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THE PRACTICAL USE OF MAGNETIC COOLING

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ABSTRACT

Today's high-field large-volume superconducting magnets remove constraints that previously confined magnetic cooling to LHe temperatures and usually to 1 K or lower. Magnetic fields of up to 15 T can significantly order a paramagnetic system as high as about 50 K. This means that a magnetic refrigerator could be an alternative to the gas working fluid refrigerator, which has low mechanical efficiency at low temperatures. Several other devices in applied magnetic fields might be practical. These include a magnetic sorption pump for helium or hydrogen vapor, a regenerator for temperatures below 20 K, and an adjustable isothermal heat source or heat sink. The useful temperature range of some of these devices may be extended higher by using ferromagnetic materials above their Curie points.

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INTRODUCTION

Physicists have used adiabatic demagnetization for decades to produce very low temperatures. [1, 2] Both one-shot and cyclic processes [3] have produced temperatures below 0.1 K. But demagnetization was begun with the magnetic material at LHe temperatures because the fields of early magnets (a few T) could not significantly order the magnetic system at higher temperatures. Now, however, superconducting magnets can make fields of over 10 T(100 KG) in large volumes. [4] These magnets should raise the demagnetization temperature limit to above 30 K, and they can contain practical amounts of magnetic material.

The new potential of magnetic cooling has not been widely discussed, although some studies are in progress. Apparently few physicists are interested in refrigeration above 4.2 K, and few engineers who would value a new cooling method are aware that magnetic cooling can acquire engineering muscle if superconducting magnets are used. The rapid growth of the lattice heat capacity above LHe temperature has discouraged study. As will be seen, however, the lattice reduces the amount of refrigeration per cycle but not the efficiency.

This paper considers an idealized paramagnetic system in order to assess the present prospects for magnetic cooling.

THE IDEAL PARAMAGNETIC CYCLE AT VERY LOW TEMPERATURES

Consider the refrigeration cycle for an ideal (noninteracting) system of magnetic moments (henceforth, called simply "spins"). The magnetization of such an ideal paramagnet is given by a Brillouin function, and the thermodynamic quantities are easily calculated. (See, for example, ref. 5.) The T-S diagram in figure 1 shows typical spin-entropy curves for several values of field H. If the spin state traces the curve ABCDA, the cycle is a Carnot cycle. The paths AB and CD are an adiabatic magnetization and an adiabatic demagnetization, respectively. Adiabatic processes are possible for the spins if the lattice entropy is negligible, as for low enough temperatures.

THE IDEAL PARAMAGNETIC CYCLE AT HIGHER TEMPERATURES

At higher temperatures where the lattice entropy is not negligible, the spins and the lattice exchange entropy when the temperature T changes. That is, the spins plus lattice can be adiabatically isolated, but not the spins alone. If the lattice and spin entropies are $S_L(T)$ and $S_s(T)$, respectively, then as T changes, the entropy required by the lattice is extracted from the spins, hence $dS_s = -dS_L$. This results in curved segments, AF and CE. Because the lattice simply absorbs and returns the same amount of entropy to the spins (for quasi-static exchange), curves AF and EC have the same shape. The efficiency of this "pseudo-Carnot" cycle equals the Carnot efficiency, $T_1/(T_2-T_1)$.

The lattice does, however, limit the refrigeration ($T_1 \Delta S$) produced per cycle and/or the sink temperature T_2. If H_{max} is the highest available field, then the spin-entropy curve for H_{max} and the extrapolated curve AF intersect to give the highest attainable temperature T_3. Any cycle beginning at A is contained inside these curves, and ΔS (equal to segments CF and EA), decreases as T_2 nears T_3. Hence, as T_2

approaches T_3, the refrigeration per cycle drops to zero.

Actually the spins can follow constant spin-entropy curves if a regenerator is used to compensate for the lattice, as suggested and analyzed by van Geunes [6] for a cycle between 4 and 15 K. Then in principle the entire entropy CB or DA is available in the cycle or alternatively, the heat rejection temperature could be raised. This could be important. But regenerators have heat transfer losses, and their analysis is difficult. Whether there is a net gain in cycle yield would depend on many factors.

In a later section cascading is discussed as a method of circumventing the T_3 limit.

The entropy transferred, ΔS, by the pseudo-Carnot cycle equals the length of segment CF in figure 1. A simple analysis shows what determines this ΔS as a function of T_2. Assume noninteracting spins with quantum number J, and let the salt have n atoms per magnetic ion. Assume the Debye model for the lattice heat capacity C_L:

$$C_L/R = 9n(T/\theta_D)^3 \int_0^{\theta_D/T} \frac{x^4 e^x \, dx}{(e^x - 1)^2}$$

where θ_D is the Debye temperature and R is 8.31 J/(gram ion K). Then

lattice entropy per gram ion is

$$S_L(T)/R = \int_0^T \frac{C_L(T')/R \, dT'}{T'}$$

and the spin entropy per gram ion is $S_s(x)/R = x \coth x - (2J + 1) x \coth [(2J + 1)x] + \ln \sinh [(2J + 1)x] - \ln \sinh x$, where

$x = \frac{\mu g H}{2kT}$, μ is the Bohr magneton, g the splitting factor, and k the Boltzmann constant. (The distinction between internal field H and the applied field is ignored in this paper.) Figure 2 shows graphical solutions for T_3 for various values of J, n, and H for $\theta_D = 300$ K.

A low value of n is desirable. For example, $J = 7/2$, $\theta_D = 300$ K, and $H_{max} = 15$ T (150 KG) gives $T_3 = 41$ K for $n = 2.5$ (appropriate for rare earth oxides, R_2O_3) but only 25 K for $n = 20$ (corresponding to a moderately dilute salt). Hence, rare earth oxides would be desirable unless interaction effects are too large near point A in the cycle.

Low values of J are undesirable. Note for $J = 1/2$, $T_3 = 23$ K for $n = 2.5$ and only 15 K for $n = 20$. Worse than the lower T_3 values however, is the fact that less ΔS can be transferred with low J.

To see the roles of θ_D and H_{max}, consider figure 3 in which $J = 7/2$ and $n = 2.5$. For $\theta_D = 300$ K (reasonable for Gd_2O_3 at low temperature) and $H_{max} = 15$ T, $T_3 = 41$ K. At 32 K, 0.2 of the maximum spin entropy, $R\ln(2J + 1) = R\ln 8$, can be transferred from a load to a sink in one cycle. The figure shows that T_3 and the entropy transferrable per cycle are reduced as θ_D is reduced. From figure 3 one can find the entropy that the cycle can reject to any T_2. High applied fields are clearly desirable. This analysis suggests that a one-stage refrigerator could reject heat at above 30 K and perhaps nearly as high as 40 K.

RAISING THE SINK TEMPERATURE LIMIT BY CASCADING (OR STAGING)

The T_3 limit can be circumvented by cascading. A second salt following curve GIKLG in figure 1 can be the heat sink for the first salt.

The second salt could even reject heat to a sink hotter than T_3. More stages would allow still hotter sinks. At higher temperature, the ΔS per mole becomes smaller, hence the upper stages in a cascade might require more salt or different salts. Practical considerations, especially irreversible losses between stages, are important in cascading. With cascading and 15 T fields, perhaps a few tenths of the maximum spin entropy could be rejected per cycle into a sink at 40 to 50 K.

USE OF MATERIALS NEAR CURIE POINTS

Even though the sink temperature is field limited for a paramagnet, hotter sinks might be reached by using a material, for an upper stage, that has a Curie point in or just below the stage's temperature range. Then the exchange interaction aids the applied field in ordering the spins. Both the isothermal ΔS and the adiabatic ΔT (magnetocaloric effect) should be enhanced. The size of these effects must depend on the ratio of the applied field to the Weiss field, if a low of corresponding states holds. Thus the higher the applied field, the better. The analysis for the ferromagnet (a cooperative system) is very difficult. A random phase approximation theory for spin 1/2 is to be presented at this conference [7], and a higher spin analysis appears feasible. Experimental work has been confined to fields of 2 T or less. A reliable theory or higher field measurements are needed to evaluate use of ferromagnets.

OTHER DEVICES BASED ON MAGNETIC COOLING

A paramagnetic salt can be an active heat sink or source because its entropy depends on an external parameter, the applied field, At 13 K, for example, where no liquid-gas phase change occurs, the entropy of a

$J = 7/2$ salt is reduced by 1.4 R by a 15 T field. This can be found from figure 3. For Gd_2O_3 this would give $\Delta S = 0.50$ J/(cm^3 K) and a heat release (or absorption) of 8.8 J/cm^3. For comparison, ΔS for LHe vaporization at 4.2 K is 0.61 J/(cm^3 K) and for LH_2 at 20.3 K it is 1.58 J/(cm^3 K). Thus an isothermal heat source or sink is possible between the LHe and LH_2 ranges with ΔS per unit volume comparable to that of He vaporization. The main advantages of this source or sink are that it can be set at any temperature, and its volume is constant. By volume, it is slightly inferior to a He phase change, but considerably inferior to H_2. By weight, the cryogen phase changes have a much larger ΔS, but the phase change temperatures are limited, and large volume changes occur.

The ΔS in the magnetic case can be spread over a temperature range. The result below 20 K or 30 K can be a heat capacity per volume higher than that of any metal. Only supercritical He can surpass this effective heat capacity, and only with a volume change.

A sorption pump for He or H_2 vapor can be based on condensing and evaporating He or H_2 with an alternately cooling and warming salt. One possible application is an oil-free pump to pump on a helium bath. More dilute salts and lower fields are required than for high temperature applications.

DISCUSSION

The analysis for ideal paramagnetism showed that cycles with sinks well above LH_2 temperature should be possible. The problems in "high" T refrigerators differ from those below 1 K. High H is needed for magnetic order at high temperature T, and lattice heat capacity is a problem.

But other problems are less serious. For example, spin-lattice relaxation time is shorter, and lattice thermal conductivity is higher. Fluids, (e.g., supercritical helium) can be used for heat transfer. More concentrated salts can be used.

Large superconducting magnets ease other problems. Smaller surface-to-volume ratios for the salts make adiabatic isolation easier. More heat transfer modes are possible to and from salts, e.g., forced convection loops. Perhaps most importantly, the refrigeration power can be large enough for engineering applications.

Magnetic refrigerators have some advantages over gas refrigerators. One is that the working material density does not change during the cycle, permitting more efficient heat transfer designs. Few moving parts are needed. Higher efficiency and lower weight may be possible, but analysis of a specific system, or actual construction of a device, will be required to verify this.

SUMMARY

With superconducting magnets, magnetothermal phenomena can be applied at much higher temperatures than before. With paramagnetism, heat sinks at 30 to 50 K appear possible. Higher temperatures, perhaps room temperature or above, might be reached with materials with appropriate Curie points. Because of the ease of entropy control by an applied field, solid, constant-volume heat sources or sinks can be devised for below about 20 K. Other devices based upon entropy changes are possible, such as magnetic sorption pumps for cryogens..

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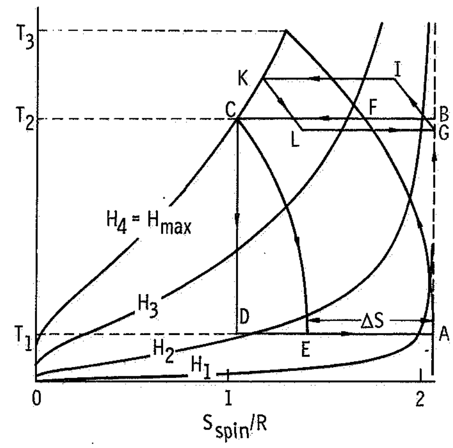

Figure 1. - T-S diagram for spin refrigeration cycles. Spin entropy curves for fields $H_1 < H_2 < H_3 < H_4$ are shown. Ideal Carnot and pseudo-Carnot cycles are shown.

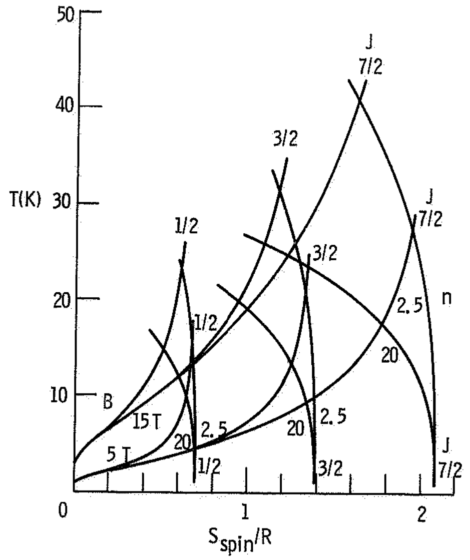

Figure 2. - Effect of J and n on T_3 and on ΔS.

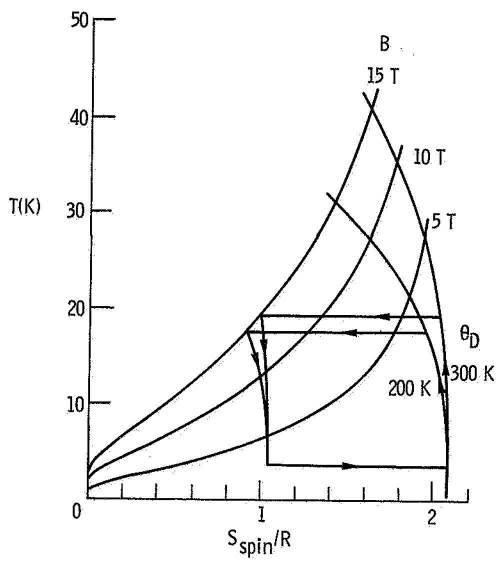

Figure 3. - Effect of B and θ_D on T_3 and ΔS for n = 2.5 and J = 7/2.