

## Refrigeration by Adiabatic Demagnetization of a Paramagnetic Salt

In the year 1922 H. Kamerlingh Onnes reached 0.83 K by pumping on his liquid  $^4\text{He}$  bath with an enormous battery of pumps. Realizing that there would be no element with a lower boiling point than helium, he predicted that this temperature would remain the minimum temperature achievable by mankind in the laboratory unless somebody discovered a completely new refrigeration technology that did not depend on the latent heat of evaporation. (Of course, he was not aware that there exists a lighter helium isotope,  $^3\text{He}$ , which pushes this limit down by about a factor of 3.) In 1926, a completely new refrigeration technology was proposed. P. Debye and W.F. Giauque independently made the proposal that lower temperatures could be reached by using the magnetic disorder entropy of electronic magnetic moments in paramagnetic salts, a method later called *adiabatic demagnetization of paramagnetic salts*. Not until seven years later, in 1933, was this proposal converted into a practical realization, when W.F. Giauque and D.P. MacDougall (Berkeley) reached 0.53 K, and a little later W.J. de Haas, E.C. Wiersma and H.A. Kramers (Leiden) reached 0.27 K. In fact, this was the first important low-temperature experiment since the end of the 19th century in which the University in Leiden was not the first to achieve success (for this early work see the relevant references in [9.1–9.3]).

Adiabatic demagnetization of paramagnetic salts was the first method of refrigeration to reach temperatures significantly below 1 K. Today this method can be applied to experiments in the range  $2\text{ mK} \leq T \leq 1\text{ K}$ . For the last decades it has not been used much, because it has been replaced by the  $^3\text{He}$ – $^4\text{He}$  dilution refrigerator, which has the substantial advantage of being a continuous refrigeration method. I will discuss adiabatic demagnetization of paramagnetic salts for historical reasons and because it may become of importance again for refrigeration in space flights. In addition, it is the basis for understanding the presently much more important nuclear adiabatic demagnetization to be discussed in Chap. 10.

## 9.1 The Principle of Magnetic Refrigeration

Let us consider paramagnetic ions with an electronic magnetic moment  $\mu$  in a solid. We assume the energy  $\varepsilon_m$  of interaction between the moments themselves as well as with an externally applied magnetic field to be small compared to the thermal energy  $k_B T$ . This means that we are considering free paramagnetic ions with magnetic moment  $\mu$  and total angular momentum  $J$  with entropy contribution

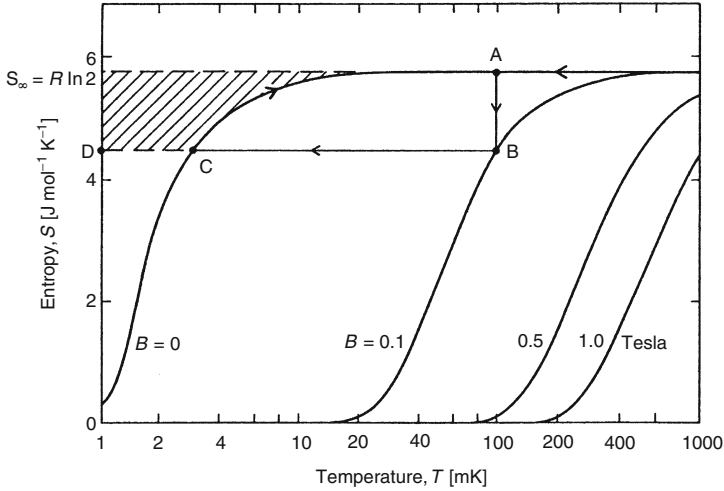
$$S = R \ln(2J + 1) \quad (9.1)$$

if they are completely disordered in their  $2J + 1$  possible orientations with respect to a magnetic field.

As in the case of Pomeranchuk cooling, it is this magnetic disorder entropy which we want to use for refrigeration. At the temperatures of interest in this chapter, this magnetic disorder entropy, which is of the order of joules per mole of refrigerant, is always large compared to all other entropies of the system, for example the lattice and conduction electron entropies, which we will therefore neglect.

If the temperature is decreased, eventually the interactions between the magnetic moments will become comparable to the thermal energy. This will then lead to spontaneous magnetic order, e.g., ferromagnetic or antiferromagnetic orientation of the electronic magnetic moments. As a result the entropy will decrease and approach zero, as required by the third law of thermodynamics. An externally applied magnetic field will interact with the magnetic moments, at least partially orienting them along its axis to create a magnetized state of higher order. Therefore, in the presence of a field the entropy will decrease at a higher temperature than without a field (Fig. 9.1).

The entropy diagram of Fig. 9.1 makes it very easy to understand magnetic refrigeration. We bring the paramagnetic salt in contact with a precooling bath to precool it to a starting temperature  $T_i$ . Then a magnetic field  $B_i$  is applied to perform an isothermal magnetization at  $T_i$  from  $B = 0$  to  $B = B_i$ . During this process the heat of magnetization has to be absorbed by the precooling bath. The next step is thermal isolation of the paramagnetic salt from the surrounding bath which then allows the adiabatic demagnetization to be carried out by reducing the external field from its starting value  $B_i$  to a final field  $B_f$ , which may be in the millitesla region. The temperature has to decrease accordingly (Fig. 9.1). Finally the cooling agent, the paramagnetic salt, will warm up along the entropy curve at  $B_f = \text{const.}$  due to an external heat leak until its cooling power has been used up. It is obvious from Fig. 9.1 that a spontaneous magnetic ordering process of the magnetic moments represents the lower limit for magnetic refrigeration. Magnetic refrigeration is a “one-shot” technique, where the demagnetization ends at a low field and then sample and refrigerant warm up.



**Fig. 9.1.** Molar entropy of a single crystal of the paramagnetic salt CMN with angular momentum  $J = 1/2$  (Sect. 9.4) as a function of temperature for magnetic fields applied along the crystallographic  $a$  axis. For the refrigeration process the salt is first isothermally magnetized (AB), and then after thermal isolation adiabatically demagnetized (BC). Eventually it warms up along the entropy curve at the final demagnetization field, which is zero in the example shown. The heat of magnetization during magnetization is given by the rectangle  $ABDS_\infty$ . The cooling power of the salt after demagnetization is given by the shaded area [9.4]

## 9.2 Thermodynamics of Magnetic Refrigeration

In this section I present some simple thermodynamic calculations relevant for the three steps of a magnetic refrigeration process.

### Heat of Isothermal Magnetization

The heat of magnetization released when the applied field is increased from zero to  $B_i$  and which has to be absorbed by the precooling bath at constant temperature  $T_i$  is given by

$$Q(T_i) = nT_i[S(0, T_i) - S(B_i, T_i)] \quad (9.2)$$

or more exactly

$$Q(T_i) = nT_i \int_0^{B_i} (\partial S / \partial B)_{T_i} dB = nT_i \int_0^{B_i} (\partial M / \partial T)_B dB, \quad (9.3)$$

where  $M$  is the magnetization (magnetic moment per unit volume). The resulting  $Q(T_i)$  is indicated in (Fig. 9.1); it is typically several joules per mole of refrigerant, so it can easily be absorbed by an evaporating helium bath, with its latent heat of several of joules per mole, or by a  $^3\text{He}$ – $^4\text{He}$  dilution refrigerator if lower starting temperatures are required.

### Adiabatic Demagnetization

For free magnetic moments the entropy is a function of just the ratio of magnetic energy to thermal energy. We therefore have for the adiabatic process

$$S(B_i/T_i) = S(B_f/T_f), \quad (9.4)$$

which results in

$$T_f/B_f = T_i/B_i. \quad (9.5)$$

We arrive at the same result by remembering that the magnetization does not change during adiabatic changes of the magnetic field. Of course, we cannot reach  $T_f \rightarrow 0$  by letting  $B_f \rightarrow 0$  because eventually the condition  $k_B T \gg \epsilon_m$  is violated and the internal interactions will align the moments and the entropy vanishes (Fig. 9.1).

### Warming-up due to External Heating

The cooling power of the salt after demagnetization to  $B_f$ , or the heat it can absorb as it is warming up, is given by

$$Q(B_f) = n \int_{T_f}^{\infty} T(\partial S/\partial T)_{B_f} dT. \quad (9.6)$$

This hatched area is indicated in Fig. 9.1. It is, of course, substantially smaller than the heat of magnetization due to the fact that the energy is absorbed at a temperature  $T < T_i$ . Hence the external heat leak should be kept as small as possible.

These results demonstrate that one has to find a compromise between a low final temperature  $T_f$  [which would require a low final field  $B_f$ ; see (9.5)], and a large cooling power (which requires a large final field; see Fig. 9.1).

For the above analysis we have to know the entropy  $S(B, T)$ , which can be calculated from data for the specific heat as a function of temperature and field according to

$$S(B, T_1) - S(B, T_2) = \int_{T_2}^{T_1} (C_B/T) dT. \quad (9.7)$$

Another possibility is to use the magnetization

$$M = \frac{\chi B}{\mu_0} \quad (9.8)$$

to calculate the magnetic entropy via the Maxwell relation  $(\partial S/\partial B)_T = (\partial M/\partial T)_B$ .

### 9.3 Non-Interacting Magnetic Dipoles in a Magnetic Field

If we have paramagnetic ions carrying a magnetic moment  $\mu$  and a total angular momentum  $J$ , then at temperature  $T$  the  $(2J + 1)$  energy levels with energies  $\varepsilon_m$  will be populated according to

$$P(m) = e^{-\varepsilon_m/k_B T} \sum_{m=-J}^{+J} e^{-\varepsilon_m/k_B T}, \quad (9.9)$$

and the partition function is given by

$$Z = \left( \sum_{m=-J}^{+J} e^{-\varepsilon_m/k_B T} \right)^{N_0}. \quad (9.10)$$

Once we have calculated the partition function, we can calculate all the required thermodynamic properties, for example

$$\begin{aligned} S &= R \partial(T \ln Z) / \partial T, \\ C_B &= T(\partial S / \partial T)_B, \\ M &= RT(\partial \ln Z / \partial B)_T, \end{aligned} \quad (9.11)$$

and hence the susceptibility  $\chi = (\partial M / \partial B)_T$  is known as well. In other words, once we know the energies  $\varepsilon_m$ , everything else can be calculated. Fortunately, if we assume non-interacting magnetic dipoles in an external magnetic field, where  $\epsilon_m \ll k_B T$ , we have

$$\epsilon_m = -\boldsymbol{\mu} \cdot \mathbf{B} = \mu_B g m B, \quad (9.12)$$

with the electronic Landé factor

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}, \quad (9.13)$$

here,  $S, J, L$  refer to the spin, the total and orbital angular momenta, respectively.

In (9.12),  $\mu_B = e\hbar/2m_e = 9.27 \times 10^{-24} \text{ J T}^{-1}$  is the Bohr magneton and  $m = -J, \dots, 0, \dots, +J$  are the magnetic quantum numbers.

Accordingly, the partition function for independent magnetic dipoles is given by

$$Z = \left( \sum_{m=-J}^{+J} e^{-mx} \right)^{N_0} = \left[ \frac{\sinh[(J+1/2)x]}{\sinh(x/2)} \right]^{N_0} \quad (9.14)$$

with  $x = \mu_B gB/k_B T$ . After some manipulation we find

$$S/R = (x/2)\{\coth(x/2) - (2J+1)\coth[x(2J+1)/2]\} + \ln \left[ \frac{\sinh[x(2J+1)/2]}{\sinh(x/2)} \right], \quad (9.15a)$$

$$C_B/R = (x/2)^2 \sinh^{-2}(x/2) - [x(2J+1)/2]^2 \sinh^{-2}[x(2J+1)/2], \quad (9.15b)$$

$$M/M_s = [(2J+1)/2J] \coth[x(2J+1)/2] - (1/2J) \coth(x/2), \quad (9.15c)$$

where  $M_s = N_0 \mu_B gJ$  is the molar saturation magnetization, and the right-hand side of (9.15c) is the polarization  $P$  or the Brillouin function  $B_J(x)$ . This function is tabulated for various  $J$  in [9.2, 9.3]. The Brillouin function  $B_J(x) = M/M_s$  for various  $J$  is shown in Fig. 10.5 as a function of  $x^{-1}$  and the dependence of the specific heat  $C_B$  on  $x$  for various  $J$  is depicted in Figs. 3.8, 3.10 and 10.4. These results demonstrate a previously mentioned fact, namely that with the above assumptions the entropy is a function of  $B/T$  only. Therefore, in Fig. 9.1 the entropy curves are simply translated if we change the field. In addition, the above results give (9.5), valid for an ideal adiabatic process:  $S = \text{const.}$  and therefore  $B/T = \text{const.}$ , which means that the starting conditions determine the final state.

The above equations cannot, of course, be used in the limit  $B_f \rightarrow 0$ , because then the assumption of negligible interactions between the moments breaks down. For very small  $B_f$  we have to replace  $B_f$  in the above equations by an effective field

$$B_{\text{eff}} = \sqrt{B_f^2 + b^2} \quad (9.16)$$

acting on the moments, where  $b$  is an internal field resulting from the neighbouring moments in the paramagnet. This then leads to

$$T_f = \frac{T_i}{B_i} \sqrt{B_f^2 + b^2}. \quad (9.17)$$

The internal field  $b$  (or the magnetic ordering temperature  $T_c$ ; see below) determines the minimum temperature  $T_{f,\min}$  that can be reached by demagnetizing to  $B_f = 0$ . Finally, we find that the magnetization and entropy are kept constant during the demagnetization process or, in other words, that the populations of the various energy levels do not change during the demagnetization (Fig. 10.2). Only their energy difference changes when we decrease the field. Figure 9.1 also demonstrates that the cooling power  $Q$  is proportional to the final field  $B_f$ . When the demagnetized salt absorbs heat it has to change the population of its energy levels, which means that the spins of the paramagnetic ions have to flip. The ions can absorb more heat if the energy change per spin flip is larger, i.e., if their energy separation, which is proportional to the field  $B_f$ , is larger.

Very often the magnetic energy  $g\mu_B B$  is substantially smaller than the thermal energy  $k_B T$ , or  $x \ll 1$ . In this approximation one does not have to use the full (9.15) but can use the so-called high-temperature approximations. I will give these approximations in Chap. 10, on nuclear demagnetization, where usually  $x \ll 1$ , because the nuclear moments are rather small.

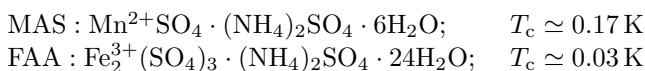
## 9.4 Paramagnetic Salts and Magnetic Refrigerators

The behavior of a magnetic refrigerator is mainly determined by the experimental starting conditions ( $B_i, T_i$ ), the heat leaks (Sect. 10.5), and the properties of the selected paramagnetic salt. Typical starting conditions for paramagnetic refrigeration,  $B_i = 0.1\text{--}1\text{ T}$ ,  $T_i = 0.1\text{--}1\text{ K}$ , are fairly easy to achieve nowadays. With these starting conditions large entropy reductions are possible (Fig. 9.1).

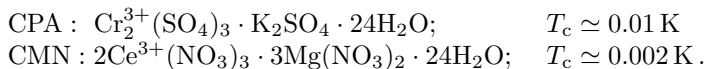
I shall not discuss here the magnetic and electric interactions of paramagnetic ions in salts; they have been covered in [9.3, 9.5]. In general, the paramagnetic refrigerant, the salt, should have a low magnetic ordering temperature  $T_c$  and a large magnetic specific heat in order to achieve a large cooling power, which means a large angular momentum  $J$  (Fig. 3.10). The ordering temperature  $T_c$  is determined by the interactions between the magnetic moments, which create the internal field  $b$ .

Paramagnetic salts suitable for magnetic cooling must contain ions with only partly filled electronic shells, i.e., either 3d transition elements or 4f rare earth elements. The following four paramagnetic substances have often been used for magnetic refrigeration in the so-called “high-temperature range” as well as in the “low-temperature range” (where  $T_c$  is the approximate magnetic ordering temperature).

“High”-temperature salts:



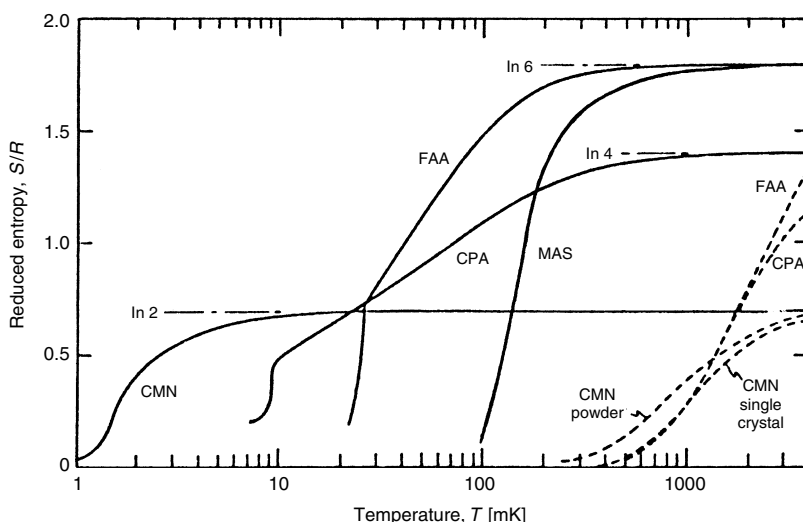
“Low”-temperature salts:



Their entropy curves are depicted in Fig. 9.2.

All these salts contain a lot of water of crystallization, which assures a large distance (about 1 nm in CMN) between the magnetic ions and therefore leads to a low magnetic ordering temperature. Details on the properties of these and other suitable salts can be found in [9.1–9.3, 9.5–9.7].

Due to the weak interactions between the rather remote and well-sheltered  $\text{Ce}^{3+}$  ions in CMN [9.6], which result in a small internal field  $b$  and a low ordering temperature  $T_c$  (Fig. 9.1), this salt has been quite en vogue as a refrigerant as well as for thermometry (Sect. 12.9). Its electronic ground state



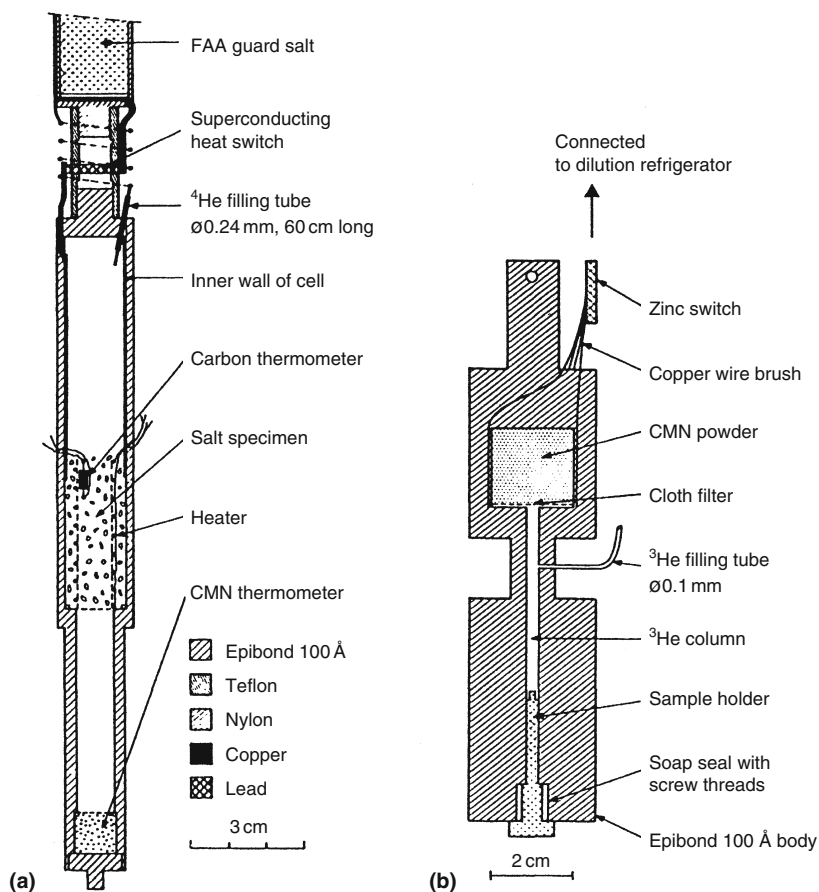
**Fig. 9.2.** Entropies  $S$  (divided by the gas constant  $R$ ) of four salts suitable for paramagnetic demagnetization as a function of temperature in zero field (—) and in 2 T (---). (For the chemical formula of the salts see the text.)

is a doublet with an effective spin of one-half at  $T < 1$  K. CMN has been extensively used by Wheatley and coworkers [9.7, 9.8] to refrigerate liquid  $^3\text{He}$  to about 2 mK. This low final temperature is possible due to a magnetic coupling between  $^3\text{He}$  nuclear moments and Ce electronic moments which strongly reduces the thermal boundary resistance (Sect. 4.3.2). Even lower temperatures can be achieved by using LCMN, a salt where the magnetic Ce ions are partly replaced by non-magnetic La ions [9.9–9.11]. This dilution, of course, reduces the cooling power/volume as well. CMN and LCMN are the salts with the lowest known electronic magnetic ordering temperature. A combination of a moderate dilution refrigerator and a magnetic refrigeration stage of CMN or LCMN at a starting field of about 1 T is a very suitable and reasonably cheap setup for  $^3\text{He}$  research. For the use of CMN and LCMN in magnetic thermometry, see Sect. 12.9.

Figure 9.3 shows some typical setups for paramagnetic refrigeration used mainly in the 1960s and 1970s before the advent of the dilution refrigerator; they are described in [9.1–9.3, 9.7–9.14] and references therein.

The advantages of paramagnetic refrigeration are that the required starting conditions can be fairly easily achieved with simple dilution refrigerators and superconducting magnets. In addition, the refrigerant can also be used as a thermometer by applying the Curie law  $\chi = \lambda/T$  to determine the temperature  $T$  by measurements of the susceptibility  $\chi$  of the salt (Sect. 12.9). However, paramagnetic refrigeration also has some severe drawbacks. The thermal conductivity of dielectric salts is rather poor; a typical value is





**Fig. 9.3.** Two paramagnetic refrigerators used by Wheatley and co-workers (a): [9.7]; (b): [9.12]. These original references and [9.1] should be consulted for details

$10^{-4} \text{ W K}^{-1} \text{ cm}^{-1}$  at 0.1 K. It is therefore difficult to achieve thermal equilibrium within the salt, leading to temperature gradients and long thermal relaxation times in the millikelvin temperature range. Similarly it is rather difficult to achieve thermal contact to the salt and special construction methods have been developed for paramagnetic refrigeration stages. Probably, the mostly applied one is to compress the powdered salt (typically at 100 bar pressure) together with some “glue” (Apiezon grease or oil or epoxy) and the ends of some fine Cu or Ag wires spread out uniformly in the pill. The other end of the wires should already have been welded to the places where the thermal contact is desired (to a heat switch connecting to the precooling stage and to a metal plate for mounting experiments and thermometers), see Figs. 12.37, and 12.39. In some cases it may be necessary to seal the

salt pill to prevent chemical changes (dehydration) leading to deterioration. Consideration of the thermal path from the spins to the lattice of the salt, to the metal wires, and to the sample/thermometer is advised to avoid unnecessary, unpleasant surprises [9.2]; these problems, of course, become more and more serious the lower the temperature range of operation. Finally, the minimum temperature is determined by interactions of the electronic magnetic moments with their surroundings and eventually by spontaneous magnetic ordering, leading to a minimum temperature of about 2 mK for paramagnetic refrigeration (reached in 1953 with CMN). Because these temperatures can nowadays also be achieved by dilution refrigerators, this latter continuous refrigeration method has replaced magnetic refrigeration with paramagnetic salts. For lower temperatures, where dilution refrigerators become inefficient, magnetic refrigeration using nuclear magnetic moments in metals is the only known refrigeration technique and will be discussed in detail in the following chapter.

Recently, compact adiabatic demagnetization refrigerators for small laboratory experiments and, in particular, for space applications have been developed [9.15, 9.16]. They have a typical minimum temperature of 30 to 50 mK, a time constant of 1 s at 100 mK, and a cooling power of about 1  $\mu$ W at this temperature. Single-stage paramagnetic refrigerators are operated from a starting temperature of 1.5 K, double-stage refrigerators can commence from the normal boiling temperature of  $^4\text{He}$  (4.2 K). By regulating the remaining magnetic field after demagnetization, a stable temperature can be maintained for many hours and the typical hold time at 100 mK is 24 h. As paramagnetic salts ferric ammonium alum (FAA) with  $J = 5/2$  or chromic caesium alum (CCA) with  $J = 3/2$  have been used. They can be applied for cooling microcalorimeters or bolometers in infrared, millimeter-wave and X-ray astronomy and as test beds for the development of detectors for millimeters, X-rays and dark matter.

Another cause for revival of adiabatic demagnetization using paramagnetic salts may result from the recent introduction of a commercial system, combining a low-vibration 4 K/1 W pulse-tube cooler (see Sect. 5.3) as a precooling stage for an adiabatic demagnetization stage. This setup is offered with a variety of experimental probes, thermometry and magnetic shielding installations for temperatures to 100 mK and as an option with a superconducting magnet supplying 12 T. The device enables the user to perform cryogen-free millikelvin/high-magnetic-field measurements.

## Problems

**9.1.** At which value of  $x$  does the high-temperature approximation (10.4) for the magnetic heat capacity deviate by 5% from the exact result given in (9.15)?

**9.2.** Calculate the cooling power of 1 mole CMN if it is demagnetized from 2 T, 1 K to zero field (Fig. 9.2). Calculate for the same experiment the heat of

magnetization which has to be removed if this salt is magnetized isothermally to 2 T. Perform the same calculation for the situation sketched in Fig. 9.1.

**9.3.** To which temperature does one have to refrigerate a solid containing paramagnetic ions with spin  $1/2$  and magnetic moments equal to one Bohr magneton in a field of 3 T so that 75% of the atoms are polarized with their spins parallel to the external magnetic field?