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MAGNETIC REFRIGERATORS FOR USE AT ROOM TEMPERATURE AND BELOW

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1. INTRODUCTION TO MAGNETIC REFRIGERATION.— More efficient and economical refrigeration would make low temperatures more accessible to researchers and to engineers. Gradually, large scale applications of low temperature phenomena, especially superconductivity, are being introduced into modern technology. Many superconducting magnets are used in particle accelerators and in particle experiments, and large magnets are being used in plasma and fusion research. Magnetically levitated trains, superconducting power transmission lines, superconducting motors and generators and other applications are currently being tested. All of these require refrigeration in the 2 K to 12 K regions.

Oxygen separation for steel production requires huge quantities of refrigeration near 80 K. Large refrigeration capacity at 20 K might be required if hydrogen succeeds as an alternative fuel.

The object of this paper is to show that modern magnetic materials and magnets provide a basis to allow the replacement of gas cycle refrigerators by more economical and efficient magnetic cycle refrigerators, at least below about 80 K. A great deal of diligent and creative hardware development is needed before that goal will be reached, however.

1.1. The Principles of Magnetic Refrigeration.— Application of a magnetic field to paramagnetic materials at low temperatures and ferromagnetic materials near their Curie temperatures causes them to warm up; alternatively, heat is expelled from such materials if the temperature is held constant during the field application. Conversely, removal of the field will cool the material or, at constant temperature, allow absorption of heat by the material. For temperatures at and below room temperature, the temperature changes can be of the order of 10–20 K if fields of about 7 T are applied to an appropriately chosen material.

The principle of a magnetic refrigerator can be illustrated with the conventional Carnot cycle device shown in figure 1. With thermal switch TS1 closed, thermal switch TS2 is opened, and a magnetic field is applied to the paramagnetic or ferromagnetic working material (WM). The field aligns the magnetic spins in the working material, decreasing the randomness (i.e., entropy S) of the spin system. The spin system is now in good thermal contact with the fixed temperature of the heat reservoir (HR), and heat will flow out of WM into HR. Next, TS1 is opened while TS2 remains open, and the magnetic field is partially removed; the spin system becomes partially randomized, requiring energy and thus cooling WM to the temperature of the heat reservoir.

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source (HS). TS2 is then closed while the magnetic field is decreased to zero, completing the spin-randomization process and allowing heat to be absorbed from HS. TS2 is then opened and a small magnetic field is applied, so that WM warms to the temperature of HR. The cycle can be repeated if TSI is closed as the full field is again applied to WM.

1.2. The Basic Concepts of Room Temperature Magnetic Refrigeration.- The magnetic Stirling-cycle refrigerator takes a ferromagnet, cools it in a magnet then removes it from the magnet, requiring a large input of work. The ferromagnet further cools upon demagnetization, allowing it to absorb heat. The ferromagnet is then heated and inserted into the magnet. The ferromagnet further warms, expelling heat at the higher temperature. Magnetic heat engines use the reverse of this cycle. The remainder of this paper will be devoted to recent developments in the low temperature adiabatic demagnetization refrigerators working on a magnetic Carnot cycle and in the higher temperature magnetic refrigerators working on a magnetic Stirling cycle. All the details of magnetic refrigerators will involve the entropy concept and entropy calculations. Magnetic devices, like all high efficiency refrigerators and heat engines, are best approached in terms of entropy, which is approximately conserved in high efficiency devices.

1.3. Actual Entropy-Temperature Diagram Illustrating the Cycles.- Figure 2 illustrates the Carnot cycle that could be executed by low temperature magnetic refrigerators like the one shown in figure 1. The material illustrated is the paramagnet Gd$_2$(SO$_4$)$_3$,8H$_2$O. From a heat source at 1.7 K, this material would absorb $Q = TAS = 9.9$ J/mol each cycle ($AS$ is the entropy change at temperature $T = 1.85$ K, as shown in figure 2, and $R$ is the gas constant). This represents 82 J/K of Gd$_2$(SO$_4$)$_3$,8H$_2$O each cycle. This number is expected to be two or three times as large for more dense Gd$_2$(SO$_4$)$_3$ and GdPO$_4$; however, measurements are needed to establish the shape of the zero field entropy curve near 2 K in these materials. Such work is currently underway at Los Alamos Scientific Laboratory (LASL).

Figure 3 illustrates the Stirling cycle executed by higher temperature magnetic refrigerators or heat engines. The material illustrated is ferromagnet gadolinium metal. It is necessary to use a ferromagnet for refrigeration above 10 or 20 K because it is impossible to provide enough magnetic field to make $\mu H = kT$ as is required to remove entropy in a paramagnet. Here $\mu$ is the magnetic moment of the ion, $H$ is the applied field and $k$ is the Boltzmann constant. In a ferromagnet near
the Curie point there are large ferromagnetic spin-spin interactions. These interactions supplement the very much smaller \( \mu H \) interaction and reduce the entropy in an applied field. From a heat source at 254 K, this material (figure 3) could absorb \( Q = 422 \) J/mol. or 21 kJ/K. Section 2 of this paper will show some devices which provide for the execution of a Stirling cycle by the gadolinium.

During the course of the measurement of the temperature-entropy curves of figures 2 and 3 and in measurements on numerous other materials, tests were made to determine the reversibility of the magnetic heating and cooling process /1,2/. High field magnetization and demagnetization was found to return the material to the original temperature although the temperature excursions were very large. Thus, no entropy creating irreversibilities could be detected in these tests.

2. SOME APPROACHES TO ACTUAL DEVICES.-

2.1. Two-Switch Refrigerator of Figure 1.- The units built so far /3,4,5/ are limited to operation below 1 K because of the character of the superconducting switches which they use. Refrigerators /6/ have been proposed which use magneto-resistive switches /7/, such as single crystals of beryllium, with switching ratios of 1000 at temperatures as high as 15 K. These would pump several watts from 2 K to 10 K with 70 % of Carnot efficiency using a Carnot cycle.

Better performance could be obtained if heat were carried to and from the paramagnetic working material by a liquid made to flow through a porous paramagnetic salt. Higher temperature operation would be feasible since switch limitations would not enter. Such a device would probably be very similar to reciprocating units discussed below.

2.2 Reciprocating Units.- The Stirling cycle reciprocating refrigerators, figure 4, proposed by Van Geuns /8/ have been developed by Brown /2/ and Barclay et al. /9/. Brown’s latest results /10/ show the production of an 80 K gradient (centered near room temperature) in the column. The rate of gradient development, following initial startup of
the gadolinium refrigerator shows 34 W capacity operating at about 0.05 Hz. Barclay's device, using Gd$_2$(SO$_4$)$_3$.8H$_2$O as a working material, pumped heat into a 4.2 K bath. The projected performance was an 8 W capacity from a heat source at 2 K at 1 Hz operation.

2.3. Rotating Devices.— Figure 5 illustrates the operation of the magnetic Stirling-cycle wheel as a refrigerator /11/. At the lower right-hand side, the fluid at $T^H$ enters the porous wheel; in a conceptual device with perfect heat transfer, the wheel is also at $T^H$ at this point. The fluid flows through the porous wheel, in contact with the wheel which was at temperature $T^C$ after leaving the high-field region. It exchanges heat with the wheel, exiting the wheel at temperature $T^C$, the same temperature as the wheel (again in the case of perfect heat exchange and flow balance). The fluid warms by an amount $\Delta$, picking up heat $Q^C$ from the low-temperature heat source and reenters the wheel at points where the fluid enters or leaves the wheel; $\Delta$ is the inherent temperature change of the working material upon entering and leaving the field. See text for description of operation.

Note that the high and low temperature extremes of this cycle are adiabats instead of the isotherms of figure 2.

A miniature version of such a device /12/, with gadolinium in the form of 0.5-mm sheets and using the field of a permanent magnet, was built and tested at Los Alamos. Because of excessive flow leakage and mechanical friction caused by the force of the magnet on the sheets, it was able to carry only a few watts over a few K temperature droop. However, the device demonstrated a Stirling rather than Carnot cycle. A more sturdy 15 cm-diameter wheel designed to pump 1 kW is currently under construction at Los Alamos /13,14/ for the Electric Power Research Institute (EPRI). It uses a porous matrix composed of fine lathe turnings of gadolinium metal. Water is the heat transfer fluid.

Figure 6 shows a low temperature rotating refrigerator /15/ operating on a Carnot cycle similar to that shown in figure 2. On the upper left-hand side of figure 6 and point A of the cycles in figure 2, supercritical helium enters the porous wheel and is forced to flow in heat exchange with the moving wheel. (Reference /15/ gives one exam-
The wheel absorbs heat from the helium as it is demagnetized to point B in the cycle shown in figure 2; the helium cools to 1.7 K. The helium then absorbs heat $Q_C$ from the load and reenters the wheel heat-exchanger area at a slightly warmer temperature. Similarly, in the lower right-hand side of figure 6, supercritical helium (at essentially the same pressure as the helium in the left-hand side) enters the porous wheel at 15 K; this corresponds to point C in the cycle in figure 2. The wheel deposits heat in the helium as the material is magnetized to point D, while the fluid leaves the wheel at a slightly warmer temperature. This heat is deposited externally, completing the cycle, with the net result that work is used to rotate the wheel and heat is absorbed at a low temperature and expelled at a high temperature. Note in figure 6 that the wheel is adiabatically magnetized as it goes from the lower left-hand to the lower right-hand side and adiabatically demagnetized as it goes from the upper right-hand to the upper left-hand side. These are the horizontal sections of the cycles shown in figure 2.

A more primitive type of rotating refrigerator has been built at Los Alamos {1}; it works also on a Carnot cycle but without using forced flow through a porous wheel. In steady state operation it carries 0.2 W from an electrical heater in a superfluid helium bath at 2.1 K into a boiling helium bath at 4 K. The refrigerator has maximum capacity at 0.25 Hz.

3. FUNDAMENTAL LIMITATIONS ON MAGNETIC REFRIGERATORS.- The Magnetic refrigeration process itself is essentially reversible. In a refrigerator that is mechanically optimized (i.e., minimum leakage around fluid seals, minimum mechanical friction, minimum heat leak, etc.) performance will be limited by heat transfer considerations. The question then becomes, how fast can heat be absorbed and expelled by the working material without excessive entropy production associated with heat flowing across a finite temperature difference $\Delta T$ and heat transfer fluid flowing across a finite pressure drop $\Delta P$?

3.1 Allowable Temperature Drops and Pressure Drops.- Consider a refrigerator absorbing heat $Q_C$ and entropy $S_C$ each cycle at the cold temperature $T_C$. The work input $W$ allows the expulsion of heat $Q_H$ and entropy $S_H$ at the hotter temperature $T_H$. Inside the real irreversible refrigerator there is a net entropy produced $\Delta S$ after the refrigerator has returned to its initial state upon completion of one cycle. Because

$$S_H = S_C + \Delta S$$

and from the first law

$$W = Q_H - Q_C$$

we can deduce that

$$W = (T_H - T_C)S_C + T_H\Delta S$$

Thus, the work in the irreversible refrigerator, compared to the work $W_R$ in a reversible refrigerator where $\Delta S = 0$, is

$$W = \frac{W_R}{1 + \frac{\Delta S}{S_C(T_H - T_C)}}$$

The relationship (4) can be used to estimate the allowable heat transfer fluid $\Delta P$ and fluid-magnetic material $\Delta T$ in a refrigerator. In a mechanically optimized refrigerator,

$$\Delta S = \Delta P \frac{V}{T}$$

is the entropy net production associated with the conversion of work from a 100% efficient pump in frictional heat at mean temperature $T$. The volume of fluid flowing through each cycle is $V$. It can be shown that

$$\Delta S_T \approx \frac{Q_T}{T^2}$$

is the net entropy production associated with an amount of heat $Q$ flowing across a temperature difference $\Delta T$ at a mean temperature $T$. The sum of $\Delta S$ from (5) and (6) when entered into (4) must not lead to excessive work $W$, or the refrigerator is very inefficient. Note that in a real refrigerator, if $\Delta S$ is too large, this simple approach fails because the working material no longer follows the ideal cycle of figures 2 or 3; (6) underestimates the performance deterioration associated with $\Delta S$.

This simple entropy calculation is useful for magnetic refrigerator design for magnetic heat engine design with the appropriate changes in (4).

In section 3.2, we will examine one particular refrigerator.

3.2. Pressure Drops and Temperature Differences in a Particular Refrigerator.- As an example of the use of (4), (5) and (6) in refrigerator/heat
engine evaluation, consider heat exchange by water
flowing through a porous gadolinium matrix in the
rotating refrigerator at room temperature. Using
the subdivision approach of figure 7, we can arrange
to keep the flow velocity of the water through
the matrix to $10^{-2}$ m/s at a rotation rate of 1 Hz
(from figure 3, in a field of 10 T, $S_c = 1.7$
J/mol-K. In 40-mesh 70% porous gadolinium filings

![Diagram](image)

Fig. 7: The approach required to minimize tempera-
ture and pressure drops in flow through porous re-
frigerator working materials. Heat transfer is a
very weak function of flow velocity $v$ while $\Delta P$
is a strong function of $v$ /15/. Consider the arrange-
ment of (b) with a total of 8 slits (5 are shown
in the figure), and with particles a factor of 3
smaller than in (a). The heat transfer is unchanged,
but $\Delta P$ is a factor of about 7 lower. Practical con-
siderations limit the number of channels which can
be cut into the material. Too many channels make
the structure mechanically weak or there is too
much heat conduction from channel to channel
through the working material. Note that properly
oriented channels do have the important benefit of
making eddy current losses manageable even if the
working material is an electrical conductor in a
changing magnetic field.

having a thickness of 11 $\mu$m, $\Delta P = 2.9 \times 10^6$ N/m$^2$
for water moving at $10^{-2}$ m/s through 1 m of mate-
rial (This can be deduced from the measurements
of reference /16/). The energy dissipation of water
flowing in a 1-m cube at $10^{-2}$m/s during a 1-s cy-
cle is $Q = 2.9 \times 10^6 \times 10^{-2} = 2.9 \times 10^4$ J/m$^3$. Because
1 m$^3$ contains about 9.5 $\times 10^3$ moles, this is a
3 J/mol. or an entropy creation of $\Delta S = Q/T = 0.01$
J/mole-K.

To calculate heat flow entropy creation from
(6), heat transfer estimates in reference /15/ ba-
sed on experimental data are used. The heat trans-
fer coefficient per unit volume in the gadolinium
filings is estimated as 1500 $\times 10^4$ W/m$^3$K or
1.8 $\times 10^5$ W/mole-K. In one cycle we must transfer
about 7.300 J/mol. (from figure 3). At 1 Hz $\Delta T$
is thus 7.300/1.8 $\times 10^5 = 0.041$ K or $\Delta S = 7.300 \times$
0.041/(294)$^2 = 0.0035$. In (4)

\[
W/K = 1 + (0.01 + 0.0035) \gamma 334 = 1 + 0.033 \gamma (7)
\]

\[
1.7 (334-254)
\]

(The net entropy creation per cycle is proportional
to the frequency $v$ since $\Delta P$ and $\Delta T$ are proportional
to $v$). Thus at $v = 10$ Hz the refrigerator requires
3.3% more work than a Carnot refrigerator.

The above calculation illustrates the prin-
ciple problem with magnetic refrigeration near room
temperature. The heat transferred is much greater
than the heat pumped. However, the large fluid-solid
heat transfer available in a porous matrix makes
this acceptable.

4. CONCLUSIONS.— Magnetic refrigerators and magnetic
heat engines are in their infancy. To date, no prac-
tical unit has been built. However, fundamental
considerations like those of the preceding section
show that magnetic refrigerator/heat engine opera-
tion at rates of 10 Hz with high efficiencies are
feasible. Economic evaluations, not reported here,
show that for above a few hertz magnetic refrigera-
tors/heat engines are economically viable near
room temperature. They also show that at low tempe-
ratures, operation somewhat below 1 Hz will result
in viable refrigerators.

However, the approach to the design and cons-
truction of magnetic units is not clear at this
point. Reciprocating and rotating units have been
tested. The reciprocating units seem to have the
advantage of simplicity. They also have the advan-
tage of being able to operate with a more porous
working material where pressure drops are much smal-
ler /16/. They have the disadvantage of requiring
a larger volume of fluid flow, as a large amount of
fluid is needed to provide a very large thermal ca-
pacity compared to the working material. At this
stage of development, there is still ample opportu-
nity for creative new approaches to magnetic refri-
gerator concepts.
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