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Cooling by Adiabatic Magnetization

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A new method of producing temperatures below 1°K is considered. It utilizes the fact that the entropy of certain paramagnetic salts is increased by the isothermal application of a magnetic field, so that, conversely, adiabatic magnetization should produce cooling. The factors limiting the temperatures which can be reached are discussed, and some suitable classes of salts proposed.

The usual method of producing temperatures below 1°K by means of adiabatic demagnetization of a paramagnetic substance relies on two properties common to most salts in use at present: (i) the entropy, S, in a given applied magnetic field, H, increases monotonically with temperature, $(\partial S/\partial T)_H>0$, and (ii) at a given temperature, the entropy decreases as H increases, $(\partial S/\partial H)_T<0$. The first of these properties implies a positive specific heat and is therefore common to all substances under normal conditions. The sign of $(\partial S/\partial H)_T$, on the other hand, is not necessarily negative and there exist paramagnetic salts for which, within certain ranges of magnetic field, it will be positive. The purpose of this note is to draw attention to the fact that for this class of substances adiabatic magnetization should produce cooling comparable with that usually achieved by means of demagnetization, and to estimate the temperature which could be reached in a practical case.[1] The effect would be exactly analogous to that which has been observed on magnetizing antiferromagnetic substances at very low temperatures.[2]

One advantage of this method would be to facilitate certain experiments which require the application of magnetic fields at temperatures below 1°K, without the need of either heat links or an arrangement for rotating the direction of the magnetic field relative to an anisotropic sample.[3] In particular it may be useful in connection with magnetic refrigerators, nuclear alignment, and Bloembergen-type masers.

The type of paramagnetic salt envisaged is one for which, in the absence of a magnetic field, the electronic degeneracy is partly removed (usually by the crystalline field), in such a way that a nonmagnetic state is lowest, with one or more magnetic states somewhat higher in energy. For optimum operation the energy separation should be large, though this may entail the use of large magnetic fields. A practical value for the energy gap, D, would be between 2°K and 10°K. Substances of this kind are, for example, salts containing Ni^{2+} ions, which have spin $S=1$, in which an axial electric field brings the $S_z=0$ state below the $S_z=\pm1$ states [see Fig. 1(a)]. In practice the $S_z=\pm1$ doublet may be further split by a rhombic term in the crystalline field, but we shall ignore this in our simple example. At temperatures such that $kT\ll D$, the entropy of such a salt will tend to $R\log 1=0$. If a magnetic field is now applied isothermally and parallel to the crystal field axis, the entropy will increase until the lower of the two magnetic states meets the ground state, when the entropy will be $R\log_e 2=0.693R$ (neglecting the population of the highest magnetic state). For larger fields the entropy again decreases towards zero [see Fig. 1(b)]. If, on the other hand, the field is applied adiabatically, so that the entropy remains constant, the temperature will fall initially, reaching a minimum when the field is again such that the two energy levels cross.

In practice it is impossible to make the energy levels exactly coincident for several reasons, and these set the limit on the lowest temperature than can be reached by this method. As in the case of conventional salts, there will be interactions between the ions, and also between the ions and nuclear magnetic moments, but in most cases the effect of these will be relatively unimportant. Much more serious is a misalignment of the crystal relative to the magnetic field, since this will usually give rise to matrix elements between the two intersecting energy levels and thus remove the desired degeneracy. Another factor which could give rise to

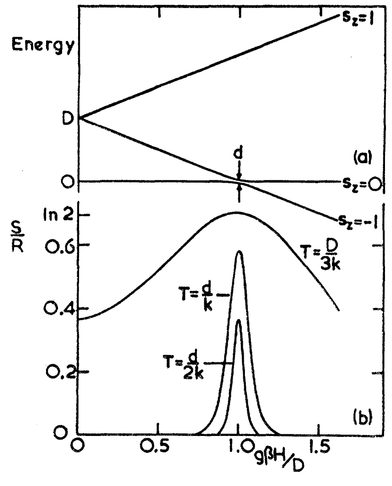

Fig. 1. (a) Variation of energy levels with magnetic field for an idealized Ni^{2+} salt with $D>0$. d = minimum energy separation between $S_z=0$ and $S_z=-1$ states. (b) Isothermal variation of entropy with magnetic field for $d\ll D$ ($d\sim D/30$).

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[1] Since these calculations were completed, the author's attention has been drawn to the fact that an outline of the method described here has recently been given independently by C. Kittel, *Proceedings of the Kamerlingh Onnes Conference on Low-Temperature Physics* [Suppl. Physica 24, S88 (1958)].

[2] N. Kurti, J. phys. radium **12**, 282 (1951).

[3] Bogle, Cooke, and Whitley, Proc. Phys. Soc. (London) **A64**, 931 (1951).

matrix elements between the lowest states is a distortion of the crystalline field. This effect could be either static (strains) or fluctuating (lattice vibrations), and in either case it would affect the properties in much the same way as a misalignment.

If we express the combined effect of these factors in terms of a minimum energy separation d, we can calculate the entropy at this separation as a function of d/kT, and equating this to the entropy at the initial temperature, T_i, find the final temperature reached on magnetizing. For a system with an energy level pattern similar to our example of Ni^{2+} ions, this gives a curve as shown in Fig. 2. From this it can be seen that if, for example, $D/k=3°K$, $T_i=1°K$, and $d/k=0.1°K$ (corresponding to an effective misalignment of about 1°), then $T_f(\text{min})=0.05°K$. If we assume that $g=2.3$, the field which would be required to reach this temperature would be 20 kilo-oersted. Unfortunately none of the Ni^{2+} salts investigated so far have energy levels quite as simple as those shown in Fig. 1(a), though there appears to be no reason why such a salt should not exist. The chief complication arises from the fact that most salts, e.g., all the Tutton salts,[4] have at least two magnetically inequivalent ions, so that the magnetic field can be applied along a favorable direction for only a fraction of the total number of ions. This reduces the degree of cooling which can be produced, but even so a useful temperature might still be reached. For example, if we were to use $Ni(NH_4)_2(SeO_4)_2 \cdot 6H_2O$[4] starting at $T_i=0.9°K$, and assume, as above, that the minimum energy separation $d/k=0.1°K$, we would reach $T_f=0.16°K$. The field required would be 19.5 kilo-oersted.

It will be obvious that in order to measure T_f experimentally it would be advantageous to use some secondary thermometer, since the susceptibility of the salt itself will be a complex function of temperature and field. The specific heat of the salt after magnetization will also depend on the field as well as on temperature, and it will be large over a wide range of conditions at a value of the order of the maximum of $0.43R$. In this respect adiabatic magnetization of a salt of this type has a great advantage over the alternative method of cooling by magnetization using a superconductor.[5] Although our example of a Ni^{2+} salt is the simplest to consider, it may in practice be more advantageous to use less common ions, such as the rare earths with even numbers of electrons (e.g., Ho^{3+}, Tb^{3+}) in suitable compounds. These ions would have the advantage of larger g values, making it possible to use a big initial splitting without the need of excessively large fields to bring the two lowest states together: also alignment might be less critical. Other possible systems include O_2 molecules trapped in a clathrate compound[6] and coupled pairs of ions with $S=\frac{1}{2}$ which have a singlet ground state (similar to those in copper acetate,[7] but with a smaller exchange coupling).

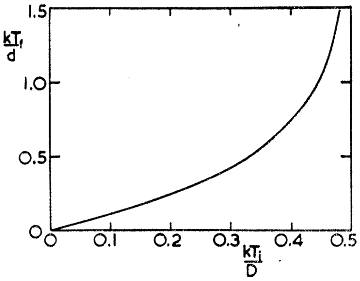

FIG. 2. Variation of minimum temperature obtainable by adiabatic magnetization, T_f, as a function of the initial temperature T_i, for a system with energy levels as shown in Fig. 1 with $d \ll D$.

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[4] J. H. Griffiths and J. Owen, Proc. Roy. Soc. (London) **A213**, 459 (1952).

[5] K. Mendelssohn and J. R. Moore, Nature **133**, 413 (1934).

[6] Meyer, O'Brien, and Van Vleck, Proc. Roy. Soc. (London) **243**, 414 (1958).

[7] B. Bleaney and K. D. Bowers, Phil. Mag. **43**, 372 (1952).