

Cooling by Adiabatic Demagnetization of Nuclear Spins

N. Kurti *Clarendon Laboratory, Oxford*

Received 24 May 1960

THE exploration of low temperatures down to about 1°K was made possible by the use of liquefied gases. The object of this article is to review briefly and in general terms the technique used to cover the temperature range down to about 10⁻³°K and to describe some recent work which shows the way the temperature range down to 10⁻⁶°K may be similarly opened up.

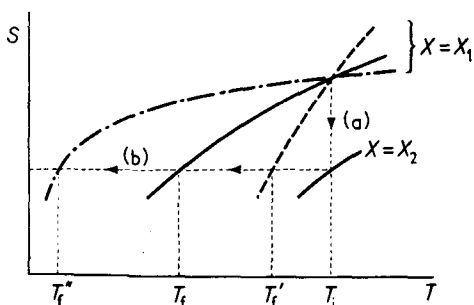


Figure 1. The cooling process in the entropy-temperature diagram: (a) Isothermal $X_1 \rightarrow X_2$; (b) Isentropic $X_2 \rightarrow X_1$

The basic principle of generating low temperatures is best explained with the help of an entropy diagram. In Figure 1, the full line represents the entropy of a system for a constant value $X = X_1$ of some external intensive parameter (e.g. pressure, magnetic field, etc.) as a function of the temperature. A brief portion of the entropy for $X = X_2$ is also indicated. The principle of the generation of low temperatures becomes clear from this diagram. At the initial temperature T_i , the entropy is reduced by an isothermal change of X from X_1 to X_2 . The system is then thermally isolated from its surroundings and the subsequent adiabatic-reversible, and therefore isentropic, change of X_2 in the opposite direction results in cooling. If X_2 is brought back to its original value X_1 , the final temperature T_f is given by the intersection of the horizontal isentropic line with the entropy curve for $X = X_1$.

As may be seen from this representation, two conditions have to be satisfied for appreciable coolings to result. First, the system must, in its initial state, possess a finite entropy, and this must be capable of an appreciable reduction by the alteration of an external parameter. Second, the degree of cooling one can obtain with a given initial isothermal entropy reduction ΔS depends on the shape of the

entropy curve for $X = X_1$. If this curve is steep (dotted line in Figure 1), the final temperature T_f' will be considerably higher than T_f , which would be obtained with a flat entropy curve (dash-dot). Remembering that the specific heat is given by $T(dS/dT)$, we can say that in order to reach low temperatures the heat capacity of the system for the final value (X_1) of the external parameter must be low. We can express this in another form by stating that the fractional cooling is given by

$$\frac{\Delta T}{T} = \frac{\Delta S}{\bar{C}}$$

where \bar{T} and \bar{C} are appropriate mean values of the temperature and of the heat capacity.

To summarize, the two essential conditions for the production of low temperatures are:

- (1) Finite entropy, entropy reduction possible;
- (2) Flat S/T curve, i.e. small specific heat for $X = X_1$ in a wide temperature range.

The first of these conditions is reasonably well satisfied in the case of a gas, as it is easy to produce sizeable entropy reduction by compression. The second condition is satisfied as long as one only considers the gas itself, but is no longer so when the additional heat capacity of the container is taken into account. In this case, one finds that the single process results in small temperature reduction, so that progressive cooling involving heat exchangers has to be employed. Only when the starting temperature T_i is low enough for lattice specific heats to become small can single or batch processes be used for gas cooling and gas liquefaction. This is, for instance, the case of the Simon expansion method for the liquefaction of helium.

The temperature of a liquefied gas can be further reduced by pumping off the vapour, but a practical limit is set by the rapidly decreasing vapour pressures. To achieve a predetermined rate of cooling dT/dt of the liquid or to absorb a given amount of heat influx \dot{Q} , the rate of evaporation has to be maintained at a definite value given by

$$\frac{C \cdot dT}{\lambda \cdot dt}$$

or

$$\frac{\dot{Q}}{\lambda}$$

respectively, where λ is the heat of evaporation and C the heat capacity to be cooled down. The lower the vapour

pressure the more difficult it is to maintain this rate of evaporation since the required pumping speed has to be increased proportionally to the reciprocal of the pressure. Let us consider, for instance, helium-3 which is the liquid with the lowest boiling point or highest vapour pressures, and thus the most suitable cryogenic liquid for reaching low temperatures. We find, assuming a pumping speed of 100 l./sec at the surface of the liquid, that the rate of heat absorption at 0.3 °K (a vapour pressure of 1.5×10^{-3} mm Hg) is 2×10^{-4} W. At 0.2 °K this is reduced to 2×10^{-6} W and at 0.15 °K to 10^{-8} W. Alternatively, we find that at 0.2 °K the rate of cooling for 1 cm³ of liquid helium-3 is about 3×10^{-5} deg.K/sec; in other words, it would take about 1 hr to lower the temperature by 0.01 °K.

It is clear from these considerations that even with liquid helium-3 the lowest practical limit is about 0.3 °K. Fortunately, just where liquefied gases lose their usefulness for producing very low temperatures, another group of substances, namely the ideal paramagnetic salts, which satisfy both essential conditions stated above, come into their own. In an ideal paramagnetic substance, the interaction energy of the elementary magnets is by definition vanishingly small. Therefore, in the absence of an external magnetic field the $2J+1$ possible orientations of the elementary magnet (J being the angular momentum) are energetically equivalent and such a system has an entropy of

$$R \times \ln (2J+1)$$

Moreover, this entropy can be appreciably reduced by means of modest magnetic fields. In a magnetic field H , the $(2J+1)$ -fold degenerate level is split into $2J+1$ equidistant levels of separation $g\beta H$, where g is the spectroscopic splitting factor and β is the Bohr magneton for the electron. For a field of 10 kgauss this energy difference is approximately $k \times 1$ °K. Therefore, at 1 °K and 10 kgauss there will be a markedly preferential population of the lower energy levels according to the Boltzmann distribution law and, correspondingly, a decrease in entropy.

Our second condition is also satisfied by such a substance. The entropy of the elementary magnets in zero field is, at least in the first approximation, temperature independent and the corresponding specific heat is zero. On the other hand, the entropy and specific heat associated with the lattice vibrations are negligibly small compared to the possible entropy reductions. It was the realization of the fact that both these conditions are satisfied by a large group of paramagnetic salts that led Debye¹ and, independently, Giauque² to propose producing very low temperatures by isentropic demagnetization of paramagnetic salts. If one knows the entropy in zero magnetic field as a function of temperature and the entropy of magnetization at the starting temperature, the method outlined in Figure 1 enables one to predict the final temperatures attainable.

The temperature changes obtainable by isentropic reduction of a magnetic field can be calculated either by a thermodynamical or by a statistical argument—just as for an ideal gas—and one obtains for a strictly ideal paramag-

netic salt with negligible specific heat the simple relation

$$T_f = H_f \frac{T_i}{H_i} \quad \dots(1)$$

where the indices i and f refer to the initial and final state. A simple way of correcting for the departure from ideal behaviour is to characterize the interaction energies by an internal field h . Equation (1) then becomes

$$T_f = \sqrt{(H_f^2 + h^2)} \frac{T_i}{H_i} \quad \dots(2)$$

(This is an approximate formula and is only valid for temperatures at which the deviation from ideal behaviour is small, in other words, when the entropy in zero field does not differ markedly from the ideal value $R \times \ln (2J+1)$. In this case we can write

$$S_i = R \ln (2J+1) - \frac{a}{2} \cdot \frac{1}{T_i^2} - \frac{\lambda}{2} \left(\frac{H_i}{T_i} \right)^2$$

$$S_f = R \ln (2J+1) - \frac{a}{2} \cdot \frac{1}{T_f^2} - \frac{\lambda}{2} \left(\frac{H_f}{T_f} \right)^2$$

λ being the Curie constant. Now $S_i = S_f$ and hence

$$T_f = \frac{\sqrt{(a\lambda + H_f^2)}}{\sqrt{(a\lambda + H_i^2)}} T_i = \sqrt{(h^2 + H_f^2)} \frac{T_i}{H_i}$$

since in most cases of practical interest $h \ll H_i$. A more rigorous derivation of this relation has been given by Abragam and Proctor.³

For the case of demagnetization to zero field ($H_f = 0$), equation (2) becomes

$$T_f = h \frac{T_i}{H_i} \quad \dots(3)$$

We see that the final temperature depends in a simple fashion on the initial temperature, the initial field, and h . That is, it depends on the interaction energies.

Thanks to suitable paramagnetic salts with small values of h , temperatures down to nearly 10^{-3} °K are becoming common in many cryogenic laboratories. This is not the place to describe in detail the various experimental techniques that have been developed for working in this range; there are quite a few informative and up-to-date survey articles on the subject.⁴⁻⁸ It seems, however, worth while to point out one fundamental difference between such a system of elementary magnets or spins and the other more common cryogenic systems. One is accustomed to dealing with systems whose energy spectrum has no upper limit. Such systems have the well-known property that at high enough temperatures where quantum effects become negligible the law of equipartition of energy holds, the energy of the system becomes infinite with temperature. In a system of spins, the energy spectrum has an upper bound and the law of equipartition of energy does not apply; in fact the specific heat of such a system tends to zero as temperature approaches infinity. This has an interesting consequence; a finite amount of energy is sufficient to bring the

system to an infinitely high temperature characterized by an equal distribution of the particles among all the energy levels. If, then, the system is made to absorb an amount of energy which is more than necessary to bring it to infinitely high temperatures, one gets a preferential population of the upper energy levels, a state that can be described by a negative absolute temperature. Such negative temperatures, corresponding to true equilibrium states, have been realized with nuclear spins⁹ which, because of the very weak coupling with their environment, can be regarded as forming a system with a bounded energy spectrum. In describing the production of negative temperatures by the absorption of a surplus of energy, one brings out clearly the essential feature of these temperatures: they are reached by passing through infinitely high temperatures and not through absolute zero, which remains an unattainable singularity of the temperature scale.

Fundamentals and practical requirements of nuclear cooling

Equation (3) shows the importance of having low interaction energies if very low temperatures are to be reached, without, however, telling the whole story. There is one unavoidable interaction, namely that between spins, and this produces a co-operative self-ordering of the spins when $\mu h \simeq kT$, μ being the elementary magnetic moment. This is accompanied by a steep drop of entropy (high specific heat), which sets a limit to the cooling by demagnetization, given by

$$T_{\text{lim}} = \frac{\mu h}{k}$$

If the interaction is dipolar,

$$h \simeq \frac{\mu}{r^3}$$

where r is the distance between two adjacent dipoles and we have

$$T_{\text{lim}} = \frac{\mu^2}{kr^3}$$

One way to reduce T_{lim} is by increasing r , e.g. by replacing the paramagnetic ions with isomorphous diamagnetic ions. But to achieve a thousand-fold reduction of T_{lim} would require a thousand-fold magnetic dilution and the maximum possible entropy change, ΔS for a given volume would be reduced in the same ratio. Since the cooling capacity of such a system, i.e. the quantity of heat it can absorb after demagnetization, is roughly $T_f \Delta S$, one should try to keep ΔS as large as possible.

For this reason it is preferable to reduce μ . This can be done by using a 'nuclear' paramagnetic substance in which the magnetization is due to the nuclear magnetic moments,^{10, 11} which are about 1,000 times smaller than the electronic magnetic moments of ordinary paramagnetics. However, the smallness of the nuclear magnetic moment raises one difficulty; to satisfy the condition $g\beta_n H \simeq kT$ (where β_n is the nuclear Bohr magneton), one needs values

of H/T , a thousand times larger than for 'electron' paramagnetic substances. Even at 0.01°K, fields of the order of 50 kgauss would be required to achieve an entropy decrease of a few per cent of the full nuclear entropy, $R \ln(2I+1)$, where I is the nuclear spin. Thus the starting temperature has to be about 0.01°K and the nuclear demagnetization temperature has to be preceded by a conventional cooling step.

A general review of the conditions to be fulfilled for successful nuclear cooling has been given by Simon.¹² The present account, without repeating his arguments, gives in a more detailed fashion the design of the actual experiments performed in the last few years at the Clarendon Laboratory.^{13, 14}

The most important requirement is to be able to transfer reasonably quickly the heat of magnetization of the nuclear spins to the heat sink at 0.01°K formed by a paramagnetic salt cooled by adiabatic demagnetization. The two principal resistances in this energy transfer are between the nuclear spin system and its own crystal lattice and between this crystal lattice and the paramagnetic salt. As to the first of these, it is well known that in dielectric crystals the nuclear spin-lattice relaxation time becomes very long at low temperatures, and at 10⁻²°K may reach days or weeks. On the other hand, in a metal the nuclear spins can transfer their energy relatively rapidly to the conduction electrons, which in turn can communicate it to the lattice. The energy transfer is accomplished by a process¹⁵ in which a change of orientation of the nuclear spin is accompanied by an equal and opposite change of orientation of the spin of a conduction electron at the top of the Fermi distribution. Angular momentum is conserved in this process while the small magnetic energy change $g\beta_n H$ of the nuclear spin can be converted into kinetic energy of the conduction electron since the states near the Fermi level are not fully occupied. The number of these unpaired conduction electrons is proportional to T ; the transition probability for a nuclear spin flip has the same temperature dependence and the relaxation time is thus inversely proportional to T . These relaxation times are of the order of ¹⁶ a second at 1°K and thus, even at 0.01°K, the time for nuclear magnetization as far as this process is concerned is of the order of minutes.

Much work has been done on the establishment of thermal contact between a metal and a paramagnetic salt at very low temperatures.^{13, 17, 18} The method which seemed to be particularly suitable for this work uses a low temperature glass as bonding agent. The paramagnetic salt specimen consists of a viscous slurry made up of powdered chrome potassium alum suspended in a mixture of about equal volumes of a saturated aqueous solution of the same salt and glycerol. The metallic link between this 'paramagnetic' stage and the nuclear stage—they have to be 15–20 cm apart so that the stray field during the nuclear magnetization does not affect the paramagnetic stage—is embedded into this mixture. On cooling, this slurry turns into a glass without any sudden volume changes, and experiments both in Leiden and Oxford have shown that reasonably good thermal contact can be maintained in this

way down to 0.01°K. For calculating the rate of heat transfer between this thermal link and the paramagnetic salt, the empirical formula

$$Q = 10^3 A(T_1^3 - T_2^3) \quad \text{ergs/sec} \quad \dots (4)$$

(where T_1 and T_2 are the temperatures of the two boundary surfaces and A is the macroscopic contact area in square centimetres) has been found useful. No great accuracy is claimed for this equation but it gives at least the right order of magnitude within a factor of 2 or 3. Using this formula we can calculate the contact area needed to remove the heat of nuclear magnetization in a reasonable time, say 1 hr for the highest field used. Let us assume $T_i = 0.012$ °K (temperature of the co-operative anomaly of chrome potassium alum) and $H_i = 30$ kgauss and take 20 g ($\frac{1}{2}$ g.atom) of metallic copper as the nuclear stage. The heat of magnetization is

$$Q_m = T_i \Delta S = \frac{1}{2} T_i \frac{\lambda}{2} \left(\frac{H_i}{T_i} \right)^2$$

where $\lambda = 3.2 \times 10^{-7}$ is the nuclear Curie constant per gram-atom. With the given numerical data we find $Q_m = 4,000$ ergs. Equation (4) then gives for the area of contact about 1,000 cm², which can be obtained with a bundle of 2,000 copper wires of 0.1 mm diameter and embedded over a length of 15 cm in the paramagnetic stage. The lower end of this thermal link serves as the nuclear stage. Such a divided specimen has the further advantage that heat evolution due to eddy currents is greatly reduced.

As shown earlier, effective cooling requires an entropy vs temperature curve which for $H = 0$ is flat over a wide temperature range. Figure 2 shows the two chief components of the entropy of a metal with nuclear spins. We see that the nuclear entropy with the constant value of $R \ln(2I+1)$ at high temperatures (in practice above

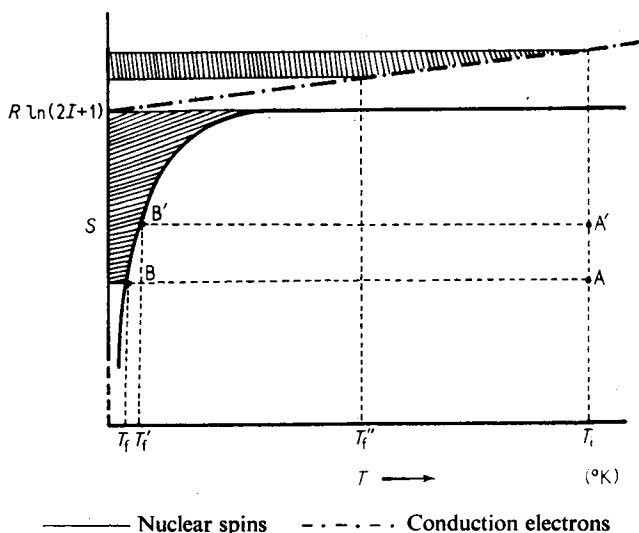


Figure 2. The relative importance of nuclear spins and conduction electrons in nuclear cooling

10^{-4} °K) satisfies this condition. Superimposed on it is the entropy of the conduction electrons which increases linearly with temperature. The Figure is not drawn to scale and it is only intended to illustrate the argument. As to the lattice entropy, it is altogether negligible compared with that of the conduction electrons at temperatures below 1°K.

We must distinguish between two cases, according to whether there is thermal equilibrium or not between the nuclear spins and the conduction electrons during demagnetization. We shall compare the temperatures reached in these two cases with the temperature T_f which would be attained (isentropic line AB) if one had the nuclear spin system by itself. Let us first consider the case where there is equilibrium (reversible and hence isentropic process). Our starting point is now given by A', the distance AA' being equal to the conduction electron entropy at T_i . Since the process is isentropic, the final temperature T_f' is again given by the intersection of the appropriate horizontal line (A'B') with the entropy curve for $H = 0$.

The position is different in the second case where during demagnetization there is no temperature equilibrium between the nuclear spins and the conduction electrons. Let us take the extreme case in which the coupling between these two systems is so weak that during demagnetization the temperature of the conduction electrons does not alter at all, so that the nuclear spins reach T_f . Now, as time goes on, there will be energy exchange between the two systems and equilibrium will be reached at a temperature at which the total heat Q gained by the nuclear spin system equals that lost by the conduction electrons. Remembering that

$$Q = \int T dS$$

we find that the final temperature T_f'' reached in this process is given by the condition that the two differently shaded areas are equal. Clearly, the irreversible process gives much poorer results than the reversible process.

We can calculate for each of these two cases the conditions under which the presence of the conduction electrons has only a small influence on the final temperature reached in nuclear cooling. For the reversible case we have $S_i = S_f$, with

$$S_i = R \ln(2I+1) - \frac{\lambda}{2} \left(\frac{H_i}{T_i} \right)^2 + \gamma T_i$$

and

$$S_f = R \ln(2I+1) - \frac{\lambda}{2} \left(\frac{h}{T_f} \right)^2$$

(where λ is the nuclear Curie constant, γT_i the electronic specific heat, and h the local internal field), since in all cases of practical interest $T_f \ll T_i$ and $h < H_i$. Remembering that T_f , the temperature that would be reached by the nuclear spin system alone, is given by

$$T_f = \frac{h T_i}{H_i}$$

we find

$$1 - \frac{T_f^2}{T_f'^2} = 2 \frac{\gamma T_i^3}{\lambda H_i^2} \quad \dots (5)$$

or, substituting numerical values for copper ($\gamma = 7.5 \times 10^8$ erg (deg.K) $^{-2}$ (g.atom) $^{-1}$ and $\lambda = 3.2 \times 10^{-7}$ (g.atom) $^{-1}$),

$$1 - \frac{T_f^2}{T_i^2} = 4.7 \times 10^7 \frac{T_i^3}{H_i^2} \quad \dots (5a)$$

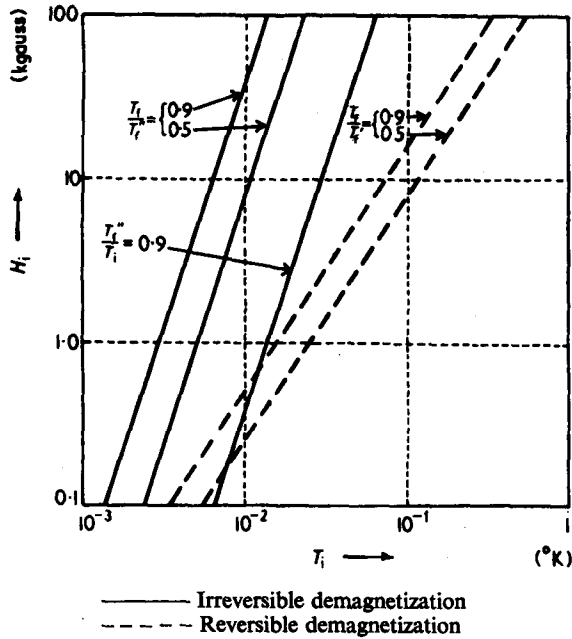


Figure 3. The effect of the conduction electrons on the final temperatures reached in the nuclear demagnetization of copper. The lines indicate limiting values of H_i and T_i for stated deviations of the actual final temperatures (T_f' and T_i') from those that would be reached in the absence of conduction electrons

Equation (5) defines pairs of values T_i, H_i , leading to T_f' not exceeding T_f by more than a given factor. Figure 3 shows two T_i, H_i lines corresponding to $T_f'/T_f = 0.9$ and $T_i'/T_i = 0.5$; only T_i, H_i values lying under these lines satisfy the respective conditions. We see that in this reversible case nuclear demagnetizations can be carried out from a wide range of initial conditions without the results being appreciably influenced by the conduction electrons.

Let us next consider the irreversible case. T_f' is now given by the condition

$$\int_T^{T_f'} C_n dT = \int_{T_i'}^{T_i} C_e dT$$

where

$$C_n = \lambda \frac{h^2}{T^2}$$

and $C_e = \gamma T$. Making the same simplifying assumptions as before we have

$$1 - \frac{T_f'}{T_f} = \frac{\gamma}{2\lambda h} \frac{T_i^3}{H_i} = 3.9 \times 10^9 \frac{T_i^3}{H_i} \quad \dots (6)$$

(with $h = 3$ gauss, the value found for copper¹⁴).

As may be seen from Figure 3, the conduction electrons have a great effect in this case; the lines for $T_f'/T_f = 0.9$ and $T_i'/T_i = 0.5$ leave only a small range of permissible T_i, H_i

values. The third line for the irreversible case refers to $T_f'/T_i = 0.9$ and defines the limits of the nuclear cooling experiments with copper under conditions of poor energy exchange between nuclear spins and conduction electrons.

The foregoing calculations show that the effect of the heat capacity of the conduction electrons is negligible in the reversible case but not if the process is irreversible. We shall next discuss whether under actual experimental conditions there is equilibrium between the nuclear spin system and the conduction electrons during demagnetization. For the simplest case of $I = \frac{1}{2}$ (two nuclear spin orientations of energy difference u , to be denoted by '+' and '-'), the approach to equilibrium between the nuclear spins and their surroundings is given by

$$\frac{dn}{dt} = \frac{1}{\tau} (n - n_0) \quad \dots (7)$$

where $n = N_+ - N_-$ is the population difference between the two states and n_0 is the distribution corresponding to temperature equilibrium with the 'temperature bath', i.e. the conduction electrons at T_0 . The relation between the relaxation time τ and the transition probability for a nuclear spin flip is given by

$$\frac{1}{\tau} = 2w \cosh \frac{u}{kT_0}$$

with

$$w_+ = w \exp(-u/kT_0)$$

and

$$w_- = w \exp(u/kT_0)$$

being the probabilities for the (+ -) and (- +) transitions, respectively. In most cases of practical interest $u/kT_0 \ll 1$ and τ is independent of the level separation; it depends, however, as mentioned earlier, on the temperature of the conduction electrons. We can define by means of n a nuclear spin temperature T ,²⁰ and as long as $u/kT \ll 1$ we have $n \propto 1/T$ and equation (7) may be written

$$\frac{dT}{dt} = \frac{T}{\tau} \left(1 - \frac{T}{T_e}\right) \quad \dots (8)$$

where T_e is the temperature of the conduction electrons. The rate of heat transfer from the conduction electrons to the nuclear spins is then given by

$$\frac{dQ}{dt} = C_n \frac{dT}{dt} = \lambda \left(\frac{H}{T}\right)^2 \frac{T}{\tau} \left(1 - \frac{T}{T_e}\right) \quad \dots (9)$$

($C_n = \lambda(H/T)^2$ being the specific heat of the nuclear spins in a magnetic field H), or by

$$-\gamma T_e \frac{dT_e}{dt}$$

(γT_e being the specific heat of the conduction electrons). Remembering that $\tau T_e = \alpha$ (constant), we have

$$\frac{dT_e}{dt} = -\frac{\lambda(H)^2}{\gamma} \frac{1}{T} \frac{1}{\alpha T_e} (T_e - T) \quad \dots (10)$$

We must now calculate the value of $(T/T_e)(T_e - T)$ which makes the cooling rate dT_e/dt of the conduction electrons

about equal to the cooling rate of the nuclear spins due to demagnetization. Let us assume that the field is reduced at a constant rate, $dH/dt = -\beta$, then for the nuclear spin system alone

$$\frac{T}{H} = \frac{T_i}{H_i}$$

and hence

$$\frac{dT}{dt} = -\frac{T_i}{H_i}\beta$$

equating this with the right-hand side of equation (8), we find

$$\frac{T}{T_e}(T_e - T) = \frac{\gamma}{\lambda}\alpha\beta\left(\frac{T}{H}\right)^2 \frac{T_i}{H_i} \approx \frac{\gamma}{\lambda}\alpha\beta\left(\frac{T_i}{H_i}\right)^2 \dots (11)$$

Substituting numerical values ($\alpha = 1$ sec/deg.K, $\beta = 10^8$ gauss/sec), we find with $T_i = 1.2 \times 10^{-2}$ °K and $H_i = 10^4$ gauss

$$(T_e - T) = 4 \times 10^{-5} \text{°K}$$

In other words, not till a temperature of about 4×10^{-4} °K is reached does the temperature difference between conduction electrons and nuclear spins exceed 10 per cent. We were thus justified in regarding T/H as constant during most of the demagnetization. It is true that while in the final stage the temperature of the nuclear spins drops from 4×10^{-4} °K to

$$T_f = h \frac{T_i}{H_i} = 3 \times \frac{1.2 \times 10^{-2}}{10^4} = 3.6 \times 10^{-6} \text{°K}$$

the conduction electrons will lag behind. But, as may be seen from Figure 3, at these temperatures even irreversible cooling of the conduction electrons will have only a negligible effect.

It can also be shown that at the end of demagnetization the time-lag is only of the order of seconds. In equation (8), T the temperature of the nuclear spins may now be taken as constant and equal to 3.6×10^{-6} °K, $H = h = 3.0$ gauss, and since $T_e \gg T$ except at the very end we have a constant cooling rate for the conduction electrons given by

$$\frac{dT_e}{dt} = -\frac{\lambda h^2}{\gamma T \alpha} = 10^{-4} \text{ deg.K/sec} \dots (12)$$

(Note: The first detailed discussion of the establishment of thermal equilibrium in a nuclear cooling experiment is due to Kittel.²¹ He based his calculations on the early experiments of Kurti et al.¹³ which gave a much higher value of h (25 gauss) than the present one. Although Kittel's numerical values have been superseded by the present ones, his main argument remains correct; in spite of the small transition probability for the Korringa relaxation process at very low temperatures (10^{-6} sec⁻¹ at 10^{-6} °K), the conduction electrons can take part in the nuclear cooling process. The physical explanation is that although the probability for a nuclear spin flip is small, very few such flips are necessary to cool the conduction electrons.)

We have assumed all along that immediately before demagnetization the thermal contact with the electronic stage is broken so that the nuclear stage as a whole—i.e. nuclear spins, conduction electrons, and lattice—is thermally insulated. While this should be possible with a superconducting heat-switch, various experimental difficulties have prevented the use of such a device and so far all experiments have been carried out *without* a heat-switch. This may seem to make nonsense of these nuclear cooling experiments, but the presence of the two thermal resistances, nuclear spin-conduction electron relaxation and heat transfer from copper to paramagnetic salt, justified the expectation of an observable cooling effect.

As mentioned above a typical specimen used in the nuclear cooling experiments consists of a bundle of insulated copper wires, about 35 cm long, whose lower end constitutes the nuclear stage and whose upper end is embedded into the electronic stage of chrome potassium alum. This specimen is suspended in a jacket whose walls are at a low enough temperature (< 0.35 °K) for heat influx due to gas to be negligible. Mutual inductance coils surrounding the electronic stage and the nuclear stage permit the measurement of their respective susceptibilities and hence their temperatures.

The apparatus used in the first experiments¹³ had two main shortcomings. The nuclear susceptibility was measured by a ballistic method; thus no continuous record of the rather rapid warming-up of the nuclear stage could be obtained, and this made the analysis of the results difficult. The second difficulty was caused by the manganous ammonium sulphate cylinder used to cool the shield surrounding the nuclear stage to about 0.1°K. Since this

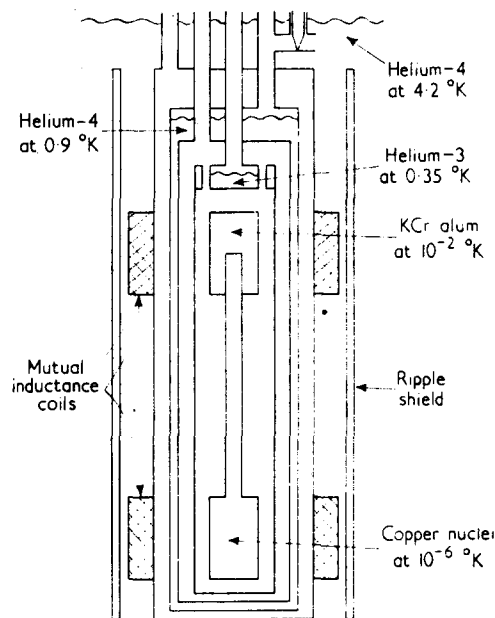


Figure 4. Schematic view of the cryostat for nuclear demagnetization

cylinder was at the height of and concentric with the electronic stage, it was impossible to determine with any accuracy the temperature of the latter and hence T_i .

To remedy these drawbacks, a new apparatus was constructed²² which uses a shield cooled by liquid helium-3 and an a.c. mutual inductance bridge permitting continuous measurement of the nuclear susceptibility starting about 2 sec after demagnetization. The apparatus is shown diagrammatically in Figure 4. Figure 5 is a photograph of the cryostat, with the magnetizing solenoid.

Results and discussion

We shall now briefly describe some of the results obtained with the new apparatus. First a series of demagnetizations were carried out, all starting from the same initial temperature, $T_i = 0.012^\circ\text{K}$, and from fields between 3 kgauss and 30 kgauss. Figure 6 shows the recorder graph of the nuclear susceptibility after a typical demagnetization. The mutual inductance was balanced at the starting temperature and the amplifier sensitivity so adjusted that the lowest temperature (highest susceptibility) gave approximately full deflection. Immediately after the nuclear stage had warmed up to the starting temperature—this usually took about 90 sec—the instrument was calibrated by altering the compensating mutual inductance in known steps. The times corresponding to integer values of the mutual inductance were then read off these warming-up curves and plotted logarithmically, as shown in Figure 7. Since the mutual inductance is proportional to the nuclear susceptibility, these plots in effect give $n = N_+ - N_-$ or $1/T$ as a function of time. If the warming-up is governed by a relaxation process between nuclear spins and conduction electrons, the latter being at a constant temperature given by the electronic stage ($T_e \gg T$), one would expect, according to equation (8), straight lines, all parallel to each other. We see that the lines are indeed nearly parallel, though there is a slight curvature.

The following simple experiment was carried out to prove that during this warming-up the conduction electrons are not in thermal contact with the nuclear spins but rather with the electronic stage. About 10 sec after demagnetization, that is as soon as the trend of the warming curve could be ascertained, the nuclear stage was exposed to a burst of γ -rays of a few seconds' duration and of an intensity calculated to generate in the specimen a quantity of heat of about 10 ergs. If the lattice and the conduction electrons had been in temperature equilibrium with the nuclear spins, the nuclear spin temperature would suddenly have risen to that of the electronic stage, since the enthalpy of the nuclear stage between 10^{-6}°K and 10^{-2}°K is only 4 ergs. The recorder graph, however, was unaffected, indicating that all the energy released by the γ -ray absorption went into the electronic stage without the temperature of even the conduction electrons being appreciably increased. Since the nuclear spin-conductance electron relaxation time is proportional to $1/T$ the warming-up curve would have become steeper if the conduction electrons had been heated.

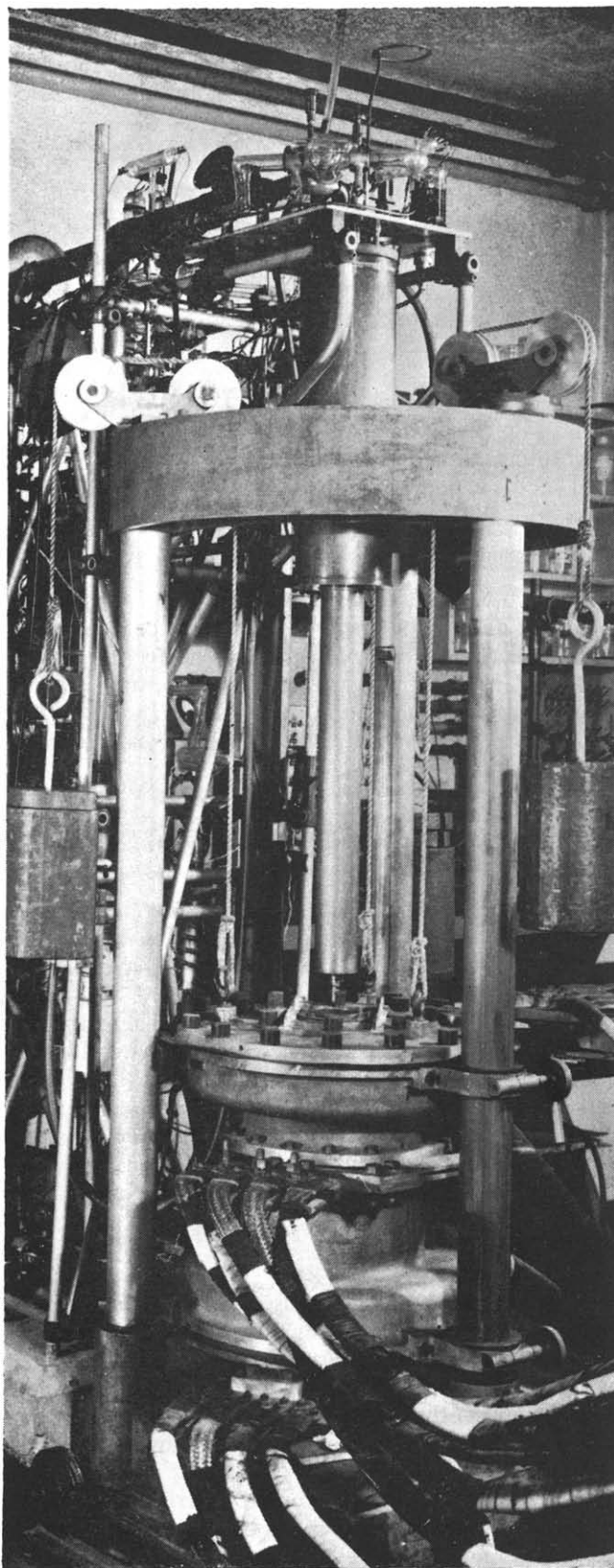


Figure 5. View of the nuclear cooling apparatus. Underneath the metal Dewar, enclosing the actual cryostat, is the water-cooled high powered solenoid

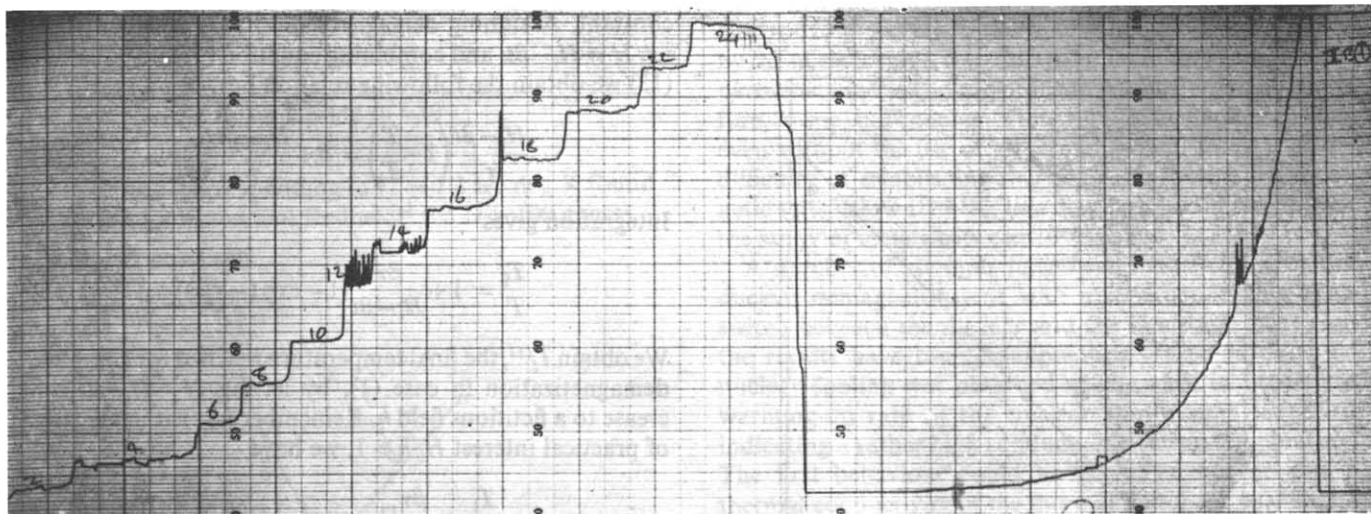


Figure 6. Recorder graph of the magnetic thermometer. Right: nuclear susceptibility after demagnetization; Left: calibration of the bridge with a variable mutual inductance. Each small division represents 5 sec

A number of nuclear demagnetizations were carried out with the electronic stage, and hence the conduction electrons, at higher temperatures, and these experiments served to determine the temperature dependence of the relaxation time. The results are given in Figure 8 which shows that the temperature dependence is not far off the predicted one. The straight line gives $\tau T = 0.4$ sec.deg.K, which agrees reasonably well with the value of $\tau T = 0.45$ sec.deg.K found by Anderson and Redfield¹⁶ in the liquid

helium temperature range and in small fields. It should be emphasized that, as shown by these authors, the relaxation time increases about 2.5 times between 1 and 100 gauss, and reaches at higher fields the value of $\tau T = 1.1$ sec.deg.K.

Figure 9 gives the final temperature reached by demagnetization from 0.012°K and from various fields. The results obey equation (3) and from the slope of the line we obtain $h = 3.1$ gauss, in good agreement with the predictions of various theories of interaction between nuclear spins in metals, and with the results from nuclear resonance experiments. Clearly, nuclear cooling is a rather cumbersome method for obtaining h ; but when it becomes possible to use 3 or 4 times larger values of H_i/T_i than has been done hitherto one would probably get below the critical temperature of the co-operative ordering of nuclear spins and

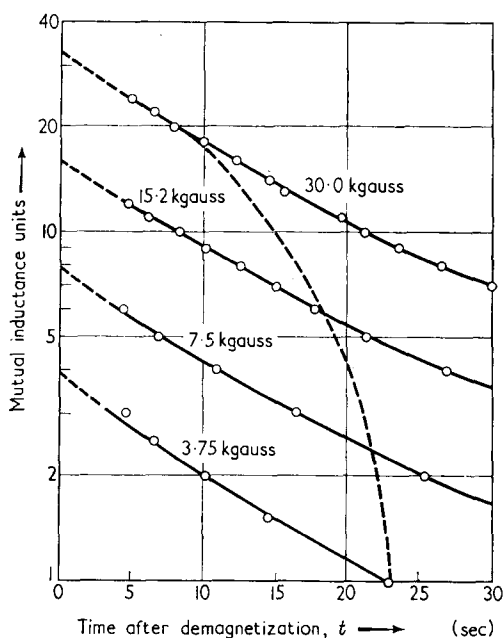


Figure 7. Nuclear susceptibility (in arbitrary units) as a function of time after demagnetizations from 0.012°K and the stated fields. The broken line (---) indicates the trend one would expect if the warming-up were governed by the heat resistance of the paramagnetic salt and the copper specimen

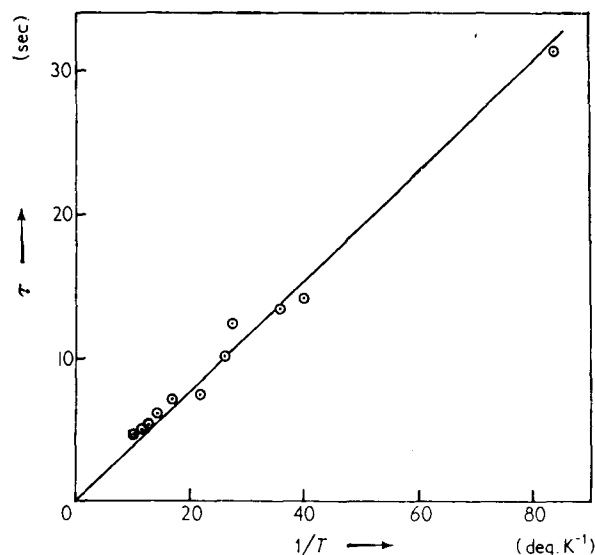


Figure 8. Relaxation time as a function of the reciprocal of the conduction electron temperature

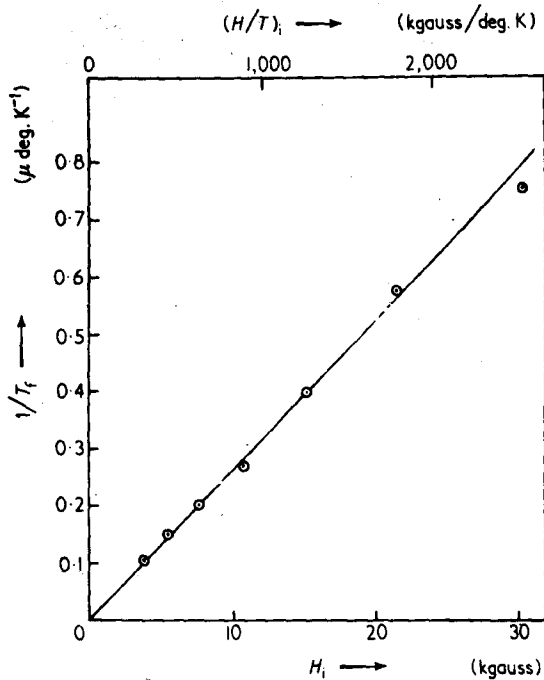


Figure 9. Temperatures attained by nuclear demagnetization from 0.012°K and various fields

then the question of whether nuclear spins are ordered in a ferromagnetic or an antiferromagnetic way may perhaps be answered.

Finally, one possible objection to the validity of these results must be discussed. Since we have used no heat-switch the nuclear stage was in, albeit weak, thermal contact with the electronic stage both after and during demagnetization. If the demagnetization could be carried out quickly the error so introduced would be small; but, in order to keep eddy current heating in the copper specimen within permissible limits, the demagnetization has to be rather slow, at the rate of about 1 kgauss/sec. We can calculate under certain simplifying assumptions how the heat contact during demagnetization affects the final temperature. There are two main heat resistances between the nuclear spin system and the paramagnetic salt of the electronic stage: at the boundary between the paramagnetic specimen and the copper, given by equation (4), and between the conduction electrons and the nuclear spins, characterized by the relaxation time τ . We shall consider the two extreme cases where one or the other of these resistances is zero.

(1) Good heat contact at the paramagnetic salt so that the heat transfer to the nuclear spins is governed by, and is given at any moment by, equation (9). On the other hand, during demagnetization, as long as $H \gg h$, we have for the rate of heat influx to the nuclear spins

$$\frac{dQ}{dt} = -H \frac{dH}{dt} = -\lambda \frac{H dH}{T} + \lambda \left(\frac{H}{T}\right)^2 dT \quad \dots (13)$$

since the internal energy of a system of ideal spins is

constant. Assuming demagnetization at a constant rate, i.e. $H = H_i - \beta t$, and combining equation (9) and equation (13) we obtain the following relation between T and H

$$\frac{H_i - \beta t}{\tau} \left(1 - \frac{T}{T_i}\right) = \beta + \frac{H_i - \beta t}{\tau} \frac{dT}{dt} \quad \dots (14)$$

Integration gives

$$\frac{T_i}{T} = 1 + \frac{\beta \tau}{H_i - \beta t} [1 - \exp(-t/\tau)] \quad \dots (15)$$

We obtain $T_f^{(1)}$, the final temperature reached for complete demagnetization in case (1), by letting $H = H_i - \beta t$ decrease to a fictitious field h . Remembering that in all cases of practical interest $H_i/h \gg 1$, we have

$$\frac{T_i}{T_f^{(1)}} = \frac{\beta \tau}{h} [1 - \exp(-H_i/\beta \tau)] \quad \dots (16)$$

Since in the ideal adiabatic-reversible case

$$\frac{T_i}{T_f^{(id)}} = \frac{H_i}{h}$$

we obtain for the ratio of final temperatures

$$\frac{T_f^{(1)}}{T_f^{(id)}} = \frac{H_i}{\beta \tau [1 - \exp(-H_i/\beta \tau)]} \quad \dots (17)$$

(2) Short relaxation time; heat leak to the nuclear spins governed by the heat influx \dot{Q} at the electronic stage. This is given by equation (4) and we can simplify the calculations by assuming this heat influx to be constant. Because of the T^3 dependence of \dot{Q} , this is a good approximation except for the initial stages of the demagnetization and will, anyway, only exaggerate the effect of this heat leak. We now have, analogously to equation (13)

$$\dot{Q} = -\lambda \frac{H}{T} \left(\frac{dH}{dt} - \frac{H dT}{T dt} \right) \quad \dots (18)$$

and, with $H = H_i - \beta t$

$$\frac{\dot{Q}}{\beta \lambda} = \frac{H}{T} \left(1 - \frac{H dT}{T dH} \right) \quad \dots (19)$$

Integration between H_i and h (i.e. T_i and $T_f^{(2)}$) gives

$$T_f^{(2)} = h \frac{T_i}{H_i} \left/ \left[1 - \frac{T_i}{H_i} \frac{\dot{Q}}{\beta \lambda} \log \left(\frac{H_i}{h} \right) \right] \right. \quad \dots (20)$$

and, as above,

$$\frac{T_f^{(2)}}{T_f^{(id)}} = \left/ \left[1 - \frac{T_i}{H_i} \frac{\dot{Q}}{\beta \lambda} \log \left(\frac{H_i}{h} \right) \right] \right. \quad \dots (21)$$

We can now calculate the effect of non-adiabatic conditions in these two extreme cases by substituting into equations (17) and (21) the following numerical values appropriate to our experiments:

$$T_i = 1.2 \times 10^{-2} \text{ }^\circ\text{K}$$

$$h = 3.1 \text{ gauss}$$

$$\lambda = 1.1 \times 10^{-7} \text{ (for } \frac{1}{3} \text{ g.atom of Cu)}$$

$$\dot{Q} = 1 \text{ erg/sec}$$

$$\tau = 90 \text{ sec (corresponding to } \tau T = 1.1 \text{ sec.deg.K found by Anderson and Redfield}^{16} \text{ for } H > 100 \text{ gauss)}$$

$$\beta = 10^3 \text{ gauss/sec.}$$

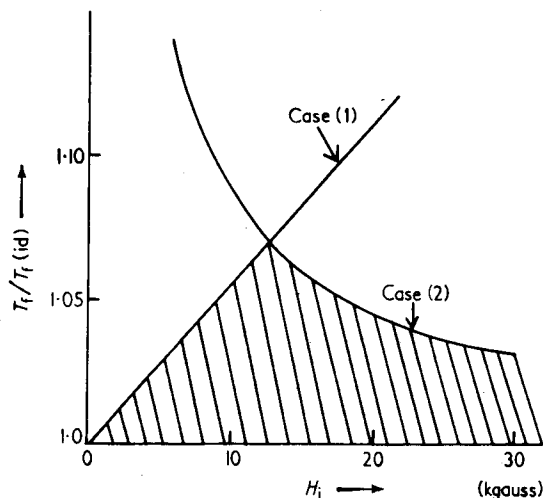


Figure 10. The effect of non-adiabatic conditions during demagnetization on the final temperatures. Case (1): Good heat contact at the paramagnetic salt, heat influx governed by the relaxation time; Case (2): Short relaxation time, heat influx governed by the thermal resistance at the paramagnetic salt

The two curves of Figure 10 representing equations (17) and (21) give the maximum deviations from ideality, since in each of these cases one of the energy transfer mechanisms was considered perfect. The actual values of $T_f/T_i^{(id)}$ lie below these curves, and in fact must always lie below the lower of the two curves, in the shaded area. The maximum possible deviation from ideal behaviour is thus 8 per cent, the actual deviation being less.

(Note: Similar calculations can be done for constant demagnetization times t_d instead of for constant field reduction rates, simply by substituting in equations (17) and (21) H_i/t_d for β . One finds that for low values of H_i the deviation may rise to 20 per cent, but for $H_i > 15$ kgauss the effect becomes comparable with that for $\beta = \text{constant}$.)

We can now discuss qualitatively what happens during demagnetization. For low values of H_i/T_i we shall have, at the beginning of the demagnetization, case (2); this is because the nuclear spin system can absorb energy from the conduction electrons at a higher rate than the heat influx \dot{Q} from the paramagnetic stage. But as the bulk copper cools the relaxation time gets longer and finally the nuclear spins and conduction electrons 'separate' (this occurs at a few thousandths of a degree according to the conditions), the latter warming to T_i and the former continuing to cool to T_f . This discussion shows that, while in the present experimental arrangement the conduction

electrons do not reach the lowest temperatures attained by the nuclear spins, they do, under favourable conditions, participate in the cooling process. It seems feasible, therefore, to cool bulk copper below 10^{-2} °K by nuclear cooling even without the use of a thermal switch. In view of the difficulty of establishing thermal contact with paramagnetic salts below 10^{-2} °K, this may be a useful method for the study of metals between 10^{-3} °K and 10^{-2} °K.

A number of attempts have been made²² to carry out nuclear demagnetizations with a superconducting heat-switch between the nuclear and the electronic stage, but the results have been disappointing. In some cases no nuclear cooling was observed at all, while in others the warming-up rate of the nuclear spin system was fast, indicating a rather high conduction electron temperature. The first behaviour could be explained by too low a thermal conductivity of the thermal switch at 0.01 °K and in a strong magnetic field, while the second behaviour may be due to heating in the switch by eddy currents or by the normal-superconducting transition. The development of a satisfactory heat-switch and an improvement in the starting conditions H_i/T_i from the present value of about 30 kgauss/deg.K to about 100 kgauss/deg.K (for some other nuclei, e.g. protons, a more modest increase would suffice) seem to be the two main short-term technical aims of nuclear cooling. The solution of these two problems would open the way to the study of ordered nuclear spin systems in thermal equilibrium with their surroundings and to investigations about the behaviour of conduction electrons down to temperatures of 10^{-7} °K.

REFERENCES

1. DEBYE, P. *Ann. Phys.* **81**, 1154 (1926)
2. GIAUQUE, W. F. *J. Amer. chem. Soc.* **49**, 1870 (1927)
3. ABRAGAM, A., and PROCTOR, N. G. *Phys. Rev.* **109**, 1441 (1958)
4. GARRETT, C. G. B. *Magnetic Cooling* (Harvard University Press, Cambridge, Mass., 1954)
5. DE KLERK, D., and STEENLAND, H. J. *Progress in Low Temperature Physics*, Vol. 1, p. 224 (North Holland, Amsterdam, 1955)
6. AMBLER, E., and HUDSON, R. P. *Rep. Progr. Phys.* **18**, 251 (1955)
7. DE KLERK, D. *Encyclopedia of Physics*, Vol. 15, p. 38 (Springer, Berlin, 1956)
8. KURTI, N. *Nuovo Cim.* **6**, Suppl. 3, 1101 (1957)
9. PURCELL, E. M., and POUND, R. V. *Phys. Rev.* **81**, 279 (1959)
10. GORTER, C. J. *Phys. Z.* **35**, 923 (1934)
11. KURTI, N., and SIMON, F. E. *Proc. roy. Soc.* **A149**, 152 (1935)
12. SIMON, F. E. *Le Magnetisme*, Vol. 3, p. 1 (Collection Scientifique, Strasbourg, 1940)
13. KURTI, N., ROBINSON, F. N. H., SIMON, F. E., and SPOHR, D. A. *Nature, Lond.* **178**, 450 (1956)
14. HOBDEN, M. V., and KURTI, N. *Phil. Mag.* **4**, 1092 (1959)
15. KORRINGA, J. *Physica*, **16**, 601 (1950)
16. ANDERSON, A. G., and REDFIELD, A. G. *Proceedings of the 5th International Conference on Low Temperature Physics*, p. 616 (University of Wisconsin Press, Madison, 1958)
17. ROBINSON, F. N. H. *Thesis* (Oxford, 1954)
18. MIEDEMA, A. R., POSTMA, H., VAN DER VLUGT, N. J., and STEENLAND, M. J. *Physica*, **25**, 509 (1959)
19. MENDOZA, E. *Les Phénomènes Cryomagnétiques*, p. 48 (Collège de France, Paris, 1948)
20. ABRAGAM, A. *Yearbook of the Physical Society*, p. 61 (1958)
21. KITTEL, C. *Phys. Rev.* **104**, 1807 (1956)
22. HOBDEN, M. V. *Thesis* (Oxford, 1960)