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Mean-Field Theory of Some Magnetized Antiferromagnets

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Two-sublattice general spin-s exchange antiferromagnets, assumed to have a stable configuration in applied uniform external magnetic fields parallel to their spontaneous spin-ordering direction in the absence of a field, are treated in the molecular- or mean-field approximation. The magnetic phase-boundary line of this antiferromagnetic configuration is shown to have simple closed parametric expressions. In the present approximate formalism the peculiar nonmonotonic phase-boundary line becomes of monotonic variation in the classical limit of $s \to \infty$. *The possibility of strongly anisotropic two-sublattice parallel-field-stable antiferromagnets to function as efficient cooling systems is explored. This arises from their magnetic entropy increase on isothermal magnetization as a consequence of the large asymmetry developed through the respective cooperation and competition of the exchange-coupled spins with the external applied field in determining the effective fields acting on the spins of the two sublattices. The competing or negative sublattice has anomalous behavior in that its component molar spin entropy exhibits its maximum limit of* $\frac{1}{2}R\ ln(2s+1)$ *at low temperatures compared to the zero-field transition temperature, as long as the applied magnetic field strength is a substantial fraction of the critical field strength, above which the system remains paramagnetic down to the absolute zero. The transformation into the antiferromagnetic state is then prevented. The enormous magnetic or spin entropy of the system, persisting down to very low temperatures, according to the mean-field formalism, makes it possible to reach quite low temperatures on adiabatic magnetization from easily accessible initial states in the presence of an external magnetic field. Within the limitations of the model and of its treatment experimental investigations into the preparation of antiferromagnets with the required anisotropy may be of particular interest in connection with their possible use for the production of low temperatures.*

1. INTRODUCTION

The main concern of this paper is the problem of using a class of antiferromagnets for the production of low temperatures. This cooling process results on adiabatic magnetization of appropriate systems in a particular magnetic configuration. In the latter the applied external magnetic field is directed parallel to the direction of spontaneous spin ordering. Such systems possess a privileged axial direction along which the magnetic moments of the two sublattices assumed here align themselves antiparallel in the ordered phase, assuring, in absence of external field, the vanishing of their resultant magnetic moment. So far the direct experimental confirmation of cooling exhibited by some antiferromagnets has been restricted to a semiquantitative verification of the thermodynamic consequences of their magnetic equation of state.[1–3] In this work we would like to explore the possibility for substantial cooling in appropriate systems. It turns out that antiferromagnets investigated experimentally so far are not suited to the production of low temperatures. It is suggested that the experimental physiochemical problems raised by the preparation of antiferromagnets useful as cooling agents should be investigated. The class of systems of interest for cooling will be shown to be those with magnetic and thermal properties describable approximately through the molecular- or mean-field formalism. Elements of the latter need not be given in any detail and the formalism will be used directly in connection with the general spin-s magnetized systems which, so far, have only been discussed in a few particular cases. If antiferromagnets satisfying the requirements imposed by the theory can be prepared, they should enable the production of quite low temperatures on adiabatic magnetization.

2. THE PARALLEL MAGNETIC FIELD CONFIGURATION OF STRONGLY ANISOTROPIC SPIN-s TWO-SUBLATTICE ANTIFERROMAGNETS

For our purposes it will suffice to outline briefly the mean-field formalism.[4] This deals with a collection of interacting spins, forming two sublattices, by assigning them the Hamiltonians, per spin,

$$\mathscr{H}_{\pm}(J, H, s) = -g\beta s H_{\mathrm{eff}\,\pm} \tag{1}$$

where, in an external magnetic field H parallel to the direction of spontaneous ordering,

$$H_{\mathrm{eff}\,\pm} = H - (2Jzs\langle s_{\mp}\rangle/g\beta s) \tag{2}$$

The effective field H_{eff} takes into account the intersublattice nearest-neighbor exchange interactions through the mean spin quantum numbers $\langle s_+\rangle$ and $\langle s_-\rangle$ of the two sublattices. These are the unknowns of the problem.

Any spin s on one sublattice is hereby assumed to be coupled to z nearest neighbors on the other sublattice. Intrasublattice or next-nearest-neighbor interactions will be assumed here to be negligibly small. The splitting factor g is taken to be isotropic in coordinate space, with β denoting the appropriate elementary magnetic dipole moment, and J the exchange energy parameter. The subscripts plus and minus differentiate between sublattices or quantities according as their direction of spontaneous spin ordering is parallel or antiparallel to the direction of the applied external magnetic field, respectively. If there are $\frac{1}{2}N$ spins per unit volume on either sublattice, their average magnetizations along the axis of the field are, respectively,

$$M_{\pm}(J, H, s) = \tfrac{1}{2}Ng\beta\langle s_{\pm}\rangle \tag{3}$$

The relative magnetizations are thus, per spin,

$$\sigma_{\pm}(J, H, s) = M_{\pm}/\tfrac{1}{2}Ng\beta s = \langle s_{\pm}\rangle/s \tag{4}$$

where, as in (2), s is the magnitude of the spin vectors of the system. The total relative mean magnetization is thus

$$\sigma_t(J, H, s) = \tfrac{1}{2}(\sigma_+ + \sigma_-) \tag{5}$$

and $\frac{1}{2}Ng\beta s$ is the sublattice saturation magnetization. On ensemble averaging at the temperature T, over the effective Zeeman levels of (1), referring to the spin components $(s, s-1, \ldots, -(s-1), (-s))$, and assuming $H_{\text{eff}\pm}$ to be known in spite of their explicit dependence, by (2), on the unknown mean spins $\langle s_+\rangle$ and $\langle s_-\rangle$, one obtains in a straightforward way

$$\sigma_{\pm}(J, H, T, s) = \langle s_{\pm}(J, H, T, s)\rangle/s = B_s(y_{\pm}) \tag{6}$$

with

$$y_{\pm} = (g\beta s/kT)H_{\text{eff}\pm} \tag{7}$$

and

$$B_s(x) = \frac{2s+1}{2s}\coth\left(\frac{2s+1}{2s}x\right) - \frac{1}{2s}\coth\left(\frac{1}{2s}x\right) \tag{8}$$

the Brillouin function of ideal spin-s systems. It is convenient to rewrite the parameters y_+ and y_- as

$$y_{\pm} = (2Jzs^2/kT)[(g\beta sH/2Jzs^2) - \sigma_{\mp}] \tag{9}$$

In the limit $H \to 0$, (6) reduces through (9) to

$$\sigma_{\pm}(J, H \to 0, T, s) = B_s(-2Jzs^2\sigma_{\mp}/kT) \tag{10}$$

and since the total magnetization of the unmagnetized antiferromagnet vanishes,

$$\sigma_+(J, T, s) + \sigma_-(J, T, s) = 0 \tag{11}$$

the sublattice magnetizations cancel, being equal and of opposite sign. Hence,

$$\sigma_+(J, T, s) = -\sigma_-(J, T, s) = \sigma(J, T, s) \tag{12}$$

and

$$\sigma(J, T, s) = B_s(2Jzs^2\sigma/kT) \tag{13}$$

The present approximate mean-field formalism defines, from below, i.e., from the low-temperature side, the transition or Néel temperature $T_N(0)$ at which spin ordering vanishes. Or, in the limit of very small relative sublattice magnetization, $\sigma \ll 1$, one has

$$\begin{aligned} \lim_{T \to T_N(0)} \sigma(J, T, s) &= \lim_{\substack{\sigma \ll 1 \\ T \to T_N(0)}} B_s(2Jzs^2\sigma/kT) \\ &\approx [(s + 1)/3s][2Jzs^2\sigma/kT_N(0)] \end{aligned} \tag{14}$$

yielding

$$kT_N(0) = \tfrac{2}{3}s(s + 1)Jz \tag{15}$$

the mean-field transition temperature.

We will be led below to compare some temperature-dependent properties of anisotropic exchange-coupled antiferromagnets of various spin quantum numbers s. The exchange parameter may thus be left largely undetermined. We will assume that $T_N(0)$ remains finite in the limit $s \gg 1$ or $s \to \infty$. If instead J had been normalized[5] as $J' \to J/s^2$, the associated Néel temperature $T_{N,s\to\infty}(0)$ would be finite. However, for direct comparison of various two-sublattice spin-s system properties with those obtained previously in particular cases, the use of the present notation appeared preferable.

We want to rewrite the parameters $y_\pm$ as

$$\begin{aligned} y_\pm &= [3s/(s + 1)][T_N(0)/T]\{[(s + 1)/3s](H/H_c) - \sigma_\mp\} \\ &= (h' - \sigma_\mp)/t' \end{aligned} \tag{16}$$

with

$$\begin{aligned} H_c(s) &= kT_N(0)/\mu_s, \qquad \mu_s = g\beta s \\ h' &= [(s + 1)/3s]h, \quad h = H/H_c \\ t' &= [(s + 1)/3s]t, \quad t = T/T_N(0) \end{aligned} \tag{17}$$

With (16) and (6), the assumed stable parallel-field configuration magnetic

equations of state of the present two-sublattice antiferromagnet subject to the nearest-neighbor exchange coupling included in (2) are then

$$\sigma_{\pm}(J, T, H, s) = B_s[(h' - \sigma_{\pm})/t'] \tag{18}$$

The two sets of reduced variables (h', t') and (h, t) of Eq. (17) become identical for spin $\frac{1}{2}$. The ranges of variation of σ_+ and σ_-, are, respectively,

$$0 \leq \sigma_+ \leq 1, \qquad -1 \leq \sigma_- \leq 1 \tag{19}$$

The values of h' are zero at $T_N(0)$, and unity at $t' \to 0$, while h is $3s/(s+1)$ in the limit $t \to 0$. By (17), one has

$$0 \leq t \leq 1, \qquad 0 \leq t' \leq (s+1)/3s \tag{20a}$$

It is to be noted, however, that the present model allows h' and h to take on values larger than the limit values of unity or $3s/(s+1)$, respectively. This will appear through the degenerate situation where the differentiation between the sublattices ceases or $\sigma_+ = \sigma_- = \sigma$. It is seen that

$$h'(J, T, s) \leq h(J, T, s), \qquad t' \leq t \tag{20b}$$

and

$$H(T \to 0, s) = [3s/(s+1)]H_c(s) = 2Jzs/g\beta = H_E(s), \tag{21}$$

a frequently used notation.[6]

The system of two equations of state (18) determines the relative sublattice magnetizations σ_+ and σ_- in terms of the reduced field strength h' and reduced temperature t', or, respectively, h and t. The transcendental B_s functions prevent one, however, from expressing σ_+ and σ_- in closed forms of h' and t'.

The mean-field magnetic equations of state of two-sublattice antiferromagnets with anisotropic intersublattice exchange coupling and anisotropic intrasublattice interactions have been discussed extensively for spin-$\frac{1}{2}$ systems by Gorter and Van Peski-Tinbergen.[7] Some aspects of these equations for general spin-s systems have been considered by Gijsman.[8] The compact general spin-s equations of state (18) are seen to reduce to those given first by Garrett[9] for spin-$\frac{1}{2}$ systems provided the fictitious isotropic Heisenberg exchange coupling between nearest neighbors is replaced by the anisotropic Ising coupling, or by postulating in the system the existence of a very large anisotropy field of magnetocrystalline or of other origin, assuring thereby the thermodynamic stability of the parallel-field configuration.

We should like to emphasize at this point that the complete or almost complete stability of the parallel-field configuration is also assumed explicitly in the present paper. In turn, this assumption is equivalent to an indirect and qualitative justification of the mean-field formalism since the configurational

stability prevents the simple spin-wave formalism[6] from being valid over most of the relevant temperature range, $0 \leq T \leq T_N(0)$.* The above additional assumption, without the explicit introduction of a strong anisotropy field, tends to extend the validity of the present treatment to systems with antiferromagnetic isotropic or Heisenberg nearest-neighbor exchange interactions.†

We turn now to the problem of the parallel-field magnetic configuration phase-boundary line of uniaxial spin-s two-sublattice antiferromagnets described approximately by the system of equations of state (18). Using the latter with (16), one has

$$h' - t'y_- = B_s(y_+), \qquad h' - t'y_+ = B_s(y_-) \tag{22}$$

These give

$$t'(y_+, y_-, s) = [B_s(y_+) - B_s(y_-)]/(y_+ - y_-) \tag{23}$$

and

$$h'(y_+, y_-, s) = [y_+B_s(y_+) - y_-B_s(y_-)]/(y_+ - y_-) \tag{24}$$

In the (h', t') plane the phase-boundary line is the locus of points where the distinction between the two sublattices disappears and both acquire the same magnetization, or

$$\sigma_+ \to \sigma_- \to \sigma, \qquad y_+ \to y_- \to y \tag{25}$$

Hence,

$$\lim_{y_+ \to y_- \to y} t'(y, s) = \lim_{y_+ \to y_- \to y} [B_s(y_+) - B_s(y_-)]/(y_+ - y_-)$$
$$= dB_s(y)/dy = d\sigma(y, s)/dy, \tag{26}$$

and

$$\lim_{y_+ \to y_- \to y} h'(y, s) = d[yB_s(y)]/dy$$
$$= B_s(y) + y(dB_s/dy) = \sigma(y, s) + yt'(y, s) \tag{27}$$

the latter resulting also at once, in the above limit, from (16). Equations (26) and (27) with

$$\sigma(y, s) = B_s(y) \tag{28}$$

*For a modification of the spin-wave formalism in systems of the type considered in the text see ref. 6. This modification is tied to the exponential decrease of the number of spin-wave excitations over most of the temperature range of antiferromagnets with almost complete parallel-field configuration stability. In this connection see Kubo.[10]

†The parallel-field configuration stability of exchange-coupled solid ^{3}He model was implicitly assumed in our mean-field treatment of the cooling on adiabatic solidification of ^{3}He in presence of a constant and uniform external magnetic field. See Goldstein.[11]

which results from (18) with (25), are the complete set of mean-field parametric equations of the parallel-field configuration phase-boundary lines of spin-s two-sublattice antiferromagnetic systems subject to nearest-neighbor exchange couplings of either totally anisotropic character or such that this configuration has thermodynamic stability.

Explicitly with the definition (8) of $B_s(y)$, one finds

$$t'(y,s) = \left(2s \sinh\frac{y}{2s}\right)^{-2} - \left\{2s\left[\sinh\left(\frac{2s+1}{2s}y\right)\right]\Big/(2s+1)\right\}^{-2} \tag{29}$$

One can also write down explicitly $h'(y,s)$ with (8) and (27)–(29). This is somewhat long and need not be given here.

The phase-boundary lines $h'(t',s)$ or $t'(h',s)$ in the (h',t') plane, and correspondingly $h(t,s)$ or $t(h,s)$ in the (h,t) plane, can only be given after elimination of y between the parametric forms $h'(y,s)$ and $t'(y,s)$, or $h(y,s)$ and $t(y,s)$. This elimination succeeds formally for spin $\frac{1}{2}$ only.

It is instructive to consider the parametric forms of t' and h' for $s = \frac{1}{2}$. As noted above, in this special case t' and h' are identical with t and h. One has at once, with (26), (27), and (29),

$$t(y, s = \tfrac{1}{2}) = 1 - \tanh^2 y = 1 - \sigma^2(y, s = \tfrac{1}{2}) \tag{30}$$

since

$$\sigma(y, s = \tfrac{1}{2}) = B_{1/2}(y) = \tanh y \tag{31}$$

Hence, by (27) and (31),

$$\begin{aligned} h(y, s = \tfrac{1}{2}) &= \sigma + yt = \sigma + (1 - \sigma^2)\tanh^{-1}\sigma \\ &= (1-t)^{1/2} + t\tanh^{-1}(1-t)^{1/2} \end{aligned} \tag{32}$$

The phase-boundary lines (30) and (32) were first given by Garrett.[9] As far as we are aware, the general parallel-field parametric phase-boundary lines (26) and (27) for arbitrary spin-s two-sublattice systems have not been written down. Gijsman[8] gave $t'(y,s)$, Eq. (29), or its equivalent $t(y,s)$, Eq. (17), with the sinh function in the denominators on the right-hand side of (29) appearing linearly, an apparent misprint. This same misprinted form reappears, however, in the $t(y, s = \frac{5}{2})$ function specialized for spins $\frac{5}{2}$. The $t(y,s)$ function has been obtained by Gijsman from a consideration of the geometric discussion of the (h,σ) plane given earlier by Gorter and Van Peski-Tinbergen.[7] The derivation of $t'(y,s)$, Eq. (26), given above appears to be direct and simple.

It is instructive to consider the limiting behavior of $t'(y,s)$ and $h'(y,s)$, or $t(y,s)$ and $h(y,s)$. One has with (29), in the limit of large y, $y \gg 1$,

$$\lim_{y \gg 1} t(y,s) \approx [3/s(s+1)]\, e^{-y/s}[1 - (2s+1)^2 e^{-2y} + \cdots] \tag{33}$$

showing that $t(y, s)$ is exponentially small at large y. Similarly, one finds

$$\lim_{y \ll 1} h(y, s) \approx [3s/(s+1)] + [3y/s(s+1)]\, e^{-y/s}[1 - (2s+1)^2\, e^{-2y} + \cdots] \quad (34)$$

Hence, $h(y, s)$ increases from its limit value of $3s/(s+1)$, at $t \to 0$ or $y \to \infty$, as t increases or y decreases. Since $h(y, s)$ must vanish at $y \to 0$, in the limit of the zero-field transition temperature $T_N(0)$ it is seen that $h(y, s)$ must have at least one maximum over the y range, or $h(t, s)$ is nonmonotonic between $t = 0$ and $t = 1$.

In the opposite limit of $y \ll 1$, near the zero-field transition $T_N(0)$, one obtains, expanding the exact mean-field parametric form $t'(y, s)$, Eq. (20), or its equivalent $t(y, s)$,

$$\lim_{y \ll 1} t(y, s) = 1 - (y^2/10s^2)(2s^2 + 2s + 1) \quad (35)$$

to order y^2. Since, by (8) and (28),

$$\lim_{y \ll 1} \sigma(y, s) = \lim_{y \ll 1} B_s(y) \approx [(s+1)/3s]y \quad (36)$$

one has

$$\lim_{y \ll 1} h'(y, s) \approx [(s+1)/3s]y[1 + t(y, s)]$$

$$\approx [(s+1)/3s](2y) \quad (37)$$

and, with (17),

$$\lim_{y \ll 1} h(y, s) \approx 2y \ll 1 \quad (38)$$

to lowest order in y, for all s. Using this connection between h and y in (35), one obtains at once

$$\lim_{h \ll 1} t(h, s) = 1 - (h^2/40s^2)(2s^2 + 2s + 1) \quad (39)$$

Or, using (17) again for t and h, the latter becomes

$$\lim_{H \text{ small}} T(H, s) = T_N(0, s) - [g^2\beta^2H^2/40k^2T_N(0, s)](2s^2 + 2s + 1) \quad (40)$$

to lowest order in H, giving the very small-field-limiting parabolic arc of the parallel-field phase-boundary line $T(H, s)$. Equation (40) was given earlier by Heller[12] and Shapira and Foner.[13]

The closed analytical expressions of $t'(y, s)$ and $h'(y, s)$, or $t(y, s)$ and $h(y, s)$, as well as of $\sigma(y, s)$, enable of course their exact calculation for any y. They are given in Figs. 1 and 2 for spins $\frac{1}{2}$ and 1, and $\frac{3}{2}$ and $\frac{5}{2}$, respectively, over the y range (0, 5). The $t(y, s)$, $\sigma(y, s)$ functions are monotonic, while $h(y, s)$ displays one maximum as implied above. The linear small-y behavior, Eq. (38), is seen to be well exhibited up to almost $y \sim 0.4$.

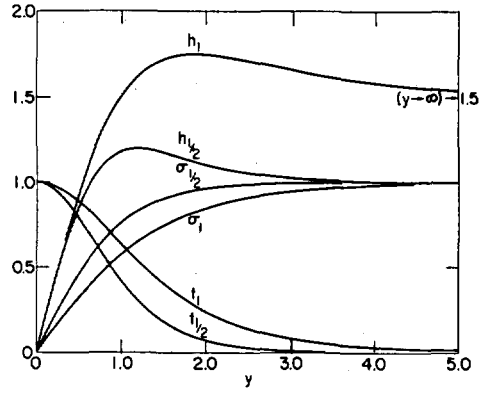

Fig. 1. Parametric representation of the reduced temperature t, reduced magnetization σ, and reduced field strength h, along the parallel-field phase-boundary line of spin-$\frac{1}{2}$ and spin-1 antiferromagnets. The parameter y is defined in the text.

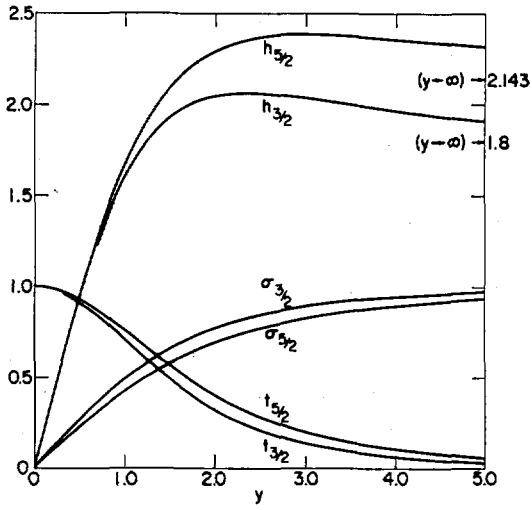

Fig. 2. Same as Fig. 1, for spins $\frac{3}{2}$ and $\frac{5}{2}$. Numerical values of the functions $h(t, s)$, $h(\sigma, s)$, or their inverses can be read off the parametric curves. The shift of the maximum values of $h(y, s)$ toward larger y values and their flattening out are seen to develop with increasing s value.

By Eq. (34), the limiting value of the phase-boundary parallel field strength at the absolute zero is

$$\lim_{T\to 0} H(T, s) = [3s/(s + 1)]H_{c,s} \tag{41}$$

The maximum of $h'(y, s)$ or $h(y, s)$ is tied to the definition (27) or

$$h'(y, s) = (d/dy)[y\sigma(y, s)] \tag{42}$$

and

$$dh'(y, s)/dy = 2(d\sigma/dy) + y(d^2\sigma/dy^2) \tag{43}$$

where on the right-hand side

$$d\sigma/dy > 0, \qquad d^2\sigma/dy^2 < 0 \tag{44}$$

as a consequence of the monotonic increase of $\sigma(y, s)$ toward its saturation limit of unity. The right-hand side of dh'/dy is the sum of two terms of opposite sign.

In order to obtain the parallel-field configuration phase-boundary lines $h(t, s)$, $h(\sigma, s)$, and $\sigma(t, s)$ in the (h, t), (h, σ), and (σ, t) planes, numerical or graphical procedures must be used for the elimination of y among the state variables, $h(y, s)$, $t(y, s)$, and $\sigma(y, s)$. The graphical elimination is quite simple, in that one has but to plot these state variables on the same graph for the given spin s and read off along the ordinates the values of h, t, and σ for the same y. Since $t(y, s)$ and $\sigma(y, s)$ are of monotonic variation, $h(t, s)$ and $h(\sigma, s)$ are nonmonotonic and have one maximum as $h(y, s)$. Figures 1 and 2 are seen to yield $h(t, s)$, $h(\sigma, s)$, $\sigma(t, s)$, etc.

For spins $\frac{1}{2}$ the nonmonotonic mean-field phase-boundary line $h(t)$ was first given by Garret,[7] and the one for $\frac{5}{2}$ by Gijsman.[8] One finds that the temperature intervals over which the phase-boundary lines $h(t, s)$ are larger than their $t \to 0$ limit decrease slowly with increasing s. Or, denoting these intervals by t_1,

$$t_1(h, s) > t_1(h, s'), \qquad s' > s \tag{45}$$

suggesting that in the limit of s becoming very large $h(t, s)$ should become monotonic throughout the spin-ordering temperature range $0 \leq t \leq 1$.

While primarily of formal interest, it appears instructive to discuss the phase-boundary line $h(y, s)$, $t(y, s)$ of the assumed exchange-coupled two-sublattice spin $s \to \infty$ antiferromagnet. Using (16), one still has

$$y_{\pm}(s \to \infty) = [h'(s \to \infty) - \sigma_{\pm}(s \to \infty)]/t'(s \to \infty) \tag{46a}$$

and

$$h'(t' \to 0, s \to \infty) = \tfrac{1}{3}h(t \to 0, s \to \infty) = \tfrac{1}{3}(H/H_{c,s\to\infty}),$$

$$t' = t/3, \qquad t = T/T_N(0, s \to \infty), \qquad H_{c,s\to\infty} = kT_N(0, s \to \infty)/\mu \tag{46b}$$

going to the limit $s \to \infty$ in (17) and assuming that μ is finite in this limit, together with $T_N(0, s \to \infty)$ and correspondingly also $H_{c,s\to\infty}$. The Brillouin function becomes the Langevin function, or

$$\lim_{s\to\infty} B_s(x) = \mathscr{L}(x) = \coth x - x^{-1}. \tag{47}$$

The magnetic equations of state, in the parallel-field configuration, of such a system are thus

$$\sigma_\pm(h', t') = \mathscr{L}[(h' - \sigma_\mp)/t'] = \mathscr{L}(y_\pm) \tag{48}$$

Along the phase-boundary line one has, by (26),

$$t'(y, s \to \infty) = d\mathscr{L}/dy = 1 + (1/y^2) - \coth^2 y \tag{49}$$

and

$$\lim_{y\gg 1} t'(y, s \to \infty) \approx 1/y^2 \tag{50}$$

and

$$\lim_{y\ll 1} t'(y, s \to \infty) \approx \tfrac{1}{3} - (y^2/15) \tag{51a}$$

or

$$\lim_{y\ll 1} t(y, s \to \infty) \approx 1 - (y^2/5) \tag{51b}$$

which is seen to result also from (35) as $s \to \infty$.

Using (27), one has

$$h'(y, s \to \infty) = (d/dy)[y\mathscr{L}(y)] \tag{52}$$

and

$$dh'(y, s \to \infty)/dy = 2y\mathscr{L}(y)/\sinh^2 y \geq 0 \tag{53}$$

showing that $h'(y)$ increases monotonically over the range of y. Consequently, the limit unity of $h'(y, s \to \infty)$ as $y \to \infty$ is reached from below. One has, indeed, with (52) and (47),

$$h'(y, s \to \infty) = \coth y + y(1 - \coth^2 y) \tag{54}$$

and

$$\lim_{y\gg 1} h'(y, s \to \infty) \approx 1 - 4ye^{-2y} < 1 \tag{55}$$

as indicated qualitatively in connection with (53).

In the limit of small y, or near the Néel point, one has, to terms linear in y,

$$\lim_{y\ll 1} h'(y, s \to \infty) \approx \tfrac{2}{3}y \tag{56a}$$

or

$$\lim_{y \ll 1} h(y, s \to \infty) \approx 2y \tag{56b}$$

which is the same as the limit (38) given above, since this very small-y limit is independent of s.

Using (56b) and (51b), one obtains

$$\lim_{y \ll 1} t(h, s \to \infty) \approx 1 - (h^2/20) \tag{57}$$

to lowest order in h. This latter limit follows also from (39) as $s \to \infty$. A glance at (39) and (57) shows that the depression of the spin-ordering transition temperature for the same applied reduced field strength is the largest for spins $\frac{1}{2}$ and decreases with increasing s as indicated by Eq. (35). This is so because the spin-ordering effect of the applied external field, of the same reduced intensity, tending to drive the system into the antiferromagnetic region is the less efficient the smaller the initial spin disorder or the smaller the spin s.

It may be of interest to mention that a detailed analysis of the spin-$\frac{1}{2}$ case, not to be included here, shows the following. The subregion of the antiferromagnetic phase limited by the chord and arc

$$h = h(t = 0, s), \qquad \text{arc } h(t, s) = (h(t = 0, s), h_{\max}, h(t = 0, s))$$

the arc defined through the ordinates of three points, is fairly complex. Namely, this limited portion of the phase diagram is further subdivided by a locus along which some derivative properties of the system vanish. On one side of this locus, on its high-temperature side, the derivative properties are similar to those of an antiferromagnet. On the low-temperature side of the locus, the derivative properties are similar to those of a paramagnet. The nonmonotonic character of the phase-boundary lines $h(t)$ or $h(\sigma)$ has the consequence that their inverse function is doubly-valued in h over the indicated subregion of the spin-ordered phase. This has no effect, however, on the entropy, for instance, either along the phase-boundary line or inside the whole parallel-field configuration of the antiferromagnetic phase.

This paper will be concerned mostly with the assumed stable parallel magnetic-field configuration of appropriate antiferromagnets. In order, however, to complete their discussion, it seems useful to consider also their perpendicular-field configuration. An abbreviated discussion of this transverse-field configuration is the subject matter of the next section.

3. THE PERPENDICULAR MAGNETIC FIELD CONFIGURATION OF SPIN-s TWO-SUBLATTICE ANTIFERROMAGNETS

The external applied magnetic field is now at a right angle to the direction of the zero-field spontaneous spin ordering. The zero-field sublattice magnetization vectors are perfectly symmetric with respect to the external field. The starting magnetic symmetry of the system, of vanishing total spontaneous magnetic moment in the limit of very small external field, must remain conserved. As a consequence of the permanent magnetic equivalence of the two sublattices with respect to the external field, the latter affects both in a similar way, and becomes thereby incapable of producing magnetic asymmetry or magnetic disorder. The application of an external field thus cannot create magnetic entropy over and above the entropy existing in the system prior to the switching on of the field. Hence the component sublattice magnetizations in their common plane perpendicular to the external field must always cancel, as in the limit of vanishing external field. As the latter increases from zero at a constant temperature a field strength is reached where paramagnetism is established, or where the permanently equal-magnitude sublattice-magnetization vectors become parallel to the direction of the external field. This state of parallel magnetization vectors reached at some critical field strength at a constant temperature has the same magnetic order as the one that existed prior to the application of the field. The magnetic entropy in the perpendicular-field configuration at a constant temperature is thus independent of the field strength. The final state of paramagnetic configuration is thus reached in the following way: The initial zero-field sublattice magnetization vectors, of constant length, must be rotated from their initial starting plane until after a rotation of $(\pi/2)$ radians, on reaching the critical field strength, they are dragged into parallelism with each other and the starting perpendicular-field direction.

In the starting zero-field configuration, one has

$$|\boldsymbol{\sigma}_+| = |\boldsymbol{\sigma}_-| = \sigma(T, H = 0) \tag{58}$$

The definition (2) of the effective field becomes now vectorial, through

$$\mathbf{H}_{\mathrm{eff}\pm} = \mathbf{H} + \mathbf{H}_{x\pm} \tag{59}$$

$$\mathbf{H}_{x\pm} = -2Jzs\boldsymbol{\sigma}_{\mp}/g\beta \tag{59a}$$

by (2). The vector triangles (59) are congruent since the sublattices are strictly equivalent. These triangles have a common side of length $|\mathbf{H}|$. Now, the effective fields arise with the magnetizations of the opposite sublattices and they are parallel to the magnetization vectors, or $\mathbf{H}_{\mathrm{eff}\pm} \parallel \mathbf{H}_{x\pm}$. Hence,

these triangles are also isosceles since the fields $\mathbf{H}_{\text{eff}\pm}$ and $\mathbf{H}_{x\pm}$ are also of the same length, the former being defined through the sublattice magnetizations, which are equal because of sublattice equivalence. One thus has in these triangles

$$\cos(\mathbf{H}, \boldsymbol{\sigma}_{\pm}(T, s)) = |\mathbf{H}|/2|\mathbf{H}_{x\pm}(T, s)| = \cos \delta_{\pm}(H, T, S) \tag{60}$$

Omitting the plus and minus subscripts, using (17), and multiplying and dividing H_x by $3s/(s + 1)$, one finds

$$\cos \delta(h', t', s) = h'(T, s)/2\sigma(t, s) \tag{61}$$

By definition, along the critical phase-boundary line the canting angle $\delta(T, s)$ must vanish, or

$$h' = [(s + 1)/3s]h = 2\sigma \tag{62}$$

along this line. On the other hand, by Eqs. (18) and (25), one must have, using (62),

$$\begin{aligned} \sigma(h', t', s) = B_s(y) = B_s[(h' - \sigma)/t'] = B_s(\sigma/t') \\ = B_s(h'/2t') = B_s(h/2t) \end{aligned} \tag{63}$$

The two sublattices behave, as far as their relative magnetizations are concerned, as classical free Weiss ferromagnets.

From (63) one has, always, along the perpendicular-field configuration phase-boundary line

$$\begin{aligned} t_s(y) = h_s/2y_s = [(s + 1)/6s]h_s'/y_s \\ = [(s + 1)/3s]\sigma_s/y_s = [(s + 1)/3s]B_s(y)/y \end{aligned} \tag{64}$$

On elimination of y among $t_s(y)$, $h_s(y)$, and $\sigma_s(y)$, one obtains the phase-boundary lines $t_s(h)$ or $h_s(t)$, $\sigma_s(t)$ or $\sigma_s(h)$, the latter being the explicit linear connection (62). The functions $h_s(t)$ and $\sigma_s(t)$ cannot be expressed in closed form, as a consequence of the transcendental character of $B_s(y)$.

By Eqs. (61) and (62), the component of the rotated sublattice relative magnetization vectors along the direction of the external field, $\sigma_{+,H}$ or $\sigma_{-,H}$, or simply σ_H, is

$$\sigma_H = \sigma(t, s) \cos \delta(t, s) = h'/2 \equiv [(s + 1)/6s]h \tag{65}$$

a quantity independent of the temperature. In the (h, t) diagram of this field configuration lines of constant reduced external field are also lines of constant component relative magnetization σ_H, and correspondingly in the (H, T) plane.

Inasmuch as

$$0 \leq \sigma_H \leq 1 \tag{66}$$

it is seen that the reduced field strength at which all the spins have been dragged parallel to the applied field is, by (63) or (66),

$$h_{c,\perp} = 6s/(s+1), \tag{67a}$$

or

$$H_{c,\perp} = [6s/(s+1)]H_c \tag{67b}$$

with H_c defined by (17).

By (63) and (64),

$$h'(t', s) = 2B_s(h'/2t') \tag{68}$$

and in the limit $t' \ll 1$, h' may be replaced by 2 in the argument of B_s, leading to

$$\begin{aligned} \lim_{t' \ll 1} h'(t', s) &= 2 \lim_{t' \ll 1} B_s(1/t') \\ &\approx 2\{1 - (1/s)\exp((-1/st')[1 - (2s+1)\exp(-2/t') + \cdots]\} \end{aligned} \tag{69}$$

the expected exponential approach toward the limit of 2 of h'.

In the opposite limit of $\sigma \ll 1, h \ll 1$ one finds after some algebra

$$\begin{aligned} \lim_{h \ll 1} t_\perp(h, s) &\approx 1 - [h^2(2s^2 + 2s + 1)/120s^2] \\ &= 1 - \{(g\beta H)^2(2s^2 + 2s + 1)/120[kT_N(0)]^2\} \end{aligned} \tag{70}$$

to order h^2 or H^2. Comparison of the coefficients of the parabolic terms in $t_\perp(h, s)$ and $t(h, s)$, Eq. (40), shows that

$$dt(h \ll 1, s)/d(H^2) = 3\, dt_\perp(h \ll 1, s)/d(H^2) \tag{71}$$

Or, at small external field strengths, the depression of the zero-field transition temperature $T_N(0)$ in the parallel-field configuration is three times larger than in the perpendicular-field configuration. The implicit phase-boundary line (68) as well as the limiting parabola (70) have also been given recently by Shapira and Foner.[13]

It is instructive to consider briefly this field configuration in the limit $s \to \infty$. One has with (64) and (47)

$$\lim_{s \to \infty} t_\perp(y, s) = \tfrac{1}{3}\mathscr{L}(y)/y \tag{72}$$

and, by (68) and (17),

$$\lim_{s \to \infty} h_{c,\perp}(t \to 0) = 6 \tag{73a}$$

or

$$H_{c,\perp}(t \to 0, s \to \infty) = 6H_{c,s\to\infty} = 6kT_N(0)/\mu \tag{73b}$$

using the definition (46) for $H_{c,s\to\infty}$. The latter critical field (73b) is again twice the critical field ($3H_{c,s\to\infty}$) needed to drag the spins parallel to the external field in the parallel-field configuration given by (46).

The approach of $h'_{s\to\infty,\perp}$ toward its $y\to\infty$ limit results at once from (68) with $h'_\perp$ taken there to be equal to 2 in the argument of $B_{s\to\infty}(h'/2t')$, or in $\mathscr{L}(h'/2t')$. To terms linear in t'

$$\lim_{t'\ll 1} h'_{s\to\infty,\perp}(t') = \lim_{t'\ll 1} 2\mathscr{L}(1/t') \approx 2(1-t') \tag{74}$$

and

$$\lim_{t\ll 1} h_{s\to\infty,\perp} = 6(1-\tfrac{1}{3}t) \tag{75}$$

according to the large-argument behavior of $\mathscr{L}(x)$.

As a consequence of the permanent magnetic symmetry of the perpendicular-field or canted configuration, the latter can not be used for cooling. A marginal cooling effect may still exist, however, but it will not be considered here.

4. MEAN-FIELD-THERMAL PROPERTIES OF MAGNETIZED ANTIFERROMAGNETS

4.1. Thermal Properties Along the Phase-Boundary Lines

The partition function of the system in the present approach is

$$Z(T,H,s) = Z_+(T,H,s)Z_-(T,H,s) \tag{76}$$

with the sublattice partition functions

$$\begin{aligned} Z_\pm^{1/(N/2)} &= \sum_{-s}^{s} \exp\left(-g\beta s H_{\mathrm{eff}\pm}/kT\right) \\ &= \sinh\left(\frac{2s+1}{2s}y_\pm\right)\Big/\sinh\left(\frac{1}{2s}y_\pm\right) \end{aligned} \tag{77}$$

with parameters $y_\pm$ defined by (10) or (16). The total entropy is thus

$$\begin{aligned} S(T,H,s)/k &= (\partial/\partial T)[T\ln Z(T,H,s)] \\ &= S_+(T,H,s) + S_-(T,H,s) \end{aligned} \tag{78}$$

and

$$S_\pm(T,H,s)/Nk = \frac{1}{2}\ln\left[\sinh\frac{2s+1}{2s}y_\pm\Big/\sinh\frac{1}{2s}y_\pm\right] - \frac{1}{2}y_\pm\sigma_\pm. \tag{79}$$

We have to consider first the entropies along the phase-boundary lines of the two supplementary field configurations. Along the parallel-field boundary $y_+ \to y_- \to y$, and one finds

$$S_{c,\parallel}(T, H, s)/Nk = \ln\left[\sinh\left(\frac{2s+1}{2s}y\right)\Big/\sinh\left(\frac{1}{2s}y\right)\right] - y\sigma$$
$$y = (h' - \sigma)/t' \tag{80}$$

Near $h' \to 0$, or $h \to 0, y \to 0, \sigma \to 0$, one has the full entropy of $Nk \ln(2s+1)$. In the opposite limit one finds

$$\lim_{y \gg 1} S_{c,\parallel}/Nk \approx (y/s)\, e^{-y/s} \tag{81}$$

Along the perpendicular-field phase boundary line we saw above that

$$y = h'/2t' = h/2t = \sigma/t' \tag{82}$$

and the entropy becomes there

$$S_{c,\perp}/Nk = \ln\left\{\sinh\left[\frac{2s+1}{2s}(\sigma/t')\right]\Big/\sinh\left[\frac{1}{2s}(\sigma/t')\right]\right\} - (\sigma^2/t'), \tag{83}$$

identical to the zero-field entropy of a spin-s Weiss ferromagnet. One has here also

$$\sigma_{\perp,s} = B_s(\sigma/t') \tag{84}$$

the magnetic equation of state of a spin-s ferromagnet.

It is appropriate to consider briefly the heat capacities along the phase-boundary lines. One finds

$$C_{c,\parallel}/Nk = t'(d/dt')(S_{c,\parallel}/Nk)$$
$$= t'(dy/dt')(-y)(dB_s/dy) \tag{85}$$

By Eq. (26) this is also

$$C_{c,\parallel}/Nk = -yt'^2(dy/dt') = -yt'^2/(dt'/dy) = -y(B_s')^2/B_s''(y) \tag{86}$$

with

$$B_s'(y) = dB_s/dy$$
$$= (2s \sinh v)^{-2} - \left(\frac{2s+1}{2s}\right)^2 (\sinh u)^{-2} \tag{87}$$

and

$$B_s''(y) = d^2B_s/dy^2 = 2\left[\left(\frac{2s+1}{2s}\right)^3(\coth u)(\sinh u)^{-2} - \left(\frac{1}{2s}\right)^3(\coth v)(\sinh v)^{-2}\right]$$
$$u = [(2s+1)/2s]y, \qquad v = y/2s. \tag{88}$$

In spin-$\frac{1}{2}$ systems

$$t' = t, \qquad t = 1 - \sigma^2, \qquad \sigma = \tanh y,$$
$$y = \tanh^{-1}(1-t)^{1/2}, \qquad dy/dt = (-)1/[2t(1-t)^{1/2}] \tag{89}$$

and

$$(C_{c,\parallel}/Nk)_{s=1/2} = \tfrac{1}{2}t(1-t)^{-1/2}\tanh^{-1}(1-t)^{1/2} \tag{90}$$

Along the perpendicular-field phase-boundary line one finds with (83) and (84)

$$C_{c,\perp}/Nk = -\tfrac{1}{2}d\sigma^2/dt'$$
$$= (\sigma/t')^2/[(dB_s/dy)^{-1} - t'^{-1}] \tag{91}$$

with dB_s/dy given by (87) and keeping in mind the relations (82). For $s = \frac{1}{2}$ this reduces to

$$(C_{c,\perp}/Nk)_{s=1/2} = (\sigma/t)^2/[\cosh^2(\sigma/t) - t^{-1}] \tag{92}$$

which is one heat capacity form we used recently for spin-$\frac{1}{2}$ systems.[14]

4.2. Thermal Properties of Magnetized Antiferromagnets in Their Spin-Ordering Phase. Cooling on Adiabatic Magnetization

The sublattice entropies, Eq. (79), complete the magnetic equations of state, Eqs. (9)–(16) and (17), of general spin-s antiferromagnets, assumed to be fully stable over the whole parallel-field configuration phase. Since the entropies have no closed analytical forms, they must be calculated numerically. This requires the calculation of the sublattice relative magnetizations σ_+ and σ_- which enter into the entropy equations through y_+ and y_-; the sublattice parametric variables.

Before analyzing these entropies it seems useful to discuss S_+ and S_- as well as σ_+ and σ_- in terms of y_+ and y_-. We will be mostly concerned with the way the sublattice and total magnetizations and entropies approach their respective limit values at the very low temperatures. As in recent work[14] in connection with the zero-field behavior of the nuclear spin-$\frac{1}{2}$

model antiferromagnet of solid ^{3}He, the Néel temperature and the experimentally determined entropy at this temperature are taken to be the empirical constants of the formalism. If $S(T_N(0), s)$ is the empirical Néel-point spin entropy of the system whose entropy is compared to the calculated mean-field entropy, the latter has to be modified so as to be expressed as

$$S(T, H, s) \doteq [S(T_N(0), s)/R \ln (2s + 1)]S_{mf}(T, H, s) \tag{93}$$

where the mean-field entropy of the magnetized system $S_{mf}(T, H, s)$ is given by (78) and (79). Clearly the heat capacities as well as all thermal properties derived from the entropies (93) will carry the constant empirical normalizing factor $[S(T_N(0), s)/R \ln (2s + 1)]$. By (78),

$$S(T, H, s) = [S(T_N(0), s)/R \ln (2s + 1)][S_+(T, H, s) + S_-(T, H, s)] \tag{94}$$

S_+ and S_- referring, by (79), to the mean-field sublattice entropies. Since the latter reduce to $\frac{1}{2}R \ln (2s + 1)$ at $T_N(0)$, $S(T, H, s)$ is seen to reduce to $S(T_N(0), s)$ at $T_N(0)$.

It is of particular interest for our purpose to discuss the entropy of the two-sublattice magnetized antiferromagnets in the limit of $T \to 0$. In this limit one has

$$y_+ \gg 1, \qquad y_- \ll -1, \qquad |y_-| \gg 1 \tag{95}$$

and the sublattice relative magnetizations become

$$\begin{aligned} \lim_{|y_\pm| \gg 1} \sigma_\pm(y_\pm, s) \lim_{|y_\pm| \gg 1} B_s(y_\pm) \\ \approx \pm\{1 - (1/s) \exp(-|y_\pm|/s) \\ \times [1 - (2s + 1) \exp(-2|y_\pm|)]\} \end{aligned} \tag{96}$$

Rewriting these to lowest order, one has

$$\begin{aligned} \lim_{y_+ \gg 1} B_s(y_+) &\approx 1 - (1/s) \exp(-y_+/s) \\ \lim_{y_- \ll -1} B_s(y_-) &\approx -1 + (1/s) \exp(-|y_-|/s) \end{aligned} \tag{97}$$

and since, by (16),

$$y_+ = (h' + |\sigma_-|)/t', \qquad y_- = (h' - \sigma_+)/t' \tag{98}$$

one sees that

$$y_+ \gg |y_-|, \qquad t' \ll 1 \tag{99}$$

Hence, while $\sigma_+(y_+)$ may already be quite close to its saturation limit, $\sigma_-(y_-)$ may still be quite far from it. Or, spin ordering on the plus sublattice may be practically complete while on the minus sublattice spin ordering

lags considerably behind that on the plus sublattice. Using (79) with $|y_{\pm}| > 1$, (97), and (99), one finds

$$\lim_{\substack{t' \ll 1 \\ y_+ \gg |y_-| \gg 1}} S(T, H, s)/R \sim \tfrac{1}{2}(y_+ + |y_-|) - \tfrac{1}{2}y_+(1 - s^{-1}\exp(-y_+/s)) + \tfrac{1}{2}y_-(-1 + s^{-1}\exp(-|y_-|/s)) = \tfrac{1}{2}(|y_-|/s)\exp(-|y_-|/s) + \tfrac{1}{2}(y_+/s)\exp(y_+/s) \approx \tfrac{1}{2}(|y_-|/s)\exp(-|y_-|/s) \tag{100}$$

The limiting very low-temperature entropy vanishes exponentially with $|y_-|, |y_-|$ being large. As a consequence of the inequalities (99), only the minus sublattice has entropy, the entropy of the plus sublattice being negligible compared with that of the minus sublattice. With

$$h' = 1 - \varepsilon, \qquad \sigma_+ \simeq 1 \tag{101}$$

the limiting entropy (100) may be written as

$$\lim_{\varepsilon \ll 1;\, t' \ll_1} S(t', h', s)/R \approx (\varepsilon/2st')\exp(-\varepsilon/st') \tag{102}$$

This shows that $S(t', h', s)$ vanishes for any finite though arbitrarily small ε, as $t' \to 0$. We may consider now the decreasing sequence of positive numbers $\varepsilon_1 > \varepsilon_2 > \cdots > \varepsilon_n > \cdots$, for all of which the terms of the entropy sequence $S(h' = 1 - \varepsilon_k, t', s)$, $k = 1, 2, \ldots, n$, vanish in the limit $t' \to 0$. For arbitrary s, two-sublattice magnetized antiferromagnets, assumed to have a stable parallel-field configuration, the above results verify the Nernst theorem since the vanishing of their entropy is proved through the intermediary of the ε sequence introduced here.

The preceding proof was obtained through the behavior of the entropy $S(t', h', s)$ as h' approached unity from below. The nonmonotonic phase-boundary lines $t'(h', s)$ or $t(h, s)$ discussed above show, of course, that in the mean-field model at $1 \leq h' \leq h'_M$, the antiferromagnetic phase does not extend down to the absolute zero. The constant-field lines $h' = \text{const}$ over the above h' interval all terminate in the spin-ordered range on the phase-boundary line, or at $t \geq 0$. These constant-field lines of the (h', t') or (h, t) diagrams are chords of finite length inside the antiferromagnetic region of these diagrams limited by the chord $h' = 1$ or $h = 3s/(s + 1)$, intercepted by the arc $h'(t')$ or $h(t)$ of the phase-boundary line at the points $t'(h' = 1) \to 0$ and $t'(h' = 1) > 0$, or at $t = 0$ and at $t(h = 3s/(s + 1)) > 0$. The problem of proving the Nernst theorem on approaching the critical limit of unity of h' from above is now the same as the one referring to the vanishing of the entropy along the critical phase-boundary line $S_{c,\parallel}(T, H, s)$ as $T \to 0$ and $H \to H_c$. This was shown to follow rigorously by Eq. (81). These two-sided approaches

of the entropy toward its vanishing limit at $h' \to 1$ and $t' \to 0$ prove satisfactorily the Nernst theorem in the mean-field description of the two-sublattice spin-s antiferromagnets assumed to have stable parallel-field configurations.

We are prepared now to discuss the entropy diagrams for their use in connection with cooling processes on adiabatic magnetization. It is convenient to consider those initial states in the cooling process that refer to the absence of external field. These states have temperatures $T < T_N(0)$. By (83), the unmodified mean-field entropy of the free unmagnetized system is

$$(S/R)_i = \ln\left[\sinh\left(\frac{2s+1}{2s}y_i\right)\Big/\sinh\left(\frac{1}{2s}y_i\right)\right] - y_i\sigma_i \tag{103}$$

Since

$$\sigma_i = B_s(y_i), \qquad y_i = \sigma_i/t'_i \tag{104}$$

$(S/R)_i$ is seen to be a function of σ_i alone or of y_i alone, on inverting the B_s function so as to yield y_i in terms of σ_i.

It is useful to consider first the adiabatic magnetization process whose final states refer to the critical magnetic phase-boundary line of entropy $S_{c,\|}(T_f, H_f, s)$ given by (80), with $y_{c,f}$ and $\sigma_{c,f}$ standing for y and σ along the critical line and

$$\sigma_{c,f} = B_s(y_{c,f}) \geq 0, \qquad y_{c,f} = (h'_{cf} - \sigma_{c,f})/t'_f \geq 0 \tag{105}$$

In the magnetization process

$$S(T_i, s) = S_{c,\|}(T_f, H_f, s) \tag{106}$$

or

$$y_i = y_{c,f}, \qquad \sigma_i = \sigma_{c,f} \tag{107}$$

In this restricted cooling process, with final states along the parallel-field phase-boundary line, adiabatic magnetization is equivalent to a transformation at constant parameter y or at constant relative sublattice magnetization σ. Both of these variables are adiabatic invariants. By (104)–(106) one thus has

$$(h'_{c,f} - \sigma_{c,f})/t'_f = \sigma_i/t'_i \tag{108}$$

which gives t'_f or t_f as a function of the initial zero-field configuration coordinates σ_i, t'_i or t_i, and the final-state reduced magnetic field strength $h'_{c,f}$. In terms of the absolute temperatures and actual field strengths one obtains, using (17) and (21),

$$T_{c,f} = T_i[H_{c,f}/H_E\sigma_i) - 1] \tag{109}$$

One might invoke here an apparent limitation imposed upon this relation. This appears to arise from the nonmonotonic phase-boundary field strength exhibiting a peculiar maximum $h'_{max} > 1$. As h' or h decrease beyond their maximum, as the temperature decreases, σ still increases toward its saturation limit. Along the phase-boundary line and over a finite σ or t range $d\sigma/dh' < 0$ or $d\sigma/dh < 0$. Both $h(t)$ and $h(\sigma)$ are double-valued functions of their argument. However, the critical entropy $S_{c,\|}$ is of monotonic variation.

We turn now to the generalized cooling process which involves the spin-ordered region of the magnetized system. It is again convenient to consider initial states referring to the antiferromagnetic configuration $T < T_N(0)$, in the absence of magnetic field. In the adiabatic magnetization process one has

$$S_f(T_f, H_f) = S_i(T_i < T_N(0), H_i = 0) \tag{110}$$

with S_i given by (103) and (104) and S_f by (79) and (94). The entropies appearing in (110) cannot yield t'_f or t_f as a function of h_f, σ_i, and t'_i or t_i in closed analytical form since Eq. (110) is transcendental in these variables. The analysis of the cooling process requires numerical methods for finding the final temperature t'_f or t_f as a function of the relevant state coordinates.

An exhaustive discussion of the adiabatic magnetization process of antiferromagnets, in their assumed stable parallel-field configuration, requires a full analysis of the response of the nuclei of the various nonmagnetic or diamagnetic atoms forming the molecule or molecular complex containing the relevant magnetic ion. In general, the effects of the external magnetic field, those of the hyperfine fields, when present, are all involved. We will assume henceforth that the latter effects have been eliminated through the use of those magnetic ions that have even–even nuclei. The effects of nuclear warming processes in the nonmagnetic atoms of the molecule or molecular complex at hand must be taken into account at the low temperatures. Since these effects vary in the different antiferromagnetic molecular systems, they can not be considered here, where we limit ourselves to the discussion of the main cooling process described by Eq. (110).

We choose to illustrate the generalized cooling process in a spin-$\frac{5}{2}$ system. As emphasized throughout this work, it is assumed that the parallel-field configuration is here freely available for the cooling process. The source of the large anisotropy required for the latter field configuration to be realized will not be discussed here. It may be of exchange origin, of the Ising type, or of the more symmetric exchange character compensated by a very-large magnetocrystalline anisotropy, for instance. While we will restrict the numerical discussion to spins $\frac{5}{2}$, it should be noted that other spin systems behave in a very similar fashion when treated by the mean-field formalism.

For our purposes, the graphs of Figs. 3 and 4, giving a series of mean-field entropies of spin $\frac{5}{2}$ systems, are to be useful. These entropies are given by the Eqs. (79) and (94). The normalization factor in (94) was chosen to be the Néel-point entropy of the only moderately anisotropic two-sublattice antiferromagnets seemingly well realized by crystallographically almost isomorphic, hydrated manganous halides ($MnCl_2 \cdot 4H_2P$) and ($MnBr_2 \cdot 4H_2O$).

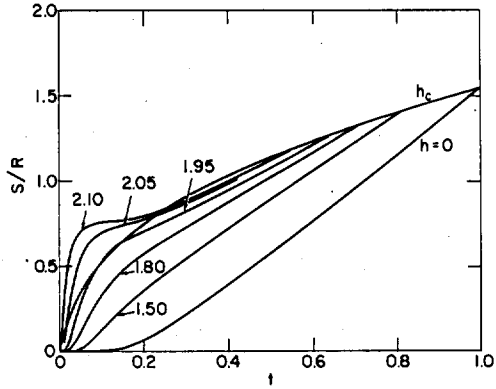

Fig. 3. Normalized, spin-$\frac{5}{2}$, antiferromagnetic-phase molar entropies S/R at the indicated reduced external field strengths h as a function of the reduced temperature t, including the critical entropy curve S_c/R along the parallel-field configuration phase-boundary line.

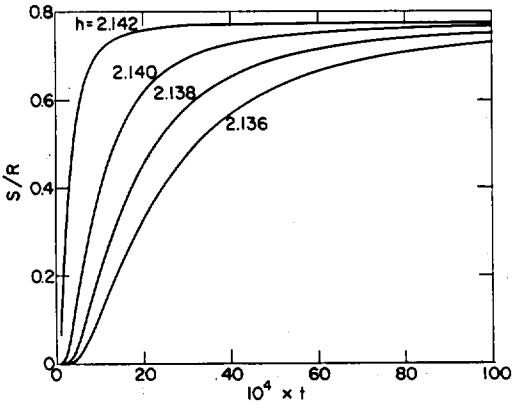

Fig. 4. Normalized molar entropy curves at the indicated reduced field strengths h close to the critical value of $3s/(s+1)$, or $15/7$, for $s = \frac{5}{2}$, at very low reduced temperatures, $0 \leq t \leq 10^{-2}$.

The Néel-point entropy[1,3] of these systems is about $1.55R$. Of the two manganous compounds the chloride is only moderately anisotropic[3] since its parallel-field configuration is only stable at field strengths $H \leq 8$ kG. In contrast, the bromide appears to have a more stable parallel-field configuration than what could have been inferred from the chloride. The parallel-field configuration of the bromide was observed to be stable[1] up to field strengths of about 12 kG. The reduced temperature t_3 of the antiferro-paramagnetic-spin-flop triple point of the chloride is about 0.76, while that of the bromide should be less than 0.52, with $H_3 > 12$–13 kG. The entropy graphs of Figs. 3 and 4 cover the reduced temperature ranges $0 \leq t \leq 1.0$ and $0 \leq t \leq 0.01$, respectively. Shown also on Fig. 3 are the zero-field entropy $S(t, h = 0)$ and the entropy $S_{c,\|}(t, h)$ along the critical parallel-field phase-boundary line. We remark, in passing, that the critical entropy $S_{c,\|}$ of spin-$\frac{1}{2}$ systems can be shown to vanish linearly in T as $T \to 0$. Such a proof is not available for spins $s > \frac{1}{2}$. The approximate linearity in T of $S_{c,\|}(T, H, s > \frac{1}{2})$ appears through the numerical values of these entropies at $t \lesssim 10^{-3}$.

Remembering the parallel-field phase diagram in the (h, t) plane, it is seen that the constant-field entropies form two classes: those of reduced field-strengths $0 < h \leq 3s/(s + 1)$, and those of $3s/(s + 1) \leq h \leq h_{\max}$. The latter do not extend to the absolute zero in the spin-ordered range. As implied at the end of Section 2, we will restrict ourselves to constant-field lines $h < 3s/(s + 1)$. This is equivalent to accepting the calculated $h(t)$ line of the phase-boundary over the t range $t(h = 3s/(s + 1)) \leq t \leq 1$, and to completing it over the remaining t range with the chord $h = 3s/(s + 1)$ parallel to the t axis. This jagged phase-boundary line excludes the region of the spin-ordered phase where $h(t)$ is double-valued in t. In completely anisotropic antiferromagnets, which have yet to be prepared, the double-valued phase-boundary line is a definite prediction of the mean-field theory.

The entropy curves at $0 \leq h \leq 3s/(s + 1)$ are seen on Fig. 3 to form two families of entropies. One of these, at the lower field strengths, starting out on the critical entropy curve $S_{c,\|}(t, h)$, stays always below this critical entropy but above the zero-field entropy curve. The limit curve $S(t, h_i)$ of this lower field strength family develops a single point of contact with $S_{c,\|}(t, h)$ at the point (t_i, h_i) defined by

$$S_{c,\|}(t_i, h_i) = S(t_i, h_i), \qquad (\partial S_{c,\|}/\partial t)_{h_i} = (\partial S/\partial t)_{h_i}, \qquad h_i < 3s/(s + 1) \quad (111)$$

The second family of entropy curves intersects $S_{c,\|}(t, h)$ at two temperatures t_1, t_2, and they are such that

$$S(t, h) \leq S_{c,\|}(t, h), \qquad h > h_i, \qquad t_1(h) < t \leq t_c(h), 0 \leq t_2 \leq t_1(h) \quad (112)$$

and

$$S(t, h) \geq S_{c,\|}(t, h), \qquad t_2 \leq t \leq t_1 \quad (113)$$

$t_c(h)$ being the reduced temperature of the starting state of $S(t, h)$ on the phase-boundary line $t(h)$ or the critical entropy value $S_{c,\|}(t, h)$.

The entropy curves at $h \leq 3s/(s+1)$ display the characteristic thermodynamic anomalies expressed by the inequalities

$$(\partial S/\partial H)_T > 0, \qquad (\partial T/\partial H)_S < 0 \tag{114}$$

which satisfy the thermodynamic relation

$$(\partial S/\partial H)_T(\partial H/\partial T)_S(\partial T/\partial S)_H = -1 \tag{115}$$

associated with the magnetic equation of state

$$\phi(T, H, S) = 0 \tag{116}$$

expressed in terms of the state variables T, H, and S. By (114), in the antiferromagnetic phase the entropy increases on isothermal magnetization, and, correspondingly, adiabatic magnetization is accompanied by cooling.

In the particular case of the diagrams of Figs. 3 and 4 referring to $s = \frac{5}{2}$, h_i defined through (111) is about 1.94. The larger field strength entropy curves, that is, those with $1.94 \leq h \leq 3s/(s+1) \sim 2.143$, are seen to develop increasingly long temperature plateaus before their final collapse toward vanishing entropies in the limit of very low temperatures. These plateaus are the longer the closer h is to its limit value of $3s/(s+1)$, or the closer H is to $[3s/(s+1)]H_c$ or H_E, as indicated through Eq. (21). This is clearly illustrated on Fig. 4, where the field strengths approach closely the critical limiting field strength.

As noted above, for a complete exploitation of the thermodynamic inequalities (114) it is required that the parallel-field configuration of the system at hand should extend up to the close vicinity of $h' \to 1$ or $h \to 3s/(s+1)$. From the standpoint of the actual realization of such antiferromagnets one is confronted with a physicochemical problem raised by the synthesis of appropriate compounds possessing the necessary stability of their parallel-field antiferromagnetic phase.

The attainment of low or very low temperatures on adiabatic magnetization of the two-sublattice model systems treated here is tied to the characteristic behavior of their minus sublattice, as far as its spin ordering and entropy are concerned. The minus-sublattice relative magnetization was shown to be given by [Eq. (9)]

$$\sigma_-(t', h', s) = B_s(y_-); \qquad y_- = (h' - \sigma_+)/t' \tag{117}$$

We want to follow the variations of the component entropy $S_-(t', h', s)$ of the minus sublattice, starting out at the phase-boundary line where

$$y_+ = y_- = y > 0, \qquad \sigma_+ = \sigma_- = \sigma > 0 \tag{118}$$

As the temperature falls below that of the phase-boundary line the field strength h', or h, being kept constant, the system leaves behind the critical line. This means that the plus sublattice increases its degree of spin ordering since σ_+ increases from its phase-boundary value $\sigma_+(t_c(h'), s)$ or $\sigma(t_c(h'), s)$, approaching unity as $t' \to 0$. In contrast, the minus sublattice, having positive relative starting magnetization $\sigma(t_c(h'), s)$ equal to that of the plus sublattice, may be said to be in a specific state of partial constrained spin order. With a temperature decrease, at $h' = \text{const}$, this sublattice penetrates into the antiferromagnetic phase and its ordering must approach the specific normal spin ordering associated with negative relative magnetization $\sigma_- < 0$. As long as $h' < 1$, y_- must decrease from its positive boundary-line value y. Hence, y_- must have a zero at t'_- where, by (117),

$$h' = \sigma_+(t'_-, h' < 1, s) \tag{119}$$

and

$$y_- < 0, \qquad t' < t'_- \tag{120}$$

At t'_-, where y_- vanishes, the minus sublattice is totally disordered. Its unmodified mean-field molar entropy reaches its maximum value there of

$$\begin{aligned} S_-(t' \to t'_-, h', s) &= \lim_{y_- \to 0} \frac{1}{2} \ln \left[\sinh \left(\frac{2s+1}{2s} y_- \right) \Big/ \sinh \left(\frac{1}{2s} y_- \right) \right] \\ &= \tfrac{1}{2} R \ln (2s+1) \end{aligned} \tag{121}$$

according to (79). Or, on leaving behind the phase-boundary line, the minus sublattice first increases its entropy for a temperature decrease at constant field strength, until y_- vanishes, where it achieves complete disorder. Beyond this zero at $t' = t'_-$, y_- becomes negative, and the minus sublattice cannot but increase its spin order. Or, at $t' < t'_-$, σ_- must approach -1 as $t' \to 0$. Hence, σ_- must sweep through the interval $(\sigma > 0, -1)$ as t' decreases from $t_c(h')$, on the phase-boundary line, to very low and vanishing temperature. By Eq. (79),

$$d(S_-/R)\, dy_- = -y_- d\sigma/dy \tag{122}$$

which vanishes with y_- at $t'_-(h')$, as we just saw, $d\sigma/dy$ being finite, or $dB_s(y_-)/dy_-$ being finite at $y_- \sim 0$. This entropy derivative vanishes also at $y_- \to -\infty$, where $\sigma_- \to -1$ and $-(d\sigma_-/dy_- \to 0$, σ_- approaching its saturation limit of -1 exponentially in y_- [Eqs. (100) and (102)]. As a consequence, $S_-(t', h', s)$ is anomalous over the y_- range between its positive boundary-line value $y(t', h', s)$ and its zero at t'_-. Formally,

$$dS_-/dt' \leq 0, \qquad t'_-(h' < h'_c) \leq t' \leq t'(h'_c) \tag{123}$$

The very large excess entropy of the minus sublattice is thus tied to the anomalous temperature region (123) over which S_- increases with decreasing temperature toward its free sublattice value at t'_-. It is only at $t' < t'_-$ that this sublattice can reduce its entropy below its maximum value. It is to be recalled that the plus sublattice achieves nearly complete spin ordering over a rather limited range of its relative magnetization $\sigma_+(t', h', s)$, and this above all at field strengths $h' \lesssim 1$. This results from the cooperation between the external field and the exchange or molecular field arising, in the present model, from the minus sublattice at $t' < t'_-$, where σ_- becoming negative causes y_+ to increase through its numerator $(h + |\sigma_-|)$ and its decreasing denominator t', Eq. (10). In contrast, the minus sublattice starts out with total spin disorder at t'_- where σ_- vanishes and where its entropy is $\frac{1}{2}R \ln (2s + 1)$ or $\frac{1}{2}S(T_N(0))$, to approach slowly its saturation value of $\sigma_- \to -1$ at $t' \to 0$. The component entropy S_- thus remains very large at first, decreasing only slowly, and causes the total entropy $S_+ + S_-$ to hover close to the maximum value of S_- over a temperature interval. To illustrate, we give in Table I some sublattice entropies S_+/R and S_-/R, for $s = \frac{5}{2}$ at the indicated constant reduced field strengths approaching h_c or $3s/(s + 1)$, or 15/7 in the present case. These sublattice entropies are mean-field entropies and do not carry the empirical normalizing factor defined through (93) and (94). As a consequence the entropy maxima of S_-/R are $\ln (2s + 1)^{1/2}$ or $\ln 6^{1/2}$. It is seen

TABLE I

Mean-Field Sublattice Entropies S_+/R and S_-/R at Various Reduced Field Strengths Near h_c or $3s/(s + 1)$ for $s = \frac{5}{2}$[a]

	$h = 2.110, t_c(h) = 0.561$		$h = 2.120, t_c(h) = 0.553$		$h = 2.130, t_c(h) = 0.546$	
t	S_+/R	S_-/R	S_+/R	S_-/R	S_+/R	S_-/R
0.50	0.469	0.833	0.480	0.8243	0.492	0.8148
0.40	0.281	0.880	0.288	0.8764	0.295	0.8723
0.30	0.134	0.8947	0.139	0.8934	0.144	0.8917
0.28	0.109	0.8955	0.114	0.8947	0.118	0.8934
0.26	0.0865	$\ln 6^{1/2}$	0.0905	0.8955	0.0948	0.8946
0.24	0.0658	0.8957	0.0694	0.8958	0.0731	0.8954
0.23	—	—	—	$\ln 6^{1/2}$	—	—
0.22	0.0476	0.8952	0.0506	0.8958	0.0539	0.8958
0.21	—	—	—	—	—	—
0.20	0.0323	0.8944	0.0347	0.8955	0.0374	$\ln 6^{1/2}$
0.10	—	0.8835	—	0.8899	—	0.8940
0.05	—	0.8485	—	0.8722	—	0.8882
0.01	—	0.3962	—	0.5484	—	0.7407
0.005	—	0.1397	—	0.2624	—	0.4999
0.0025	—	0.0164	—	0.0615	—	0.2191
0.001	—	—	—	—	—	0.0180

[a]The maxima of S_-/R refer to $\ln 6^{1/2}$ or 0.8959.

that S_+ decreases fairly rapidly as t decreases, while S_- first develops its broad maximum, followed by a long plateau extending to t values of 0.005–0.0025. At field strengths $h \lesssim h_c$, the minus sublattice must lose a significant fraction of its entropy over a rather small temperature interval.

This state of affairs is further illustrated in Figs. 3 and 4 referring, as mentioned above, to the normalized entropies of the hydrated manganous halides with $S(T_N(0)) \sim 1.55R$ and $s = \frac{5}{2}$. The entropy plateaus are seen to develop around $\frac{1}{2}S(T_N(0))/R$, or about 0.75–0.76, and are seen to hover around this value as $h \to 3s/(s+1)$. These same graphs give directly the lower-bound final temperatures accessible on adiabatic magnetization, with initial states either in the zero-field configuration or in the parallel-field configuration at various initial field strengths. As emphasized above, all additional thermal effects arising from the hyperfine interactions of the magnetic ions themselves or of the nuclear warming processes of the other constituent atoms of the antiferromagnetic molecular unit, crystallization water molecules included, have been omitted. Within the limitations of neglecting these effects as well as those of the approximate mean-field formalism of totally anisotropic antiferromagnets, the entropy diagrams of Figs. 3 and 4 suggest the possibility of appropriate ionic antiferromagnets to function as efficient cooling agents. In such systems, starting with initial states in the absence of magnetic field at temperatures $T < T_N(0)$, $T_N(0) \sim 1$ K, significant cooling may be achieved on adiabatic magnetization in the parallel field configuration at easily available field strengths. An experimental search for appropriate antiferromagnets with the required anisotropy and the nuclear behavior discussed above appears to be of great interest from the standpoint of their use for the production of low temperatures.

We should like to close with an additional remark. This refers to the shape of the higher-field-strength entropies. It is seen that the associated heat capacities, at constant field strength, develop a maximum at low temperatures. The appearance of these parallel-field-configuration, very low-temperature mean-field capacity maxima was first noticed by Garrett[9] in his treatment of spin-$\frac{1}{2}$ antiferromagnets assumed to have stable parallel-field configurations.

In concluding it may be justified to emphasize that experimental investigations into the physicochemical problems raised by the preparation of strongly anisotropic two-sublattice antiferromagnets appear to be of interest, both for their intrinsic magnetic behavior and for their use as possibly efficient cooling agents on adiabatic magnetization.

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