MAGNETIC REFRIGERATION

The application and subsequent removal of a magnetic field causes cooling in certain materials—the magnetocaloric effect (or magnetic refrigeration). In the laboratory it is possible to pump over liquid helium and so provide considerable cooling power at ~1 K. For this reason magnetic refrigeration has usually been used to reach temperatures below 1 K. It is also the case that the high magnetic fields required are usually provided through superconducting magnets which must operate below ~5 K. There are two types of magnetic refrigerator,

adiabatic demagnetization refrigerators (ADR) and nuclear demagnetization refrigerators. The ADR uses the interaction of electrons with an applied magnetic field whereas nuclear demagnetization uses the interactions of the nuclei. The temperature region of operation for an ADR depends on the magnetic material used. This can range from tens of Kelvin down to mK (1); whereas for a nuclear demagnetization refrigerator the region is 10 mK to several microkelvin. Cooling power (the amount of energy that can be absorbed) decreases strongly with decreasing temperature. For an ADR cooling powers in the region of microwatts at low temperature can be obtained whereas for nuclear demagnetization it is nanowatts or less. Such low cooling powers from nuclear demagnetization refrigerators leads to extreme measures in order to avoid unwanted heat entering the system, for example, seismic isolation. The use of nuclear demagnetization refrigerators is therefore restricted to specialized low temperature research laboratories. For ADRs with their higher cooling power such extreme measures are not required, making such refrigerators easier to use in a more typical laboratory environment, so that they are the more common of the two.

Principle of Magnetic Refrigeration

A cooling process may be regarded to be an entropy reducing process. Since entropy (or degree of disorder) of a system at constant volume or constant pressure decreases with decreased temperature, cooling can be achieved within a medium via any process which results in the decrease of entropy of that medium. For example, the liquefaction of gases is achieved by the isothermal reduction of entropy through compression of a volume V_1 at temperature T_1 to a smaller volume V_2 generating heat, which is extracted by contact with a cold reservoir, followed by adiabatic or isentropic expansion which results in cooling of the gas to below T_1. In the magnetic cooling process the disordered collection of magnetic dipoles associated with a particular ion within a medium (paramagnetic material) constitutes such a system described here. For such a material the application of a magnetic field causes alignment of the dipoles with the magnetic field and thus a reduction in entropy. The dipoles used are either electronic (electron cooling due to the electron spins) or nuclear (nuclear cooling due to the nuclear spins) depending on the required final temperature, millikelvin temperatures for electronic (ADRs) and microkelvin temperatures for nuclear demagnetization refrigerators. The principle of operation is the same the main difference being the starting temperature. For electron cooling starting temperatures of up to 20 K or more can be used whereas for nuclear cooling a starting temperature in the region of 0.01 to 0.02 K is needed in order for the magnetic interaction to dominate over the thermal energy.

Components of a Magnetic Refrigerator

An ADR is essentially composed of the following three items which need to be housed in a cryostat (2) to provide a bath temperature:

1. A paramagnetic material. This is suspended via low thermal conductivity supports within an enclosure at the bath temperature, usually pumped, liquid helium in laboratory systems. The paramagnetic material is integrated with a stage or platform, upon which the experimental items under investigation may be mounted.
2. A magnet. This may either be a permanent or superconducting magnet. The latter is usually used due to their ease of operation and compactness. It is housed within the liquid helium vessel and so sufficiently cooled for superconductivity.
3. A heat switch. This is used to make and break a high thermal conductivity path between the paramagnetic material and the cold bath (e.g., liquid helium). This is used in order to cool the paramagnetic material to the starting temperature and to extract the heat of magnetization. The form of this switch may be mechanical, gaseous, or superconducting (2).

A schematic of a "classical" ADR is shown in Fig. 1. Variations on the classical form arise due to requirements to (1) increase the low temperature hold time and (2) increase the bath temperature. Increasing the low temperature hold time can be achieved by reducing the parasitic heat leak through the supports by using a second higher temperature intermediate paramagnetic material. This intercepts the heat flow from the bath to the low temperature paramagnetic material. The intermediate material comprises a higher temperature paramagnetic material which has a high heat capacity, for example, gadolinium gallium garnet. The operation of the ADR is the same as the conventional form except the intermediate paramagnetic material will demagnetize to a temperature between that of the bath and the low temperature material. Such a refrigerator is commonly called a two stage ADR (3). Increasing the bath temperature without decreasing the hold time can be accomplished by using a second ADR to cool a classical or two stage ADR. It is essentially two ADRs in series, one configured for high temperatures and the other for low temperatures. The high temperature ADR is used to cool the low temperature ADR prior to the demagnetization of that stage. This effectively simulates a lower temperature

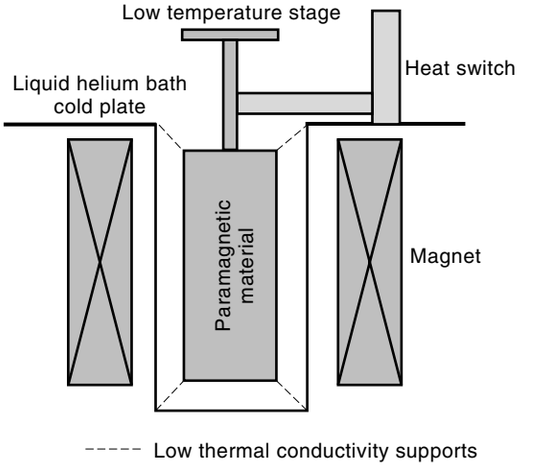

Figure 1. Conventional ADR schematic. A paramagnetic material is shown in a pill arrangement with a stage where samples can be attached. The pill is housed in the bore of a superconducting magnet via low thermally conducting supports. The magnet is housed in a liquid helium container and the heat switch is used to cool the pill to the temperature of the liquid helium.

bath for a conventional or two stage ADR. This kind of refrigerator has been called a double ADR (4).

A further variation of the classical ADR is the "hybrid". This consists of a conventional ADR coupled to a low temperature cryogenic stage provided by He^3. The He^3 stage is used to provide a temperature of 0.3 K reducing the parasitic heat load and providing a very low starting temperature for the paramagnetic material.

The composition of a nuclear demagnetization refrigerator is essentially the same as a conventional ADR except that its bath temperature must be in the region of 0.01 K. The bath is provided by either an ADR or, more typically, a He^3–He^4 dilution refrigerator (2,5).

HISTORY AND CURRENT STATUS OF MAGNETIC REFRIGERATORS

Cooling by affecting the electron spins was proposed by Debye (6) in 1926 and Giauque (7) in 1927. The first practical demonstration was by De Haas, Wiersma, and Kramers (8), Giauque and MacDougall (9) in 1933, and Kurti and Simon (10) in 1934. The nuclear demagnetization refrigerator was suggested by Gorter in 1934 and Kurti and Simon in 1935. However it was not until 1956 when Kurti et al. successfully obtained cooling from 12 mK to 20 μK via the demagnetization of nuclear spins. Since those pioneering days numerous texts on magnetic refrigeration have been published and most low temperature physics books contain a chapter describing it. For further information see Refs. 2, 5, and 11.

The advent of dilution refrigerators in the 1960s saw the demise of ADRs because of the higher cooling power and continuous operation offered by dilution refrigeration. In recent years ADRs have become more popular due to the increased use of low temperatures (0.1 to 0.01 K) for the operation of detectors for astronomy and particle physics and the development of mechanical coolers to replace the use of liquid helium (12). In astronomy the need for better signal to noise leads to low temperature detectors (10 to 100 mK) and exotic telescope locations (Antarctica, on top of high mountains, and in space). X-ray astronomy can only be conducted by space-borne instrumentation due to the absorption of X rays by the earth's atmosphere. The cost and practicalities involved require low mass systems which are gravity independent and highly reliable. The use of a consumable cryogen in space—helium—limits the duration of missions. For infrared and optical astronomy space also has enormous advantages in the form of "seeing" and sky background.

The first demonstration of an ADR in space occurred with a sounding rocket flight in 1996 (13). This was a conventional ADR comprising a liquid helium cooled magnet and an ferric amonium alum (FAA) salt pill housed in a pumped liquid helium cryostat operating at 2 K. A similar ADR is under development (14) at the Goddard Space Flight Center for the X-ray spectrometer (XRS) experiment due to fly on the Japanese ASTRO-E mission in 2000. Advances in miniaturizing ADRs and increasing their operating temperature range further are ongoing and brought about by real-use practicalities. Such development is being achieved through new materials (especially for thermal isolation), new magnet technology (low current), and high temperature paramagnetic materials. Until recently the superconducting magnet used to generate the magnetic field would have to be housed in the liquid helium bath. The advent of conduction cooled superconducting magnets, in which the magnet is cooled via conduction through the magnet housing, enables the ADR to be a unit which is simply attached to a cold plate. This enables the ADR to be connected to a mechanical cooler thereby eliminating the need for a liquid helium bath to cool the magnet and provide the bath temperature for the ADR. Cryogen-free operation could enable the ADR to become a general purpose instrument capable of autonomous computer control without the need for the user to have either cryogenic experience or special helium handling equipment.

THEORY

Certain paramagnetic materials are suitable for use as magnetic refrigerants. The magnetic ions of these materials have an interaction energy, ϵ with their crystalline environment and each other which is smaller than the average thermal energy kT. In such a situation each magnetic ion is relatively "free" resulting in a distribution of randomly oriented dipoles with $2J + 1$ degeneracy, where J is the angular momentum quantum number, that is, there are $2J + 1$ possible orientations of the ions. This gives an $R \ln(2J + 1)$ per mole contribution to the entropy of the material from the magnetic dipoles, where R is the gas constant. The entropy (S) of a paramagnetic material can be thought of comprising two components. One arises from the magnetic ion (e.g., chrome in chromium potassium alum, CPA) and is given the subscript m (S_{m}). The other component arises from the rest of the molecule and is refer to as the lattice (S_{lattice}). The total entropy is given by

$$S = S_{\mathrm{m}} + S_{\mathrm{lattice}}$$

As the temperature of the paramagnetic material is reduced the lattice contribution to the entropy of the material reduces and a point is reached where the magnetic entropy given by $R \ln(2J + 1)$ dominates. As the temperature decreases further the entropy will remain at the value given by $R \ln(2J + 1)$ until the thermal energy approaches the interaction energy ϵ at which point spontaneous ordering of the dipoles occurs, due to their own weak magnetic fields, and the entropy falls. When $\epsilon \sim k\theta$, where θ is the magnetic ordering temperature of the material (or Néel temperature), the entropy drops rapidly. At very low temperature the internal interactions between ions removes the degeneracy and the system resides in a singlet ground state of zero entropy. At a temperature greater than θ the entropy of the spin system of the magnetic ions can be reduced significantly if the interaction of the dipoles and the applied magnetic field is greater than the thermal excitation given by kT.

If the internal interaction energy is very low the magnet ions can be considered as free and the entropy (S) of a collection of magnetic ions can be given by Eq. 1. Figure 2 shows the typical form of the entropy curve as a function of temperature and applied magnetic field:

$$\frac{S(B,T)}{R} = \ln\left[\frac{\sinh(2J+1)x/2}{\sinh(x/2)}\right] + \frac{x}{2}\coth\left(\frac{x}{2}\right) - \frac{(2J+1)}{2}x\coth((2J+1)x/2) \tag{1}$$

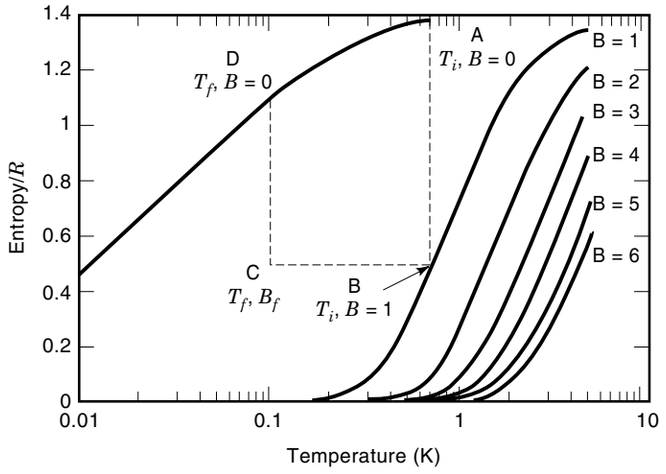

Figure 2. Typical behavior of entropy with temperature and magnetic field, with the operational sequence of an ADR. The sequence starts at point A, proceeding to point B on application of the magnetic field (heat switch engaged). Cooling, transfer to point C, occurs with the partial removal of the magnetic field (heat switch open). The temperature is held (transferring from C to D over time) by further reduction of the magnetic field at the correct rate.

where

$$x = g\beta B/kT \tag{2}$$

and

g = spectroscopic splitting factor
β = Bohr magnetron
B = magnetic field (Gauss)
k = Boltzmann constant
T = temperature (K)

This equation is only valid if the ions are free and for high (>1 T) magnetic fields. For low magnetic fields additional terms which take into account the weak internal field have to be added. The zero magnetic field entropy curve is determined from

$$S = \int C/T\, dT$$

where

S = total entropy
C = heat capacity
T = temperature

A detailed account of paramagnetic theory as applied to magnetic refrigeration can be found in Ref. 11.

PARAMAGNETIC MATERIALS

The paramagnetic material "the refrigerant" is the core of the refrigerator. It determines the temperature to which cooling can be achieved and how much energy can be absorbed. Cooling over a wide temperature range is possible due to the varied materials available. These can be divided roughly into four temperature ranges (~10 to 40 mK, 40 to >100 mK, >0.3 K to 1 K, and >1 K). The substances widely used in these temperature ranges are detailed in Table 1. A detailed review of the first three temperature ranges can be found in Ref. 11 and for the fourth, high temperature range (15).

Refrigerant Construction (Salt Pill)

Traditionally, the refrigerant stages in an ADR have been called salt pills because in the early days all refrigerants were made from a "salt". Although other forms of paramagnetic refrigerant are now available the term salt pill has remained in common use and now, incorrectly, refers to the whole refrigerant assembly used in the ADR. The refrigerant materials commonly used and listed in Table 1 are hydrated salts (CMN, CPA, CCA, FAA, and MAS), garnets (O_{12} compounds) or perovskites (AlO_3 compounds). Salt pills comprised of the following four components, (1) a stage, to which items can be attached for cooling, (2) A thermal bus connecting the stage to the paramagnetic material, (3) the paramagnetic material, and (4) a container for the paramagnetic material. The stage and thermal bus are made from high thermally conducting material, usually copper, and the container is either a high electrical resistivity material in order to minimize eddy current heating, for example, stainless steel, or fibre glass. Garnets and perovskites, which are very large dense crystals, can be bonded via an epoxy or low temperature cement to the thermal bus. In the case of hydrated salts the thermal bus comprises many hundreds of high thermally conducting (cop-

Table 1. Magnetic Details of Some Paramagnetic Materials

Temperature Range	Material	Formation	J	g	T_n (K)
10–40 mK	Cerium magnesium nitrate (CMN)	$Ce_2Mg_3(NO_3)_{12} \cdot 24H_2O$	1/2	2	~0.01
40–>100 mK	Chromic potassium alum (CPA)	$CrK(SO_4)_2 \cdot 12H_2O$	3/2	2	~0.01
	Cesium chromic alum (CCA)	$CsCr(SO_4)_2 \cdot 12\ H_2O$	3/2	2	~0.01
	Ferric ammonium alum (FAA)	$FeNH_4(SO_4)_2 \cdot 12H_2O$	4/2	2	~0.03
>0.3 K	Manganese ammonium sulfate (MAS)	$MnSO_4(NH_4)_2SO_4 \cdot 6H_2O$	5/2	2	~0.1
>1 K	Dysprosium gallium garnet (DGG)	$Dy_3Ga_5O_{12}$	1/2	8	~0.4
	Erbium orthoaluminate (ErOA)	$ErAlO_3$	1/2	9	~0.6
	Ytterbium orthoaluminate (YbOA)	$YbAlO_3$	1/3	7	~0.8
	Gadolinium gallium garnet (GGG)	$Gd_3Ga_3O_{12}$	7/2	2	~0.8
	Dysprosium aluminum garnet (DAG)	$Dy_3Al_5O_{12}$	1/2	11	~2.5
	Dysprosium orthoaluminate (DOA)	$DyAlO_3$	1/2	14	~3.5
	Gadolinium orthoaluminate (GOA)	$GdAlO_3$	7/2	2	~3.8

per) wires attached to the stage and spreading into the salt enclosure. The hydrated salts are produced via an aqueous solution and the slow evaporation of the water. They fall into two categories, those that can be readily grown around copper wires and those that cannot. In the case where the salt will not grow around wires (CPA) small crystals have to be grown in a vessel (beaker) and then compressed along with the wires to form a solid mass which is then sealed in the pill enclosure. For the salts which will readily grow around wires (CMN, CCA, FAA, and MAS) the aqueous solution is allowed to evaporate from the enclosure which holds the wires and thermal bus. For CMN, where the orientation of the crystals to the magnetic field is important, seed crystals have to be cemented in place first with the correct orientation. The salts listed in Table 1 are all corrosive to copper and so if used this metal has to be plated with gold. A thickness of 30 to 50 μm is usually sufficient. The hydrated salts have to be hermetically sealed within the enclosure in order to ensure that water of crystallization is not lost when exposed to vacuum. Such sealing can be achieved by the use of epoxy, for example, Stycast 2850.

MAGNETIC REFRIGERATOR OPERATION

The operation of a magnetic refrigerator requires the system to be at a temperature in which the lattice entropy does not dominate the paramagnetic material in order that the applied magnetic field can reduce the entropy of the material. The process of cooling can be separated into three stages. The first is isothermal magnetization of the paramagnetic material at a temperature T_1, transferring the paramagnetic material from point A (Fig. 2) to point B. This process generates heat (magnetization energy) which has to be extracted to a heat sink at a temperature of T_1, via a heat switch. The magnetization energy (Q Joules per mole) is given by

$$Q = \int T dS \tag{3}$$

and since T is constant

$$Q = T_1[S_A - S_B] \tag{4}$$

Adiabatic demagnetization forms the second stage in which the magnetic field is reduced to a value B_f which corresponds to the desired final temperature T_f. During this stage the entropy of the paramagnetic material remains constant, resulting in cooling as given by

$$\frac{(B_i^2 + b^2)^{1/2}}{T_i} = \frac{(B_f^2 + b^2)^{1/2}}{T_f} \tag{5}$$

where

B_i = Initial magnetic field
B_f = Final magnetic field
b = Internal magnetic field associated with each magnetic ion
T_i = Initial temperature
T_f = Final temperature

The third stage can be effective in two ways, the first and most thermally efficient is isothermal demagnetization. This provides stability at T_f by reducing the magnetic field B from B_f to zero at a rate which counteracts the thermal input from the surrounding environment. The total amount of energy the paramagnetic material can be absorbed is given by Eq. (3) and Eq. (6) next, since T is constant,

$$Q = T_2[S_C - S_D] \tag{6}$$

The duration in seconds of operation at T_f, called the hold time, is given by

$$\text{Hold Time} = \frac{n T_f[S_C - S_D]}{dQ_{th}/dt} \tag{7}$$

where

n = Number of moles of magnetic ion
dQ_{th}/dt = Total power into the paramagnetic material (e.g., parasitic heating)

Once the magnetic field reaches zero the whole process must be repeated (recycled) from stage 1. The second approach is for the magnetic field to be reduced to zero, completely demagnetizing the paramagnetic salt to a temperature of T_{min}. A constant temperature above T_{min} can be achieved by using a stage which is heated via a resistor and which has a weak thermal link to the paramagnetic material. The heater power needs to be reduced as the paramagnetic material warms under the parasitic load. Since the temperature of the paramagnetic material is not constant the energy which can be absorbed is given by Eq. (3) only. This process is less thermodynamically efficient to the isothermal process since heat is being added, however, it does not require active control of the magnetic field and therefore is simpler in some respects.

TEMPERATURE REGULATION

As previously stated the third stage of operation of an ADR, namely the holding of the final required temperature, can be achieved via demagnetizing at a rate to counteract the heat flowing into and thus warming up the salt pill. Temperature regulation is achieved via a computer controlled servo system in which the rate of reduction in magnetic field is controlled in order to maintain the temperature at the desired value. For superconducting magnets the magnetic field is proportional to current and thus it is the current that is controlled. The degree of stability is limited to the sensitivity of the thermometry and the step size in magnetic field/current. Temperature regulation of ± 1 μK is possible with room temperature resistance bridge phase sensitive detection (PSD) electronics and germanium thermometers. The thermometry readout is limited by the Johnson noise associated with the resistance bridge resistors. Cooling of these resistors to approximately 10 K should make it possible to achieve ~a few hundred nanokelvin stability of an ADR when operated at a temperature of 0.1 K.

Magnetic Field Servo

Constant temperature is maintained by the reduction of electrical current (I) by a value dI every dt seconds. The value of dI/dt is determined by the servo algorithm based on how well

the temperature is being maintained. With every new value of dI/dt the current is stepped down at the corresponding value of dI, (dt is kept constant) until the new value of dI/dt is calculated. Intervals of a minute or less are appropriate for most systems depending upon the application.

The current–temperature control equation (16) is:

$$dI_i/dt = (c/\Delta t)[(T_i - T_{\text{set}}) + (\Delta t/\tau)\sum(T_{i-j} - T_{\text{set}})]$$

where

i = Current value
j = previous $(i-1)$ value
dI_i/dt = ith current ramp rate
T_i = ith temperature
T_{i-j} = $i-j$th temperature
T_{set} = Servo temperature
Δt = time interval
τ = system time constant
Σ = Sum over $j=0$ to $i-1$
c = system constant

SUMMARY

Millikelvin refrigeration is becoming necessary for many applications (astronomy, particle physics, material science, and biophysics). Adiabatic demagnetization refrigerators are seen as one of the most attractive ways of achieving such temperatures. Their compactness, ease of operation (turn key is a possibility since the process is purely electrical and cryogen free) and gravity independence gives many advantages over helium based apparatus. Cryogenic engineering advances now mean that an ADR can be a small bench top instrument rather than requiring a well equipped cryogenic laboratory. With this simplification and miniaturization of cryogenic instrumentation the user will no longer have to be an experienced cryogenic physicist which will open millikelvin refrigeration to a much broader community of scientists and engineers. Such an expansion process has not yet occurred with nuclear demagnetization refrigeration, however, with the constant development of lower operating temperature detectors and advances in cryogenic science and engineering it is probably only a matter of time.

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