NASA TECHNICAL MEMORANDUM

NASA TM X-73676

NASA TM X-73676

(NASA-TM-X-73676) MAGNETIC STIRLING CYCLES: A NEW APPLICATION FOR MAGNETIC MATERIALS (NASA) 6 p HC A02/MF A01 CSCL 10A

N77-26616

Unclas
G3/44 31872

MAGNETIC STIRLING CYCLES--A NEW APPLICATION FOR MAGNETIC MATERIALS

by Gerald V. Brown
Lewis Research Center
Cleveland, Ohio 44135

TECHNICAL PAPER to be presented at the
International Magnetics Conference
sponsored by the Institute of Electrical and Electronics Engineers
Los Angeles, California, June 6-10, 1977

STAR Category 76

MAGNETIC STIRLING CYCLES--A NEW APPLICATION FOR MAGNETIC MATERIALS

Gerald V. Brown
NASA Lewis Research Center
21000 Brookpark Road
Cleveland, OH 44107

Summary

There is the prospect of a fundamental new application for magnetic materials as the working substance in thermodynamic cycles. Recuperative cycles which use a rare-earth ferromagnetic material near its Curie point in the field of a superconducting magnet appear feasible for applications from below 20K to above room temperature. The elements of the cycle, advanced in an earlier paper, are summarized. The basic advantages include high entropy density in the magnetic material, completely reversible processes, convenient control of the entropy by the applied field, the feature that heat transfer is possible during all processes, and the ability of the ideal cycle to attain Carnot efficiency. The mean field theory is used to predict the entropy of a ferromagnet in an applied field and also the isothermal entropy change and isentropic temperature change caused by applying a field. Results are presented for J=7/2 and g=2. The results for isentropic temperature change are compared with experimental data on Gd. Coarse mixtures of ferromagnetic materials with different Curie points are proposed to modify the path of the cycle in the T-S diagram in order to improve the efficiency or to increase the specific power.

E-9196

Introduction

The surprising capacity of appropriate ferromagnetic materials to pump heat at temperatures far above that of liquid helium was pointed out in a previous paper.[1] A ferromagnetic material (FM) can refrigerate, pump heat, or produce work from heat even at room temperature or higher in cycles that are analogous to those that use a gaseous working material or refrigerant. The high field superconducting magnet makes this possible, although permanent magnets and even normal electromagnets may be suitable in some applications. Three previously known principles were combined in Ref. 1 to yield a practical class of magnetic cycles: choose a rare-earth-based FM, use it near its Curie point T_c, and use a recuperative thermodynamic cycle. The reasons are first, that for a given T_c, the response to an applied field of a rare-earth FM is far greater than that of a transition-element-based material; in fact above T_c, the susceptibility depends quadratically on J, the total angular momentum quantum number. Secondly, the isothermal change in entropy and the isentropic change in temperature that are produced by applying a field H are larger near T_c than at higher or lower temperatures. Thus T_c should be carefully chosen. Thirdly, just as gas refrigeration cycles employ recuperation in counterflow heat exchangers or regenerators in order to span a large temperature range, the magnetic cycle must be recuperative, too. In the magnetic case, much more heat must be recuperated, but higher heat transfer coefficients more than offset the disadvantage.

The use of FM's in thermal cycles constitutes a basically new practical application. In existing power applications magnetic materials merely interchange electrical and mechanical energies. Until now FM's have not effected the conversion between (low grade) thermal and (high grade) mechanical or electrical energies, except near absolute zero.

The Recuperative Cycle

The recuperative cycle is easy to describe in an embodiment which employs a regenerator composed of a liquid column in a vertical tube.[1] The rare earth FM, fabricated into a movable element with a large heat transfer area, passes up and down through the fluid cyclicly. In steady state operation a temperature gradient exists in the fluid with the hotter end at the top. In the steady state of a heat pump (or refrigerator) cycle there are four steps (see Fig. 1).

(1) Isothermal magnetization at the top of the liquid column. The heat of magnetization is transferred to a heat sink as it is produced (process A→B).
(2) Cooling at approximately constant field as the FM passes down through the liquid column to its bottom (process B→C).
(3) Isothermal demagnetization at the bottom of the column, during which heat is absorbed from a heat source (process C→D).
(4) Zero-or low-field warming as the FM passes to the top of the column to begin another cycle (process D→A or D→E).

This embodiment strongly resembles the Stirling refrigerator with a gaseous refrigerant. In other embodiments the recuperation could be more like counterflow heat exchange and the cycle like a Linde-Hampson cycle or a Claude cycle.

As reported in Ref. 1, this method has been demonstrated over a temperature span of 47K between 272K and 319K.

Basic Advantages

Several advantages of the magnetic cycle should be stressed. The advantages arise from the ease of varying the external parameter (field) and from the fact that heat transfer to or from the FM can be maintained even during changes in field. So, for example, the FM can reject heat isothermally as it is magnetized, whereas it is not practical to compress a gas isothermally. Nonisothermal compression is the most serious cause of inefficiency in conventional refrigerators. The efficiency of the ideal magnetic cycle

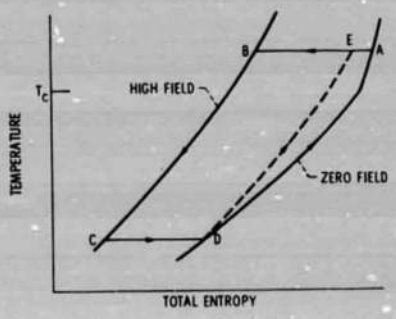

Figure 1. T-S Diagram for the Recuperative Ferromagnetic Cycle.

(with isotherms and perfect recuperation) can approach the Carnot efficiency if the process D→A in fig. 1 is replaced by the process D→E (drawn parallel to BC). This can be done either by changing the field H appropriately as the FM warms or by using FM mixtures as described below. The possibility of changing H at will during the cycle also permits non-isothermal sources and sinks to be efficiently utilized. Furthermore the ideal cycle contains no inherently irreversible processes (such as Joule-Thomson expansion of a gas). Note that the field may be reversibly raised or lowered incrementally while heat transfer occurs; pressure cannot be so flexibly controlled. The use of a solid working medium offers another advantage--all heat exchange can be between the solid and a liquid (or in some low temperature ranges, a high density gas). Hence the heat transfer coefficients are much higher than for solid-to-gas; enough higher to more than offset the higher viscosity of the liquid and to permit the greater degree of recuperation needed by the solid over the gas.

Possible Applications

A full engineering and economic analysis of specific machine designs is needed to predict in what applications the magnetic cycle can compete economically. However, the basic advantages cited above suggest that it should be evaluated for all refrigeration applications. Obvious applications to be studied are refrigeration for superconducting devices such as magnets, power transmission lines, and rotating machinery; liquification of gases including He, H_2, N_2, and natural gas; the separation of air; and numerous special purposes such as cooling of infrared sensors, etc. Near room temperature magnetic refrigerators, heat pumps and air conditioners should be evaluated, as should magnetic heat engines above room temperature. Higher efficiency would be welcome in all these applications.

It is expected that the Curie point of a pure rare earth can be decreased to any lower value desired for these applications by a rather modest dilution of the rare earth to reduce the conduction-electron-mediated exchange interaction. Rare earth combinations may also be useful but the hoped-for entropy change may be reduced if crystal fields decrease the effective moment or if complex magnetic structures arise. In any case it appears that materials with T_c optimized for any application can be produced.

Mean-Field Calculation of Entropy

To evaluate the magnetic cycle, one needs to know the entropy as a function of temperature and field. Very little experimental data exists. In this section the Weiss mean field theory is shown to predict moderately well the entropy and temperature changes caused in simple ferromagnets by applied fields. The agreement between theory and experiment is good enough to justify the use of the mean field theory in feasibility studies.

Following the treatment in Ref. 2, we suppose the magnetization M is proportional to the Brillouin function B_J:

$$M = Ng\mu_B JB_J(x) \qquad (1)$$

where N is the number density of dipoles, g the Lande factor, μ_B the Bohr magneton, and

$$x = \mu_B gJ(H + KM)/kT \qquad (2)$$

where k is Boltzmann's constant and K is the mean-field coupling constant. K can be eliminated in favor of T_c by noting that above T_c no spontaneous M exists, so there equations (1) and (2) must have only a trivial solution for M. That condition reduces to

$$Ng^2\mu_B^2 J(J + 1)K = 3kT_c. \qquad (3)$$

Equations (1)-(3) can be solved simultaneously for any value of H by graphical or numerical methods. The magnetic entropy S_m is given by.

$$S_m/R = \log\left\{\sinh\left[(2J+1)x/(2J)\right]/\sinh\left[x/(2J)\right]\right\} - xB_J(x) \qquad (4)$$

where the value of x is taken from the solution of (1)-(3).

It is convenient to introduce nondimensional variables defined by

$$t = T/T_c \text{ and } h = H/\left[3kT_c/(J + 1)\mu_B g\right] \qquad (5)$$

The magnetic entropy, calculated from (4) is presented in figure 2 in terms of t and h for J=7/2 and g = 2, values appropriate for materials based on Gd. Conduction electron contributions are not included. The failure of the theory to include short range order is evident at zero field in the abrupt corner and in the attainment of the full magnetic entropy at T_c. The isothermal entropy change ΔS caused by a field change Δh follows immediately and is plotted in figure 3. The entropy pumping capacity of any FM based on Gd with any T_c in the plot's range can be estimated from figure 3 and the definitions (5).

As an example of the isothermal entropy and heat pumping capacity of an FM, the theory predicts for Gd that at 273K a 10 Tesla change in field gives ΔS=12 J/kg-K which corresponds to a heat of 3.2 kJ/kg.

To compare theoretical and experimental results, the total entropy S_{tot} was calculated by $S_{tot}=S_m+S_L$, where S_L is the lattice entropy based on a Debye model with the Debye temperature taken to be 172K. The isentropic change in temperature caused by applying a field was found numerically and is presented in figure 4 along with new experimental data. The data were taken on a cast cylindrical polycrystalline sample 2.29 cm diameter and 9.33 cm long with hemispherical ends. The new data are more accurate than the first high field data that were reported in Ref. 1. The applied field and effective field are considered identical in the plot; based on the calculated value of M, the two fields differ by at most 3%. The mean field theory

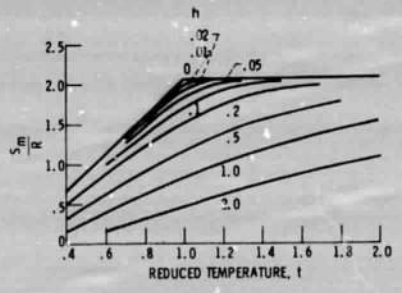

Fig. 2. Magnetic Entropy in Units of R as a Function of the Reduced Temperature t and the Reduced Applied Field h for J=7/2, g=2.

cannot distinguish between the ferromagnetic Curie point T_f and the paramagnetic Curie point T_p; only one quantity, T_c, occurs in the equations (3) and (5). It is interesting to compare the results of setting $T_c=T_f$ with those of setting $T_c=T_p$. Hence figure 4 presents three theoretical curves with the experimental data. Curve F results from setting $T_c=T_f=293K$. Curve P1 results from setting T_c equal to an older value of T_p ($302.5K$[2]); curve P2 from a more recent value (310K for polycrystalline samples[4]).

It is interesting that the P curves give better agreement except near T_f. Somewhat above T_p the paramagnetic value must give the correct Curie-Weiss behavior; below T_f the agreement is apparently better because the mean field acts in a basically paramagnetic way on each ion. Thus the appropriate value of the coupling constant is better reflected by T_p in the Curie-Weiss law than by the ordering temperature T_f. Near T_f the use of T_f gives the best agreement. Above about $1.1T_f$ the P1 curve is best, and below about $0.9\ T_f$ the P2 choice is best. The choice of T_c to use to evaluate a particular FM in a cycle must be made in the context of the intended temperature range and the positions of T_f and T_p in it. For such a simple theory it is surprising that those quantities which depend upon entropy differences are not badly predicted.

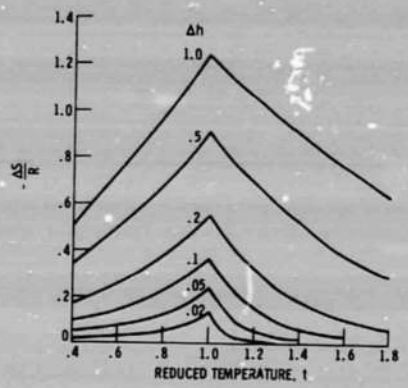

Fig. 3. Isothermal Entropy Change ΔS in Units of R in Terms of Reduced Temperature t and Change in Reduced Field Δh. Initial field is zero. (J = 7/2, g = 2.)

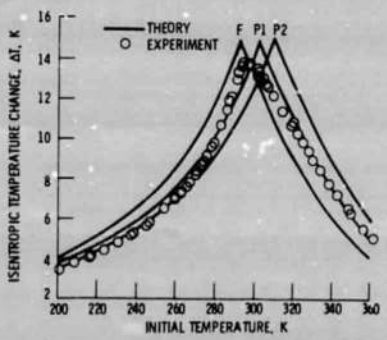

Fig. 4. The Isentropic Temperature Change Produced by Applying a 7T Field to Gd.

Modifying the T-S Diagram to Improve Efficiency

As noted under "Advantages" above, the Carnot efficiency is not achieved in the unmodified cycle ABCDA in Fig. 1. One aspect of the unmodified cycle is that the average heat capacity of the FM is usually not the same at zero field as at high field, and this would cause a problem in the regenerator. To achieve the "parallel sides" of the cycle in the T-S diagram, which indicate equal heat capacities during warming and cooling and are characteristic of a high efficiency recuperative cycle, is straightforward because the field can be changed during regeneration. As the FM warms in the regenerator, the field is simply increased to cause the state of the FM to follow D→E rather than D→A.

Another way to get the same (or greater) improvement in the T-S diagram is to employ a macroscopic mixture of FM's with different Curie points. The mixture may be formed physically in any manner that preserves the Curie point of each material. The combined entropies at zero field can be made to approach line DE in Fig. 1 as closely as desired. (The high field curve changes, too, but less markedly.) Similarly, the FM mixture technique can be used to reshape the entropy curves for special purposes such as to provide distributed rather than isothermal refrigeration.

Permanent Magnets and Normal Electromagnets

The isothermal entropy change is roughly proportional to ΔH, so a permanent magnet ($B\lesssim 1T$) or a normal electromagnet with an iron core ($B\lesssim 2T$) would be less effective than a superconducting coil (B up to 17T). However, it may be desirable for some applications to avoid the cryogenics required for a superconducting magnet, and permanent and/or normal magnets should be considered in cases where the temperature span is small or where several stages can be used.

Conclusions

Ferromagnetic materials bring to thermodynamic cycles fundamental advantages which include high entropy density, fully reversible processes, entropy control by an external parameter (field) that can be varied up or down incrementally at will, and a constant shape and density that permits heat transfer at all times. The performance of the FM can be estimated fairly well by the mean field theory. The efficiency of the FM cycle can approach the Carnot value if the field strength is varied appropriately during recuperation or if a suitable mixture is used.

(1) G. V. Brown, J. Appl. Phys. 47, 3673 (1976).
(2) A. H. Morrish, Physical Principles of Magnetism, Wiley, N.Y., (1965).
(3) J. S. Smart, Effective Field Theories of Magnetism, Saunders, Philadelphia (1966).
(4) K. N. R. Taylor and M. I. Darby, Physics of Rare Earth Solids, Chapman and Hall, Ltd., London (1972), page 132.

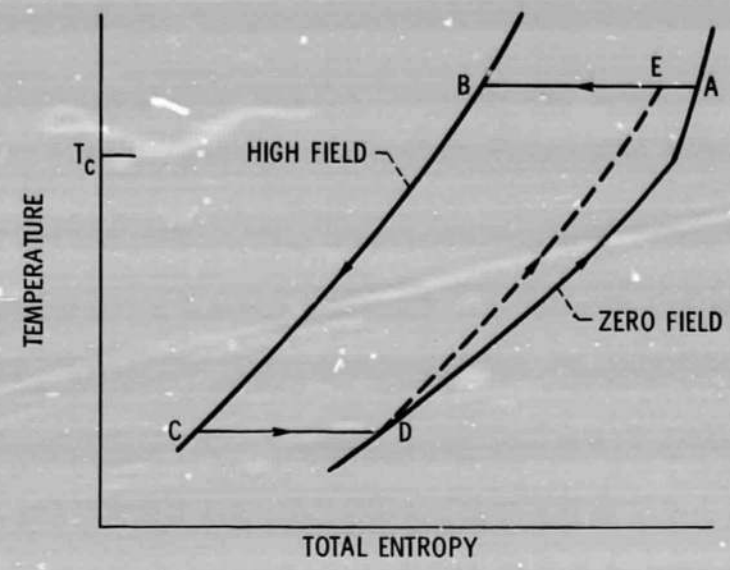

Figure 1. - T-S Diagram for the recuperative ferromagnetic cycle.

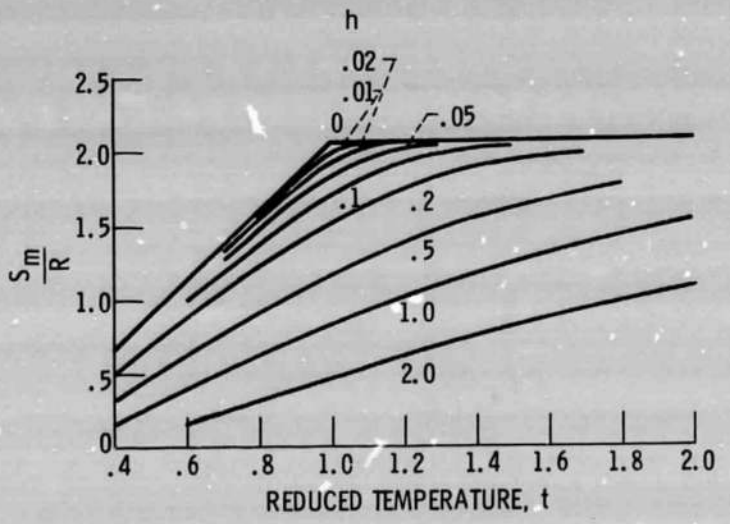

Figure 2. - Magnetic entropy in units of R as a function of the reduced temperature t and the reduced applied field h for J = 7/2, g = 2.

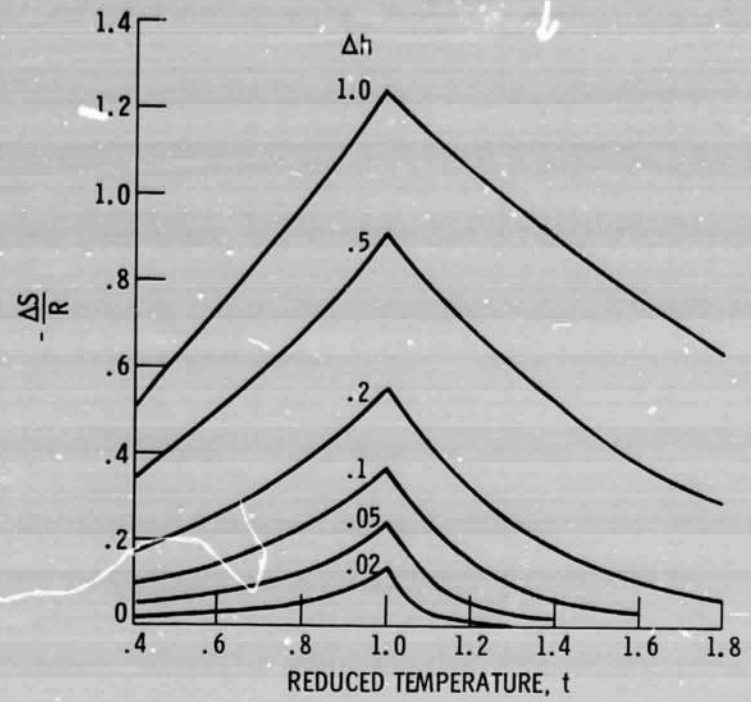

Figure 3. - Isothermal entropy change ΔS in units of R in terms of reduced temperature t and change in reduced field Δh. Initial field is zero. (J = 7/2, g = 2.)

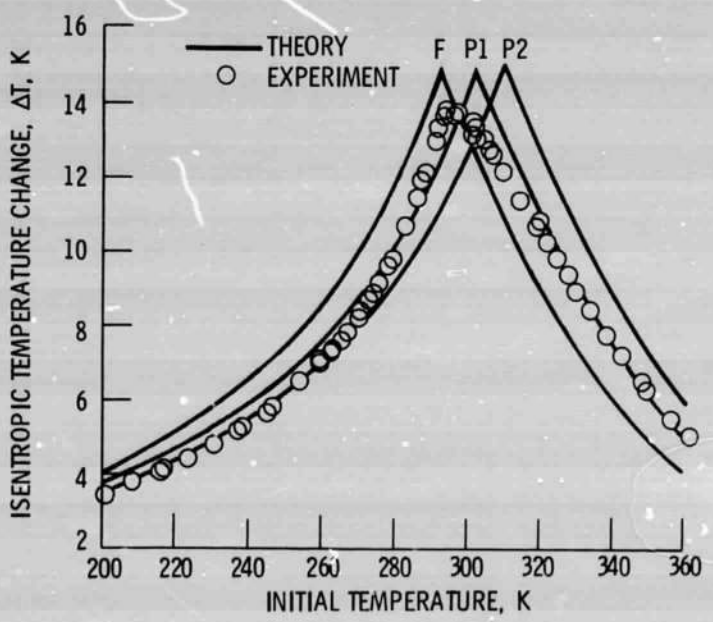

Figure 4. - The isentropic temperature change produced by applying a 7T field to Gd.

NASA-Lewis