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MAGNETIC STIRLING CYCLES--A NEW APPLICATION FOR MAGNETIC MATERIALS

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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.

**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. 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: (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→B).

This embodiment strongly resembles the Stirling refrigerator with a gaseous refrigerant. In other embodiments the recuperation could be more like countercflow 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. Non-isothermal compression is the most serious cause of inefficiency in conventional refrigerators. The efficiency of the ideal magnetic cycle
(with isotherms and perfect recuperation) can approach the Carnot efficiency if the process $\mathrm{D}\rightarrow\mathrm{A}$ in fig. 1 is replaced by the process $\mathrm{D}\rightarrow\mathrm{B}$ (drawn parallel to $\mathrm{BC}$). 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 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; liquefaction 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 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 $T_c$ in the plot's range can be estimated from figure 3 and the definitions (5).

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 by 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 $\mu$ is proportional to the Brillouin function $B(x)$

$$\mu = N g x B(x)$$

where $N$ is the number density of dipoles, $g$ the Landé factor, $\mu_B$ the Bohr magneton, and

$$x = \frac{\mu_B \mu (1 + K)}{kT}$$

(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 $T_c$ spontaneous $M$ exists, so there equations (1) and (2) must have only a trivial solution for $H$. That condition reduces to

$$N g^2 \mu_B^2 (J + 1)k = 3kT_c.$$  

(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

$$S_m / R = \frac{1}{2} \log \left( \frac{\sinh \left( \frac{2B(1+J)}{B(1+J)} \right)}{\sinh \left( \frac{B(1+J)}{B(1+J)} \right)} \right) - R J(x)$$  

(4)

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

It is convenient to introduce nondimensional variables defined by

$$t = T/T_c \quad \text{and} \quad h = H/[3kT_c/(J + 1)g]$$  

(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$_3$C$_8$, 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 $\Delta S$ caused by a field change $\Delta h$ 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 $\Delta S = 12 \text{ J/kg-K}$ which corresponds to a heat of 3.2 kJ/kg.

To compare theoretical and experimental results, the total entropy $S_{tot}$ was calculated by $S_{tot} = S_{lat} + S_{m}$, where $S_{lat}$ is the lattice entropy based on the 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 diametet 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 seen to be identical in the plot based on the calculated value of $H$, the two fields differ by at most 5%. 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 $J=7/2$, $g=2$.](image-url)
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 P 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); curve P2 from a more recent value (310K for polycrystalline samples).

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 1.11$T_f$ 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.

Modifying the T-S Diagram to Improve Efficiency

As noted under "Advantages" above, the Carnot efficiency is not achieved in the unmodified cycle ANKDA 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. 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 PE 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 $AH$, so a permanent magnet (0≤1T) or a normal electromagnet with an iron core (0.5≤2T) would be less effective than a superconducting coil (0 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 or cycled incrementally and smoothly, and 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.

(3) J. S. Smart, Effective Field Theories of Magnetism, Saunders, Philadelphia (1966).
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 $\Delta S$ in units of $\mathcal{R}$ in terms of reduced temperature $t$ and change in reduced field $\Delta h$. Initial field is zero. ($J = 7/2$, $g = 2$.)

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