

Magnetic Field Dependence of Thermodynamic Properties of Antiferromagnets; Adiabatic Magnetization^{*†}

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(Received June 21, 1962; revised manuscript received August 2, 1962)

The thermodynamic properties of cubic or uniaxial antiferromagnets are examined using spin wave theory. The specific heat, magnetization, and parallel susceptibility are shown to be exponentially increasing functions of applied field for values of H_0 less than the critical spin-flopping field. Since this field dependence suggests that an antiferromagnet can be cooled by the adiabatic application of a magnetic field, the theory of adiabatic magnetization is investigated. Field-dependent nuclear spin effects are evaluated on an effective field model by perturbation theory and are included in the analysis. It is found that when spin wave effects are dominant, cooling should be observed; at lower temperatures, when nuclear effects are non-negligible, either cooling or heating may be observed, depending on the initial temperature and final value of the magnetic field. The dependence of the cooling on the physical parameters of the antiferromagnet is discussed and detailed calculations are made for MnF_2 .

I. INTRODUCTION

THE low-temperature thermodynamic properties of antiferromagnets were first examined in detail by Kubo,¹ using the method of spin waves. This analysis was for zero external field and primarily in the limit of negligible anisotropy, except where the latter was necessary to avoid singularities. The spin wave specific heat was found to be proportional to T^3 and the sublattice magnetization to T^2 .

The presence of anisotropy, however, is greatly enhanced by interplay with the exchange energy and introduces a gap of a few degrees' magnitude into the spin wave spectrum. For finite anisotropy and low temperature, Kubo expressed the free energy and thermodynamic quantities derivable therefrom in terms of Schlömilch series.² He noted that for very low temperature there is an exponential decrease with temperature for these quantities.

Eisele and Keffer³ elaborated on the finite anisotropy effects in the thermodynamic theory of antiferromagnets. It was pointed out that when the absolute temperature is below the gap temperature, the specific heat and magnetization are much smaller than their zero-anisotropy values since the number of spin waves excited falls off exponentially with decreasing temperature. Well above the gap temperature, however, the values of the thermodynamic properties approach the zero-anisotropy values first given by Kubo.

One of the effects of an applied field can be described in the following way. The degeneracy of the spin wave

modes of an antiferromagnet is removed by the application of a magnetic field. The modes will therefore contribute differently to the specific heat. For an increasing applied field, the increasing specific heat of the lower energy mode more than compensates for the decreasing specific heat of the higher energy mode. In other words, $\partial C/\partial H > 0$ for antiferromagnetic spin waves; the same quantity is negative for ferro- and ferrimagnetic spin waves (and for antiferromagnetic spin waves when the magnetic field is perpendicular to the spin axis). This difference was pointed out by Kouvel and Brooks⁴ who calculated the spin wave specific heat of a simple cubic antiferromagnet by graphical integration.

Since the specific heat depends strongly (exponentially) on the applied field, particularly when $g\mu_B H_0/k_B$ approaches the gap temperature, it may be possible to cool an antiferromagnet by applying a magnetic field under adiabatic conditions as was suggested by Akhiezer, Bar'yakhtar, and Kaganov.⁵ These authors describe the thermodynamic properties with sets of equations, each of which is valid for a particular range of values of temperature and magnetic field relative to the Néel and gap temperatures and critical field characterizing the antiferromagnet. Earlier, Turov⁶ suggested that it might be possible to effect a measurable change in the temperature of an antiferromagnet by the adiabatic rotation of a crystal in a magnetic field, since the field dependence of the specific heat is anisotropic.

In the present paper the magnetic field dependence of the measurable, macroscopic properties of cubic or uniaxial antiferromagnets is examined theoretically and the results are presented in an analytical form (Sec. II). These properties include the total and sublattice

^{*}This work was done in the Sarah Mellon Scaife Radiation Laboratory and was supported by the U. S. Air Force through the Air Force Office of Scientific Research. Numerical computation was supported in part by National Science Foundation Grant No. G-11309 to the University of Pittsburgh Computing Center.

[†]Part of a thesis submitted to the Graduate Faculty of the University of Pittsburgh in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1962.

¹R. Kubo, *Phys. Rev.* **87**, 568 (1952).

²G. N. Watson, *A Treatise on the Theory of Bessel Functions* (Cambridge University Press, New York, 1952), 2nd ed., Chap. XIX.

³J. A. Eisele and F. Keffer, *Phys. Rev.* **96**, 929 (1954).

⁴J. S. Kouvel and H. Brooks, *Cruft Laboratory, Harvard University, Technical Report No. 198, 1954* (unpublished).

⁵A. I. Akhiezer, V. G. Bar'yakhtar, and M. I. Kaganov, *Uspekhi Fiz. Nauk* **71**, 533 (1960) [translation: *Soviet Phys.—Uspekhi* **3**, 567 (1961)]. In the latter reference, in the discussion preceding Eq. (9.5) on p. 590, in place of "switching-on," which appears twice, read "switching-off."

⁶E. A. Turov, *J. Expl. Theoret. Phys. (U.S.S.R.)* **34**, 1009 (1958) [translation: *Soviet Phys.—JETP* **7**, 696 (1958)].

magnetizations, the parallel susceptibility, and the magnetic specific heat. In Sec. III the anisotropy-exchange temperature is considered further and the general expressions of Sec. II are simplified by making some approximations with a fairly wide range of validity. Since the temperature span of interest will often extend below 2–3°K, the field-dependent nuclear spin contribution to the magnetization and specific heat of the system is evaluated on an effective-field model (Sec. IV). The results of the previous sections are combined in Sec. V to provide a theoretical description of adiabatic magnetization of an antiferromagnet, and in Sec. VI this theory is applied to manganous fluoride. Section VII contains a general discussion of the dependence of adiabatic magnetization cooling on the physical parameters of the antiferromagnetic material.

II. MAGNETIC FIELD DEPENDENCE

The antiferromagnetic spin wave properties described in this and following sections are based on a two sublattice model with uniaxial anisotropy and a single exchange integral, J , coupling nearest neighbors. A crystalline field, H_A , is used to represent the anisotropy, being directed along the preferred axis in opposite senses for the two sublattices. This field is allowed to be temperature dependent as a substitute for explicit treatment of the higher-order spin wave interactions which cause the macroscopic anisotropy constant to decrease with rising temperature. This temperature-dependent H_A is also useful as a substitute for magnetic dipole interactions in the Hamiltonian. The dipolar form of anisotropy requires the evaluation of dipole-wave sums and depends on \mathbf{k} , and thus would necessitate the use of numerical integration to determine the thermodynamic properties.

The model contains N_0 magnetic cells, each cell having a magnetic ion from both the $+$ and $-$ sublattices. With the applied field, H_0 , in the preferred direction and smaller than the critical spin-flopping field, H_c , the spin Hamiltonian for this model may be written as

$$\mathcal{H}_0 = 2J \sum_{\langle l, m \rangle} \mathbf{S}_l \cdot \mathbf{S}_m + g\mu_B H^+ \sum_l S_l^+ + g\mu_B H^- \sum_m S_m^-, \quad (1)$$

where g is the gyromagnetic ratio and μ_B is the Bohr magneton (both >0), and

$$H^\pm = H_0 \pm H_A. \quad (2)$$

The \pm superscript indicates the sublattice with magnetic moment essentially parallel or antiparallel to H_0 , respectively, and the symbol $\langle l, m \rangle$ represents pairs of nearest neighbors, l being the index for $+$ sublattice and m for $-$ sublattice.

By using the spin wave formalism developed by Holstein and Primakoff⁷ for ferromagnets and modified

by Kubo¹ for antiferromagnets, the Hamiltonian is diagonalized and brought into the form

$$\mathcal{H}_0 = C' + \sum_k (n_k^+ + \frac{1}{2}) \epsilon_k^+ + \sum_k (n_k^- + \frac{1}{2}) \epsilon_k^-, \quad (3)$$

where

$$C' = -2N_0 S(S+1)JZ - 2N_0(2S+1)JZ\alpha, \quad (4)$$

$$\epsilon_k^\pm = 2SJZ \{ [(1+\alpha)^2 - \gamma_k^2]^{1/2} \pm \alpha_0 \}, \quad (5)$$

$$\alpha = \frac{1}{2} g\mu_B (H^+ - H^-) / 2SJZ = g\mu_B H_A / 2SJZ, \quad (6)$$

$$\alpha_0 = \frac{1}{2} g\mu_B (H^+ + H^-) / 2SJZ = g\mu_B H_0 / 2SJZ, \quad (7)$$

and

$$\gamma_k = Z^{-1} \sum_h \exp(i\mathbf{k} \cdot \mathbf{r}_h), \quad (8)$$

with Z being the number of nearest neighbors and \mathbf{r}_h the nearest-neighbor vector. This equation has been derived by Kubo,¹ Ziman,⁸ and others, and is a special case of a more general equation given by Keffer.⁹

The frequencies of the uniform precession modes given by Eq. (5) with $\mathbf{k}=0$ do not quite agree with those of Keffer and Kittel¹⁰ which were derived classically and are, in the notation of the present paper,

$$\hbar\omega^\pm = 2SJZ [(2\alpha + \alpha^2)^{1/2} \pm \alpha_0 (1 - \frac{1}{2}\chi_{11}/\chi_1)], \quad (9)$$

where χ_{11} (χ_1) is the susceptibility of the electronic spin system in a magnetic field applied parallel (perpendicular) to the preferred axis. The factor $(1 - \frac{1}{2}\chi_{11}/\chi_1)$ affecting the applied field does appear in higher-order spin wave theory⁹ and expresses the fact that the spin system has less energy to gain by flopping to a hard axis as χ_{11} approaches χ_1 near T_N . In what follows the α_0 of Eqs. (5) and (7) will be replaced by

$$\alpha_0 = g\mu_B H_0 (1 - \frac{1}{2}\chi_{11}/\chi_1) / 2SJZ. \quad (10)$$

Equation (9) now leads to a critical spin-flopping field given by

$$H_c^2 = (2H_B H_A + H_A^2) / (1 - \chi_{11}/\chi_1), \quad (11)$$

where $H_B = 2SJZ/g\mu_B$, which is in agreement with the value predicted by Néel.¹¹

A. Spin Wave Energy

The total spin wave energy is obtained by summing the ϵ_k^\pm over Bose distributions in the first Brillouin zone of the magnetic unit cell. For small \mathbf{k} in cubic lattices,

$$\gamma_k^2 \approx 1 - (2a_0^2/Z)k^2, \quad (12)$$

where a_0 is the length of a side of the elementary cubic cell, and the sum over \mathbf{k} may be approximated by an integral to infinity. Thus

$$E(T, H_0) = \frac{V}{2\pi^2} \int_0^\infty \{ \epsilon_k^+ [\exp(\beta\epsilon_k^+) - 1]^{-1} + \epsilon_k^- [\exp(\beta\epsilon_k^-) - 1]^{-1} \} k^2 dk, \quad (13)$$

⁸ J. M. Ziman, Proc. Phys. Soc. (London) **A65**, 540, 548 (1952).

⁹ F. Keffer, in *Handbuch der Physik* (Springer-Verlag, Berlin, 1963) (to be published).

¹⁰ F. Keffer and C. Kittel, Phys. Rev. **85**, 329 (1952).

¹¹ L. Néel, Ann. Phys. (New York) **5**, 232 (1936).

⁷ T. Holstein and H. Primakoff, Phys. Rev. **58**, 1098 (1940).

where V is the sample volume and $\beta = (k_B T)^{-1}$. The Bose function for $\langle n_k^- \rangle$ has no singularities when $H_0 < H_c$.

Equation (13) is evaluated by expanding the Bose functions,

$$[\exp(\beta \epsilon_k^\pm) - 1]^{-1} = \sum_{p=1}^{\infty} \exp(-p\beta \epsilon_k^\pm), \quad (14)$$

and making the replacement

$$(2\alpha + \alpha^2)^{1/2} \cosh y = [(2a_0^2/Z)k^2 + 2\alpha + \alpha^2]^{1/2}. \quad (15)$$

To simplify notation, effective temperatures are substituted for the exchange, anisotropy-exchange, and magnetic-field energies:

$$T_E = 2SJZ/k_B, \quad (16)$$

$$T_{AE} = (2\alpha + \alpha^2)^{1/2} T_E, \quad (17)$$

$$T_H = \alpha_0 T_E. \quad (18)$$

Each of these quantities is an implicit function of the absolute temperature; however, T_E will be considered constant. After substituting Eqs. (14)–(18) in (13), the spin wave energy becomes

$$\begin{aligned} E(T, H_0) = & \frac{V}{\pi^2} \left(\frac{Z}{2a_0^2} \right)^{3/2} k_B T_{AE} \left(\frac{T_{AE}}{T_E} \right)^3 \\ & \times \left\{ \sum_{p=1}^{\infty} \int_0^{\infty} \left[\cosh \left(\frac{pT_H}{T} \right) \cosh y - \frac{T_H}{T_{AE}} \sinh \left(\frac{pT_H}{T} \right) \right] \right. \\ & \left. \times \exp \left[- \left(\frac{pT_{AE}}{T} \right) \cosh y \right] \sinh^2 y \cosh y dy \right\}. \quad (19) \end{aligned}$$

The integrals are Hankel functions,¹² and the final expression for the total spin wave energy is

$$\begin{aligned} E(T, H_0) = & \frac{1}{4} A_i N_0 k_B T_{AE} \left(\frac{T_{AE}}{T_E} \right)^3 \sum_{p=1}^{\infty} \left\{ \cosh \left(\frac{pT_H}{T} \right) \right. \\ & \times \left[K_4 \left(\frac{pT_{AE}}{T} \right) - K_0 \left(\frac{pT_{AE}}{T} \right) \right] - 2 \left(\frac{T_H}{T_{AE}} \right) \\ & \left. \times \sinh \left(\frac{pT_H}{T} \right) \left[K_3 \left(\frac{pT_{AE}}{T} \right) - K_1 \left(\frac{pT_{AE}}{T} \right) \right] \right\}, \quad (20) \end{aligned}$$

where $A_i = (1/2\pi^2)(Z/2)^{3/2}$. The series is convergent for $T_H < T_{AE}$, which is equivalent to the condition for nonsingularity of the Bose function, $H_0 < H_c$. In the absence of an applied field the summations are known as Schlömilch series and are rapidly convergent; the zero-field limit of Eq. (20) is equivalent to Eq. (11) of reference 3.

The temperature dependence of the spin wave energy is illuminated by a further revision:

$$E(T, H_0) = (2\pi^4/15) A_i N_0 k_B T (T/T_E)^3 \mathcal{E}, \quad (21)$$

where

$$\begin{aligned} \mathcal{E} = & \frac{15}{8\pi^4} \left(\frac{T_{AE}}{T} \right)^4 \sum_{p=1}^{\infty} \left\{ \cosh \left(\frac{pT_H}{T} \right) \right. \\ & \times \left[K_4 \left(\frac{pT_{AE}}{T} \right) - K_0 \left(\frac{pT_{AE}}{T} \right) \right] \\ & \left. - 2 \frac{T_H}{T_{AE}} \sinh \left(\frac{pT_H}{T} \right) \left[K_3 \left(\frac{pT_{AE}}{T} \right) - K_1 \left(\frac{pT_{AE}}{T} \right) \right] \right\}. \quad (22) \end{aligned}$$

Below T_{AE} and H_c , the temperature and field dependence of \mathcal{E} are basically exponential. When the external field is zero,

$$\mathcal{E} \rightarrow \left(\frac{15}{8\pi^4} \right) \left(\frac{T_{AE}}{T} \right)^4 \sum_{p=1}^{\infty} \left[K_4 \left(\frac{pT_{AE}}{T} \right) - K_0 \left(\frac{pT_{AE}}{T} \right) \right], \quad (23)$$

and, when T is much greater than T_{AE} and T_H , the value of \mathcal{E} goes to 1. The limit of vanishing anisotropy for finite applied field is inappropriate since the corresponding ground state with spins perpendicular to the field is not represented by Eq. (1).

B. Spin Wave Specific Heat

The specific heat is the derivative of Eq. (20) with respect to T , holding H_0 constant, and has the value

$$C_H(T, H_0) = (8\pi^4/15) A_i N_0 k_B (T/T_E)^3 \mathcal{C}, \quad (24)$$

where

$$\begin{aligned} \mathcal{C} = & \frac{15}{8\pi^4} \left(\frac{T_{AE}}{T} \right)^4 \sum_{p=1}^{\infty} \left\{ \cosh \left(\frac{pT_H}{T} \right) \left[K_4 \left(\frac{pT_{AE}}{T} \right) - \frac{T}{T_{AE}} \left(\frac{\partial T_{AE}}{\partial T} \right) K_0 \left(\frac{pT_{AE}}{T} \right) \right. \right. \\ & + \left[1 + 2 \left(\frac{T_H}{T_{AE}} \right)^2 - \frac{T}{T_{AE}} \left(\frac{\partial T_{AE}}{\partial T} \right) - 2 \frac{T T_H}{T_{AE}^2} \left(\frac{\partial T_H}{\partial T} \right) \right] K_2 \left(\frac{pT_{AE}}{T} \right) \left. \right\} - \frac{T_H}{T_{AE}} \sinh \left(\frac{pT_H}{T} \right) \left[\left[3 - \frac{T}{T_H} \left(\frac{\partial T_H}{\partial T} \right) \right] K_3 \left(\frac{pT_{AE}}{T} \right) \right. \\ & \left. + \left[1 - 2 \frac{T}{T_{AE}} \left(\frac{\partial T_{AE}}{\partial T} \right) - \frac{T}{T_H} \left(\frac{\partial T_H}{\partial T} \right) \right] K_1 \left(\frac{pT_{AE}}{T} \right) \right] \right\}. \quad (25) \end{aligned}$$

¹² See reference 2, p. 172.

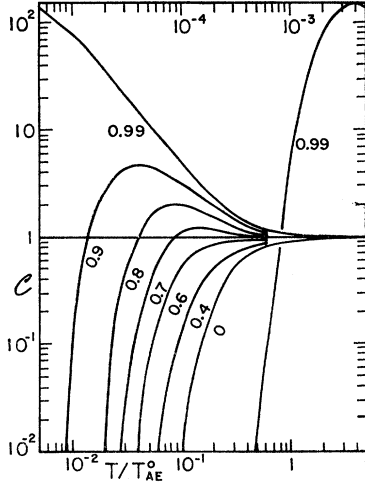


FIG. 1. The temperature variation of the function \mathcal{C} for cubic or uniaxial symmetry showing the effects of applied field and anisotropy. The number below each curve is the value of the ratio T_H^0/T_{AE}^0 . The 0.99 curve on the right-hand side is a lower temperature extension to be used with the scale at the top of the figure.

This expression is plotted in Fig. 1 for the case of constant T_{AE} and T_H . In the limit of zero applied field,

$$\mathcal{C} \rightarrow \frac{15}{8\pi^4} \left(\frac{T_{AE}}{T} \right)^4 \times \sum_{p=1}^{\infty} \left\{ K_4 \left(\frac{pT_{AE}}{T} \right) - \frac{T}{T_{AE}} \left(\frac{\partial T_{AE}}{\partial T} \right) K_0 \left(\frac{pT_{AE}}{T} \right) + \left[1 - \frac{T}{T_{AE}} \left(\frac{\partial T_{AE}}{\partial T} \right) \right] K_2 \left(\frac{pT_{AE}}{T} \right) \right\}. \quad (26)$$

The expression for \mathcal{C} in reference 3 was developed holding T_{AE} constant, but is otherwise equivalent to Eq. (26). When T far exceeds T_{AE} and T_H , the value of \mathcal{C} is 1. In this case, the specific heat, Eq. (24), follows the usual T^3 law for Bose particles.

C. Magnetization

The magnetic moments of the sublattices and of the antiferromagnetic material as a whole are determined in the usual method from the partition function corresponding to Eq. (3), with the integrals being evaluated by the procedure which led to Eq. (20). A net magnetization exists only when H_0 is finite causing a difference in the two sublattice magnetic moments. Since the sublattice moments are separately determinable from nuclear magnetic resonance experiments, their individual values, as well as the total magnetic moment, are of interest. The net sublattice moments are

$$M_s^{\pm} = k_B T (\partial \ln \mathfrak{M} / \partial H^{\pm}) \\ = \pm M_{s0} \mp \Delta M_{s\beta} \mp \Delta M_s(T, H_0) + \frac{1}{2} M(T, H_0), \quad (27)$$

in which $M_{s0} = N_0 g \mu_B S$ and is the moment for complete

alignment,

$$\Delta M_{s\beta} = \frac{1}{2} g \mu_B \sum_k [(1+\alpha)(2\alpha+\alpha^2+2a_0^2 k^2/Z)^{-1/2} - 1] \quad (28)$$

and is the field- and temperature-independent zero-point deviation ($\sim 2\%$ of M_{s0}) from the completely aligned trial ground state, and

$$\Delta M_s(T, H_0) = (\pi^2/6) A_i N_0 g \mu_B (1+\alpha) (T/T_E)^2 \mathfrak{M}_s, \quad (29)$$

with

$$\mathfrak{M}_s = \frac{3}{\pi^2} \left(\frac{T_{AE}}{T} \right)^2 \times \sum_{p=1}^{\infty} \cosh \left(\frac{pT_H}{T} \right) \left[K_2 \left(\frac{pT_{AE}}{T} \right) - K_0 \left(\frac{pT_{AE}}{T} \right) \right], \quad (30)$$

represents the deviation due to finite T and H_0 . Eisele and Keffer³ have given Eqs. (27)–(30) for $H_0 = 0$. The expression for \mathfrak{M}_s is shown in Fig. 2; it is defined to have a value of 1 at high T . In this limit the sublattice magnetization exhibits the usual T^2 dependence.

The final term in Eq. (27) is the total magnetic moment of the sample,

$$M(T, H_0) = (2\pi^2/3) A_i N_0 k_B (T_H/T_E) \times (T/T_E)^2 (\partial T_H / \partial H_0) \mathfrak{M}_s, \quad (31)$$

where

$$\mathfrak{M} = \frac{3}{4\pi^2} \frac{T_{AE}}{T_H} \left(\frac{T_{AE}}{T} \right)^2 \times \sum_{p=1}^{\infty} \sinh \left(\frac{pT_H}{T} \right) \left[K_3 \left(\frac{pT_{AE}}{T} \right) - K_1 \left(\frac{pT_{AE}}{T} \right) \right]. \quad (32)$$

At high temperature the limit of \mathfrak{M} is 1 and $M(T, H_0)$ is proportional to T^2 . In the absence of a field, $M(T, 0)$ is zero. Equation (32) is plotted in Fig. 3.

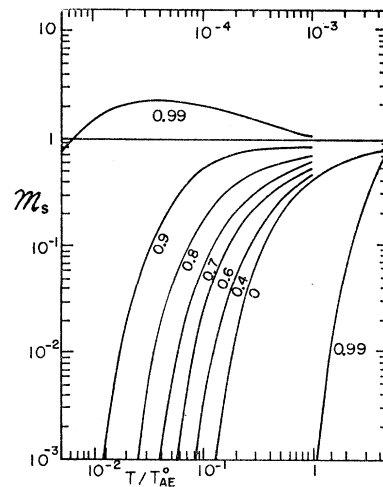


FIG. 2. The temperature variation of the function \mathfrak{M}_s for cubic or uniaxial symmetry showing the effects of applied field and anisotropy. The number below each curve is the value of the ratio T_H^0/T_{AE}^0 . The 0.99 curve on the right-hand side is a lower temperature extension to be used with the scale at the top of the figure.

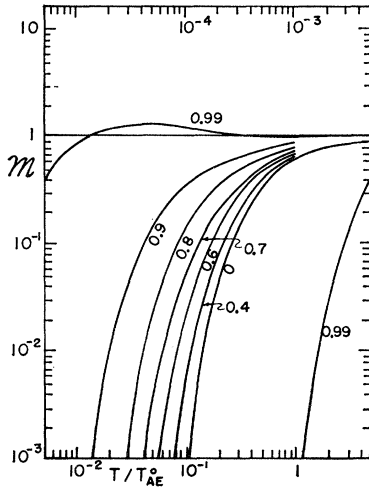


FIG. 3. The temperature variation of the function \mathcal{M} for cubic or uniaxial symmetry showing the effects of applied field and anisotropy. The number below each curve is the value of the ratio T_H^0/T_{AE}^0 . The 0.99 curve on the right-hand side is a lower temperature extension to be used with the scale at the top of the figure.

D. Susceptibility

With reference to Eqs. (10) and (18), the partial derivative in Eq. (31) is seen to be

$$k_B(\partial T_H/\partial H_0) = g\mu_B[1 - \frac{1}{2}(\chi_{||}/\chi_{\perp}) - \frac{1}{2}H_0\partial(\chi_{||}/\chi_{\perp})/\partial H_0]. \quad (33)$$

Thus the equation for the differential parallel susceptibility, $\chi_{||} = V^{-1}[\partial M(T, H_0)/\partial H_0]$, becomes a second-order, inhomogeneous, differential equation in $\chi_{||}$ which must be solved consistently. This situation results from the inclusion of the higher-order spin wave correction, Eq. (10), in the quadratic approximation Hamiltonian, Eq. (3). The expression for the parallel susceptibility is evaluated in the following manner.

Since $\frac{1}{2}(\chi_{||}/\chi_{\perp}) \ll 1$ for $T \ll T_N$, and since $\chi_{||}$ is zero at $T=0$ for the two sublattice antiferromagnet, the hyperbolic functions are expanded in Taylor's series about T_H^0 , keeping only terms linear in $\chi_{||}$. [Note that $k_B T_H^0 = g\mu_B H_0[1 - \frac{1}{2}\chi_{||}(0)/\chi_{\perp}(0)] = g\mu_B H_0$.] In this order of approximation the differential equation becomes an algebraic equation and the resulting expression for the susceptibility is

$$\chi_{||}(T, H_0) = (2\pi^2/3)A_L N_0 V^{-1}(g^2 \mu_B^2/k_B T_E)(T/T_E)^2 \chi, \quad (34)$$

with

$$\chi = \frac{3}{\pi^2} \left(\frac{T_{AE}}{T} \right)^2 \sum_{p=1}^{\infty} \cosh\left(\frac{pT_H^0}{T}\right) K_2\left(\frac{pT_{AE}}{T}\right). \quad (35)$$

Equation (35) goes to 1 at high T and the susceptibility then exhibits the usual T^2 dependence of an antiferromagnet. The expression for χ is plotted in Fig. 4. Reference 3 gives the value of χ for $H_0=0$.

The Weiss molecular field value for the perpendicular

susceptibility is

$$\chi_{\perp}^0 = N_0 V^{-1} g^2 \mu_B^2 S/k_B T_E, \quad (36)$$

and consequently,

$$\chi_{||}/2\chi_{\perp}^0 = (\pi^2/3)(A_L/S)(T/T_E)^2 \chi \ll 1 \quad (37)$$

in the temperature range where spin wave theory is applicable. Thus, even for MnF_2 , which has a relatively high $T_{AE} \approx \frac{1}{6}T_E$, the approximations used in arriving at Eq. (34) are valid to at least $T \sim T_{AE}$ and the parallel susceptibility should be well represented by that equation.

An improvement in χ_{\perp} over the molecular field value is obtained as follows. In a field applied perpendicularly to the easy axis the susceptibility is

$$\chi_{\perp} = 2V^{-1}M_s(T, 0) \sin\theta/H_0, \quad (38)$$

where θ is the angle the sublattice magnetization vector makes with the preferred direction. At equilibrium the net torque on the sublattice moment must be zero, thus determining

$$\sin\theta \approx \theta \approx H_0/(2H_E + H_A). \quad (39)$$

The improved perpendicular susceptibility can now be written as

$$\chi_{\perp}(T) = \frac{\chi_{\perp}^0}{1 + \frac{1}{2}\alpha} \left[1 - \frac{\Delta M_{s\beta}}{M_{s0}} - \frac{\Delta M_s(T, 0)}{M_{s0}} \right]. \quad (40)$$

This equation, including higher order spin wave corrections, is given by Keffer.⁹ Equation (40) is independent of the applied field and only varies slowly with temperature.

III. T_{AE} ; ZERO-ORDER EQUATIONS

By using Eqs. (38) and (39) the anisotropy-exchange temperature defined in Eq. (17) can be put in the

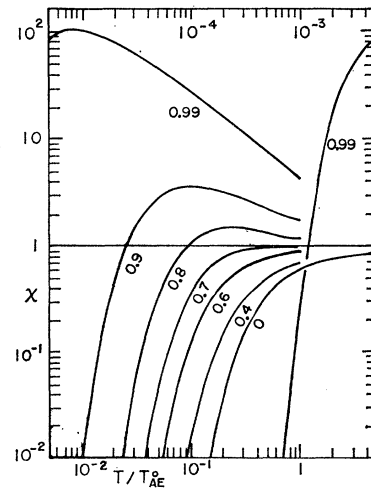


FIG. 4. The temperature variation of the function χ for cubic or uniaxial symmetry showing the effects of applied field and anisotropy. The number below each curve is the value of the ratio T_H^0/T_{AE}^0 . The 0.99 curve on the right-hand side is a lower temperature extension to be used with the scale at the top of the figure.

form

$$k_B T_{AE} = g\mu_B (2H_A M_s / \chi_1)^{1/2} = g\mu_B [2\kappa(T) / \chi_1(T)]^{1/2}, \quad (41)$$

where $\kappa(T)$ is an anisotropy coefficient. Pincus¹³ has shown that the temperature dependence of anisotropy energy in antiferromagnets is related to the temperature dependence of the sublattice magnetization by the expression

$$\kappa(T) / \kappa(0) = [M_s(T) / M_s(0)]^{n(n+1)/2}, \quad (42)$$

where n is the order of the principal surface harmonic in the expansion of the anisotropy energy, and the magnetization value is for zero applied field. If the temperature dependence (very slight) of the factor $(1 + \frac{1}{2}\alpha)$ in the denominator of Eq. (40) is ignored, then the gap temperature, Eq. (41), becomes

$$T_{AE} = T_{AE}^0 [M_s(T) / M_s(0)]^{(n+2)(n-1)/4}, \quad (43)$$

where T_{AE}^0 is the spin wave energy-gap temperature at $T = 0^\circ\text{K}$ and is given by the expression

$$k_B T_{AE}^0 = g\mu_B [2\kappa(0) / \chi_1(0)]^{1/2}. \quad (44)$$

The temperature dependence of T_{AE} is made more explicit by substituting Eqs. (29) and (30) in Eq. (43) and using the binomial expansion:

$$T_{AE} = T_{AE}^0 \left\{ 1 - \frac{1}{8}(n+2)(n-1)(1+\alpha) \left(\frac{A_i}{S} \right) \left(\frac{T_{AE}^0}{T_E} \right)^2 \times \sum_{p=1}^{\infty} \left[K_2 \left(\frac{pT_{AE}^0}{T} \right) - K_0 \left(\frac{pT_{AE}^0}{T} \right) \right] \right\}. \quad (45)$$

This expansion retains only terms linear in $(A_i/S) \times (T_{AE}^0/T_E)^2$, thus making it consistent with the expansions used to determine the parallel susceptibility. Obviously, T_{AE}^0 should now replace T_{AE} in Eq. (35).

The Hankel functions approach zero exponentially with the temperature; since $(A_i/S)(T_{AE}^0/T_E)^2 \ll 1$, most low-temperature calculations will be sufficiently accurate using both T_{AE}^0 and T_H^0 in place of T_{AE} and T_H . The resulting expression for $E^{(0)}(T, H_0)$ is obtained by direct replacement of T_H and T_{AE} in Eq. (22) with their 0°K values. The corresponding zero-order expressions for C_H , ΔM_s , M , and χ_{11} are given below for convenience.

$$C_H^{(0)}(T, H_0) = A_i N_0 k_B \frac{T_{AE}^0}{T} \left(\frac{T_{AE}^0}{T_E} \right)^3 \sum_{p=1}^{\infty} \left\langle \cosh \left(\frac{pT_H^0}{T} \right) \times \left[K_4 \left(\frac{pT_{AE}^0}{T} \right) + \left[1 + 2 \left(\frac{T_H^0}{T_{AE}^0} \right)^2 \right] K_2 \left(\frac{pT_{AE}^0}{T} \right) \right] - \frac{T_H^0}{T_{AE}^0} \sinh \left(\frac{pT_H^0}{T} \right) \left[3K_3 \left(\frac{pT_{AE}^0}{T} \right) + K_1 \left(\frac{pT_{AE}^0}{T} \right) \right] \right\rangle; \quad (46)$$

¹³ P. Pincus, Phys. Rev. **113**, 769 (1959).

$$\Delta M_s^{(0)}(T, H_0) = \frac{1}{2}(1+\alpha) A_i N_0 g\mu_B \left(\frac{T_{AE}^0}{T_E} \right)^2 \times \sum_{p=1}^{\infty} \cosh \left(\frac{pT_H^0}{T} \right) \left[K_2 \left(\frac{pT_{AE}^0}{T} \right) - K_0 \left(\frac{pT_{AE}^0}{T} \right) \right]; \quad (47)$$

$$M^{(0)}(T, H_0) = \frac{1}{2} A_i N_0 g\mu_B \left(\frac{T_{AE}^0}{T_E} \right)^3 \times \sum_{p=1}^{\infty} \sinh \left(\frac{pT_H^0}{T} \right) \left[K_3 \left(\frac{pT_{AE}^0}{T} \right) - K_1 \left(\frac{pT_{AE}^0}{T} \right) \right]; \quad (48)$$

$$\chi_{11}^{(0)}(T, H_0) = 2 A_i N_0 V^{-1} \left(\frac{g^2 \mu_B^2}{k_B T_E} \right) \left(\frac{T_{AE}^0}{T_E} \right)^2 \times \sum_{p=1}^{\infty} \cosh \left(\frac{pT_H^0}{T} \right) K_2 \left(\frac{pT_{AE}^0}{T} \right). \quad (49)$$

The sums in these expressions converge for $H_0 < H_c$, but the rate of convergence is very slow for H_0 near H_c and T near T_{AE}^0 . For example, the sum which is slowest to converge is the one in Eq. (49) and in other expressions pertaining to the susceptibility: about 460 terms are required to obtain better than 99% convergence for $H_0 = 0.99 H_c$ and $T = T_{AE}^0$.

IV. NUCLEAR CONTRIBUTION

The magnetic hyperfine interaction between atomic and nuclear spins is treated as a perturbation on the electron-electron interaction Hamiltonian, Eq. (1):

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}', \quad (50)$$

where

$$\mathcal{H}' = -g_N \mu_N \mathbf{I} \cdot (\mathbf{H}_S + \mathbf{H}_0). \quad (51)$$

In Eq. (51), $g_N I$ is the magnitude of the nuclear magnetic moment in units of the nuclear magneton, μ_N ; \mathbf{I} is the nuclear spin in units of \hbar ; \mathbf{H}_S is the field at the nucleus due to the electron spins; and \mathbf{H}_0 is the external field. The effective field \mathbf{H}_S is taken proportional to \mathbf{S} and the perturbing Hamiltonian becomes

$$\begin{aligned} \mathcal{H}' = & -g_N \mu_N A \left(\sum_l I_l^z S_l^z + \sum_m I_m^z S_m^z \right) \\ & - \frac{1}{2} g_N \mu_N B \left[\sum_l (S_l^+ I_l^- + S_l^- I_l^+) \right. \\ & \left. + \sum_m (S_m^+ I_m^- + S_m^- I_m^+) \right] \\ & - g_N \mu_N H_0 \left(\sum_l I_l^z + \sum_m I_m^z \right). \quad (52) \end{aligned}$$

The entire perturbation can be expressed in terms of the spin wave operators for which \mathcal{H}_0 is diagonal as

Marshall¹⁴ has done for ferromagnets, but it is sufficient at present to take $S_l^z \approx -S$, $S_m^z \approx S$, and $S^\pm \approx 0$. The neglected terms are of order $(T/T_E)^r$, where $r=3/2$ for a ferromagnet and $r=2$ for an antiferromagnet. These terms and other effects not included in this simple model are accounted for by replacing AS with an experimentally determined effective field. In the metals and transition element ions in salts, the effective field is primarily due to core polarization and is antiparallel to the electronic magnetization.¹⁵ This means that $A > 0$. With these approximations and substitutions the hyperfine perturbation reduces to

$$\mathcal{H}' = -g_N\mu_N[(H_0 - H_{\text{eff}})\sum_l I_l^z + (H_0 + H_{\text{eff}})\sum_m I_m^z]. \quad (53)$$

Since the off-diagonal matrix elements of \mathcal{H}' are zero in the set of electronic eigenstates of \mathcal{H}_0 , the perturbed energy levels through second order in quantum perturbation theory are

$$E_n = E_n^{(0)} + \mathcal{H}_{nn}'. \quad (54)$$

The eigenstates $|n\rangle = |I\rangle|S\rangle$ are functions of both the nuclear and electronic coordinates, but the unperturbed eigenvalues $E_n^{(0)}$ depend only on the electronic quantum numbers. Following Landau and Lifshitz,¹⁶ this expression is inserted in the formula for the free energy,

$$e^{-\beta F} = \sum_n e^{-\beta E_n}, \quad (55)$$

and the right side of Eq. (55) is expanded to second order in \mathcal{H}' . The free energy is then determined to be (by making a similar expansion of the logarithm):

$$F = F_0 + \sum_n \mathcal{H}_{nn}' e^{\beta(F_0 - E_n^{(0)})} + \frac{1}{2}\beta \left[\sum_n \mathcal{H}_{nn}' e^{\beta(F_0 - E_n^{(0)})} \right]^2 - \frac{1}{2}\beta \sum_n (\mathcal{H}_{nn}')^2 e^{\beta(F_0 - E_n^{(0)})}. \quad (56)$$

The second and third terms are zero since positive and negative values of the quantum numbers appearing in \mathcal{H}_{nn}' can be matched in pairs, but

$$\begin{aligned} \sum_n (\mathcal{H}_{nn}')^2 e^{\beta(F_0 - E_n^{(0)})} \\ = 2(g_N\mu_N)^2(H_0^2 + H_{\text{eff}}^2)e^{\beta F_0} \sum_n e^{-\beta E_n^{(0)}} \left[\left(\sum_l I_l^z \right)^2 \right]_{nn} \\ = \frac{2}{3}N_0(g_N\mu_N)^2 I(I+1)(H_0^2 + H_{\text{eff}}^2). \end{aligned} \quad (57)$$

Since F_0 is the free energy corresponding to the unperturbed spin wave Hamiltonian, only the portion

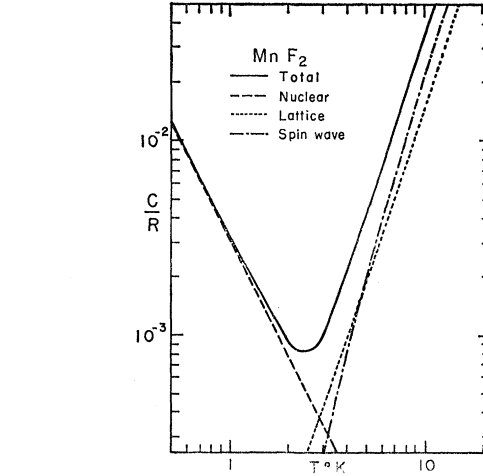


FIG. 5. The temperature variation of the specific heat per mole of MnF_2 in the absence of applied field. The dashed line is the nuclear contribution C_N/R , the dotted line is the lattice contribution C_L/R , and the dashed-dotted line is the magnetic contribution C_H/R . The sum of these is represented by the solid line.

turbed spin wave Hamiltonian, only the portion

$$F_N = F - F_0 = -\frac{1}{3}N_0(g_N\mu_N)^2 I(I+1)(H_0^2 + H_{\text{eff}}^2)/k_B T \quad (58)$$

is needed to determine the nuclear contribution to the thermodynamic properties of the system.

The nuclear spin specific heat is

$$C_N = \frac{2}{3}N_0 k_B I(I+1)(g_N\mu_N)^2(H_0^2 + H_{\text{eff}}^2)/(k_B T)^2; \quad (59)$$

the sublattice magnetic moments are

$$M_N^\pm = \mp \frac{1}{3}N_0 I(I+1)(g_N\mu_N)^2 H_{\text{eff}}/k_B T + \frac{1}{2}M_N, \quad (60)$$

where the total nuclear moment is

$$M_N = \frac{2}{3}N_0 I(I+1)(g_N\mu_N)^2 H_0/k_B T; \quad (61)$$

and the parallel susceptibility is

$$\chi_N = \frac{2}{3}N_0 V^{-1} I(I+1)(g_N\mu_N)^2/k_B T. \quad (62)$$

The \pm superscript above refers to the sublattice with electronic magnetization essentially parallel or antiparallel to the applied field, respectively. Each of the nuclear properties represented by Eqs. (59)–(62) is usually negligible at liquid helium temperature or above, compared to the spin wave properties calculated in Sec. II. However, the nuclear contribution begins to dominate the thermodynamic properties as the absolute temperature is lowered to 1 or 2°K. The nuclear and spin wave specific heats of MnF_2 are compared in Fig. 5. The equations of this section are valid as long as the perturbation energy per particle is much less than $k_B T$. For effective fields at the nucleus of a few hundred kilogauss, the minimum temperature for which this condition is satisfied is a few tenths of a degree.

¹⁴ W. Marshall, Phys. Rev. **110**, 1280 (1958).

¹⁵ R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 2027 (1961). This paper includes other appropriate references.

¹⁶ L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1958), p. 93.

If the substitutions introduced in the discussion following Eq. (52) are modified, the subsequent equations are easily adapted to the cases of ferro- and ferrimagnets. For the former, both S_l^z and $S_m^z \rightarrow -S$ with the result that

$F_N(\text{ferro})$

$$= -\frac{1}{3}N_0(g_N\mu_N)^2I(I+1)(H_0-H_{\text{eff}})^2/k_BT, \quad (63)$$

an expression equivalent to Marshall's lowest order term.¹⁴ The ferrimagnetic case requires $S_l^z \rightarrow -S_a$ and $S_m^z \rightarrow S_b$ with two effective fields, $H_a = A_a S_a$ and $H_b = A_b S_b$. The nuclear contribution to the ferrimagnetic free energy is then

$F_N(\text{ferri})$

$$= -\frac{1}{6}N_0(\mu_N^2/k_BT)[g_a^2I_a(I_a+1)(H_0-H_a)^2 + g_b^2I_b(I_b+1)(H_0+H_a)^2]. \quad (64)$$

V. ADIABATIC MAGNETIZATION

The basic assumptions used in deriving the equations of Sec. II were that (1) $T \ll T_N$ and (2) $H_0 < H_c \approx k_BT_{AE}^0/g\mu_B$. Condition (1) was necessary to presume the applicability of spin wave theory and to allow the simplification of extending the integral over the first Brillouin zone to infinity; condition (2) assures that the spins are basically aligned in the preferred direction, the arrangement for which Eq. (1) is expected to be appropriate. The qualitative discussion in Sec. I indicated that cooling of an antiferromagnet by adiabatic magnetization might be possible when the net specific heat shows a rapid increase with increasing applied field. This implies condition (3), that $T < T_{AE}^0$, since the exponential dependence of the thermodynamic properties on H_0 and T disappears for $T > T_{AE}^0$.

The methods described in Sec. II are used to determine the field- and temperature-dependent magnetic spin wave entropy:

$$S^{(0)}(T, H_0) = \frac{1}{3}A_l N_0 k_B \frac{T_{AE}^0}{T} \left(\frac{T_{AE}^0}{T} \right)^3 \sum_{p=1}^{\infty} \left\{ \cosh \left(\frac{pT_{H^0}}{T} \right) \times \left[K_4 \left(\frac{pT_{AE}^0}{T} \right) - K_2 \left(\frac{pT_{AE}^0}{T} \right) \right] - \frac{3}{2} \frac{T_{H^0}}{T_{AE}^0} \sinh \left(\frac{pT_{H^0}}{T} \right) \times \left[K_3 \left(\frac{pT_{AE}^0}{T} \right) - K_1 \left(\frac{pT_{AE}^0}{T} \right) \right] \right\}. \quad (65)$$

The nuclear contribution to the entropy follows from Eq. (58):

$$S_N = -\frac{1}{3}N_0 k_B (g_N\mu_N)^2 I(I+1)(H_0^2 + H_{\text{eff}}^2)/(k_BT)^2. \quad (66)$$

Finally, using the Debye model, the lattice specific heat

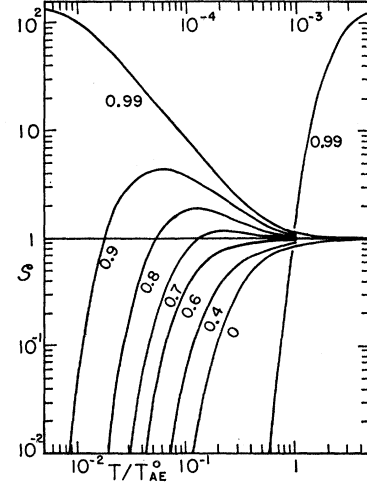


FIG. 6. The temperature variation of the function S for cubic or uniaxial symmetry showing the effects of applied field and anisotropy. The number below each curve is the value of the ratio T_H^0/T_{AE}^0 . The 0.99 curve on the right-hand side is a lower temperature extension to be used with the scale at the top of the figure.

is given by

$$C_L = (12\pi^4/5)mR(T/\Theta_D)^3, \quad (67)$$

and

$$S_L = \frac{1}{3}C_L, \quad (68)$$

where m is the number of moles, R is the universal gas constant, and Θ_D is the Debye temperature based on treating the molecular formula unit as a single (three-dimensional) harmonic oscillator.

Since the total entropy of a sample remains unchanged in an adiabatic experiment, the isentropic function $T(H_0)$ is the solution of the transcendental equation

$$S^{(0)}(T, H_0) + S_L + S_N = \text{const.} \quad (69)$$

This equation contains so many sample-dependent parameters that a general analytic solution is not attempted. The spin wave entropy, Eq. (65), however, can be given reasonable generality by plotting the function

$$S = (45/8\pi^4 A_l N_0 k_B) (T_E/T)^3 S^{(0)}(T, H_0) \quad (70)$$

vs T/T_{AE}^0 using T_H^0/T_{AE}^0 as a parameter; this is done in Fig. 6. The quantity S is defined analogously to \mathcal{E} , \mathcal{C} , etc., and approaches unity for $T \gg T_{AE}^0$. Equations (66) and (68) are easily calculable and can be combined with the general results of Fig. 6 to determine the adiabatic effect for a specific material. In the preceding discussion it was implicitly assumed that the adiabatic condition would be met by isolating the sample in a vacuum so that with the pressure and its differential change equal to zero, the specific heats at constant volume or pressure would be equivalent.

A rough estimate of the temperature change and its functional dependence on T_{AE}^0 is made in the following way. Ignore all but the spin wave contribution in Eq. (69); assume the initial temperature, T_i , to be of the order of T_{AE}^0 , and the final temperature, T_f , to be much less than T_{AE}^0 . Let the applied field which is switched on adiabatically be of the order of the critical field. Then, by equating the initial and final values of the entropy, it is found that

$$T_f \sim 0.7 T_i^2 / T_{AE}^0. \quad (71)$$

If the major contribution to the initial entropy comes from the lattice waves rather than the spin waves, i.e., if $\Theta_D \ll 3T_E$, then the expression for the final temperature is

$$T_f \sim (5T_E / \Theta_D)^2 T_i^2 / T_{AE}^0. \quad (72)$$

Except for the numerical factor, this equation is equivalent to one given in reference 5. Both (71) and (72) are very crude numerical approximations; however, they serve to indicate that, for a given initial temperature, an antiferromagnet with a large anisotropy-exchange temperature would exhibit greater cooling than one with a lower T_{AE}^0 . This dependence on T_{AE}^0 is tested in Sec. VII. It should be noted that the increased cooling will be at the expense of applying a larger field, since most of the cooling effect occurs in the range $0.75 < H_0/H_c \lesssim 1.0$ and H_c is proportional to T_{AE}^0 .

The differential thermodynamic equation for an adiabatic process is given in many texts, such as Epstein¹⁷; in a vacuum this equation is simply

$$\frac{dT}{dH} = - \frac{T(\partial M / \partial T)_H}{C_H}, \quad (73)$$

where M and C_H represent all contributions to the magnetic moment and specific heat of the sample. This equation is, of course, equivalent to Eq. (69), but shows explicitly how the rate of adiabatic temperature change depends on the macroscopic properties. In this equation the sign of $(\partial M / \partial T)_H$ dictates whether the sample will be cooled or heated by magnetizing it, while the size of the effect is determined by the field dependence of both M and C_H . The qualitative discussion of cooling in Sec. I, based solely on knowledge of the behavior of C_H rather than of M , is entirely equivalent since C_H and M are connected through the Cauchy relations,

$$\frac{\partial}{\partial H} \left(\frac{C_H}{T} \right)_T = \frac{\partial}{\partial T} \left[\left(\frac{\partial M}{\partial T} \right)_H \right]_H. \quad (74)$$

Although Eq. (73) generally represents cooling by adiabatic magnetization for an antiferromagnet, it is

interesting to note that the nuclear contribution to $(\partial M / \partial T)$ is opposite in sign to the spin wave contribution. Thus at low temperatures, the adiabatic switching on of a magnetic field can result in cooling or heating an antiferromagnet, depending on the initial temperature and final value of the field. It can be shown that the limit as T approaches zero of dT/dH for spin waves is zero. Since the perturbation theory used to evaluate the nuclear properties is not valid below a few tenths of a degree, the limit of the total dT/dH cannot be examined rigorously. However, the temperature dependence of C_N and M_N , Eqs. (59) and (61), is such that if the perturbation limit is ignored, the total dT/dH also approaches zero with decreasing temperature.

VI. APPLICATION TO MnF_2

The crystal structure of MnF_2 is body-centered tetragonal with $c_0/a_0 = 0.68$. This ratio is such that nearest-neighbor Mn^{++} ions are actually c -axis pairs rather than corner and body-center pairs. Measurements¹⁸ of Mn impurities in ZnF_2 , however, give a very small, probably ferromagnetic, interaction between c -axis neighbors and a larger ($\times 10$) antiferromagnetic interaction between corner and body-center neighbors. In addition, Smart¹⁹ has shown that the Néel temperature, Curie-Weiss constant, and specific heat anomaly of MnF_2 are explained consistently by a single corner-center exchange interaction. The body-centered tetragonal structure can be reduced mathematically to bcc in \mathbf{k} space integrations by the simple substitution $k_z' = (c_0/a_0)k_z$. Thus the equations of Sec. II for total energy, magnetic moment, etc., are applicable to MnF_2 . Justification of the use of spin wave theory is mentioned later in connection with the experimental data.

The effective exchange temperature, T_E , is theoretically related to the perpendicular susceptibility by Eq. (36). The latter quantity was measured by Bizette and Tsai²⁰ and the experimental data result in a value for T_E of 77.0°K ($T_N \approx 68^\circ\text{K}$).

Johnson and Nethercot²¹ have excited the $\mathbf{k}=0$ spin wave resonance in MnF_2 at low temperatures using millimeter waves. The zero-field resonance frequency extrapolated to 0°K was found to approach 261.4 kMc/sec within experimental error. This result determines T_{AE}^0 as 12.54°K since the resonance frequency is directly proportional to the gap energy for $\mathbf{k}=0$ spin waves.

Oguchi²² has used spin wave theory to calculate the anisotropy constant, $\kappa(T)$, in good agreement with experiment,²³ and has shown it to be proportional to

¹⁸ M. R. Brown, B. A. Coles, and R. W. H. Stevenson, *Phys. Rev. Letters* **7**, 246 (1961).

¹⁹ J. S. Smart (to be published).

²⁰ H. Bizette and B. Tsai, *Compt. rend.* **238**, 1575 (1954).

²¹ F. M. Johnson and A. H. Nethercot, Jr., *Phys. Rev.* **114**, 705 (1959).

²² T. Oguchi, *Phys. Rev.* **111**, 1063 (1958).

²³ S. Foner, *Phys. Rev.* **107**, 683 (1957).

¹⁷ P. S. Epstein, *Textbook of Thermodynamics* (John Wiley & Sons, Inc., New York, New York, 1937), p. 352.

TABLE I. Adiabatic magnetization of MnF_2 ; $\Delta T/T_i$ in percent.

T_i (°K) (H_0/H_c) ^a	0.6 (0.048) ^b	1.0 (0.08)	2.0 (0.16)	4.0 (0.32)	6.0 (0.48)	8.0 (0.64)	10.0 (0.80)	12.0 (0.96)
0.10	0.00875	0.00865	-0.0374	-0.258	-0.171	-0.111	-0.0762	-0.0554
0.20	0.0347	0.0342	-0.159	-1.025	-0.678	-0.439	-0.302	-0.220
0.30	0.0777	0.0762	-0.401	-2.31	-1.53	-0.988	-0.681	-0.497
0.40	0.138	0.133	-0.825	-4.11	-2.73	-1.76	-1.21	-0.886
0.50	0.215	0.201	-1.53	-6.46	-4.29	-2.77	-1.91	-1.39
0.60	0.309	0.269	-2.63	-9.38	-6.24	-4.03	-2.78	-2.02
0.70	0.419	0.304	-4.31	-12.9	-8.62	-5.56	-3.82	-2.78
0.75	0.478	0.287	-5.44	-14.9	-9.99	-6.44	-4.42	-3.21
0.80	0.536	0.222	-6.79	-17.2	-11.5	-7.39	-5.06	-3.67
0.85	0.588	0.0791	-8.41	-19.6	-13.1	-8.43	-5.77	-4.17
0.90	0.620	-0.191	-10.35	-22.3	-15.0	-9.58	-6.53	-4.72
0.95	0.602	-0.672	-12.7	-25.4	-17.0	-10.84	-7.37	-5.32
0.99	0.499	-1.34	-15.1	-28.2	-18.8	-12.0	-8.11	-5.83

^a $H_c = 93.3$ kOe.^b The column headings in parentheses are values of T_i/T_{AE}^0 ; $T_{AE}^0 = 12.54^\circ\text{K}$.

$M_s^{2.9}$. [Macroscopic arguments leading to Eq. (42) predict M_s^3 .] Kanamori and Tachiki²⁴ have calculated $\chi_1(T)$ from an equation similar to (40), but including corrections for higher-order spin wave interactions, and, with their own calculation of $M_s(T)$, have evaluated $T_{AE}(T)$ in very good agreement with the measured T_{AE} of reference 21.

The nuclear magnetic resonance (NMR) frequency of F^{19} in MnF_2 has been measured with great precision by Jaccarino and Shulman.²⁵ The shift of this frequency due to M_s is expected to be proportional to M_s with a temperature independent constant of proportionality.²⁶ Keffer²⁷ has calculated the sublattice magnetization using spin wave theory, taking account of discrete lattice and zone boundary effects, and has found that $M_s(T)$ fits the experimental curve of the NMR frequency shift up to $T \sim T_{AE}^0$.

The nuclear spin specific heat of MnF_2 was measured from 0.5–2.0°K by Cooke and Edmonds²⁸ who found it to have an inverse T^2 dependence with a numerical coefficient corresponding to $H_{\text{eff}} = 650$ kOe in Eq. (59). This value of the effective field is in good agreement with values determined by other experimental and theoretical means.¹⁵

The low-temperature specific heat of MnF_2 was also measured by Catalano and Phillips²⁹ in the range 1–5°K. Their analysis of the T^3 lattice contribution gave a Debye temperature of 253°K at about 1–2°K.

This value falls off slowly with the temperature and is estimated to be about 242°K at 15°K from higher temperature data.³⁰ A value of $\Theta_D = 250^\circ\text{K}$ is used in the present calculations. Other data for manganous fluoride are $S = 5/2$, $g = 2$, $I = 5/2$, and $g_N I = 3.468$.

The differential equation (73) was solved numerically for values of the applied field up to 99% of the critical spin-flopping field, which is about 93.3 kOe in MnF_2 . Maximum cooling by adiabatic magnetization was found to occur for an initial temperature of 3–4°K; the effect amounts to a 25–30% decrease in temperature for the maximum applied field, 92.4 kOe. The isentropic functions $T(H_0)$ are shown in Fig. 7 for initial temperatures between 2°K and 5°K. From 6°K to 12°K the curves are nearly parallel to the one starting at 5°K, i.e., the slope has only a weak dependence on tempera-

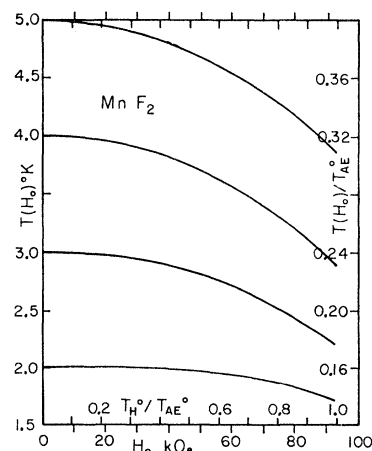


FIG. 7. The isentropic functions $T(H_0)$ for the adiabatic magnetization of MnF_2 . The critical spin-flopping field is 93.3 kOe.

²⁴ J. Kanamori and M. Tachiki (to be published).²⁵ V. Jaccarino and R. G. Shulman, Phys. Rev. **107**, 1196 (1957); R. G. Shulman and V. Jaccarino, *ibid.* **108**, 1219 (1957); V. Jaccarino and L. R. Walker, J. phys. radium **20**, 341 (1959).²⁶ T. Oguchi and A. Honma, J. Phys. Soc. (Japan) **16**, 79 (1961).²⁷ F. Keffer (unpublished).²⁸ A. H. Cooke and D. T. Edmonds, Proc. Phys. Soc. (London) **71**, 517 (1958).²⁹ E. Catalano and N. E. Phillips, Proceedings of the International Conference on Magnetism and Crystallography, Kyoto, Japan, September, 1961 (to be published).³⁰ J. W. Stout and E. Catalano, Jr., J. Chem Phys. **23**, 2013 (1955).

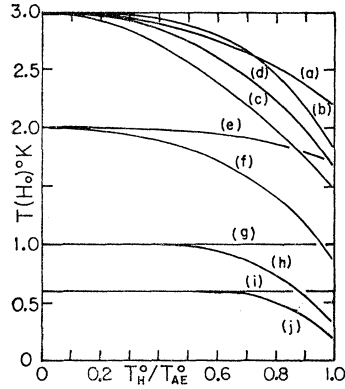


FIG. 8. Dependence of adiabatic magnetization on individual parameters. Curves (a), (e), (g), and (i) represent MnF_2 as in Fig. 7. In each of the other curves one parameter differs from the MnF_2 value: (b) $T_{AE}^0 = 25^\circ\text{K}$; (c) $T_E = 38.5^\circ\text{K}$; (d), (f), (h), and (j) $g_N I = 0$.

ture in this range [see Eq. (76)]. The magnitude of the temperature change decreases slowly from 1.1° at 6°K to 0.70° at 12°K . At 1°K and below both cooling and heating are observed theoretically, but the size of the effect is negligible. Complete data for the temperature range $0.6^\circ\text{K} \leq T \leq 12^\circ\text{K}$, equivalent to $0.048 \leq T/T_{AE}^0 \leq 0.96$, are given as percent temperature changes in Table I.

VII. DISCUSSION

It is apparent now that the basic premise, $T_f \ll T_i$, which led to the approximate temperature-change formula of reference 5 [rederived as Eq. (72) in the present paper], is not generally appropriate. A better approximation is the following. Let $T_i \sim T_{AE}^0$ so that \mathcal{C} and $\mathfrak{M} \sim 1$; write

$$C_H = C_H(T, H_0) + C_L \sim C_H(T) [1 + (3T_E/\Theta_D)^3], \quad (75)$$

which is proportional to T^3 . The nuclear contribution is negligible at this temperature. Equation (73) becomes

$$\frac{dT}{dH_0} \sim -\frac{5}{2\pi^2} \left(\frac{g\mu_B}{k_B} \right)^2 \frac{H_0}{(1+\delta)T}, \quad (76)$$

where $\delta = (3T_E/\Theta_D)^3$. Define $\Delta T = T_f - T_i$ and $T_{av} = \frac{1}{2}(T_f + T_i)$; let $g\mu_B H_f/k_B \sim T_{AE}^0$ (equivalent to the critical field) and $H_i = 0$. The solution of Eq. (76) is then

$$\Delta T \sim -0.13(T_{AE}^0)^2/(1+\delta)T_{av}. \quad (77)$$

Since ΔT is fairly small, T_{av} can be replaced by T_i . The MnF_2 value of ΔT predicted by Eq. (77) for $T_i = 6^\circ\text{K}$ is -1.6° , and for $T_i = 12^\circ\text{K}$ it is -0.82° . Both of these values are in much better agreement with the detailed calculations than are the predictions of either Eq. (71) or Eq. (72).

Aside from the nuclear terms, the differential equation (73) can be formulated using the reduced variables T/T_{AE}^0 and T_H^0/T_{AE}^0 (or H_0/H_c) and the ratio T_E/Θ_D . Consequently the data in Table I are indicative of the

effect of adiabatic magnetization on any antiferromagnet which fits the model described in Sec. II and for which $T_E/\Theta_D \sim 0.3$ as in MnF_2 . With this in mind, the data of Table I can be used to check the functional dependence of Eqs. (71), (72), and (77) on T_{AE}^0 . All three equations indicate that for a given T_i , an increase in T_{AE}^0 will result in a greater ΔT (at the expense of a larger H_0). Since halving T_i has the same effect on the ratio T_i/T_{AE}^0 as doubling T_{AE}^0 , the data in the last line of Table I (maximum applied field) show that $|\Delta T/T_i|$ increases from about 6% to 19% as the ratio T_i/T_{AE}^0 is reduced from 1 to 0.5. The approximation, Eq. (77), predicts a factor of four increase in ΔT . Comparison of curves (a) and (b) in Fig. 8 shows the effect of doubling T_{AE}^0 in MnF_2 while holding all other parameters constant.

Adiabatic magnetization depends on the exchange temperature, T_E , more qualitatively than quantitatively. A T_E small compared to the Debye temperature enhances the importance of the magnetic specific heat relative to the lattice specific heat. Thus the total C_H depends more strongly on the applied field when $T_E \ll \Theta_D$, resulting in a larger ΔT . The effect of reducing T_E to one-half its original value while other MnF_2 parameters are unchanged is shown by comparing curves (a) and (c) in Fig. 8. Because the electronic moment and magnetic specific heat are proportional to the same power of T_E , the differential equation describing the adiabatic temperature change is essentially independent of the value of T_E . Furthermore, if T_E is very low, the inverse dependence of C_H on the exchange temperature means that the magnetic specific heat will also be much greater than the nuclear specific heat, even at very low temperatures, again improving the prospect of a large ΔT .

Since, in the absence of the nuclear terms, dT/dH is always negative for nonzero T , it is the nuclear magnetic moment which effectively sets a low-temperature limit on the cooling effect. The nuclear moment and hyperfine field of manganese are particularly large with the result that the nuclear specific heat is the dominant specific-heat term in MnF_2 below 3°K . In Fig. 8, curves (d), (f), (h), and (j) were calculated using the physical constants of MnF_2 except $g_N I = 0$; they are to be compared with normal MnF_2 curves (a), (e), (g), and (i) in that order. Although $dT/dH \rightarrow 0$ as $T \rightarrow 0$, it is apparent that the cooling process extends to a much lower temperature in the absence of the magnetic hyperfine interaction.

Antiferromagnetic structures containing even-even nuclei, such as Cr^{52} , Fe^{56} , and $\text{Ni}^{58,60}$, as the magnetic ions should be much more useful for very low temperature cooling by adiabatic magnetization than those containing Mn^{55} or $\text{Cu}^{63,65}$ ions. Even Cr^{53} , Fe^{57} , and Ni^{61} may be suitable since their nuclear moments are, at least, an order of magnitude smaller than that of Mn^{55} . An example would seem to be Cr_2O_3 , which has

been extensively investigated by Foner.³¹ The effective nuclear moment of this crystal is very small since natural chromium contains less than 10% Cr^{53} . Chromic oxide has a gap temperature of about 7.9°K (critical field about 59 kOe) which can be increased by the addition of Al_2O_3 . Less favorable, however, is the relatively high Néel temperature of Cr_2O_3 , $T_N = 308^\circ\text{K}$. With T_N reduced to 266°K by the addition of corundum, preliminary calculations indicate that $(\text{Cr}_2\text{O}_3)_{0.9}(\text{Al}_2\text{O}_3)_{0.1}$ would be cooled from 1.0 to 0.5°K or from 0.6 to 0.24°K by a near-critical field of 81 kOe.

In general, the optimum conditions for observing or causing cooling in an antiferromagnet by adiabatic magnetization are: (1) $g_N I \sim 0$ or $T \gtrsim 1\text{--}2^\circ\text{K}$ so that the nuclear (heating) effect is negligible (this condition

is not important if T_E is very small); (2) $T < T_{AE}^0$ so that the number of spin waves excited depends exponentially on temperature; (3) T_{AE}^0 large, but no greater than $g\mu_B/k_B$ times the maximum magnetic field available; and (4) $T_E \ll \Theta_D$ so that the magnetic specific heat is dominant. A possible use for the effect of adiabatic magnetization on an antiferromagnet, other than the cooling *per se*, would be as a sink for the heat generated when a paramagnetic (or ferromagnetic) material is magnetized prior to cooling by adiabatic demagnetization.

ACKNOWLEDGMENT

The author is grateful to Professor Frederic Keffer for suggesting this investigation and for his continued interest and advice.

³¹ S. Foner, Suppl. J. Appl. Phys. **32**, 63 (1961).