0.3 \Delta$ and decreases at lower temperatures as $(k_{\rm B}T/\Delta)^{\rm 3/2}$ (10). In particular, for temperatures smaller than the gap, $k_{\rm B}T \ll \Delta$, we can obtain from Eq. (25) the following result for the cooling power of the junction:

$$P(\Delta/e) \simeq \frac{\sqrt{\pi}(\sqrt{2}-1)\zeta(3/2)}{4} \frac{\Delta^2}{e^2 R_{\rm T}} \left(\frac{k_B T}{\Delta}\right)^{3/2}$$
(29)

The power supplied by the voltage source is $P_{\rm e}(V) = VI(V)$. The electric current at the optimal bias, for low temperatures, can be calculated in a similar way as the heat current. As a result, the supplied power at the optimal voltage is

$$P_{\rm e}(\Delta/e) \simeq \frac{\sqrt{\pi}(\sqrt{2}-1)|\zeta(1/2)|}{\sqrt{2}} \frac{\Delta^2}{e^2 R_{\rm T}} \left(\frac{k_{\rm B}T}{\Delta}\right)^{1/2}$$
(30)



Figure 3. The heat current for a NIS junction as a function of the bias voltage. From top to bottom the curves correspond to temperature $T = 0.3, 0.2, 0.15, 0.1 \Delta$. The inset shows the normalized heat current $P(V_{opt})e^2R_T/\Delta^2$ under optimal bias voltage conditions, as a function of the temperature k_BT/Δ . (From Ref. 10.)

If we introduce the efficiency at the optimal point of operation of the device, $\eta = P(\Delta/e)/P_{e}(\Delta/e)$, Eqs. (29) and (30) read

$$\eta = \frac{\sqrt{2}}{4} \frac{\zeta(3/2)}{|\zeta(1/2)|} \frac{k_{\rm B}T}{\Delta}$$
(31)

For typical values of the gap for conventional low-temperature superconductors $\Delta \approx 2$ K and T = 200 mK, the estimated efficiency is of the order of 7%.

In the initial experiment (9), a small metallic film of copper with volume $U = 0.4 \ \mu \text{m}^3$ and ambient temperature of T =100 mK was cooled down to 85 mK. The barrier resistance $R_{\text{T}} = 10 \ \text{k}\Omega$ was much larger than the resistance of the metallic island, approximately 10 Ω . The cooling power was about 7 fW at the ambient temperature. The refrigerating device was consisted of a tunnel junction between Cu (normal metal) and an aluminum superconducting electrode (NIS). The current was driven through the system with another superconducting electrode (Pb) which was in metallic contact (SN) with the normal thin film.

A dramatic improvement of the performance of the NIS microrefrigerator was achieved recently (11). Leivo et al. (11) combined two NIS junctions in series to form a symmetric SINIS hybrid superconducting structure. Because the heat power is a symmetric function of the voltage, when the junction is biased symmetrically at the optimal points, that is, $V \simeq \pm \Delta/e$, even though the current passes through the normal metal in one direction, the heat flows out of the metallic island through both junctions. Moreover, one of the advantages of this structure is the efficient thermal isolation of the metallic island that we desire to refrigerate. The junction resistances were approximately 1 k Ω , and the volume of the metallic island was about 0.05 μ m³. Starting from 300 mK, a 75% decrease in the electronic temperature was obtained. The achieved cooling power 1.5 pW was three orders of magnitude larger than before.

A schematic diagram of the SINIS microrefrigerator is depicted in Fig. 4. The two superconducting electrodes on the top of the metallic island can be used to measure its temperature. The current voltage characteristic (I-V) is recorded, from which the temperature of the metal can be calculated. It should be mentioned that in the tunneling limit the I-V char-



Figure 4. A schematic of the SINIS Peltier refrigerator. A metallic island (N) is connected via thin insulating regions (I) to superconducting electrodes (S). The two junctions are characterized by the same resistance, R_T . The symmetrically biased junctions effectively reduce the electron temperature of the island, which is recorded via the thermometer. (Based on Ref. 11.)



Figure 5. Performance of the SINIS cooling device. By varying the bias voltage the temperature of the metallic island is recorded. Each curve corresponds to different ambient temperature. Solid lines represent the theoretical fit with one fitting parameter Σ . In the inset the optimal cooling power is plotted as a function of the ambient temperature. Asterisks represent the experimental result, and the solid line is twice the result of Eq. (25). (From Ref. 11.)

acteristics depend only on the electronic temperature. Figure 5 shows the performance of the SINIS Peltier refrigerator at various ambient temperatures (value of T when V = 0). The value of the bias voltage at the temperature dips is approximately $V \simeq 2\Delta/e$; each junction is biased symmetrically eV/2 with respect to the metal. Namely, the superconducting gap of the aluminum is $\Delta = 180 \ \mu eV$. The voltage dependence of the temperature can be calculated from the energy balance equation:

$$P(V) = P_{\rm e-p} = \Sigma U (T^5 - T_{\rm L}^5)$$
(32)

For V = 0 we have $T_{\rm L} = T$. For the SINIS system, one has to calculate in a self-consistent way the electric current and heat current because there is a voltage drop across the normal metal which shifts the chemical potential of the metallic island. The temperature dependence of the maximum cooling power is plotted in the inset of Fig. 5.

When comparing the NIS Peltier microrefrigerator to conventional millikelvin refrigeration schemes like adiabatic demagnatization or dillution cryostats, there are many advantages and disadvantages. Some of the advantages are: smaller size and weight (can operate even at zero gravity); faster cooling; easier to construct, operate, and maintain; reliability. One of the major drawbacks is the small cooling power; the superconducting electrodes can remove only some picowatts of power, and the cooling is basically efficient only for small volume conductors. The cooling power of a dillution refrigerator at temperatures below 100 mK is in the range of tens to hundreds of microwatts. In addition, the cooling properties of the NIS junctions are related only to the electronic temperature. Attempts to cool down the lattice based on tunneling principles show even smaller cooling power. However, the NIS Peltier microrefrigerators are of importance for devices that dissipate small amounts of power lie x-ray or infrared detectors. Furthermore, cryogenic NIS junctions can be used as sensitive bolometers to detect particles and radiation. When some incident radiation is absorbed by the metal, it affects mostly the electronic temperature due to weak coupling of lattice with the electrons. The extra energy is deposited in a form of highly energetic thermal excitations that tunnel to the superconductor. Temperature increments can be detected via changes in the I-V characteristics of the device (12). As a final remark, Peltier microrefrigerators can serve as an alternative solution for the cooling of bolometric detectors (which operate best below 100 mK) and as temperature sensors that are carried by satellites for astronomical observations.

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PERCEPTION, ACTIVE. See ACTIVE PERCEPTION.