MAGNETIC COOLING

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CONTENTS

Abstract. After a historical introduction the general principles of the magnetic cooling method are outlined. First, the case of the ideal paramagnetic salt is treated, and this is followed by a discussion of the electric and magnetic interaction effects which cause departures from ideal behaviour, and set a lower limit to the temperatures which can be reached upon adiabatic demagnetization. A description of experimental techniques and procedures includes the subjects of cryostat and magnet design. The methods which have been used to establish the absolute temperature in the range below 1 °K are surveyed and a summary of the results obtained is presented. Apart from their usefulness as coolants and thermometers, paramagnetic salts have intrinsically interesting thermal and magnetic properties, e.g. specific heat anomalies and hysteresis effects, associated with the internal ordering which proceeds as the temperature approaches the absolute zero. These properties are discussed in a separate section; another deals with the properties of other substances in the region below 1 °K—mainly metals and liquid helium. A section is also included on the difficult problems associated with providing adequate thermal insulation for a low temperature system on the one hand, and thermal contact within such a system on the other. The comparatively new developments of cascade demagnetizations and continuous cooling cycles are described. Finally, the principles involved in a recent striking application of the magnetic cooling method, viz. the spatial orientation of atomic nuclei, are outlined.

§ 1. INTRODUCTION

The temperature region below 1 °K constitutes a wide and relatively new field for physical research and may only be entered, effectively, by means of the process of ' magnetic cooling '. It was less than thirty years ago, in 1926, that Debye (1926) and Giauque (1927) suggested, independently of each other, that the reversible temperature effects connected with the magnetization of certain paramagnetic salts might be used for producing temperatures well below those obtainable by means of liquid helium. The first experiments with this method were carried out in 1933 (Giauque and MacDougall 1933) and since then magnetic cooling has become an established cryogenic technique, both for studying the properties of the paramagnetic salts used as cooling agents and for carrying out experiments on other substances in this new temperature region.

Langevin (1905) was the first to point out that changes in the magnetization of paramagnetic substances must generally be accompanied by reversible temperature changes. Langevin's theory was based on the assumption of an assembly of non-interacting magnetic dipoles which, in the absence of an external magnetic field, are pointed at random. Upon application of a magnetic field H the energy of a given dipole depends upon its orientation with respect to the field direction and a statistical equilibrium is produced, depending on the temperature T in accordance with the Boltzmann statistics. It followed from this theory that the magnetic moment M should depend only upon the ratio H/T, and for small values of H/T this leads to Curie's law, according to which the paramagnetic mass susceptibility, that is, the magnetic moment per unit mass divided by H, is inversely proportional to the absolute temperature. (The symbol χ will be used to denote the volume susceptibility i.e. magnetic moment per unit volume I divided by H; χ also obeys Curie's law provided that one may neglect thermal expansion—as is the case at low temperatures.)

If pressure and volume effects are neglected one may write down the expression for the enthalpy E as $E=U-HM$, where U is the internal energy. The condition for dE $(=TdS-MdH)$ to be a total differential gives

$$\left(\frac{\partial T}{\partial H}\right)_S = -\left(\frac{\partial M}{\partial S}\right)_H \qquad \ldots\ldots(1)$$

$$= -\frac{T}{C_H}\left(\frac{\partial M}{\partial T}\right)_H$$

where $C_H = T(\partial S/\partial T)_H$ is the specific heat in constant magnetic field. If $(\partial M/\partial T)_H$ is negative, as is the case with a substance obeying Curie's law, isentropic magnetization will be accompanied by heating and demagnetization by cooling.

On the kinetic picture, any degree of alignment of the dipoles with the magnetic field results in a decrease in potential energy. Since the internal energy is, by definition of an ideal paramagnetic substance, independent of the relative orientation of the dipoles, the energy of magnetization appears in the form of heat. Langevin pointed out that the effect is bound to be small at ordinary temperatures, where $\partial M/\partial T$ is small and the heat capacity large.

The position altered completely with the discovery by Woltjer and Kamerlingh Onnes (1923) that some paramagnetic salts, e.g. gadolinium sulphate, behaved according to Langevin's theory even at the temperature of liquid helium. The conditions for appreciable magnetocaloric effects, namely small specific heats and high values of $\partial M/\partial T$, could now be satisfied and it was the recognition of this fact that led Debye and Giauque to put forward their suggestions for the magnetic cooling method.

In their first experiment Giauque and MacDougall, using gadolinium sulphate, reached 0·53°K, starting from 3·4°K and 8 kilo-oersteds, and subsequently 0·25°K with the same initial field but demagnetizing from 1·5°K. The final temperatures were estimated by measuring the magnetic susceptibility and extrapolating the Curie relationship. Giauque's experiments were followed very soon by those of de Haas, Wiersma and Kramers (1933 a) who used cerium fluoride in their first experiments and reached 0·27°K starting from 1·26°K and 30 kilo-oersteds. Here again the temperature was estimated from the susceptibility, which was determined by a balance method. The final field after demagnetization had to be, therefore, of the order of 1000 oersteds and this was one of the reasons why, in spite of the high initial field, lower temperatures were not reached. Better results were obtained by using cerium and dysprosium ethyl sulphates and potassium chromic alum (de Haas, Wiersma and Kramers 1933 b).

Kurti and Simon (1934) carried out their first adiabatic demagnetization experiments with manganous ammonium sulphate, and by cooling other substances in contact with the paramagnetic salt these authors found some new superconductors with transition points below 1°K (1934, 1935 a, b).

The determination of the absolute temperature scale below 1°K soon became one of the chief preoccupations of workers in this field. The first experiments using a purely thermodynamic method were made by Giauque and MacDougall (1935 a) on gadolinium phosphomolybdate and by Kurti and Simon (1935 c) on ferric ammonium alum, while de Haas and Wiersma (1936) estimated the temperatures reached with caesium titanium alum by a 'magnetic method'. Knowledge of the absolute temperature scale made it possible to obtain more detailed information on the nature and magnitude of the interactions in paramagnetic salts and to discuss the experimental results in the light of theoretical work by Van Vleck (1937) and by Hebb and Purcell (1937).

Experiments on thermal conductivities and relaxation phenomena in paramagnetic salts below 1°K were begun in 1936 (Kurti, Rollin and Simon 1936, Cooke and Hull 1937). The period up to 1939 also saw the first experiments on liquid helium below 1°K (Kurti and Simon 1938 a), extension of the work on the properties of paramagnetic salts (Casimir, de Haas and de Klerk 1939 a, b), on heat transfer and relaxation effects (Shire and Allen 1938, Shire and Barkla 1939), and the investigation of the occurrence of co-operative phenomena in paramagnetic salts at very low temperatures (Kurti, Lainé, Rollin and Simon 1936 a, Kurti, Lainé and Simon 1937).

After 1946, work with magnetic cooling restarted with great intensity and at present more than a dozen laboratories throughout the world are known to be actually employing this technique.

§ 2. COOLING BY ADIABATIC DEMAGNETIZATION

2.1. *Theory*

(*a*) *General.*

The aim of the theory is the prediction of the various thermal and magnetic properties of paramagnetic salts, such as entropy S, and magnetization M, and their correlation with the experimental data. All these functions can be readily derived from the partition function Z of the assembly of paramagnetic ions contained in the salt. The well-known expressions of statistical mechanics give

$$S=k\frac{\partial}{\partial T}(T\log Z) \qquad \ldots\ldots(2)$$

and

$$M=kT\frac{\partial}{\partial H_e}(\log Z) \qquad \ldots\ldots(3)$$

where H_e is the ' external ' magnetic field, i.e. the value which would exist in the absence of the specimen, and k Boltzmann's constant. In the limiting case of very elongated specimens placed parallel to the field H_e is equal to H, the magnetic field within the specimen, which appears in the definition of the susceptibility, i.e. $\chi=I/H$.

If the dipoles can be regarded as identical and independent of each other, the partition function can be written $Z=z^N$ where N is the number of dipoles and z is the partition function for a single dipole. The entropy is then given by $S/R=\partial(T\ln z)/\partial T$ where S/R is a dimensionless quantity, not depending on the quantities of material considered, and R is the gas constant.

In this report we shall only be concerned with salts of the iron group and of the rare earth group. Their paramagnetism is due to the magnetic moment associated with the electrons in the incompletely filled shell of the metallic ion. It is advantageous to begin a discussion of the theory with a treatment of the case of free ions, for which the Russell–Saunders coupling scheme applies. At liquid helium temperatures only the lowest of the multiplets need be considered. It is characterized by a quantum number J which determines the resultant angular momentum of the electrons, and a quantum number M_J which determines the component of the angular momentum along a chosen axis. M_J can only take one of the $2J+1$ discrete values $J, J-1, \ldots -J$, the corresponding components of the magnetic moment along the axis being $gM_J\beta$, where β is the Bohr magneton and g the spectroscopic splitting factor. In zero external field these magnetic substates are degenerate, the partition function $z=2J+1$ and $S/R=\ln 2J+1$.

In a magnetic field H one has

$$z=\sum_{M_J=-J}^{M_J=+J}\exp\left[-gM_J\beta H/kT\right]$$

and by suitable differentiation one obtains

$$M = M_\infty\left[\frac{2J+1}{2J}\coth\frac{2J+1a}{2J} - \frac{1}{2J}\coth\frac{a}{2J}\right] \qquad \ldots\ldots(4)$$

$$S = R\ln(2J+1) + \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH \qquad \ldots\ldots(5)$$

where $M_\infty = NgJ\beta$ is the saturation moment. The expression on the right-hand side of equation (4) is the familiar Brillouin function. These functions have been tabulated by Hull and Hull (1941) for $J=1/2$, $3/2$, $5/2$, by Giauque, Stout, Egan and Clark (1941) for $J=7/2$, and by Schmid and Smart (1954) for $J=1/2$, $1, \ldots,$ $9/2$. Although they correspond to the cases of completely free ions, it turns out that they are of use for calculating the entropy of paramagnetic salts used in the magnetic cooling process under the starting conditions, i.e. at temperatures of about 1°K, if the appropriate quantum number is used for J—see § 2.1 (*b*).

For the majority of salts used in the magnetic cooling process, the lattice entropy is quite negligible compared with the 'magnetic entropy' even at the initial temperature, which nowadays is usually about 1°K. Hence a description of the process which equates the increase of magnetic entropy to the decrease of thermal entropy of the lattice no longer applies. One must rather view absolute temperature in its statistical aspect, i.e. as a parameter in the partition function determining the distribution among the different states. Then upon adiabatic demagnetization the temperature will fall until the various internal constraining forces produce the same degree of order in zero field as that produced by the external magnetic field at the starting temperature. Two different types of constraining forces together bring about the reduction in entropy in zero field; one is the effect of the electric field due to other ions distributed on crystal sites round the paramagnetic ion, and the other the effect of direct interactions between the magnetic ions. Two curves, ABO and ACO, have been drawn in figure 1 to represent the behaviour of two hypothetical salts, showing an entropy reduction to R ln 2 due to the effect of the crystalline electric field (see § 2.1 (*c*)), followed by the further reduction due to interactions. The magnitude of the interactions is smaller in the salt represented by ABO. The numbers marked along the 1°K ordinate give typical values of the magnetic field in kilo-oersteds (corresponding roughly to the case of $J=5/2$) which must be applied at that temperature in order to obtain the corresponding entropy reductions.

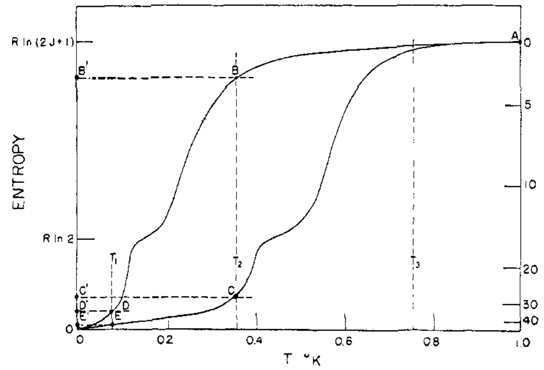

Figure 1. Entropy as a function of temperature for two hypothetical paramagnetic salts.

With a given magnetic field it is possible to reach a lower temperature with the salt wherein the interactions are smaller. Furthermore, since this salt has a bigger heat content ($\int TdS$) in the low temperature range T_1 to T_2—compare areas BB′D′D and CC′E′E—it would be possible to *maintain* the temperature for a longer period of time. Similarly, the salt represented by curve ACO would be most suitable for work in the range T_2 to T_3, where its entropy is falling most rapidly and where its specific heat is consequently greatest.

(*b*) *Effect of crystalline electric field.*

In the salts most commonly used each metallic ion is surrounded by six water molecules situated at the corners of an octahedron. When this octahedron is regular the electric field at the central ion has cubic symmetry; it may be distorted, however, to give components of lower symmetry. Bethe (1929) was the first to treat the problem of the splitting of a degenerate level through the effect of this electric field and showed how the splitting depends upon the nature of the term and the symmetry of the electric field. The theory has been applied in detail to various paramagnetic salts by Kramers (1930), Penney and Schlapp (1932), Van Vleck and Penney (1934) and, with particular respect to the magnetic cooling method, by Hebb and Purcell (1937).

The splittings may be quite small ($\sim 0{\cdot}1\ \mathrm{cm}^{-1}$) in the case of ions in S states, e.g. Fe^{3+}, or they may be very large ($\sim 1000\ \mathrm{cm}^{-1}$) in cases where there is a resultant orbital angular momentum, e.g. Cr^{3+} and Co^{2+}. In either case, however, the result usually is that we have a low-lying group of levels so well separated in energy from higher levels that they only are populated at the temperatures used at the start of adiabatic demagnetization experiments. This low-lying group of levels cannot usually be characterized by the same quantum numbers which were used to specify states of the free ion, and their behaviour magnetically may be quite complicated.

When the splitting pattern is known, the task of writing down the partition function is fairly simple. To illustrate the general principles of the method, one may take the historically interesting case of gadolinium nitrobenzene sulphonate, which was studied experimentally by Giauque and MacDougall (1935 a) and MacDougall and Giauque (1936) and discussed theoretically by Hebb and Purcell (1937). If one assumes a field of cubic symmetry, the ^{8}S level of the gadolinium ion splits into two doubly degenerate levels and one quadruply degenerate level lying between.† The spacings between the quadruplet and the two doublets are in the ratio 5:3 but since theory does not predict the position of the spacings the partition function in zero magnetic field can be either,

$$z_c = 2(1+2\exp(-3\delta/8kT)+\exp(-\delta/kT)) \qquad \ldots\ldots(6a)$$

or

$$z_c = 2(1+2\exp(-5\delta/8kT)+\exp(-\delta/kT)) \qquad \ldots\ldots(6b)$$

where δ is the overall energy separation. Hebb and Purcell found that the experimentally determined entropy–temperature curve agrees better with the theoretical curve calculated from (6*a*); δ/k was found to be 1·4 degrees.

In order to calculate the susceptibility it is necessary to know how the levels split when a small magnetic field is applied. Hebb and Purcell summarize this

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† Paramagnetic resonance experiments on other gadolinium salts (Bleaney, Elliott Scovil and Trenam 1951, Trenam 1953, Bogle and Heine 1954) indicate, however, that the correct splitting pattern is one of four doublets.

information by giving the magnetic moment matrix in a representation which makes the energy diagonal. The elements of this matrix are substituted into the standard formula for the magnetic susceptibility (see for example Van Vleck 1932). They find $\chi = \gamma\tau/3T$ where $\tau = Ng^2\beta^2 J(J+1)/k$ with $g=2$, $J=S=7/2$ and N the number of ions per cm^3; γ is a function of δ/kT which we shall not quote here.

Until about 1946, adiabatic demagnetization experiments were the most important source of information for these small energy splittings occurring in paramagnetic salts. Recently, however, microwave spectroscopy has provided a much more powerful tool for determining splitting patterns and splitting constants, and for predicting entropy reductions caused by the crystalline electric field. It is all the more useful in that it allows one to examine whether, as is often the case, there are different sets of ions in the unit cell of the crystal which have different axes of symmetry and different splitting patterns. The results of microwave spectroscopy are usually expressed by giving the values of certain constants in a ' spin Hamiltonian' (Abragam and Pryce 1951) which is a function of an angular momentum operator S. The value of S is obtained by setting $2S+1$ equal to the total number of levels (including degeneracy) in the lowest-lying group, and may or may not be the same as the actual value of the electron spin of the free ion. The energies of the states of the paramagnetic ion (as a function of an externally applied magnetic field) are the same as the eigenvalues of the spin-Hamiltonian. An excellent detailed discussion, including a derivation of the spin-Hamiltonian in many special cases, has been given recently by Bleaney and Stevens (1953). Here it will suffice to quote one example by way of illustration, namely that of the Cr^{3+} ion ($L=3$, $S=3/2$) in the alums. The crystalline electric field has predominantly cubic symmetry and splits the seven-fold orbital level into two triplets, and a singlet lying about 10^4 cm^{-1} below the nearest triplet. Under these conditions there is very little contribution to the susceptibility from orbital motion (the orbital angular momentum is said to be ' quenched ') and the g-value is only very slightly less that the free spin value of 2. The four-fold spin degeneracy of the lowest orbital level is removed, however, by the combined action of spin–orbit coupling and a smaller component of the crystalline electric field possessing trigonal symmetry, and there result two doublets separated in energy by an amount δ. The spin-Hamiltonian is given as

$$g\beta\ \mathbf{H.S} + D(S_z^2 - 5/4) \text{ with } S=3/2.$$

The second term describes the splitting of the spin levels due to the crystalline field and one can see that $\delta = D\{(3/2)^2-(1/2)^2\}=2D$. Here the z-axis is the trigonal axis of the crystalline electric field. It should be noted that in the alums there are four sets of non-equivalent ions, each set having its z-axis in one of the four directions corresponding to the body diagonals of the basic cube.

In general the spin-Hamiltonian is somewhat more complicated; for example, the g-factor may be anisotropic, or the crystal field may have lower symmetry so that terms in S_x^2 and S_y^2 have to be introduced. However, one can always construct the energy matrix from it and, in principle, obtain the partition function and hence derive expressions for S/R and χ.

In adiabatic demagnetization experiments one is generally interested in (*a*) the expression for the entropy of the specimen under the initial magnetizing conditions at temperatures around 1°K, and (*b*) the expressions for the entropy and susceptibility in zero field at temperatures below 1°K. The former usually involves computing a small correction to be applied to the expression given in equation (5). It has been done for the important example of Cr^{3+} in the alums for the case of a single crystal with the magnetic field applied along the direction of a cube edge, i.e. when the magnetic field makes the same angle with each of the trigonal axes of the four sets of ions (Hudson 1952) and for the case of a powdered specimen (Daniels and Kurti 1954). The case of copper potassium sulphate in which the Cu^{2+} ion has a slightly anisotropic g-factor has been treated by Garrett (1950 a).

In principle, the expressions for the entropy in zero magnetic field and the susceptibility are obtainable directly from the spin-Hamiltonian. In practice, however, only the values in the higher temperature region turn out to be useful on account of the complicating effects of the direct interactions between ions (discussed in the next section). In the high temperature region the susceptibility may be expressed in a power series in $1/T$ by, for example, first expanding the partition function in the same way. The first term in the expansion gives the Curie constant and the second a contribution to the Curie–Weiss constant Δ, as may be seen by writing the Curie–Weiss law,

$$\chi=\frac{c}{T-\Delta}=\frac{c}{T}+\frac{c\Delta}{T^2}+\ldots.$$

It should be pointed out that in substances having an isotropic g-factor the average value of Δ vanishes for powdered specimens, and also for single crystals of substances like the alums where the non-equivalent ions have their axes arranged in cubic symmetry (Penney and Schlapp 1932). For example, the first part of the expansion for the susceptibility of the Cr^{3+} ion in the alums is, considering only the effect of the crystalline electric field,

$$\chi=\frac{5N\beta^2}{k}\left\{\frac{1}{T}-\frac{\delta^2}{30T^3}\right\}.$$

(c) *Interaction of magnetic ions.*

It follows from a theorem by Kramers (1930) that for paramagnetic ions with an odd number of electrons (this condition is fulfilled by all those used in magnetic cooling) the crystalline electric field cannot entirely remove the degeneracy. The remaining (two-fold) degeneracy can only be removed by interaction between the ions themselves. The forces concerned here may be either of the magnetic dipole type, the exchange type, or both. One now has to deal with an N-body problem, N being the number of paramagnetic ions in the crystal as a whole, and there will be a band of 2^N energy levels. The crystal in its lowest state could be either ferromagnetic with all the dipoles pointing in the same direction, thus giving rise to a spontaneous magnetization, or antiferromagnetic, consisting of some ordered array of mutually compensating dipoles. The behaviour of paramagnetic salts in this co-operative region is not too well understood; discussion on this aspect will be postponed until § 4.5. For the present it is sufficient to say qualitatively that in most cases the final reduction of the entropy to zero will be brought about by a co-operative action of the dipoles and will be steeper than is the case for the effect of the crystalline field. This means that the temperature remains substantially constant over a considerable range of entropy or, in other words, for a wide range of values of the magnetic field used for the adiabatic demagnetization process.

The effect of these interactions in the higher temperature region is quite well understood, however, and it is this aspect with which this section will be mainly concerned. There are three main approaches. In the Lorentz method one represents the magnetic interaction of the dipoles by a local field nI, where $n=4\pi/3$ for a cubic lattice. This approach is formally the same as the Weiss molecular field treatment of ferromagnetism, and predicts ferromagnetism at low temperatures except for the case of a spherical specimen. As was pointed out by Onsager (1936) however, the Lorentz theory applies to a system of induced, as distinct from permanent, dipoles. Onsager, using classical magnetostatics and treating the surroundings of a given dipole as a continuum, attempted a more rigorous approach. The two formulae become identical at small values of the susceptibility but the Onsager theory predicts that the susceptibility will only become infinite at the absolute zero. Pirenne (1949), however, has shown how it may be logically modified to allow the existence of a Curie point.

The results which are frequently used are the modifications which these theories make to the susceptibility. Denoting by χ_0 the susceptibility calculated with allowance for the effects of the crystalline electric field alone, the following expressions are obtained for the susceptibility with dipole interaction:

$$\text{Lorentz}\ \chi=\chi_0\left(1-\frac{4\pi\chi_0}{3}\right)^{-1} \qquad \ldots\ldots(7a)$$

$$\text{Onsager}\ \chi=\chi_0\left[\frac{3}{4}-\frac{3}{16\pi\chi_0}+\left(\frac{9}{16}+\frac{3}{32\pi\chi_0}+\frac{9}{256\pi^2\chi^2_0}\right)^{\frac{1}{2}}\right] \ldots\ldots(7b)$$

Both of these approaches are phenomenological, in contrast to the third which is the quantum mechanical method developed by Waller (1936) and in particular by Van Vleck (1937). Van Vleck takes as the Hamiltonian of the system,

$$\mathcal{H}=\sum_i \Phi_i+\sum_{j>i} W_{ij}-H_\mathrm{e}\sum_i(\mu_i)_z \qquad \ldots\ldots(8)$$

where μ_i is the magnetic moment of the ith ion, Φ_i the energy due to the crystalline electric field and H_e an external field applied along the z axis. The term W_{ij} represents the interactions between two ions

$$W_{ij}=\frac{1}{r_{ij}^{\ 3}}\left[\boldsymbol{\mu}_i.\boldsymbol{\mu}_j-\frac{3(\boldsymbol{\mu}_i.\mathbf{r}_{ij})(\boldsymbol{\mu}_j.\mathbf{r}_{ij})}{r_{ij}^{\ 2}}\right]+V_i \qquad \ldots\ldots(9)$$

where r_{ij} is the distance between ions i and j. The first term is the familiar expression for the potential energy of two dipoles, the second is an exchange term. Van Vleck takes $V_{ij}=v_{ij}(\boldsymbol{\mu}_i.\boldsymbol{\mu}_j)$, where v_{ij} is a constant given in formula (8) of Van Vleck's paper, so that the energy due to exchange is proportional to the cosine of the angle between the individual dipoles. This is referred to as isotropic exchange. The essence of the method is to write down the partition function and to expand it in a power series in $1/T$, obtaining

$$Z=\text{Spur}\left\{1-\frac{\mathcal{H}}{kT}+\frac{\mathcal{H}^2}{2k^2T^2}-\ldots\right\} \qquad \ldots\ldots(10)$$

On account of the theorem concerning the invariance of the spur of a matrix, the above spurs may be evaluated in any representation and it is not necessary to attempt to solve the eigenvalue problem. Herein lies the advantage of the method, which has been much used subsequently in the theory of paramagnetism (see for example Bleaney 1950 a, Cooke, Duffus and Wolf 1953, Daniels, 1953 a, Garrett 1950 b).

Van Vleck's theory gives the following results at high temperatures (i.e. $T \gg \tau$)

$$\frac{S_0-S}{R}=\frac{Q\tau^2}{12T^2} \qquad \ldots\ldots(11)$$

where $\tau = Ng\beta^2 J(J+1)/k, \qquad S_0 = R \log (2J+1)$

and $Q=\frac{1}{N^2}\sum_i r_{ij}^{-6}(2+v_{ij}^2).$

Q is a factor which depends upon the type of crystal lattice and which Van Vleck evaluates for simple, body-centred and face-centred cubic structures. He also finds that to this approximation the above entropy reduction and that due to the effect of the crystal field are additive, a fact which is made use of in computing the correction to the ' Brillouin entropy ' for magnetization at 1°K (see, for example, Gardner and Kurti 1954). The expression for the susceptibility, neglecting exchange, is given by

$$\chi=\chi_0(1-\frac{4\pi}{3}\chi_0+12\eta\chi_0^2)^{-1} \qquad \ldots\ldots(7c)$$

where $\eta=\frac{Q}{12}\left[1+\frac{3}{8J(J+1)}\right].$

The effect of isotropic exchange on the high temperature behaviour of χ can be included as a Curie–Weiss Δ, which is simply related to the constant a in the expression for the entropy, $(S_0-S)/R = a/RT^2$, by the relation $2a/R\Delta^2 = 3/4f$, where $2f$ is the number of nearest neighbours. It was formerly thought that exchange effects in the dilute salts used in this field would be negligible on account of the comparatively large distance between ions. The theory of indirect, or anisotropic, exchange [' superexchange '] however, shows that it is possible for exchange to take place through intervening atoms (Kramers 1934). Opechowski (1948) considered a general type of exchange interaction and showed that in this case also a relation exists between Δ and a. This relation depends on the interaction constants which, unfortunately, are not easily calculated. One important conclusion drawn is that, whereas the contributions to the $1/T^2$ term in the entropy from dipole–dipole interaction and isotropic exchange are additive, this is not so for anisotropic exchange. The theory has been extended further by Daniels (1953 a) to cover the case of ions having anisotropic g-factors.

(*d*) *Hyperfine splitting.*

The pattern of the energy levels for a magnetic ion may be further modified if its nucleus possesses a spin. There are two types of interaction which can cause this; the interaction between the nuclear magnetic moment and the magnetic field caused by the electrons in the unfilled shell, and the interaction between the nuclear electric quadrupole moment and the gradient of the electric field at the nucleus. A further source of entropy associated with the $2I+1$ magnetic substates of the nucleus is provided, the overall splitting of which is usually of the order of 0·01 degree.

The theory of hyperfine structure in paramagnetic salts has been given by Abragam and Pryce (1951), and the effect can be described by adding terms to the spin Hamiltonian. For substances where the crystalline electric field has axial symmetry the extra terms are

$$AS_zI_z+B(S_xI_x+S_yI_y)+Q[I_z^2-\tfrac{1}{3}I(I+1)]. \qquad \ldots\ldots(12)$$

The constants A and B describe the splitting due to the magnetic interaction and Q describes that due to the quadrupole interaction. These constants may be determined from paramagnetic resonance experiments. The pattern of the energy levels due to these interactions has been discussed in a paper by Bleaney (1951 a) to which we shall again refer in § 8. The effect of the hyperfine splitting is to give rise to a Schottky-type specific-heat anomaly, wherein $C \propto 1/T^2$ at 'high' temperatures. The constant of proportionality has been derived by Bleaney (1950 a) who also showed that at such temperatures the hyperfine splitting has no effect on the susceptibility. Furthermore, the contributions to both entropy and susceptibility from hyperfine splitting and direct interactions between ions are additive as far as the term in $1/T^3$ (Daniels 1953 a).

2.2. *Experimental*

The salt specimen, usually spheroidal in shape (see § 3.1), is enclosed in a vacuum space the outer wall of which is in contact with liquid helium. The temperature of the latter is reduced as far as possible by pumping, and temperatures in the range 0·9°–1·3°K are usual.

The magnetic cooling process comprises three stages: (i) The salt is magnetized isothermally, the heat of magnetization being conducted to the liquid helium by 'exchange gas' (helium at a pressure of 10^{-3}–10^{-2} mm Hg) introduced into the vacuum space. (ii) When, after a suitable time interval, the heat transfer is complete, the salt is thermally isolated from its surroundings by pumping off the exchange gas. (iii) The magnet is now de-energized and during this isentropic process the temperature of the salt falls. The specimen thereupon acts as its own 'getter' in removing traces of residual gas by condensation. The success of the adiabatic demagnetization process depends upon the degree to which the salt is thermally isolated from its surroundings. It must be suspended or supported by materials of low thermal conductivity, and room-temperature radiation must be efficiently screened off.

Figures 2 and 3 show two typical cryostats; the essential features are common to both but there are differences in detail. The paramagnetic salt may be in the form of a single crystal, a dense compress of small crystallites, or a loose powder held in a glass or plastic container. By compressing powdered salt under a pressure of a few tons per square inch a specimen is obtained of a density very little less than that of the crystal, and which may, with care, be shaped as desired. The specimen is either suspended by fine nylon fibres in a cylindrical frame which slides into the vacuum case, or is supported rigidly by a thin-walled tube of glass or some other good thermal insulator. Care must be taken to avoid loss of the water-of-crystallization of hydrated salts; for instance the vacuum chamber must never be evacuated unless the specimen is first cooled well below 0°C. Further experimental details relevant to thermal insulation will be given in § 5.

The determination of the susceptibility, which is required for both the study of magnetic properties and the indication and measurement of temperature (see § 3), is usually made by an induction method (see, however, the balance method used by de Haas, Wiersma and Kramers 1933 b). A coil of a few hundred to a few thousand turns of thin copper wire, immersed in liquid helium or liquid hydrogen so that its electrical resistance is small and constant, surrounds the specimen. Its self-

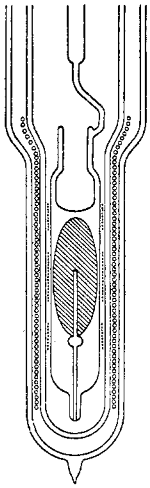

Figure 2. Demagnetization cryostat (*after* Casimir, de Haas and de Klerk 1939 a). An ellipsoidal salt specimen is shown mounted on a glass pillar within a vacuum jacket. This is surrounded by two concentric dewar vessels, the inner one containing liquid helium and the outer one liquid hydrogen (or nitrogen). The secondary coil of the mutual inductance is wound on to the vacuum jacket and the primary on to the ' tail ' of the helium dewar.

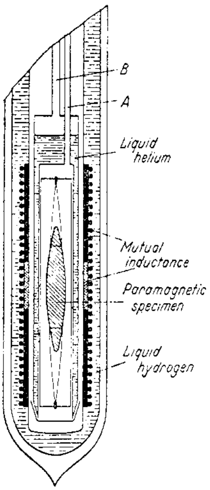

Figure 3. Demagnetization cryostat (*after* Kurti 1952). The mutual inductance is wound on to a former which fits over the vacuum case and is surrounded by liquid hydrogen. The liquid helium cryostat is pumped through tube B. Exchange gas may be admitted and removed from the salt space through tube A.

inductance, or more commonly its mutual inductance relative to a second concentric coil, being a linear function of the susceptibility, serves for this measurement. Since the change in mutual inductance due to the change of magnetic susceptibility is small, it is customary to reduce the total circuit mutual inductance by means of compensating coils. The susceptibility may be determined ballistically by observing the deflection of a ballistic galvanometer in series with the secondary coils when the current in the primary coils is reversed. Alternatively, it may be measured by an a.c. method, e.g. a Hartshorn mutual inductance bridge. The frequency is normally within the range 50–500 c/s and a vibration galvanometer or a cathode-ray oscilloscope (in either case preceded by an amplifier) serves as a null detector (Casimir, de Haas and de Klerk 1939 a, Benzie and Cooke 1950 a[†]).

Compared with the ballistic method, the a.c. method has the advantages of high sensitivity and of being capable of adaptation for automatic recording. On the other hand, at very low temperatures, where relaxation and hysteresis effects become important, the frequency dependence of the susceptibility and the heating effect caused by the alternating primary field are a disadvantage from which the ballistic method does not suffer. The measuring fields are, in both methods, of the order of a few oersteds and may be reduced in favourable cases to a few tenths of an oersted.

The entropy reductions for any given H/T for ideal paramagnetic salts may be obtained from the tabulated values referred to at the end of § 2.1 (*a*) (as mentioned in § 2.1 (*b*), departure from ideal behaviour due to crystalline field effects will

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[†] *Note added in proof.* See also R. A. Erickson, L. D. Roberts and J. W. T. Dabbs, *Rev. Sci. Instrum.*, 1954, **25,** 1178.

necessitate a small correction to the entropy reduction so calculated). In order to enter the region where co-operative effects may be investigated it is essential to reduce the entropy to a value below $R \ln 2$. It is clear that with the limited magnetic fields usually at one's disposal it is of great advantage to reduce the starting temperature as much as possible, since this is equivalent to a proportionate increase of the magnetic field. The temperature that can be reached by pumping on liquid helium is mainly determined by the film of He II creeping up the walls of the container, and is higher than one could achieve if liquid helium were a normal liquid (Rollin 1936, Kurti, Rollin, and Simon, 1936, Rollin and Simon 1939). It has been shown, however, that by suitable design it is possible to reach about 0·8°K even with pumps of relatively small speed, such as 2–3 litres per second (Blaisse, Cooke and Hull 1939, Cooke and Hull 1939, Lasarew and Esselson 1941, Ambler and Kurti 1952 a). Taking 1°K as a round figure for the starting temperature, one may see from the tables that a field of 10–15 kilo-oersteds should bring one into the region of the co-operative anomaly. But if one wants to remove the magnetic entropy to within a few per cent of its full value much higher fields are required, e.g. 4×10^4 oersted deg^{-1} would be necessary to get into a temperature region corresponding to room temperature for the case of ordinary ferromagnetic metals such as iron or nickel.

The simplest way of increasing the field obtainable from a given piece of equipment is to reduce the size of that part of the cryogenic apparatus that has to be brought into the magnetic field. Now to ensure tolerable warm-up rates, the diameter of the salt specimen should not be less than about 5 mm and this would bring to about 25 mm the overall outside diameter of the apparatus, which usually consists of two or three layers of liquefied gases with intervening vacuum spaces. Somewhat larger cryostats are, however, more convenient to assemble, and in most demagnetization apparatus a compromise is reached with outside diameters of 35–50 mm permitting samples of 15–25 mm diameter to be used.

Fields of 10–15 kilo-oersteds in pole gaps of up to 40–50 mm can be obtained from medium-sized laboratory electromagnets equipped with cooled windings, and difficulties arise only when fields of about 20 kilo-oersteds are required. There are two ways of producing fields of this intensity and extension: either with electromagnets having large diameter cores and tapered pole pieces (e.g. the electromagnets of the Kamerlingh Onnes Laboratory in Leiden and of the Bellevue Laboratory near Paris) or with efficiently cooled high-powered iron-free solenoids. This latter method has been considerably developed in recent years, due mainly to the work of Cockcroft (1928), Bitter (1936), Ashmead (1944) and Tsai (1947), and the technique of winding such coils has received much attention (Gaume 1946, Daniels 1950, Daniels 1953 b). Solenoids consuming 1000 kw or more and producing fields of 40–50 kilo-oersteds for considerable periods of time have been in operation in the last few years. The following rough and ready formula (Hudson 1949 a) is useful for obtaining a conservative estimate of the field produced by an iron-free solenoid: $H(\text{kilo-oersted}) = 4(W/D)^{1/2}$. Here W is the power consumed in kilowatts, D the internal diameter of the solenoid in centimetres and it is assumed that the shape of the coil is not far off optimum, i.e. that both the outside diameter and the length are between $3D$ and $5D$. The temperature rise of the copper conductor has been taken into account and a space factor consistent with efficient cooling has been allowed for.

Solenoids with liquid air or liquid nitrogen cooling have also been used (Kurti 1933, Collins 1950). They have the advantage of lightness, simple construction, and a reduction of the necessary power by about a factor of six, corresponding to the reduced electrical resistivity. If the field need not be kept on for long periods the consumption of liquid nitrogen (about 1 litre/min for 10 kilo-oersteds in a coil of 50 mm inside diameter) is not prohibitive.

The relative merits of iron magnets and iron-free solenoids from the point of view of magnetic cooling experiments (leaving aside questions of capital cost, running cost, etc.) may be summarized as follows. Iron magnets have the advantage that, by virtue of their relatively high self-inductance in their pre-saturation range, they act as chokes and reduce the ripple which is a troublesome feature of d.c. supplies provided by rectifiers or motor generators; with solenoids, separate chokes or smoothing circuits may have to be installed. As to ease of handling, small iron magnets (say up to two tons) can be almost as easily moved from the cryostat as solenoids; with large iron magnets one has to move the cryostat (de Haas and Wiersma 1933, Kurti, Lainé, Rollin and Simon 1936 b, de Klerk and Hudson 1954).

The main advantage of working with an iron-free solenoid lies in the wider possibilities it offers for measuring the magnetization. With the inductance method it is relatively easy to determine the differential susceptibility in an external field, and if measuring field and external field are parallel to each other the total magnetic moment can be obtained by integration. It was mainly for this reason that Giauque and his collaborators did all their experiments with an iron-free solenoid. With an iron magnet the magnetic moment can of course be measured directly by means of a balance method but because of its other shortcomings this technique has not been used since the first experiments of de Haas and Wiersma.

The difficulty of measuring the susceptibility by an inductance method in the presence of an iron magnet lies in the influence of the iron on the self or mutual inductance, especially as this effect varies with the degree of saturation of the pole-pieces. Casimir and de Haas (1940), however, succeeded in determining the magnetization by means of a mutual inductance set at right angles to the external field produced by an iron-magnet. If I and H_e are the magnetization and external field respectively, and χ the differential susceptibility measured at right angles, we have for an isotropic, spherical specimen $I=\chi H_e$. For ellipsoidal specimens the anisotropy of the demagnetizing factor necessitates a correction.

Many important experimental details of magnetic cooling technique have been omitted from this section; they will be mentioned in later sections under the appropriate topics. A detailed description of the technique practised in Oxford has been given by Hull (1947), and of a recent magnetic cooling installation at the U.S. National Bureau of Standards by de Klerk and Hudson (1954).

§ 3. The Determination of Temperatures below 1°K

3.1. *The 'Magnetic Scale'*

The determination of temperatures below 1°K presents unusual difficulties in that all the conventional methods fail. For example, gas thermometry is inapplicable owing to the rapid decrease of the vapour pressure of helium, which by 0·5°K is of the order of 10^{-5} mm Hg. The problem is to find a suitable thermometric parameter, i.e. any easily measured physical property which is a single-valued and sufficiently rapidly varying function of the absolute temperature. The magnetic susceptibility χ of the actual salt used for the cooling satisfies this condition over an appreciable temperature range and is most commonly used. Since in the helium range χ obeys Curie's law, i.e. is inversely proportional to the absolute temperature T, it is logical to define a 'Curie' (or magnetic) scale of temperature T^* by extrapolating Curie's law into the demagnetization range.

A magnetic temperature is defined by using the value of the 'external' susceptibility, i.e. $\chi_e = I/H_e = c/T^*$, where c is the Curie constant per cm^3. On account of demagnetizing effects we obtain different scales for differently shaped specimens, and it was proposed by Kurti and Simon (1938 b) to reduce them all to that appropriate to a spherically shaped specimen, $T^{\circledast}$, by means of the relation $T^{\circledast} = T^* + \beta$ where $\beta = (n_s - n)c$, n_s being the demagnetizing coefficient for a sphere ($=4\pi/3$) and n that for the specimen actually used. It is essential that specimens should always be ellipsoidal in shape so that n can be calculated. The proposal to correct the various magnetic scales to the particular one for a sphere was not made arbitrarily but has a special advantage.

One may define an 'ideal susceptibility', χ_0, as the ratio of the magnetic moment to the field actually *acting upon the ions*, $\chi_0 = M/H_{\text{loc,}}$ and this quantity should obey Curie's law to a lower temperature than does χ_e. In the higher temperature region, one may accurately describe the effect of dipole interactions by the Lorentz internal field; for a sphere, the Lorentz and demagnetizing fields cancel and $H_{\text{loc,}} = H_e$, $\chi_0 = \chi_e$, and thus $T^{\circledast}$ should be a better approximation to T than any other magnetic temperature.

In fact, in the absence of appreciable Stark splitting $T^{\circledast}$ should be equal to the absolute temperature in the range of validity of the Lorentz treatment. (Some salts actually obey a Curie–Weiss law, $\chi = c/(T - \Delta)$ and Δ may be determined by careful calibration in the liquid helium range or from measurements of the field dependence of the adiabatic susceptibility (Garrett 1950 a).)

For the purpose of correlating results obtained for differently shaped specimens the proposal of Kurti and Simon remains of use, of course, even outside the range where $T^{\circledast} = T$. They pointed out, however, that at the very lowest temperatures where co-operative effects occur, the values of $T^{\circledast}$ computed from the values of T^* obtained with differently shaped specimens would not necessarily agree, and hence in quoting results the value of β used should always be given. The experiments of Steenland, de Klerk, Potters and Gorter (1951) showed this to be the case.

3.2. *Calorimetric Methods*

From the Kelvin definition of thermodynamic temperature, $T = dQ/dS$, it follows that absolute temperatures may be obtained directly if the change in entropy corresponding to the introduction of a known amount of heat can be determined. Using the magnetic temperature T^* as a thermometric parameter one may write $T = (dQ/dT^*)/(dS/dT^*)$. The (S, T^*) relation is obtained by measuring T^* immediately after each of many demagnetizations, the corresponding entropies being calculated from the initial conditions of H and T. (See § 2.1 (*a*)). It is the determination of the (Q, T^*) relation which presents the greatest problem. Ideally, one simply introduces a uniformly distributed known amount of heat dQ and measures the resulting change in T^*, i.e. the experiments comprise, essentially, measurement of a specific heat C^*, defined by

$$C^* = dQ/dT^* = T(dS/dT^*). \qquad \ldots\ldots(13)$$

In practice it is difficult to supply heat uniformly to the sample and, especially, to make adequate correction for the effects of stray heating. The latter is always a surface effect and at very low temperatures, where the thermal diffusivity becomes very small, a pronounced temperature gradient will persist across the sample (Kurti and Simon 1938 c, Cooke and Hull 1942). The measured susceptibility is then a mean value, so that the derived value of T^* is not unique and the resulting (Q, T^*) curve cannot be correlated with the known (S, T^*) relation. One ingenious method of dealing with this problem has been discussed by Daniels and Kurti (1954). It relies on the fact that in powder specimens at very low temperatures the thermal diffusivity is so extremely small that, to a good approximation, the state of affairs may be described by the following simple model. There are two distinct zones (i) a core which, under the influence of background heating alone, remains at constant temperature, and (ii) a surrounding shell at a much higher, but also constant, temperature. As the stray heat influx continues the boundary between the zones moves steadily inwards, and if the further assumption is made that the deliberately introduced heat has a noticeable effect on the core alone, the analysis of the observations is tractable.

As far as deliberately introducing heat into the salt specimen is concerned the most obvious method is that of passing current through a resistance which is in good contact with the salt. The method fails below a few tenths of a degree Kelvin through deterioration in the quality of this contact. An elegant method introduced by Kurti and Simon (Simon 1935, Kurti and Simon 1935 c) is to irradiate the specimen with gamma rays. A good degree of uniformity may be achieved by symmetrically disposing a number of sources at a suitable distance, or by automatically rotating two sources, set equidistant from the specimen and diametrically opposite each other. If the absorption remains independent of temperature the rate of heating will remain constant, and the source may be calibrated by continuing the measurements into the ' high temperature ' region where the relation between T^* and T is known already (see §§ 3.1 and 3.4).

At very low temperatures, in the region of the susceptibility maximum, the a.c. susceptibility becomes complex (Giauque and MacDougall 1935 b) thus one may write

$$\chi = \chi' - i\chi'' \qquad \ldots\ldots(14)$$

and it may be shown that the application of an alternating magnetic field dissipates energy in the salt at a rate given by $dW/dt = \frac{1}{2}h_0^2\omega\chi''$ where h_0 is the peak-value of the a.c. field, ω is the angular frequency and χ'' the loss-component of the susceptibility (Casimir, de Haas and de Klerk 1939 b). For zero stray heat influx, we have $dQ = dU - dW = 0$ hence $C^* = dU/dT^* = dW/dT^*$. While χ'' is increasing with decreasing entropy the a.c. heating tends to restore homogeneity of temperature, upset by stray heating effects, and the degree of success of this method depends upon the degree to which this compensation is provided. (If χ'' also shows a maximum at a certain entropy the method cannot be used at lower entropies, since inhomogeneities would then be magnified.)

Yet another method of doing work upon the substance is by executing a large number of hysteresis cycles during ballistic measurements. The area of a hysteresis loop is a measure of the energy dissipation per cycle (Steenland, de Klerk and Gorter 1949).

In practically all cases where a given substance has been investigated in the same entropy range by the two calorimetric methods, gamma-ray and χ'' heating (this has never been done, unfortunately, in any one laboratory), the χ'' method has given much lower temperature values. It has been suggested (de Klerk, Steenland

and Gorter 1948, 1949) that the discrepancies may be due to unreliability of a gamma-ray source as a constant-rate heat supply when applied to a paramagnetic salt at very low temperatures. To particularize, the absorbed energy might be, in part, stored elsewhere in the crystal rather than all being communicated at once as heat to the spin system. This question has been discussed at some length by Platzman (1953) who concludes that a partial inhibition of the final conversion of the absolute energy to heat is entirely possible, especially through ‘ permanent ’ dissociation of molecules. Kurti and Simon (1953) have commented on Platzman's analysis, pointing out that the experimental evidence is against the possibility of such effects being serious for the temperature range and substances investigated so far. Finally, it should be mentioned that the loss-component χ'' and the remanence may also be used as thermometric parameters (de Klerk, Steenland and Gorter 1949) as well as for introducing heat. In the final analysis, the accuracy of all types of low-temperature calorimetric determination depends upon the extent to which the stray heat influx may be reduced by improvement in design of apparatus (see § 5.1).

3.3. *Magnetic Methods*

The temperature change upon isentropic application of a magnetic field can be calculated from equation (1), and for a finite change,

$$[\Delta T]_S = -\int_H^{H'} \left(\frac{\partial M}{\partial S}\right)_H dH. \qquad \ldots\ldots(15)$$

By obtaining a lattice of (M, H) curves at various entropies ranging between ‘ high ’ known temperatures and low unknown temperatures, the latter may be determined from this relation. This is essentially the method proposed by Giauque (Giauque 1936, 1953, Giauque and MacDougall 1938). Since the value of the absolute temperature being determined is very much less than 1°K, and the high known temperature is about 1°K, the former enters as a small difference between two relatively large quantities. Furthermore the derivation of ΔT can be seen from equation (1) to be a rather involved procedure, so that extremely accurate magnetic measurements are necessary to achieve a moderate degree of accuracy in the absolute temperature. Since at least comparable accuracy can be obtained by simpler methods, the above procedure has not been used extensively.

It is an important point, however, that this method is available and that absolute temperature determinations may be made without the necessity of deliberately introducing heat into the salt specimen. The method has recently been discussed at length (Giauque 1953) and its merits *vis-à-vis* the calorimetric procedure outlined.

The above type of experiment permits the determination of absolute temperatures in both ‘ zero ’ and finite magnetic field. A second approach to the latter was described by de Haas and Wiersma (1936) which makes use of the fact that the magnetic moment M during adiabatic demagnetization remains constant down to a very small value of the magnetic field. Using a thermodynamic argument they obtained the general relation for this situation, that M is a function of $(H-K)/T$, where K depends only on the initial conditions of H and T. The constant K can, in principle, be determined by accurate measurements of magnetization curves in the liquid helium region. (Note that for an ideal paramagnetic K is zero.) The values obtained for very low temperatures are highly sensitive to the value of K, thus here again extremely accurate magnetic measurements are required to give a moderate accuracy for the values of the absolute temperature.

3.4. *The ' Theoretical Method '*

This is an indirect method of obtaining a ($T^{®}$, T) correlation based on the Hebb–Purcell theory, and has proved to have a limited applicability. Paramagnetic resonance experiments have shown that, in many cases, the Hebb–Purcell theoretical treatment contains over-simplified assumptions concerning the symmetry of the crystalline electric field and neglects hyperfine structure and exchange effects which are often significant. It is, however, a very simple method and the experimental determinations involved can be made with high accuracy. In no case does the range of validity extend very far below 0·1°K.

The theory [see §§ 2.1 (*b*), (*c*)] leads to expressions for the susceptibility and the entropy as functions of the absolute temperature. The principle of the method is to combine these two relations to obtain a third, or (χ_0, S), relation. This may be checked by direct experiment and within the range of agreement it is assumed that the two original formulae are individually correct, whence T may be calculated from the experimentally observed χ_e if the relation between χ_e and χ_0 is known. The latter is an ' idealized susceptibility ' expressed in terms of the field actually acting upon the ions, H_{loc}, and differs from χ_e on account of the effects of magnetic interaction and the external shape of the specimen. The latter is taken care of by reducing the measured susceptibility to the case of a sphere and the former may be taken into account by theories developed by Lorentz, Onsager and Van Vleck. In general, the Onsager approach is found to be most satisfactory.

The ' Leiden convention ' is to compare theory and experiment in terms of magnetic temperature and to reverse the above procedure by correcting experimentally observed values of T^* to those which would be obtained without interactions. Use of the three methods for allowing for the interactions leads to symbols T^*_{Lor}, T^*_{Ons} and T^*_{VV} [T^*_{Lor} is identical with $T^{®}$].

3.5. *Secondary Thermometers*

Carbon resistors offer many practical advantages such as compactness, stability under the heating which is sometimes necessary during assembly of apparatus, and essentially field-independent behaviour. Colloidal carbon films were investigated by Giauque, Stout and Clark (1938) and some data for carbon-composition resistors down to 0·3°K have been published by Clement, Quinnell, Steele, Hein and Dolecek (1953). The latter authors conclude that carbon-composition resistors exhibit more reproducible behaviour after warming to room temperature and being recooled, while the colloidal carbon films offer a much wider range of thermometric sensitivity. Howling, Darnell and Mendoza (1954) have investigated a carbon resistor down to 0·05°K, using the resistance as a thermometric parameter (rather than the susceptibility of the paramagnetic salt) in making absolute temperature determinations. (In several recent experiments (see § 6) carbon resistors have been used to indicate temperatures below 1°K, after calibration against a ' magnetic thermometer ', but no pertinent data have been published.)

Leaded phosphor bronze wires have been studied as resistance thermometers down to $T^*=0{\cdot}027°$ (ferric ammonium alum) by Allen and Shire (1937) and by Van Dijk, Keesom and Steller (1938) who found a linear dependence of R on T^* down to 0·25°. The resistance is markedly dependent on current and on magnetic field by virtue of the presence of small occlusions of superconducting lead, which are, in fact, responsible for the temperature-dependent resistivity.

3.6. *The Results*

Absolute temperature determinations below 1°K have been made on relatively few paramagnetic salts although one or two of these have received special attention from various investigators. Salts for which data have been obtained will be dealt with below in the (approximately) chronological order of their first investigation. The brief summaries of spectroscopic data have been taken largely from the review article of Bleaney and Stevens (1953).

(*a*) *Ferric ammonium alum*, $Fe_2(SO_4)_3(NH_4)_2SO_4.24H_2O$.

Gramme ionic weight 482·2. Density† 1·71 g cm^{-3}.

The free Fe^{3+} ion is in a $^6S_{5/2}$ state and a crystalline electric field of cubic symmetry would split the six-fold degenerate ground level into a doublet and a quadruplet. A field of lower symmetry would, however, give rise to a separation into three doublets (Meijer 1951), as appears to be required by the shape of the 'T^{-2} region' of the specific heat curve (Benzie and Cooke 1950 b). Resonance measurements on diluted specimens showed g to be isotropic and equal to 2 within less than 1% (Ubbink, Poulis and Gorter 1951, Whitmer and Weidner 1951).

The relation between T^{*} and T was first investigated, using gamma-ray heating, by Kurti and Simon (1935 c) and has been published in graphical form by Cooke (1949); the data below 0·2°K are given in table 1.

Table 1. (T, T^{*}) Correlation for Ferric Ammonium Alum

T(°K)	T^{*}(°K)	T(°K)	T^{*}(°K)	T(°K)	T^{*}(°K)
0·015	0·0720	0·043	0·0850	0·090	0·1390
0·020	0·0702	0·045	0·0910	0·100	0·149
0·025	0·0683	0·050	0·0970	0·120	0·168
0·030	0·0670	0·055	0·1008	0·140	0·183
0·035	0·0666	0·060	0·1050	0·160	0·198
0·040	0·0666	0·070	0·1150	0·180	0·214
0·042	0·0668	0·080	0·1273	0·200	0·229

The Curie point was found to be 0·042°K, reached from initial conditions of $H_i/T_i=11500$. Steenland, de Klerk, Potters and Gorter (1951) find, in general, lower values of absolute temperature and give 0·030°K for the Curie point; they introduced energy into their specimen by utilizing a.c. losses and, below the Curie point, d.c. hysteresis losses.

De Klerk (1948) used the 'theoretical method' (§ 3.4) and obtained agreement with the Hebb–Purcell theory down to 0·27°K using a value of 0·183 degree for the overall splitting, and assuming the doublet–quadruplet pattern. (The paramagnetic relaxation experiments of Benzie and Cooke (1950 b) indicated 0·23 degree for a system of three equispaced doublets; their heat capacity values would correspond with a splitting of 0·20 degree, were the doublet–quadruplet pattern correct.)

(*b*) *Gadolinium phosphomolybdate*, $GdPO_4(MoO_3)_{12}.30H_2O$.

Gramme ionic weight 2520.

The free Gd^{3+} ion is in an $^8S_{7/2}$ state. The eight-fold degenerate ground level is split by a cubic field into two doublets and a quadruplet.‡ The latter lies between

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† The densities given here and in subsequent sections refer to room temperature.

‡ See footnote to § 2.1 (*b*)

the two former and the spacing is in the ratio 3:5 (cf. the case of the nitrobenzene sulphonate, § 2.1 (*b*)).

Giauque and MacDougall (1935 a, 1938) measured the specific heat by an induction method of heating and compared their results with the (S, T^*) data. They concluded that, down to 0·15°K, T^* does not differ from T by more than 0·03°K.

(*c*) *Chromic potassium alum*, $Cr_2(SO_4)_3.K_2SO_4.24H_2O$.

Gramme ionic weight 499. Density 1·83 g cm^{-3}.

The free Cr^{3+} ion is in a $^4F_{3/2}$ state but the effect of the crystalline electric field is so strong that the phenomenon of ' quenching of the orbital momentum ' occurs and the ion is in, effectively, a ^4S state. The spin quadruplet remains degenerate in a cubic field but is split into two Kramers doublets by any field of lower symmetry. The magnitude of the splitting, in ' degrees ', has been found to be 0·263 (Casimir, de Klerk and Polder 1940), 0·27 (de Klerk 1948), 0·251 (de Klerk, Steenland and Gorter 1949), 0·245 (Bleaney 1950 b), 0·258 (P. H. Keesom 1948) and $0{\cdot}25_0$ (Ambler and Hudson 1954 a).

The variable behaviour of this salt, as evidenced by the splittings quoted above, is probably due to the occurrence of a structural transition which may be observed at about 80°K (Kraus and Nutting 1941). The individual features of its behaviour appear to be irreconcilable and it is, strictly speaking, not permissible to apply the Hebb–Purcell theory to this salt owing to the as yet unexplained appearance of *two* splittings (Bleaney 1950 c). Any calorimetric type of investigation will yield a root mean square value for the splitting (Daniels and Kurti 1954).

Bleaney (1950 b), using gamma-ray heating, measured absolute temperatures down to 0·05°K and these are given in table 2. Temperatures in the region of the Curie point have been measured by de Klerk, Steenland and Gorter (1949) and by Daniels and Kurti (1954). These are presented as an entropy–temperature curve in figure 4, wherein a marked disagreement between the two sets of measurements may be observed. As usual, at the lowest entropies the Leiden values of T are much smaller than the Oxford values. The triangles in this diagram are points obtained by Ambler and Hudson (1954 a) using the Leiden method of a.c. heating and are of interest in that the temperatures they represent are unusually *high*. The temperatures of the Curie point are 0·004°K (Leiden), 0·011°K (Oxford), and $(H/T)_c = 16000$.

Table 2. (T, $T^{\circledast}$) Correlation for Chromic Potassium Alum

$\ln(4-S/R)$	T(°K)	$T^{\circledast}$(°K)	$\ln(4-S/R)$	T(°K)	$T^{\circledast}$(°K)
0·008	1·000	1·000	0·187	0·180	0·195
0·022	0·600	0·604	0·226	0·160	0·174
0·034	0·480	0·485	0·271	0·140	0·156
0·047	0·400	0·406	0·329	0·120	0·138
0·057	0·360	0·368	0·404	0·100	0·121
0·072	0·320	0·330	0·503	0·080	0·103
0·091	0·280	0·291	0·616	0·060	0·086
0·120	0·240	0·252	0·682	0·050	0·079
0·158	0·200	0·215	0·720	0·045	0·075

(*d*) *Manganous ammonium sulphate*, $MnSO_4.(NH_4)_2SO_4.6H_2O$.

Gramme ionic weight 391. Density 1·83 g cm^{-3}.

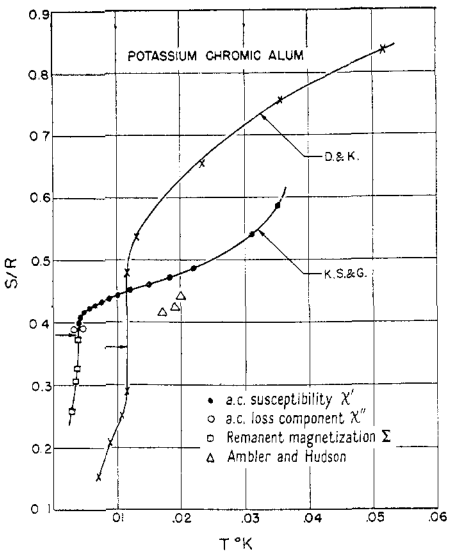

Figure 4. Entropy versus temperature for potassium chromic alum in the region of the Curie point. Curve D. & K., results of Daniels and Kurti (1953) using gamma-ray heating and the ballistic susceptibility as a thermometric parameter. Curve K.S. & G., results of de Klerk, Steenland and Gorter (1949) using heating by a.c. losses and, as thermometric parameter, a.c. susceptibility χ', a.c. loss component, χ'', remanent magnetization Σ. Results of Ambler and Hudson (1954 a) using χ'' heating and χ' as thermometric parameter.

This is a Tutton salt, the crystalline electric field having tetragonal symmetry. The free Mn^{2+} ion is in a $^6S_{5/2}$ state and the interaction with the crystalline electric field is very small. Resonance experiments (Bleaney and Ingram 1951 a) show that $g=2{\cdot}000$ and is isotropic to about 1 part in 10^4.

Adiabatic demagnetization experiments by Cooke and Hull (Cooke 1949) indicated that $T_c=0{\cdot}14$°K and $(H/T)_c=6200$. Their (T^*, T) correlation was presented in graphical form and is summarized in table 3. Their calibration of the γ-ray source was made, however, by assuming that the Hebb–Purcell theory was valid down to 0·5°K and that the quadruplet–doublet splitting pattern was correct. Actually, resonance experiments show that the pattern consists of three unequally spaced doublets, which is considerably modified by a surprisingly large hyperfine splitting (Bleaney and Ingram 1951 a, Abragam and Pryce 1951). Steenland, van der Marel, de Klerk and Gorter (1949) made absolute temperature measurements, using χ'' heating, in the region of, and below, T_c. The latter was found to be 0·10°K, which is appreciably lower than the value of Cooke and Hull.

Table 3. (T, T^*) Correlation for Manganous Ammonium Sulphate

T(°K)	T^*(°K)	T(°K)	T^*(°K)
0·13	0·115†	0·315	0·35
0·13	0·15	0·37	0·40
0·16	0·20	0·425	0·45
0·205	0·25	0·48	0·50
0·26	0·30		

† minimum

(*e*) *Gadolinium sulphate*, $Gd_2(SO_4)_3.8H_2O$.

Gramme ionic weight 373. Density 3·010 g cm^{-3}.

Bleaney, Elliott, Scovil and Trenam (1951) reported paramagnetic resonance experiments on gadolinium ethylsulphate and noted that the spectrum is of the same nature in gadolinium sulphate. For the former, g is isotropic and equal to 1·993. The recent experiments of Bogle and Heine (1954) have shown the splitting pattern to consist of four doublets (rather than two doublets and a quadruplet as assumed heretofore) lying at 0, 0·20, 0·48 and 0·82 cm^{-1}.

Van Dijk (1946) has published extensive data on absolute temperatures, measured calorimetrically, down to 0·22°K.

(*f*) *Copper potassium sulphate*, $CuSO_4.K_2SO_4.6H_2O$.

Gramme ionic weight 442. Density 2·22 g cm^{-3}.

This is a Tutton salt. The free Cu^{2+} ion is in a $^2D_{5/2}$ state. In a cubic field the orbital levels split into an upper triplet and a lower doublet. In a tetragonal or rhombic field the doublet is further split into two singlets. The latter are still spin-degenerate and at low temperatures one has effectively $S=\frac{1}{2}$. Bleaney, Bowers and Ingram (1951) find that $g_{\parallel}=2{\cdot}45$, $g_{\perp}=2{\cdot}14$. The susceptibility follows a Curie–Weiss law with $\Delta=+0{\cdot}034°$ (Garrett 1950 a, Benzie and Cooke 1950 b) and Garrett (1950 a) finds that $T=0{\cdot}987\ T^{*}+0{\cdot}033°$ down to $T^{*}=0{\cdot}025°$.

De Klerk (1946) obtained a (T^{*}, T) correlation for a powder specimen, T being measured by means of a potassium chromic alum ‘ thermometer ’, and reported a much larger value for Δ, viz. $+0{\cdot}052$ degree.

Demagnetization experiments by Steenland, de Klerk, Beun and Gorter (1951), in which g was taken to be 2·18, yielded $T_c=0{\cdot}05$°K for $H_i/T_i=11500$ and approximate absolute temperature values in the range 0·0046°–0·025°K. Their lowest values have been criticized, however, by Daniels (unpublished) as being incompatible with the entropy due to hyperfine structure. The latter contributes notably to the specific heat (Garrett 1950 b).

(*g*) *Cobalt ammonium sulphate*, $CoSO_4.(NH_4)_2SO_4.6H_2O$.

Gramme ionic weight 395·2. Density 1·902 g cm^{-3}.

The free Co^{2+} ion is in a $^4F_{9/2}$ state. In a cubic field the seven-fold orbital state is split into two triplets and a singlet, with one triplet the lowest. The latter, with its four-fold spin-degeneracy, is then split into a number of doublets by the combined effect of the spin–orbit coupling and the tetragonal field of this Tutton salt. For the lowest doublet $g_{\parallel}=6{\cdot}45$, $g_{\perp}=3{\cdot}05$ (Bleaney and Ingram 1951 b). Garrett (1951 a), taking $g_{\parallel}=6{\cdot}2$, $g_{\perp}=3{\cdot}0$ (from early data), obtained (T^{*}, T) data for the K_1, K_2 and K_3 axes; $T_c=0{\cdot}084$°K.

(*h*) *Chromic methylammonium alum*, $Cr_2(SO_4)_3.(CH_3NH_3)_2SO_4.24H_2O$.

Gramme ionic weight 492. Density 1·645 g cm^{-3}.

The paramagnetic resonance measurements of Bleaney (1950 c) showed there to be a unique value of the ground-state splitting δ. It should therefore be more suitable as a standard thermometric substance than the potassium alum.

Adiabatic demagnetization experiments by Hudson and McLane (1954) indicated that the Hebb–Purcell theory provides a good description of the behaviour down to about 0·08°K, using the Onsager internal field formula and $\delta/k=0{\cdot}269$

degree; the appropriate (T^*, T) correlation was given in a table. Their value of δ/k is in good agreement with the value 0·275 for a powder specimen (de Klerk and Hudson 1953) and 0·27 (Gardner and Kurti 1954). The latter authors measured absolute temperatures by the gamma-ray method of heating in the range 0·013–0·396°K and their results are summarized in table 4. They found $T_c = 0{\cdot}02$°K at $(S/R)_c = 0{\cdot}500$, $(H/T)_c = 13\,900$, and suggest that the difference between their value of δ/k and the paramagnetic resonance value of 0·245 obtained by Bleaney (1950c) indicates that a small amount of anisotropic exchange is contributing to the specific heat.†

Table 4. (T, T^*) Correlation for Chromic Methylammonium Alum

S/R	T^*(°K)	T(°K)	S/R	T^*(°K)	T(°K)
0·350	0·053	0·013	0·900	0·121	0·096
0·400	0·052	0·016	0·950	0·132	0·109
0·450	0·051	0·018	1·000	0·143	0·122
0·500	0·051	0·020	1·050	0·157	0·137
0·550	0·053	0·023	1·100	0·175	0·153
0·600	0·061	0·028	1·150	0·196	0·180
0·650	0·071	0·032	1·200	0·224	0·210
0·700	0·083	0·039	1·250	0·266	0·254
0·750	0·092	0·048	1·300	0·336	0·326
0·800	0·102	0·065	1·350	0·404	0·396
0·850	0·111	0·077			

(*i*) *Cerium magnesium nitrate*, $2Ce(NO_3)_3.3Mg(NO_3)_2.24H_2O$.

Gramme ionic weight 765.

The free Ce^{3+} ion is in a $^2F_{5/2}$ state; the next lowest level to the ground state, $^2F_{7/2}$, is about 2500 cm^{-1} above. Cooke, Duffus and Wolf (1953) assumed the ground state to be split into doublets characterized to a first approximation by $J_z = \pm 1/2$, $\pm 3/2$, $\pm 5/2$. The lowest doublet was identified as $J_z = \pm 1/2$ with $g_\perp = 1{\cdot}84$, $g_\parallel = 0{\cdot}25 \pm 0{\cdot}05$.

Daniels and Robinson (1953) employed gamma-ray heating in demagnetization experiments and found that $T^* = T$ down to 0·006°K. Their (T^*, T) data between $T = 0{\cdot}003$° and 0·006°K are summarized in table 5.

Table 5. (T, T^*) Correlation for Cerium Magnesium Nitrate

S/R	T(10^{-3} deg K)	T^*(10^{-3} deg K)	S/R	T(10^{-3} deg K)	T^*(10^{-3} deg K)
0·100	3·08	3·20	0·525	3·76	4·35
0·300	3·08	3·20	0·550	4·25	4·72
0·350	3·08	3·28	0·560	4·50	4·90
0·400	3·08	3·38	0·570	4·79	5·09
0·425	3·08	3·49	0·580	5·12	5·32
0·450	3·12	3·66	0·590	5·46	5·56
0·475	3·23	3·88	0·600	5·86	5·86
0·500	3·43	4·09			

In this salt, owing to the smallness of the magnetic specific heat, the contribution to the specific heat from the lattice is not negligible and has been estimated to become comparable with the magnetic specific heat at about 0·5°K. It should be

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† The most recent analysis of paramagnetic resonance data (J. M. Baker, unpublished), assuming a small rhombic component in the crystal field, indicates that $\delta/k = 0{\cdot}255$. The possible existence of some anisotropic exchange still remains.

stressed that the property of obeying Curie's law down to 0·006°K potentially makes this salt an extremely valuable ' thermometer '. Owing to its marked anisotropy it cannot be used in powdered form; on the other hand, this feature may be of considerable use in another connection (see § 7.4).

3.7. *Note on Discrepancies*

Although a rather large amount of data on temperature measurements has now been published it is largely confined to a few salts and to the region above 0·1°K. Below this point the data are sparse and the work of one laboratory rarely overlaps that of another; where this does occur the agreement is generally bad. For example, the Curie point of ferric ammonium alum is given as 0·030°K (Leiden) and 0·042°K (Oxford), and that of chromic potassium alum as 0·004°K (Leiden) and 0·011°K (Oxford). The questioned validity and the defence of the gamma-ray method have already been mentioned in § 3.2; it appears most probable that the cause of the discrepancies lies elsewhere (see below). It is now generally agreed that in order to resolve the present difficulties, measurements should be made using both methods on the same specimen in several laboratories.

The two curves of figure 4 (§ 3.6 (*c*)) illustrate the magnitude of the discrepancy between the Leiden and Oxford temperature values. Since the triangle points were obtained using the ' Leiden method ' (Ambler and Hudson 1954 a), these points provide evidence, though slight, that the divergence is not due to invalidity of the gamma-ray method. The most probable cause is the difficulty of making an accurate correction for the effects of stray heating (see § 3.2) and a general improvement in experimental technique to permit measurements under conditions of negligible ' drift ' is now highly desirable.

§ 4. PROPERTIES OF PARAMAGNETIC SALTS BELOW 1°K

§ 4.1. *Susceptibility*

The susceptibility may be measured either ballistically or by an a.c. bridge method and, as mentioned before, is readily obtained as a function of entropy. As the entropy decreases it is observed that the ' zero-field ' susceptibility first increases at a rate roughly proportional to the square root of the entropy diminution, then much more rapidly and ultimately goes through a maximum. In the region of the maximum the d.c. susceptibility is usually found to be a few per cent higher than the a.c. susceptibility; (χ, S) curves for chromic potassium alum and chromic methylammonium alum are shown in figures 5 (*a*) and 5 (*b*) respectively. One may note that in the methylammonium alum the rapid increase in χ sets in at entropy $R \ln 2$, in accordance with expectations, whereas this does not occur in the potassium alum until a much lower entropy. This latter behaviour is not understood.

From the theoretical point of view the relationship between χ and T is, of course, more useful than that between χ and S. Since χ is inversely proportional to T^* this is equivalent to a (T^*, T) correlation, discussed previously.

4.2. *Relaxation and Hysteresis Phenomena*

The decrease of entropy below the value $R \ln 2$ and the appearance of a susceptibility maximum are evidence of the temperature decreasing to such a point that kT has become of the order of the magnetic interactions. The latter give rise to a co-operative effect with a final spatial ordering of the spins towards an entropy

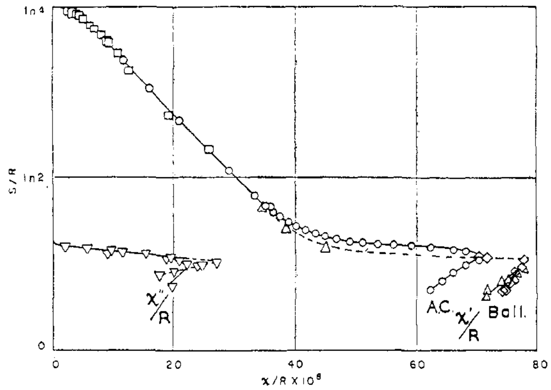

Figure 5(*a*). Chromic potassium alum: entropy plotted against susceptibility (*after* de Klerk 1952, p. 215, fig. 44.3).

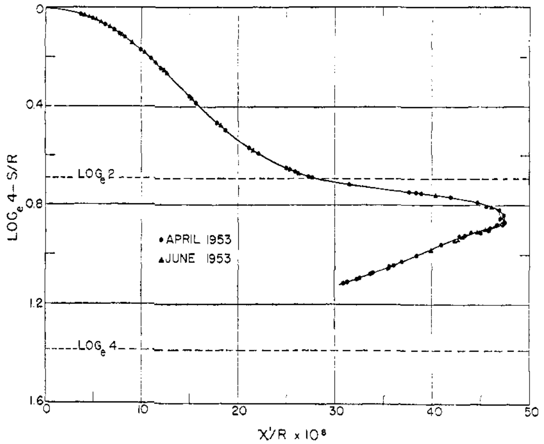

Figure 5(*b*). Chromic methylammonium alum: entropy plotted against a.c. susceptibility (*after* Hudson and McLane 1954).

of zero at 0°K. Experiments suggest that the most probable arrangement is an antiparallel, or antiferromagnetic, one.

In the early experiments of Kurti, Lainé, Rollin and Simon (1936 a) upon ferric ammonium alum an associated phenomenon was observed, namely the appearance of hysteresis effects below the entropy corresponding to $\chi_{\max}$. The remanence is found to increase at first with increasing magnitude of the cycled field, but the hysteresis disappears in fields of about 100 oersteds and greater. In the case of chromic methylammonium alum, the remanence when plotted as a function of entropy goes through a maximum (Hudson and McLane 1954). This type of behaviour has not been reported for the other salts investigated, e.g. chromic potassium alum (Steenland, de Klerk and Gorter 1949, Ambler and Hudson 1954 a), manganous ammonium sulphate (Steenland, van der Marel, de Klerk and Gorter 1949), ferric ammonium alum (Kurti, Lainé, Rollin and Simon 1936 a, Steenland, de Klerk, Potters and Gorter 1951). In these latter cases the remanence is found to increase continuously as the entropy is lowered.

Conventionally the ‘ Curie point ’ is taken to be defined by the appearance of remanence, which generally occurs at a slightly higher entropy (or temperature) than does the maximum in susceptibility. The observed remanent magnetizations are always very small (being only a few per cent of the magnetization at the limits of the cycle, which in turn is only a few per cent of the saturation magnetization) and tend to support the argument against the ordered state being ferromagnetic.

Coincident with the rapid increase of χ towards its maximum and the appearance of hysteresis effects, the a.c. susceptibility is found to become complex (see § 3.2). The out-of-phase component of the susceptibility χ'' increases continuously with decreasing entropy in the cases of cobalt ammonium sulphate (Garrett 1951 a) and ferric ammonium alum (Steenland, de Klerk, Potters and Gorter 1951) but goes through a very sharp maximum just below the Curie point in the case of chromic methylammonium alum (Hudson and McLane 1954). There is conflicting evidence on the behaviour of chromic potassium alum: de Klerk, Steenland and Gorter (1949) report a maximum, while Ambler and Hudson (1954 a) could detect no maximum but only an inflection at roughly the same entropy.

Cooke and Hull (1937) investigated the variation of χ'' with temperature and with frequency ν in ferric ammonium alum (above the Curie point) by observing rates of warming in an a.c. field, using frequencies of 328 and 455 c/s. Making use of the concept of a relaxation time τ within which the spins take up their stable orientation after a change has taken place in H, these authors found that τ varied with temperature according to the relation $\tau = 2{\cdot}3 \times 10^{-7} \exp(-T/0{\cdot}035)$ sec within the range of measurement, 0·04° to 0·12°K. Interpreting the results of MacDougall and Giauque (1936) for gadolinium nitrobenzene sulphonate heptahydrate in a similar way, they find $\tau = 5 \times 10^{-7}$ sec at 0·25°K. This is comparable with the values obtained for ferric ammonium alum. The evidence points to τ representing the time constant for mutual interaction between the spins. The heating effect was found to be proportional to the square of the frequency, implying, $\chi'' \propto \nu$ and ruling out any explanation of the phenomenon on the basis of simple magnetic hysteresis. On the other hand, Shire and Barkla (1939), using the same salt, found the heating to be proportional to frequency in the range 75–400 c/s at temperatures in the region of 0·1°K.

De Klerk, Steenland and Gorter (1949) measured χ'' directly in chromic potassium alum for the frequencies 225, 375 and 525 c/s but the measurements were not sufficiently reproducible to permit conclusions to be drawn as to the frequency dependence. By using the frequencies 225 and 525 c/s alternately in the same run, however, it was deduced that, in the range 0·01°–0·05°K, the heating was proportional to $\nu^{1\cdot 7}$, in fair agreement with the results of Cooke and Hull for ferric ammonium alum.

The fact that χ'' is closely associated with the appearance of a Curie point strongly suggests that it has its origin in the magnetic interaction forces which produce the transition. In contrast to the spin–spin relaxation observed at higher temperatures (see, for example, Cooke 1950) the relaxation time is temperature dependent. It is not impossible that the two phenomena are basically the same: in the low temperature case we have a situation which is more difficult to examine analytically due to kT becoming comparable with the interaction energy, to the anisotropy of electric interactions, and to the possible development of domain structure.

4.3. *Specific Heat Anomalies*

Any process within a substance which brings about a change of entropy will contribute to the heat capacity. As the temperature is lowered redistribution of the ionic magnetic moments over the allowed energy levels, split by the crystalline field, will occur giving rise to a Schottky-type anomaly. The removal of the final $\boldsymbol{R}\ln 2$ of electronic entropy occurs through magnetic (or exchange) interaction and this, being a co-operative effect, results in a very rapid decrease in S with a consequent sharp-peak anomaly. A third source of entropy lies in the splitting of nuclear magnetic energy levels by the magnetic field of the electrons surrounding the nucleus. This entropy amounts to $\boldsymbol{R}\ln(2I+1)$ where I is the nuclear spin.

These three effects may or may not overlap, depending upon the relative magnitude of the interactions. For example, in the case of chromic potassium alum the magnetic and crystal field anomalies are centred on 0·01°K and 0·10°K respectively, and are thus clearly separated. The relative abundance of ^{53}Cr, the only stable isotope having non-zero spin, is only 9% and the hyperfine splitting is very small (Bleaney and Bowers 1951) so that the hyperfine structure contribution to the specific heat is negligible. In contrast, in the case of manganous ammonium sulphate, all three interactions are important and their contributions to the specific heat overlap.

When overlap does occur it is frequently possible to determine the various contributions by making measurements upon crystals wherein some of the paramagnetic ions have been replaced by suitable diamagnetic ions. This technique has been used by Benzie and Cooke (1949) in the liquid helium region and by Garrett (1950 a, b) and Malaker (1951) below 1°K. At ' high ' temperatures each interaction contributes a term proportional to $1/T^2$ to the specific heat, and may be determined by extrapolating the results to infinite dilution. The measured specific heat, less the hyperfine structure and Stark contributions, represents the combined effect of the dipole–dipole and exchange interactions. The dipole quantity is usually calculated from the Van Vleck formula (corresponding to equation (11)) and the remainder ascribed to exchange. As discussed in § 2.1 (*d*), the nuclear specific heat may also be calculated from paramagnetic resonance data and the values so obtained are generally in good agreement with those obtained by the dilution method. Care must be exercised in operating on the assumption that Stark splittings are unaffected by dilution. Kurti (private communication) has pointed out that this would be very wrong in the case of ferric rubidium alum, for example.

4.4. *Free Radicals and F-Centres*

The magnitude of the interactions in a paramagnetic determines the temperature of the rapid fall in entropy, and hence the temperature which may be reached by adiabatic demagnetization (see figure 1). Such interactions should be smallest in a spin one-half paramagnetic having a high degree of magnetic dilution. For this reason, some investigations have been undertaken recently into the magnetic behaviour of free radicals (van den Handel 1952, Gerritsen *et al.* 1954) and colour centres in alkali halides (Heer and Rausch 1953).

The evidence to date is not encouraging, however, since it appears that in these situations large exchange interactions (Hutchinson 1949, Holden *et al.* 1950, 1951, Schneider and England 1951) and significant hyperfine interactions (Pake, Townsend and Weissman 1952, Lloyd and Pake 1954) are present. Adiabatic demagnetizations have been made with diphenyl-picrylhydrazyl (Ambler and Hudson 1954, unpublished) but merely to confirm the existence of a susceptibility maximum in the upper tenths-of-degree range. Above 2°K this substance was found to obey a Curie–Weiss law with $\Delta \simeq -0{\cdot}06$ degree; below 2°K, $\chi(T-\Delta)$ decreased rapidly with falling temperature.

4.5. *Antiferromagnetism*

At or close to the Curie point the susceptibility reaches a maximum value. If measurements are made at lower entropies in superimposed steady fields H it is found that the isentropic differential susceptibility $(\partial M/\partial H)_S$ first increases with increasing H and then goes through a maximum. If one plots such results as a lattice of $(\mathrm{M}, \mathrm{S})_H$ curves, the sealso show a maximum, provided that H does not exceed a certain critical value, $H_c{}^0$; the latter varies considerably from substance to substance. The locus of the maxima constitutes a phase boundary. Within the boundary, $(\partial M/\partial S)_H$ is positive, corresponding to a negative magnetocaloric effect, as may be seen at once from the thermodynamic relation of equation (1). That is to say, isentropic application of a magnetic field results in a cooling. Outside the boundary the reverse situation holds and the substance is paramagnetic, with a positive magnetocaloric effect. The behaviour within the boundary is readily explained for the case of antiferromagnetism:

We may write
$$\left(\frac{\partial T}{\partial H}\right)_S = -\frac{(\partial S/\partial H)_T}{(\partial S/\partial T)_H}$$
and since $\partial S/\partial T$ is always positive, a negative $(\partial T/\partial H)_S$ corresponds to a positive $(\partial S/\partial H)_T$, i.e. isothermal application of a magnetic field *increases* the entropy or disorder. Such an effect would be expected in an antiferromagnetic since the effect of applying a small field will be partially to disrupt the antiparallel alignment of the spins.

The phase-boundary feature appears to be common to all low temperature paramagnetics. It has been reported by Kurti (1951) for a compressed powder 3–1 ellipsoid of ferric ammonium alum, by Garrett (1951 a) for single crystal sphere of cobalt ammonium sulphate along the K_1-axis only, by Ambler and Hudson (1954 b) for a single crystal sphere of chromic methylammonium alum measuring along a cubic axis, and may also be derived from the results of Steenland (1952) for a single crystal sphere of chromic potassium alum.

Garrett first drew attention to the phase boundary and discussed his results on the cobalt Tutton salt in the light of a theory of antiferromagnetism, due to Sauer and Temperley (1940), based on dipole–dipole interaction. This predicted a transition curve quite similar to that observed experimentally. Comparison was made on the basis of a $(T, H)_S$ diagram, which is essentially the same as a $(M, S)_H$ diagram by virtue of equation (1). The transition curve is roughly parabolic in shape and along it the field (termed ‘ critical field ’ and denoted by H_c) varies between zero at the normal Curie point T_c and a limiting value $H_c{}^0$ at the absolute zero.

The Sauer–Temperley theory, designed for the alums (face-centred cubic lattice) and with the simplifying assumptions of no crystalline field effects and a unique direction of alignment, requires $T_c = 3{\cdot}6\ N\mu^2/k$ and $H_c{}^0 = 1{\cdot}8\ N\mu$ where N is the number of ions per cm^3 and μ is the magnetic moment of each ion. The crystalline electric field in the cobalt Tutton salt has tetragonal symmetry and there are two sets of magnetic ions with different tetragonal axes. Garrett took for his value of the critical field $H_c{}^0$ the component along a tetragonal axis of the ‘ external critical field ’. The theoretical and observed values of T_c and $H_c{}^0$ were respectively 0·065°K and 0·084°K, 160 oersteds and 340 oersteds.

For chromic methylammonium alum, Ambler and Hudson (1954 b) obtained $H_c{}^0 = 120$ oersteds, which has a component of 70 oersteds along each of the trigonal axes—the presumed directions of alignment. The theoretical value is 100 oersteds. The value of T_c for this salt is 0·02°K (Gardner and Kurti 1954); the theoretical value is 0·04°K. In contrast, T_c for chromic potassium alum is either 0·004°K or 0·011°K (see § 3.7) and H_c^0 appears to be of the order of 15 oersteds.

Dipole–dipole interaction is present and is of roughly the same order of magnitude in all low-temperature paramagnetics, but the above results make it extremely unlikely that it is solely responsible for the co-operative transitions. If this were so, the Curie points of these two chromic alums should be very nearly the same, since the magnetic ion is the same and the inter-ionic distance differs by only 3%. Garrett (1951 b) has been able to show that an extension of Van Vleck's theory of direct exchange interaction (applicable to a simple cubic or body-centred cubic arrangement) leads to results remarkably similar, in main features, to those obtained by Sauer and Temperley for the case of dipole–dipole coupling. Direct exchange, however, can almost certainly be excluded, theoretically by reason of the high dilution, and experimentally on the basis of no detectable Curie–Weiss Δ, but indirect exchange can be admitted. The existence of indirect exchange has been invoked to account for otherwise unidentifiable contributions to the heat capacity, but the theory is not sufficiently well developed to be applied to co-operative phenomena. (See, however, the extension by Gorter and Haantjes (1952) of Néel's phenomenological theory.)

4.6. *Thermal Conductivity*

The thermal conductivity k of paramagnetic salts is an important factor in research at very low temperatures. It is found to be very small and thus any stray heat-leak to a cooled specimen will tend to raise the temperature of the surface preferentially and give rise to an inhomogeneous temperature distribution. It is difficult to apply a satisfactory correction for this effect, and the ' useful time ' after a demagnetization is severely limited, being inversely proportional to the heat-leak and probably of the order of a few minutes for a typical case of 2–3 erg min^{-1} cm^{-2}. Again, k partly determines the degree of thermal equilibrium between a paramagnetic salt used as a coolant and a second substance which is being cooled through thermal contact (see § 5.2).

Relatively few measurements have been made of k for paramagnetic salts; the data available have been summarized and discussed by Berman (1953). The standard experimental methods are of little use below 1°K owing to the difficulties of establishing thermal contact between the salt specimen and heaters or thermometers, and of minimizing heat-leaks. The usual procedure has been to measure a mean conductivity by observing the rate of temperature equalization of the ends of paramagnetic crystals demagnetized from inhomogeneous fields. An average magnetic susceptibility is measured for each end of the crystal, from which one derives an average T^* and hence an average T. The rate of heat flow is calculated from heat capacity data, a correction being applied for the heat-leak. Considering the inaccuracies involved at each step of this treatment, it may be appreciated that no more than an order-of-magnitude determination can be expected.

Measurements were made by Kurti, Rollin and Simon (1936) on cylinders, 7 mm in diameter, cut from crystals of ferric ammonium alum (23 mm long) and chromic potassium alum (30 mm long). Values for k (in cal deg^{-1} cm^{-1} sec^{-1}) were obtained as follows: for the ferric alum, $k = 0{\cdot}6 \times 10^{-5}$ at $T^* = 0{\cdot}07$ degree and $1{\cdot}8 \times 10^{-5}$ at 0·10 degree; for the chromic alum $k = 2{\cdot}3 \times 10^{-5}$ at $T^* = 0{\cdot}18$ degree.

Bijl (1949) measured k for chromic potassium alum between 1·4° and 3·9°K by a conventional heating method, determining the temperature gradient by the susceptibility method; k was found to be proportional to a power of the temperature of about 2·3. It was also found that the conductivity depended on the rate at which the specimen was cooled below 70°K. Garrett (1950 c) examined the same salt between 0·16° and 0·29°K by a method not very different from that of Kurti *et al.* In this region k varied as T^3 within the experimental accuracy and seemed to fit on to an extrapolation of the ‘ slow cooling ’ curve of Bijl.

The thermal conductivity may be expressed in terms of a mean free path l (Debye 1914), the distance which a lattice wave travels before its intensity is reduced to 1/e of its initial value. Retaining the concept of a mean free path when discussing heat transfer in terms of phonons, the Debye expression $k=\frac{1}{4}Cvl$ is modified to $k=\frac{1}{3}Cvl$ where C is the lattice specific heat per unit volume and v is the velocity of sound. The mean free path should increase with decreasing temperature (Peierls 1929) and at very low temperatures, l should be determined by the size of the specimen being investigated, or by that of the grains of which it may be composed, and k should vary as C, i.e. as T^3. Although the latter type of variation was observed by Garrett, his results indicate that l was about 0·5 mm while the crystal diameter was 15 mm. Berman points out that this suggests there are boundaries within the crystal sufficiently definite to scatter phonons and limit the mean free path to 0·5 mm. The results of Kurti *et al.* on ferric ammonium alum indicate $l \sim 0{\cdot}25$ mm, whereas the crystal diameter was 7 mm.

The earliest measurements showed that specimens in the form of compresses of finely ground crystals exhibited a thermal conductivity lower by a factor ten than that of a single crystal. Van Dijk and Keesom (1940) obtained the relation $k=0{\cdot}00312\times(T^*)^3$ calorie units for the conductivity of compressed, powdered ferric ammonium alum in the range $T^*=0{\cdot}04$–$0{\cdot}3$ degree. At 0·1°K this gives a value about one sixth that of the single crystal value of Kurti *et al.* The density of the specimen was very close to that of the single crystal. Hudson (1949 b) investigated a powder specimen of the same substance in the range 0·10–0·22°K. At 0·10°K the conductivity was about fifty times less than the single crystal value; the filling factor was again very close to unity and the size of the crystallites was estimated to vary between 10^{-3} and 10^{-2} cm. Berman points out that these results suggest a mean free path of the order of the size of the crystallites.

In cooling a non-paramagnetic substance indirectly by means of the magnetic cooling method, a frequently used technique is to establish thermal contact between the substance and paramagnetic refrigerant by immersing both in liquid helium. It may be seen, therefore, that as far as the properties of the salt are concerned, heat transfer should be made quite efficient by using the salt in finely powdered form, the transmission area increasing as d^2 while k decreases as d, where d is the average linear dimension of the grains. The temperature discontinuity at the liquid-salt interface is another important consideration; this is taken up in § 5.2.

§ 5. THERMAL INSULATION AND THERMAL CONTACT BELOW 1°K

5.1. *Thermal Insulation*

Heat influxes to the salt arise through absorption of radiation, condensation of helium gas, conduction along supports, and dissipation of energy stored in vibrations of the specimen and supports. By taking suitable precautions the total heat influx can be brought down to 20–50 erg min^{-1}, which is small enough to allow most salts to remain below 1°K for many hours.

Radiation falling on the salt should not be allowed to come from surfaces at temperatures above a few degrees absolute.† The walls of the salt chamber are accordingly made opaque and radiation traps are included in pumping lines connected to the chamber.

Although after demagnetization the pressure of helium in the salt chamber must become very small on account of the 'gettering' action of the salt, there remains a layer of helium absorbed on the walls, part of which gradually desorbs and condenses on the salt. This may be removed before demagnetization by prolonged pumping, but when metal cryostats are used and the starting temperature is very low (e.g. 0·9°K) this may take an inconveniently long time. The effect may be reduced considerably by a 'degassing' technique when precise knowledge of the initial temperature, i.e. T_i, is unimportant. The cryostat is pumped at a temperature of about 1·5°K for some time, then just before demagnetizing the temperature is reduced as low as possible. In any case, when the temperature of the salt rises above about 0·5°K, helium begins to desorb from the salt, the vacuum in the salt chamber consequently deteriorates and the heat-leak increases considerably. This makes it difficult to carry out experiments between 0·5°K and 1°K.

Some of the difficulties inherent in the use of exchange gas can be overcome by using a metallic link between the salt and the helium bath through which the heat of magnetization can flow. Heat contact must be broken before demagnetization, however, and this may be done either mechanically (Collins and Zimmerman 1953) or by a superconducting switch (Heer and Daunt 1949). The ratio of the thermal conductivity of a pure superconductor in its normal and superconducting states k_n/k_s increases strongly for decreasing temperature and for tin or tantalum, for example, is about 50 at 0·5°K (see § 6.1 (*c*)). The switch is operated by means of a magnetic field greater than the threshold value. Additional information can be found in papers by Gorter (1948 a), Mendelssohn and Olsen (1950 a), Steele and Hein (1952), Nicol and Daunt (1952), Croft, Faulkner, Hatton and Seymour (1953), and de Vries and Daunt (1954).

The support for a salt specimen should be designed with two points in mind: the heat conducted along it must be small and the system should not be free to execute large vibrations. By using fine enough supports of low thermal conductivity material there is usually not much difficulty in reducing the heat conduction to a tolerable value. For example, if one extrapolates data by Berman (1951) for the thermal conductivity of glass, a spill 1 mm diameter, of 0·1 mm wall thickness and 5 cm long would conduct roughly 5 erg min^{-1} from a helium bath at 1°K to the salt. High warming up rates due to vibration in the system (see, for example, Hull, Wilkinson and Wilks 1951, Darby, Hatton, Rollin, Seymour and Silsbee 1951) have been attributed to frictional losses, either internally in the suspension material or superficially at the points of contact with the salt, and steps should be taken to insulate the apparatus from likely sources of vibration such as vacuum pumps. A more rigid suspension for the salt often helps, but this may result in an increased heat-leak due to conduction. The fact that good thermal contacts at very low

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† At 300°K, 90°K and 20°K, $2{\cdot}8\times10^7$, $2{\cdot}2\times10^5$ and $5{\cdot}5\times10^2$ erg min^{-1} respectively are emitted per cm^2 of a black body, and the spectrum of the radiation has a maximum intensity for wavelengths λ about 10μ, 30μ and 150μ respectively. In the infra-red region, radiation for which $\lambda > 5\mu$ is not transmitted by ordinary glasses.

temperatures are extremely difficult to make may be exploited and a high thermal resistance introduced at the point of contact between salt and support. There is also the possibility of interposing a guard ring at some point along the support, consisting of a piece of paramagnetic salt, having a large specific heat at a temperature of about 0·2°K, which is demagnetized at the same time as the specimen.

Although a heat influx of 20–50 erg min^{-1} can be reproducibly achieved, this is not the case for smaller heat influxes, and there are very few such cases reported (Cooke and Hull 1942, Darby *et al.* 1951, Malaker 1951). In fact one of the main technical problems still to be solved is that of designing a system into which there is, reproducibly, a very small heat influx, say 1 erg min^{-1}. This is very important if appreciable progress is to be made in the field of absolute temperature determinations at the lowest temperatures, and if nuclear demagnetizations are to be carried out successfully (see § 7.2).

5.2. *Thermal Contact*

Below about 0·7°K thermal contact can only be made in two ways, (*a*) mechanically, by pressing the substance to be cooled to the salt, (*b*) through the intermediary of liquid (or solid) helium.

(*a*) Cooling by mechanical contact was first used by Kurti and Simon (1934) to discover new superconductors. The superconductor was finely divided, mixed with powdered ferric ammonium alum, and the mixture compressed to form a very compact pill. The method has been modified by many workers to study a variety of problems, and individual cases are discussed in § 6. Mendoza (1948) mixed a lacquer with the powdered salt to improve the contact between the salt and copper fins embedded in the mixture. He measured the equilibrium times for heat transfer between two such pills of chromic potassium alum, the copper fins being connected by a copper rod some 10 cm long. He found that at temperatures down to about 0·15°K the main thermal resistance was that of the contact between the salt and the fins, the rate of heat flow through which obeyed the relation,

$$dQ/dt=(\beta A/3)(T_1^3-T_2^3) \qquad \ldots\ldots(16)$$

where A was the area of contact, T_1-T_2 the temperature difference across the contact and β a constant $=3\times10^{-5}$ watt cm^{-2} deg^{-3}. This relation was subsequently verified by Goodman (1953) who obtained, however, a somewhat larger value for β.

(*b*) Two methods have been developed using liquid helium:

(α) The sealed high pressure capsule method was devised by Kurti, Rollin and Simon (1936) and has been used by Kurti and Simon (1938 a), Shire and Allen (1938), and Hull, Wilkinson and Wilks (1951). A similar but less efficient method has been used by de Haas, Casimir and van den Berg (1938). The substance under investigation is placed in a thick-walled metal capsule together with powdered paramagnetic salt. The capsule is then filled at room temperature with helium gas at a pressure of 120 atmospheres and sealed off. The procedure has been described in detail by Hull (1947). The volumes of salt and container are so chosen that when the capsule is cooled and the helium liquefies, the salt and specimen are completely covered with liquid.

(β) The open capsule method was devised by Hudson, Hunt and Kurti (1949) and has been used in many different experiments which will also be described in detail in § 6. The apparatus is shown in figure 6. The open container A holding the liquid helium, salt and specimen is suspended by the capillary tube C inside a vacuum case suspended in the helium cryostat. In the original experiment C was 7 cm long with internal diameter 0·2 mm and external diameter 0·5 mm. The main source of the heat influx is due to the helium, which, after creeping up the walls of the connecting tube C, evaporates in the warmer parts of the apparatus and condenses back into the container. The action of the capillary is twofold; it limits the amount of film creeping out by providing only a small transfer perimeter, and it limits the amount of gas condensing back by providing a big flow resistance. By this technique the heat influx to A was kept down to 300 erg min^{-1} and by using a double-container system, in which the upper one acted as a guard-ring for the lower, the leak was reduced to 50 erg min^{-1}. An attempt was made to keep the pressure at the top of C as low as possible by connecting it to a wider tube and pumping on the latter with a fast diffusion pump. It has been found, however, that the pumping of C does not significantly reduce the heat influx into A (Hudson 1949 b), but that the heat influx increases considerably with increasing cryostat temperature. It would seem therefore that the pressure at the top of C must always be that corresponding to the vapour pressure of helium at the cryostat temperature and that the essential points of good design are to have as low a cryostat temperature as possible and a big flow resistance in C. (A similar method has been used by de Klerk (1946), who inserted a valve at the bottom of the tube connected to the capsule.)

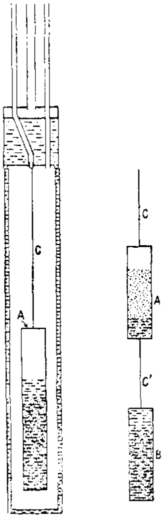

Figure 6. Open-container arrangements for cooling liquid helium below 1°K (*after* Hudson, Hunt and Kurti 1949).

It becomes more and more difficult to use liquid helium as a heat transmitting agent at very low temperatures on account of the falling off in the thermal conductivity. (The measurements of Kurti and Simon (1938 a) between 0·2°K and 0·5°K give $k = 2{\cdot}5 \times 10^{-2} T^3$ cal cm^{-1} sec^{-1} deg^{-1}.) Furthermore, with liquid helium there is another thermal resistance to be considered, namely the contact resistance between the liquid and a solid surface, discovered by Kapitza (1941). From measurements made above 1°K (Kapitza 1941, Osborne 1951, Beenakker, Taconis, Lynton, Dokoupil and van Soest 1952) one may take heat flow through such a contact across which there is a temperature difference ΔT as being approximately given by $dQ/dt = T^3 \Delta T/32$ cal cm^{-2} sec^{-1}. Measurements of Ambler (1953) indicate that this temperature relationship can be extrapolated at least down to 0·1°K. This means that contact resistance is extremely important when liquid helium is used as the transmitting agent; indeed it has the same effect as a layer of liquid helium 8 mm thick. Theories of this contact resistance have been developed by Kronig and Thellung (1950), Gorter, Taconis and Beenakker (1951), Khalatnikov (1952).

The use of solid helium for establishing thermal contact within an open capsule has been suggested by Swenson (see Wilkinson and Wilks 1951). Webb, Wilkinson and Wilks (1952) found that at temperatures below about 0·2°K, its normal conductivity at densities obtainable with quite moderate pressures ($\sim$50 atmospheres) is about ten times that of the liquid and furthermore, on the basis of all the above theories, one would expect a smaller surface thermal resistance effect than is encountered with the liquid.

Another important factor in the design of apparatus for cooling by contact below 1°K is the thermal diffusivity of paramagnetic salts. The thermal conductivity varies as T^3 (see § 4.6) but the specific heat varies with T in a complicated way and a rigorous analysis of heat flow is impossible. At any given temperature, however, one can make a rough computation.

For example, consider an arrangement where one is establishing thermal contact by means of copper fins embedded in the salt, the separation of adjacent fins being l. One may estimate the thermal time constant τ for a slab of salt (say chromic potassium alum) of thickness l by supposing that there exists a small temperature inhomogeneity across it, and using the relation $\tau \simeq l^2/\delta\pi^2$, where δ is the thermal diffusivity. Using single crystals, the smallest one could conveniently make l would be about 0·5 mm. Taking Garrett's value for the thermal conductivity $k = 1{\cdot}25 \times 10^{-2} T^3$ cal cm^{-1} sec^{-1} deg^{-1}, one finds that at 0·1°K, $\tau \simeq 0{\cdot}1$ sec, and at 0·01°K this is increased to several minutes. The situation would be somewhat worse if one used salt in the form of a powder compress since the thermal conductivity is about ten times smaller; in this case, however, one could conveniently make l still smaller.

§ 6. Experiments below 1°K

6.1. *Properties of Metals*†

(a) Electrical conductivity.

As the temperature of a metal is lowered the electrical resistivity is found to fall until in the liquid hydrogen or liquid helium region a levelling off occurs. This residual resistance is probably due to the mean free path of the electrons reaching a limit determined by the presence of various types of impurities, physical and chemical. At still lower temperatures the resistivity is sometimes found to drop abruptly to zero (superconductivity); in other cases the resistivity has occasionally been found to rise again, thus demonstrating the phenomenon of a resistance minimum.

The latter has not been investigated very much below 1°K due mainly to the inherent experimental difficulties. De Haas, Casimir and van den Berg (1938) studied the behaviour of a gold wire down to 0·4°K, their limit of good thermal

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† *Note added in proof.* Some measurements have been reported recently by J. Rayne (*Phys. Rev.*, 1954, **95**, 1428) on the specific heats below 1°K of a number of metals.

equilibrium. The wire was mounted in a glass tube (containing helium gas for heat transfer) enclosed in a quantity of ferric ammonium alum. A phosphor bronze wire, also in the tube, was used as a resistance thermometer. The resistivity of the gold was found to increase continuously with falling temperature and the measurements suggested that the rate of rise would become extremely rapid below 0·2°K.

Mendoza and Thomas (1951) investigated gold, silver and copper down to about 0·1°K. The paramagnetic salt was pressed around copper fins connected by a copper wire to a copper former which supported the wire specimen under investigation. Insulation was provided by a thin coating of bakelite varnish on the former, and electrical contacts to the wire were made through thin superconducting (high thermal resistivity) leads and the copper fins. All three metals showed a rise in electrical resistivity, becoming very rapid at the lowest temperatures. The minimum resistance decreased when the physical purity of a specimen was enhanced by annealing. Mendoza and Thomas found that the low-temperature rise in resistance was steeper the greater was the value of the minimum resistance.

Further measurements were made by Thomas and Mendoza (1952) on magnesium and molybdenum. The resistivity of the latter reached a constant value at the lowest temperatures, after rising exponentially with decreasing temperature over a considerable range. The electrical resistivity of gold was measured down to 0·006°K by Croft *et al.* (1953) and found to obey a relation of the form $R=a \log (b/T)$. Two methods were employed in these determinations, the open-capsule technique and a two-stage demagnetization technique (see § 7.1).

The phenomenon of the resistance minimum is not well understood and it is possible that such minima may be produced by different mechanisms in different metals. Various explanations have been put forward, e.g. scattering of electrons by unfilled d-shells of impurity atoms (Gerritsen and Korringa 1951), limitation of the electron mean free path due to the physical size of the specimen, and especially (MacDonald 1951) a size effect due to internal boundaries, a rearrangement of the lattice to cause a gap at the top of the electron distribution and resultant semi-conductor behaviour (Slater 1951). MacDonald (1952) has recently reported the results of a series of measurements on a variety of alloys—not below 1°K—and points out that no existing theory is adequate to account for these results.

(*b*) *Superconductivity.*

One of the earliest applications of the magnetic cooling method was the discovery of new superconductors with transition temperatures below 1°K (Kurti and Simon 1934, 1935 a). By embedding the metal under investigation in a powdered paramagnetic salt and observing the change of susceptibility during warm-up, a transition may be detected by the appearance of a large discontinuity in χ due to the disappearance of the superconductor's diamagnetism. Transitions were observed for cadmium, hafnium and zirconium.

For investigating the detailed behaviour of the superconductor it is best to employ the technique of Goodman and Mendoza (1951) in which the metal is separated from the salt by means of a copper rod. These workers measured the temperature dependence of the threshold magnetic field in aluminium, cadmium, gallium and zinc, and confirmed the parabolic relation for these substances. Superconducting transitions in osmium and ruthenium have been observed by Goodman (1951).

The method of mixtures has been employed by Daunt and co-workers to obtain critical field data for titanium (Daunt and Heer 1949 a), aluminium and zinc (Daunt and Heer 1949 b), and zirconium, hafnium, cadmium and titanium (Smith and Daunt 1952). In the latter work attention was paid to the considerable effects of impurities and strain, which were further emphasized by subsequent measurements on a well-annealed, pure specimen of titanium by Smith, Gager and Daunt (1953). These gave values of T_c and $(dH_c/dT)_{Tc}$ considerably smaller than those obtained with the specimen investigated earlier. Discrepancies between the results of different workers for the same metals are very probably due to varying degrees of strain in the specimens, especially in hard materials such as Hf, Zr and Ti. The possibility of errors in temperature measurements, however, cannot be entirely discounted.

Calorimetric measurements are difficult to make by reason of the extremely small specific heats of metals in this region. Samoilov (1952) has investigated cadmium between 0·3 and 0·9°K; above the transition point he found $C=1{\cdot}70\times10^{-4}T+464(T/300)^3$ cal mol^{-1} deg^{-1}, the linear term being in fair agreement with the figure derived from magnetic measurements (Samoilov, 1951), and below T_c the specific heat varied as T^3 (as in most superconductors).

(*c*) *Thermal conductivity.*

The thermal conductivity of metals, both normal and superconducting, at very low temperatures is not only of great fundamental interest but it is also of considerable practical importance in applications of the magnetic cooling method. As discussed more fully in § 5.2 (*a*), a convenient and satisfactory way of cooling a second substance is by means of a ' thermal link ' of, for instance, copper to the paramagnetic salt. The marked decrease in k which occurs when a pure metal enters the superconducting state forms the basis of the ' superconducting heat switch ', which is discussed in §§ 5.1 and 7.1.

The first measurements below 1°K were made by Heer and Daunt (1949) who investigated tin and tantalum down to 0·2°K by using a metal specimen as a link between two ' thermometers ' of chromic potassium alum. For both metals the thermal conductivity in the superconducting state k_s was found to be much smaller than that in the normal state k_n, the ratio k_n/k_s in the region of 0·5°K being about 60 for tin and 40 for tantalum. For tin, $k_s=1{\cdot}1\times10^{-2}T^3$ watt unit. By extrapolation of these results it was estimated that for tin at 0·01°K the ratio k_n/k_s would be of the order of 10^5.

The heat conductivity of lead down to 0·4°K has been measured by Olsen and Renton (1952). Measurements were made for the superconducting and ' intermediate ' states, but the normal-state conductivity was too large to permit measurements on the same specimen. Heat was supplied electrically at one end of the specimen, the other end being embedded in a ' pill ' of compressed paramagnetic salt which served as a heat sink. The temperature gradient was measured by means of carbon resistance thermometers (§ 3.5), attached at two intermediate points, a method which avoids uncertainties due to contact-resistance encountered (especially with magnetic thermometers) when the temperatures at the ends of the specimen are measured. Up to 0·9°K, k appeared to be proportional to T^3, with a stronger dependence on T above this point. In the intermediate state the rise in thermal resistivity and marked hysteresis effects observed by Mendelssohn and Olsen (1950 b) occurred. Similar results were obtained by Mendelssohn and Renton

(1953) for tin, indium, thallium, columbium, tantalum and aluminium. The conclusion was reached that in the T^3 region, only the crystal lattice is contributing to the conductivity, although the numerical values of k were five to ten times smaller than those predicted theoretically for ideal single crystals.

Goodman (1953) published data obtained for five tin specimens of widely differing purity. Here again the specimen rod joined two pills of paramagnetic salt, via copper inserts as described by Mendoza (1948). The results were discussed in terms of the separate contributions to the conductivity from the electrons and from the lattice. The former was found to be in agreement with the theoretical predictions of Heisenberg (1948).

The thermal conductivity of copper down to 0·25°K was studied by Nicol and Tseng (1953) using the same technique as Heer and Daunt and applying a correction for contact resistance. A linear relation, $k=\alpha T$, was verified with $\alpha=1{\cdot}76$w cm^{-1} deg^{-2}, which held over the temperature range 0·25–4·2°K. Previous results in the region 1·2–4°K give for α the values 0·6 (Allen and Mendoza 1947), 0·58 (Andrews, Spohr and Webber 1950), 4·7 (Berman and MacDonald 1952) and 2·9 (Mendelssohn and Rosenberg 1952).

6.2. *Properties of Helium*

(*a*) *Liquid helium.*

The striking properties of liquid helium which are manifested below 2·2°K (i.e. by liquid helium II) such as superfluidity, enhanced heat transport, and second sound, are strongly temperature dependent. How they are modified by a progressive lowering of the temperature below 1°K is a subject which has lately become of great interest to both experimental and theoretical physicists.

The experiments of Pellam and Scott (1949) conclusively demonstrated a marked rise in the second sound velocity u_2 below 1°K and resolved the conflict between the theoretical predictions of Tisza (1940) and Landau (1941) in favour of the latter. Higher velocities at still lower temperatures were observed by Atkins and Osborne (1950) and appeared to confirm the prediction of Landau that u_2 would tend towards a limiting value of $u_1/\sqrt{3}$ where u_1 is the velocity of sound. More recently de Klerk, Hudson and Pellam (1953, 1954) measured the variation of u_2 with temperature over the range 0·02° to 1°K. Their results, illustrated in figure 7, demonstrated the occurrence of a sharp rise in u_2 at 0·7°K followed by a tendency to flatten off at the ' Landau velocity ' at 0·5°K and a subsequent rise as the temperature was lowered further. The indications are that the value of u_2 approaches that of u_1 at very low temperatures. The shape of the received pulses becomes very much spread out below 0·6°K and gives rise to the speculation (Pellam and Scott 1949) that at the lowest temperatures one may have to do with a return to normal diffusive heat flow. In the Landau terminology, the contribution of roton (high temperature) excitations to ' the normal fluid ' density varies exponentially with temperature and, below a few tenths of a degree Kelvin, phonons will be entirely responsible for the thermal transport properties. Explanations of the observed pulse broadening and anomalous increase in u_2 towards the value of u_1 at very low temperatures have been given in terms of phonon mean-free-path effects (Atkins 1953, Mayper and Herlin 1953, de Klerk, Hudson and Pellam 1953) and Ziman (1954) has been able to account for the observed shape of the received pulses in a quantitative analysis.

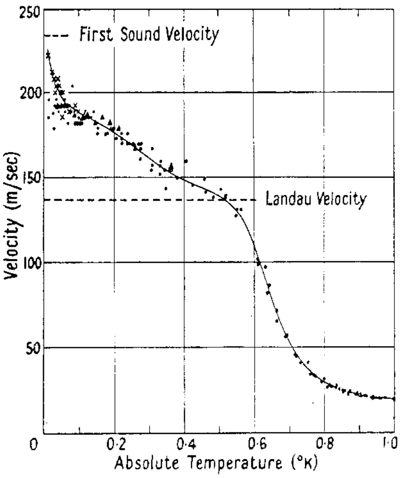

Figure 7. Velocity of second sound in liquid helium II as a function of temperature (*after* de Klerk, Hudson and Pellam 1954).

The thermal conductivity of liquid helium below 1°K has only been measured to date by rather rough methods. Kurti and Simon (1938 a) used two sealed capsules each containing about 1 gramme of ferric ammonium alum and helium gas under high pressure, and connected by a capillary, 18 mm long with 0·5 mm internal diameter. In the range 0·2–0·5°K, k appeared to vary as T^3 and the authors concluded that at such temperatures the conductivity was entirely ' lattice-type ' and no longer enhanced by the superflow properties. During his measurements on the specific heat of copper potassium sulphate, de Klerk (1946) obtained some values for k in the range 0·2 to 0·9°K. Two glass spheres 36 mm in diameter were connected by a glass tube 10·5 cm long and 3·2 mm internal diameter and for this part of the experiment were both filled with chromic potassium alum. The apparatus was provided with a valve to reduce heat influx due to film flow. The rate of temperature rise of the lower sphere after demagnetization provided a measure of the heat transfer through the liquid filling the connecting tube. The measurements showed a rather abrupt increase in the rate of variation of k with T at about 0·55°K, k apparently being roughly proportional to T^5 above this temperature. The interpretation was given, however, in terms of a ' mean heat conductivity ' defined by heat flux divided by average temperature gradient. Since k is obviously a strong function of T, however, one could better write $k = aT^n$ and this leads to (approximately) a T^6 dependence at the higher temperatures. In a similar way, one may deduce from the measurements at the lower temperatures that the index n is 3, at least in the range 0·25–0·50°K, and the value of a is here about 9×10^5 erg $\sec^{-1}$ cm^{-1} $\deg^{-4}$. This is in quite good agreement with the results of Kurti and Simon. In a preliminary account of recent experiments, Fairbank and Wilks (1954) report values of k some ten times greater in the low-temperature region than those above. Below 0·6°K the heat flow was found to be linear with temperature gradient and the index n was found to be less than 3.

The velocity of the liquid helium film has been measured by Ambler and Kurti (1952 b) below 1°K. A double-walled beaker was filled with compressed manganous ammonium sulphate and liquid helium was initially introduced into the inner vessel. To determine the rate at which the liquid flowed out of the inner space into the annular volume through the agency of the mobile film, visual observations were made on the meniscus in the inner beaker. This was viewed through vertical slits, cut in the salt cylinder, and illuminated by a collimated monochromatic light beam (mercury green). Especial care has be taken to prevent light falling directly on the salt, as this would have caused a prohibitively fast warming-up rate. The results are shown in figure 8; a striking feature is the resemblance which this curve bears to the second sound velocity curve shown in figure 7.

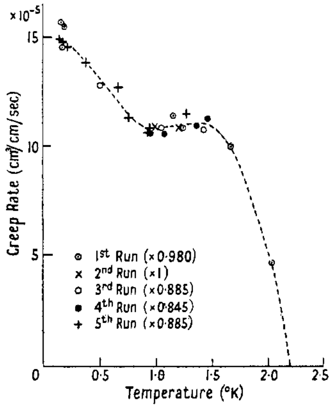

Figure 8. Flow-rate of the liquid helium film as a function of temperature (*after* Ambler and Kurti 1952)

The specific heat of liquid helium at low temperatures was first measured by Pickard and Simon (1939), who found a T^3 dependence below 0·8°K. Keesom and Westmijze (1941) reported a T^6 dependence down to 0·6°K, summarized by $C = 0{\cdot}023\ T^6$ cal g^{-1} deg^{-1}. Hull, Wilkinson and Wilks (1951) obtained $C = 0{\cdot}024\ T^{6{\cdot}2}$ for the region above 0·6°K, and good agreement with the Landau theoretical curve. In these experiments, measurements below 0·6°K were not possible because of the dominantly large heat capacity of the ferric ammonium alum used for cooling. Kramers, Wasscher and Gorter (1952) obtained more favourable conditions by using copper potassium sulphate and were able to continue their measurements down to 0·25°K. They made use of the open-container technique whereas the earlier work had all been done with a sealed-capsule assembly. Below 0·6°K the specific heat was found to be given by $C = 5{\cdot}62 \times 10^{-3}\ T^3$ cal g^{-1} deg^{-1}, in good agreement with the theoretical value calculated for a phonon gas. Above 0·6°K the specific heat will contain, on the Landau picture, a roton term in addition to the phonon contribution. The theoretical expression for the roton contribution has the form (Landau 1947) $C_r = Af(T) \exp(-\Delta/kT)$ and Kramers *et al.* noted reasonably good correspondence between theory and experiment for $\Delta/k = 8$°K. It appears that a choice of 9·6°K is even better (de Klerk, Hudson and Pellam 1954) and this agrees with the second sound velocity results and Landau's original evaluation.

(*b*) *Solid helium.*

The thermal conductivity of solid helium at a density of 0·194 g cm^{-3} was measured by Webb, Wilkinson and Wilks (1952) between 0·3° and 0·7°K. k was found to vary approximately as $T^{2{\cdot}3}$ with a value of about 0·1 w cm^{-1} deg^{-1} at 0·6°K.

Thus in this region, the behaviour of helium is normal in that the thermal conductivity of the solid is appreciably greater than that of the liquid. These results and others obtained by the same authors in the liquid helium region point to a maximum in k occurring at about 0·9°K. The specific heat as a function of temperature down to 0·55°K was also measured for three different densities.

(*c*) *Helium* 3.

In the last year or two, experiments have been reported on liquid ^{3}He. The properties of the light isotope are considerably different from those of ^{4}He and the presence of small quantities of ^{3}He in ^{4}He notably affects the properties of the latter. For example the lambda-point, or temperature of transition from He II to He I, is depressed and the second sound velocity drastically modified. Daunt and Heer (1950) cooled ^{3}He–^{4}He mixtures of various concentrations in an open container and detected the lambda-point by observing, during warm-up, the temperature at which the heat influx to the salt suddenly diminished. An 89% ^{3}He mixture showed a lambda-point of 0·38°K and these authors deduced that pure ^{3}He will not undergo a transition above 0·25°K and probably not even at any lower temperature. King and Fairbank (1953) measured the velocity of second sound between 0·2° and 1·1°K for ^{3}He–^{4}He mixtures of various concentrations. The results were in general agreement with the prediction of Pomeranchuk (1949) that u_2 would go through a maximum with decreasing temperature and fall to a small finite value at 0°K. No significant pulse distortion was observed down to the lowest temperatures, indicating the absence of long-mean-free-path effects such as are encountered in pure ^{4}He.

Roberts and Sydoriak (1954) measured the vapour pressure of pure ^{3}He down to 0·47°K, and the ratio of specific heat at the saturation vapour pressure to latent heat, C_{sat}/L, down to 0·54°K. The vapour pressures agreed within 2% with the equation of Tchen and London (1953). The derived entropy was found to be approaching zero at 0°K, indicating no liquid phase transition at low temperatures. These authors calculated that S/R reaches ln 2 at 0·5°K and falls to about 1·2 at 0·4°K. Measurements of the specific heat have also been reported by de Vries and Daunt (1954) down to 0·57°K and by Osborne, Abraham and Weinstock (1954) down to 0·42°K; in both cases use was made of a carbon resistance thermometer for temperature measurement. The results of Osborne *et al.* were summarized by the expression $C_{\mathrm{sat}}=0{\cdot}53+0{\cdot}48\ T$ cal mol^{-1} deg^{-1} which was used, in conjunction with their own vapour pressure data obtained above 1°K, to derive an expression for the entropy. This indicated a value for S/R of 1·35 at 0·42°K. (The decrease of the entropy below the value R ln 2 is of interest in connection with the alignment of the nuclear spins, discussed below.) The three sets of specific heat data agree quite well and show only a small increase of C in the range 0·4–1·0°K.

Weinstock, Abraham and Osborne (1952) measured the melting pressure of ^{3}He down to 0·16°K, extending their earlier investigations in the region above 1°K. Between 0·5° and 1·5°K the data lie on the curve $P=26{\cdot}8+13{\cdot}1\ T^2$ atmospheres. The curve showed a rather sudden flattening just below 0·5°K, the experimentally determined pressure rapidly approaching a constant value of 29·3 atmospheres. The results were later discussed more fully by the same authors (Weinstock *et al.* 1953) and the conclusion reached that no appreciable nuclear alignment occurs in the liquid down to 0·5°K. The Clapeyron–Clausius relation gives $dp/dT=(S_{\mathrm{liq}}-S_{\mathrm{sol}})/(V_{\mathrm{liq}}-V_{\mathrm{sol}})$ and since the entropy of the solid probably remains at R ln 2 down to $T \sim 10^{-7}$°K (Pomeranchuk 1950), any nuclear alignment in the liquid at much higher temperatures than this should be accompanied by a negative sign for dp/dT. Roberts and Sydoriak (1954) pointed out, however, that the existence of a minimum in the melting pressure curve would be obscured by the blocked capillary technique, which was used by Weinstock *et al.* Nuclear alignment should also be evidenced by the entropy of the liquid falling below the value R ln 2 but the computations of Roberts and Sydoriak were in conflict with those of Osborne *et al.* (see above) and the question of alignment at 0·5°K remained somewhat in doubt until the publication of the nuclear resonance results discussed below.

A point of great interest is whether the behaviour of liquid ^{3}He approximates to that of an ideal Fermi–Dirac gas. At low temperatures, the spins of the particles in such a gas should take up an anti-parallel ordering as the entropy is reduced toward zero and the magnetic susceptibility should therefore deviate from the Curie law, finally becoming temperature independent. A study of the nuclear magnetism of liquid ^{3}He therefore offers the most precise and direct information, the measurements of vapour pressure, specific heat and melting pressure providing additional information on this question.

A definitive experiment below 1°K has recently been carried out by Fairbank, Ard and Walters (1954) who measured the susceptibility (down to 0·2°K) by observing the amplitude of a nuclear magnetic resonance signal. The results are shown in figure 9. Here curve A represents the Curie law and curve C the behaviour of an ideal Fermi–Dirac gas with the same density and atomic mass as liquid ^{3}He, i.e. with degeneracy temperature $T_0 \sim 5$°K. The experimental points are seen to deviate widely from the latter curve, a significant deviation from curve A only commencing at about 1·2°K. Curve B corresponds to a Fermi–Dirac gas with $T_0 = 0·45$°K, the degeneracy temperature which provides the best fit to the data. This agreement is probably fortuitous since the *thermal* properties of such an ideal F–D gas would be very different from those observed. Nevertheless one may conclude from the susceptibility data that the *nuclear-spin entropy* is considerably less than R ln 2 at 0·5°K. (For a more detailed discussion on the various experimental results and their possible theoretical interpretation† the reader is referred to the recent paper by Temperley (1954).)

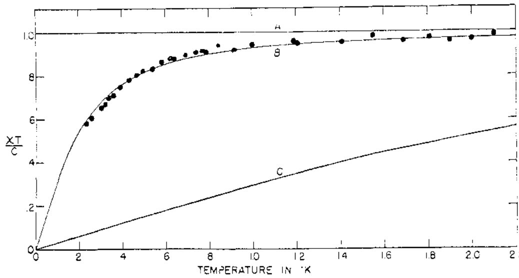

Figure 9. $\chi T/C$ against T for liquid ^{3}He; χ = susceptibility and C = Curie constant (*after* Fairbank, Ard and Walters 1954).

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† *Note added in proof.* See also L. Goldstein (*Phys. Rev.*, 1954, **96**, 1455), P. J. Price (*Ibid.*, 1955, **97**, 259) and O. K. Rice (*Ibid.*, 1955, **97**, 263).

§ 7. Further Developments in Magnetic Cooling

7.1. *Two-Stage Demagnetization*

To attain temperatures below 0·01°K from an initial temperature of 1°K it is usually necessary to have magnetic fields of about 25 kOe available. Such fields can only be produced by large iron-cored magnets or high-power solenoids, the installation of which is rather expensive. By carrying out a two stage demagnetization process, however, where the first stage is cooled to 0·1°K say, and is used as a sink for the heat of magnetization of the second stage, very much smaller fields can be used. Darby *et al.* (1951) describe such an experiment in which a field of only 9000 oersteds is used to obtain a final estimated temperature of 0·001°K. The first stage consisted of a compressed powder specimen of iron ammonium alum which was cooled to 0·25°K and the second stage a similar but smaller specimen of dilute potassium chromic alum.

The success of the experiment depended largely upon securing a very small heat leak into the second stage which had a small heat capacity, and upon the design of the thermal switch between the stages. The thermal switch, for which a superconducting wire was used, allows good thermal contact between the stages when the lower stage is being magnetized, but after demagnetization isolates them thermally (see § 5.1). The apparatus used is shown in figure 10 (*a*), and the warming up curve for the lower stage in figure 10 (*b*). Darby *et al.* actually used a lead wire 3 cm long and 0·3 mm diameter. The demagnetization of the upper stage and magnetization of the lower stage were carried out slowly so that heat transfer took place under conditions approaching reversibility.

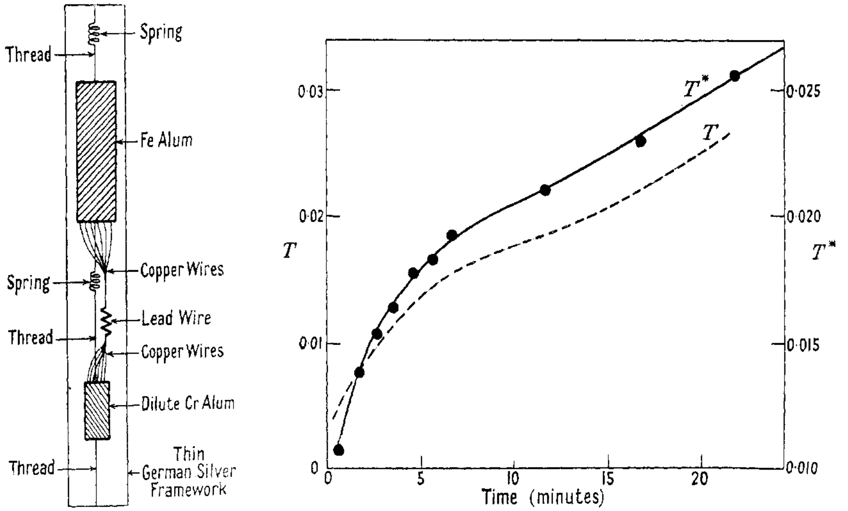

Figure 10. (*a*). Experimental arrangement for two-stage demagnetization. (*b*). Warm-up rate of lower stage (*after* Darby, Hatton, Rollin, Seymour and Silsbee 1951).

7.2. *Nuclear Demagnetization*

The lower limit of temperature attainable by demagnetizing paramagnetic salts is probably about 0·001°K and is set by the strength of the interactions between the paramagnetic ions. Although the effect of the interactions can be reduced by diluting the salt with suitable diamagnetic ions there is a limit to the usefulness of this technique since the heat capacity becomes very small, and at the limit of extreme dilution the dominant contribution to the entropy at 1°K will be that of the lattice. The suggestion was made independently by Gorter (1934) and Kurti and Simon (1935 d) that use could be made of nuclear paramagnetism to obtain still lower temperatures. The limit would be set by the strength of the direct interactions between nuclei but it is expected that temperatures as low as 10^{-6} deg K might be reached. The problem has been discussed in some detail by Simon (1939), who pointed out that if the temperatures reached after demagnetization are to be held for a usefully long period of time, even assuming a most favourable heat leak of 1 erg min^{-1}, initial magnetizing conditions of $H/T=10^7$ kilo-oersted deg^{-1} at least are needed. Since the biggest magnetic field which one supposes would be available for the purpose in the near future would be about 100 kilo-oersteds, a starting temperature of 0·01°K would be needed, and a two-stage demagnetization process would have to be carried out. Simon also lists substances which would be most suitable for the nuclear stage.

Although it is now twenty years since the suggestion was made, a successful experiment has not yet been carried out, although one should mention the interesting experiments of Rollin and Hatton (1949), Pound (1951) and Purcell and Pound (1951). The reason for this is that there are considerable difficulties in designing a switch which would be capable of transmitting the heat of magnetization from the nuclear stage to the electronic stage. Suppose that one has a large quantity of potassium chromic alum for the first stage which has been cooled somewhat below 0·01°K. In order to be able to reduce the stray field at the electronic stage to a sufficiently small value while maintaining an intense field at the nuclear stage, the two stages would have to be placed about 20 cm apart. The problem is to design the link so that the nuclear stage will be cooled to 0·01°K in a reasonable time, say an hour. (For the heat flow between the stages to be as nearly as possible reversible, and for ease of heat transfer within the first stage, it would be better to demagnetize the chrome alum initially to some intermediate temperature, say 0·1°K, and then slowly to reduce it to 0·01°K, but the present example will illustrate the difficulties involved.) The change in entropy dS due to a temperature change dT in a field H kilo-oersteds is given by (Simon 1939)

$$dS/dT=2{\cdot}15\times10^{-10}R\mu^2\frac{I+1}{I}\frac{2H^2}{T^3} \qquad \ldots\ldots(17)$$

where I is the spin and μ the nuclear magnetic moment in nuclear magnetons. From this formula and a knowledge of the thermal resistance controlling the heat flow, one can then compute how long the cooling of the nuclear stage will take.

The use of a copper rod of 1 cm^2 cross section has been shown by Kurti (1948) to provide adequate heat transfer. Two points must be borne in mind with this arrangement. First, copper has a large nuclear magnetic moment μ so that if it is situated in a very high magnetic field an appreciable amount of heat of magnetization will be produced which will also have to be conducted away; this problem could be avoided by having a short length of a more suitable material with small μ, such as lead, in the highest field; the lead could then also act as a thermal switch. Second, there may be appreciable eddy current heating due either to magnetic current ripple or even just through demagnetizing, so that the copper would have to be laminated.

Where the nuclear stage is a metal there would be no difficulty in making a good contact with the metallic link leading to the electronic stage. At the latter, however, the situation is quite different. For a mechanical type contact with a resistance equal to that given by equation (16) one finds that a contact area of the order of 10^5 cm^2 is needed. The situation if liquid helium is used is somewhat more favourable, provided one considers only the thermal conductivity (Kurti 1948). Assuming contact to be made through layers of thickness 0·01 cm then an area of 250 cm^2 will suffice. However, when one takes into account the surface resistance it turns out to be the most important factor and an area of the order of 50 000 cm^2 would be needed. One may summarize the difficulty in carrying out a nuclear demagnetization therefore as being that of overcoming contact resistance.

7.3. *Continuous Cooling Cycles*

The possibility of setting up a continuously operating refrigerator for producing temperatures below 1 °K using a paramagnetic salt as working substance was pointed out by Daunt and Heer (1949 c). The advantage of such a system is that one would have a constant temperature bath below 1 °K and so be in position to perform experiments in which quite big heat influxes could be tolerated. The steps of a cycle undergone by the working substance (ferric ammonium alum) working in a Carnot cycle are shown in figure 11. There are two isothermals AB and CD and two adiabatics BC and DA. Along AB the salt is magnetized isothermally at 1 °K, the heat being rejected to a liquid helium bath. After thermal isolation it is demagnetized to the point C. It then takes in heat from the cold reservoir along CD, and at the same time the magnetic field is further reduced so that the temperature of the working substance remains constant. It is finally magnetized adiabatically along DA until its temperature reaches 1 °K, when it is placed in thermal contact with the helium bath and the magnetization completed isothermally. The heat extracted from the cold reservoir $= T_C(S_D - S_C)$ (i.e. the area MNCD) where T_C is the temperature at C and S_C and S_D the entropies at C and D respectively. The material for the working substance is chosen so that this quantity is large, i.e. the paramagnetic ion should have a large value of J and should not deviate markedly from ideal behaviour in this region.

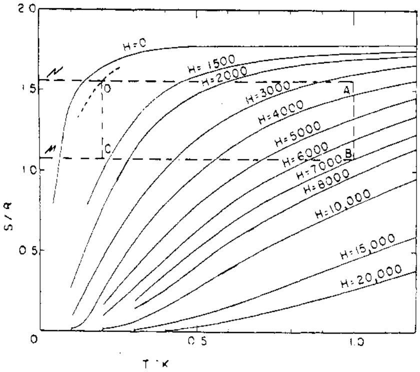

Figure 11. Entropy plotted against temperature for ferric ammonium alum for different magnetic fields, showing the ideal path for the working substance in a heat pump (*after* Heer, Barnes and Daunt 1954 b).

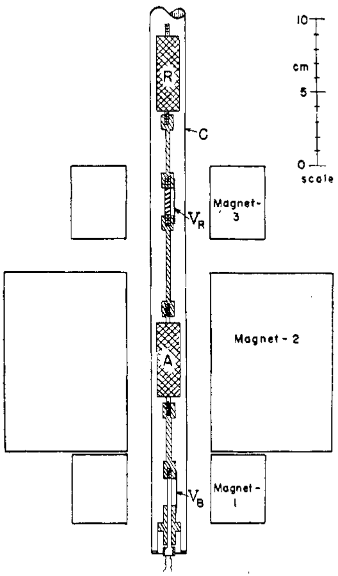

Figure 12. Schematic layout of a heat pump for producing and maintaining temperatures below 1°K (*after* Heer, Barnes and Daunt 1954 b).

Two experimental arrangements have been described, one by Collins and Zimmerman (1953) and the other by Heer, Barnes and Daunt (1953, 1954 a, b). In the former arrangement mechanical make-and-break thermal valves were used, which, however, caused an appreciable heating through the mechanical vibrations they introduced. A temperature of 0·73°K was maintained, the heat sink being at 1·13°K. In the latter arrangement, which is illustrated in figure 12, superconducting lead ' valves ' were used. The whole assembly is enclosed in a german silver tube C which is surrounded by liquid helium. The working substance A is 15 g of ferric ammonium alum and can be connected thermally either to the helium bath through valve V_B, or to the cold reservoir R, a 15 g sample of chromic potassium alum, through valve V_R. Magnets 1 and 3 are used for opening and closing the valves, and magnet 2, which can produce 7000 Oe, is used for magnetizing A.

The actual cycle deviated from ideality for several reasons. There were extraneous heat influxes, partly due to generation of eddy currents in the copper links in the system through switching the magnetic fields on and off, and partly due to an imperfect vacuum within C. The thermal contacts were imperfect and there was difficulty in following the true isothermal path CD.

Working on a 2-minute automatic cycling period, a reservoir temperature of 0·2°K could be reached. At 0·3°K the rate of heat extraction from the reservoir was $1{\cdot}4 \times 10^4$ ergs/cycle. Heer *et al.* pointed out that further developments of the thermal switches and contacts would bring about a more efficient refrigerator, and proposed addition of a further stage to enable temperatures of 0·05°K to be reached.

7.4. *The Use of Anisotropic Paramagnetic Salts*

It was proposed by Cooke (1953) that two novel types of experiment could be performed by making use of the fact that at very low temperatures certain rare-earth salts (e.g. cerium ethylsulphate, cerium magnesium nitrate and neodymium magnesium nitrate) show paramagnetic susceptibilities which are extremely anisotropic.

In the first, adiabatic demagnetization could be carried out by rotation (Bogle, Cooke and Whitley 1951). That is, a single crystal of the salt could be magnetized at 1°K along an axis of high susceptibility and then demagnetized by rotating it until an axis of low susceptibility coincided with the direction of the applied field. For example, demagnetization of cerium ethyl sulphate from 0·95°K and 1800 oersteds along the high-susceptibility axis yields a temperature of 0·20°K. If the same field is then applied perpendicular to the axis, the temperature is raised only to 0·23°K. The advantage of this technique is that it is possible to carry out experiments below 1°K involving the use of a magnetic field (e.g. the investigation of the threshold field of a superconductor) without having to employ the more elaborate techniques of cooling by contact.

The second type of experiment involves a method of measuring the susceptibility of another (isotropic) salt below 1°K. The two salts, in thermal contact, are cooled together and the resultant magnetic moment determined in two different directions. Since the contribution from the anisotropic salt is known, that from the isotropic salt can be determined. Cerium magnesium nitrate is an ideal substance from this point of view, for not only is it markedly anisotropic, but it also obeys Curie's law down to 0·006°K.

§ 8. NUCLEAR ORIENTATION

The production of oriented nuclear systems in the solid state has been a recent achievement of the magnetic cooling method and has proved to be of use in the study of problems in nuclear physics. We shall not attempt to discuss here, however, the nuclear data obtained. A detailed discussion of the four methods which have been proposed for producing oriented nuclei at low temperatures (two of which have been carried out so far) has been given by Simon, Rose and Jauch (1951) and by Bleaney (1951 a). A distinction is drawn between two types of orientation; one is a *polarization* where there is a net magnetic moment, and the other is an *alignment* where, although orientations close to a given axis or plane in the solid are preferred, there is no distinction between parallel and anti-parallel directions for the nuclear spins. The experiments which gave the first clear-cut demonstration of nuclear *alignment* were reported by Daniels, Grace and Robinson (1951) using a method proposed by Bleaney (1951 a); similar experiments were reported shortly afterwards by Gorter, Poppema, Steenland and Beun (1951). The first experiments in which a significant nuclear *polarization* was obtained were reported by Ambler, Grace, Halban, Kurti, Durand, Johnson and Lemmer (1953). In all these experiments ^{60}Co nuclei were oriented.

The most direct way of orienting nuclei, i.e. by applying a very large external magnetic field at a sufficiently low temperature, is essentially the same problem as that of nuclear demagnetization and a successful realization of the method is held up for the same technical reasons. However, the proposal made independently by Gorter (1948 b) and Rose (1949), that use could be made of the large magnetic field (10^5–10^6 oersteds) acting on nuclei of paramagnetic ions due to the electrons in the unfilled shell, has been successfully carried out. The interaction between this magnetic field and the nuclear magnetic moment in certain ions causes a large hyperfine splitting so that at temperatures of the order of 0·01°K only the lowest hyperfine level is populated, corresponding to an alignment of the nuclear spin with respect to the electron moment. Thus polarization of the electron moments, which can be achieved at these very low temperatures by a field of only a few hundred oersteds, results also in a polarization of the nuclear moments. In principle, the procedure would be to magnetize a suitable salt at 1°K with a field strong enough to saturate the electron paramagnetism, then to demagnetize to a field of a few hundred oersteds. The method was tried by Gorter, de Klerk, Poppema, Steenland and de Vries (1949) with ferric ammonium alum, but only a very small and non-reproducible effect was produced. Later it was effectively used by Bernstein, Roberts, Stanford, Dabbs and Stephenson (1954) to produce a polarization of about 17% of the saturation value of ^{55}Mn nuclei in manganous ammonium sulphate. It has been pointed out, however, that this method cannot be employed to produce very high degrees of nuclear polarization since the hyperfine splitting limits the lowest temperature which can be attained. We can see that magnetization at 1°K will remove most of the entropy from the electron spin system but practically none from the nuclear spin system, whereas for high degrees of nuclear polarization we must remove as much entropy as possible from both systems. It was suggested by Gorter (1948 a) that the salt under investigation could be cooled by contact with another salt having no hyperfine structure. Although in this case one encounters the difficulty of contact cooling below 1°K, the method has been used by Roberts, Bernstein, Dabbs and Stanford (1954) to produce a 12% polarization of ^{149}Sm nuclei in samarium ethyl sulphate by cooling this salt to 0·12°K by contact with ferric ammonium alum at 0·06°K. A more direct method is to incorporate in the same salt ions which have a very small hyperfine structure or none at all (see for example Daniels 1951). Yet another consideration was put forward by Bleaney (1951 b), namely that in the salt chosen the small externally applied magnetic field should be the dominant force tending to align the electron moments. In many salts this is not the case and there are strong forces arising from the effect of the crystalline electric field, unless a salt is chosen in which the ions are magnetically isotropic. Both of the above conditions were fulfilled in the experiment by Ambler *et al.* (1953) in which over a 90% polarization of the cobalt nuclei, incorporated in the salt $3[0{\cdot}5\%\ \mathrm{Co},\ 99{\cdot}5\%\ \mathrm{Mg}\ (\mathrm{NO_3})_2]\ 2\mathrm{Ce}(\mathrm{NO_3})_3.24\mathrm{H_2O}$, was obtained.

In the experiment of Daniels, Grace and Robinson (1951) ^{60}Co nuclei were aligned in a Tutton salt of composition $(1\%\mathrm{Co}, 12\%\mathrm{Cu}, 87\%\mathrm{Zn})\mathrm{Rb_2(SO_4)_2.6H_2O}$. The method relies on the fact that in certain paramagnetic salts, in particular the cobalt Tutton salts, magnetic interaction between the unpaired electrons of the magnetic ion and the nucleus is anisotropic due to the effect of the crystalline electric field; the hyperfine splitting then depends not only upon the relative orientations of the electronic and nuclear spins, but also upon their orientation with respect to the axis of symmetry of the crystalline electric field. In other words, the magnitude of the magnetic field at the nucleus depends upon the orientation of the electron spin with respect to the symmetry axis. Alignment occurs, at a sufficiently low temperature, in zero external field; we have an alignment rather than polarization because the energy of an ion is unaltered by reversing the directions of both nuclear and electron spins. Data on the suitability of salts for this type of alignment can be readily obtained by paramagnetic resonance and have been discussed by Bleaney (1951 a, b) in terms of the constants D, A and B appearing in the spin-Hamiltonian.

The fourth method of orienting nuclei, suggested by Pound (1949), produces an alignment and relies on the interaction between the nuclear quadrupole moment and an electric field gradient. A suitable substance would be one in which the associated hyperfine splitting is large and anisotropic. The difficulty of finding such a substance and cooling it to a sufficiently low temperature has so far precluded a successful realization of this suggestion.

The experiments which can be carried out with oriented nuclei fall into two groups. One group, for which polarized nuclei must be used, comprises a study of the scattering of polarized nucleons by polarized nuclei. The other, for which either polarized or aligned nuclei may be used, comprises a study of the directional effects in emission from radioactive nuclei. The experiments which have been performed in the former class to date have been carried out at the Oak Ridge National Laboratory, U.S.A., by Roberts, Bernstein and collaborators, on the interaction of polarized slow neutrons with polarized ^{55}Mn and ^{149}Sm nuclei. When polarized slow neutrons are captured or scattered by a target in which the nuclear spins are also polarized, the cross section is different from that observed when the spins are randomly oriented.

In the ^{55}Mn (Bernstein *et al.* 1954, Dabbs and Roberts 1954) experiment, the change in cross section was determined by measuring the difference between the numbers of radioactive ^{56}Mn nuclei produced. The 2·6-hour half-life of ^{55}Mn was long enough to permit the counting to be done after the sample had been removed from the cryostat.

In the ^{149}Sm experiment a somewhat different method was used, the nuclear polarization being measured by determining the state of polarization of an originally unpolarized beam of neutrons after transmission through a samarium salt. The salt actually used, samarium ethyl sulphate, is unsuitable for self-cooling, and ferric ammonium alum was employed as a coolant, thermal contact being established by means of a copper rod.

The experiments in the second group comprise a study of the emission pattern of γ-rays from aligned radioactive nuclei (Spiers 1948). The polar diagram for the intensity can be written

$$I(\theta)=\sum_M W_M I_M(\theta) \qquad \ldots\ldots(18)$$

where W_M is the relative population of the nuclear magnetic substate M and $I_M(\theta)$ is the angular distribution for the radiation originating from this state (θ being the angle between the axis of alignment and direction of emission). $I_M(\theta)$ depends only upon the spin and spin changes involved in the decay (see for example Tolhoek and Cox 1953, Steenberg 1953). It is a polynomial in $\cos^2\theta$ containing terms up to $\cos^{2l}\theta$ where l is the multipolarity of the emitted γ-ray. W_M depends only on the hyperfine structure and the temperature. A measurement of the angular distribution can be used to obtain, through the term $I_M(\theta)$ in equation (18), information about the decay scheme of the aligned nucleus; it is especially easy to obtain the multipolarity of a γ-ray transition. Through the term W_M in equation (18) one can also obtain information concerning the hyperfine splitting, and hence a value for the nuclear magnetic moment.

Many experiments of this type have been reported, but since the conclusions lie in the realm of nuclear physics they will only be mentioned here and not described in detail: ^{60}Co by Bleaney *et al.* (1952), Bleaney *et al.* (1954), Poppema *et al.* (1952), Gorter *et al.* (1952), Bishop *et al.* (1952); ^{58}Co by Daniels *et al.* (1952), Grace and Halban (1952), Bishop *et al.* (1952); ^{54}Mn by Daniels and Kurti (1953); Grace *et al.* (1954) and Bishop *et al.* (1954); and ^{141}Ce and ^{147}Nd by Ambler, Hudson and Temmer (1955).

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