

TABLE IV. Elastic constants of alkali halides at low temperatures in units of 10^{11} d/cm².^a

| | F | Cl | Br | I |
|----|--------------------|--------------------|--------------------|--------------------|
| | | C_{11} | | |
| Li | 12.42 _H | | | |
| Na | | 5.730 _N | | |
| K | | 4.832 _H | 4.17 _H | 3.38 _H |
| Rb | | | | |
| Cs | | | 3.355 _N | 2.669 _N |
| | | C_{12} | | |
| Li | 4.24 | | | |
| Na | | 0.986 | | |
| K | | 0.54 | 0.58 | 0.22 |
| Rb | | | | |
| Cs | | | 1.002 | 0.753 |
| | | C_{44} | | |
| Li | 6.49 | | | |
| Na | | 1.32 | | |
| K | | 0.663 | 0.505 | 0.368 |
| Rb | | | | |
| Cs | | | 0.972 | 0.814 |

^a Subscript *H*—at liquid helium temperature; subscript *N*—at liquid nitrogen temperature.

As a possible explanation for the same anisotropy value for all lithium halides, one surmises that the halide ions touch each other in lithium salts and that the

lithium ions occupy the available holes in the lattice. For salts where the alkali ion size is larger, the value of the anisotropy increases, since the lattice departs from being a simple face-centered cubic lattice. For the other alkali ions, increasing the halide ion size also increases the anisotropy of the salt. When considering cesium chloride type halides, the observed sudden drop in the value of the anisotropy may be due to the increased number of nearest neighbors tending to make the crystal more isotropic.

The meager low-temperature data in Table IV indicates that as the temperature is lowered, the anisotropy increases in general, while the departure from the Cauchy relation is decreased as a rule. The scarce temperature-dependent data on C_{12} and C_{44} would also suggest that the slopes for the above two constants are somewhat coupled (possibly by the Cauchy relation), the slope of C_{12} being, as a rule, less than that of C_{44} for any particular salt.

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Spin-Wave Contribution to Specific Heat and Magnetization in Canted Spin Arrays

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The dispersion law for spin waves in a cubic canted spin array has been derived. From this dispersion law the spin-wave contributions to the specific heat and magnetization have been obtained. The integrals involved in the expressions for these quantities have been evaluated numerically for a moderate range of the system description parameters B and F . In a special case the behavior of the spin wave contribution has been shown to change from T^3 at very low temperature to T^2 at somewhat higher temperatures. This phenomenon is discussed in terms of some available data on low-temperature spin system specific heats.

INTRODUCTION

THE subject of spin waves has been of interest ever since Bloch¹ initially proposed the method as a way of describing the deviations of the magnetization at low temperatures from that at absolute zero. Recent direct observations of the spin-wave resonance² have tended to increase our faith in the model. An excellent review³ includes calculations typical of those to be found in the literature.

One of the most interesting facets of spin-wave theory is the study of such waves in canted arrays. This interest was stimulated by Dzyaloshinsky's⁴ observation that the observed weak transverse ferromagnetism⁵ of α -Fe₂O₃ could be explained in terms of a turning towards one another of the two antiferromagnetically coupled sublattices. This in turn could reasonably be due to canted anisotropy fields. Orbach⁶ has pursued this question from the spin-wave viewpoint and has obtained the spin-wave dispersion law and the static magnetization due to canted arrays.

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¹ F. Bloch, *Z. Physik* **61**, 206 (1930).

² M. H. Seavey, Jr., and P. E. Tannenwald, *Phys. Rev. Letters* **1**, 168 (1958).

³ J. Van Kranendonk and J. H. Van Vleck, *Revs. Modern Phys.* **30**, 1 (1958).

⁴ I. Dzyaloshinsky, *J. Phys. Chem. Solids* **4**, 241 (1958).

⁵ F. J. Morin, *Phys. Rev.* **78**, 819 (1950) and references cited there.

⁶ R. Orbach, *Phys. Rev.* **115**, 1189 (1959).

In this paper we derive the spin-wave dispersion law under slightly more general conditions than those employed by Orbach. Proceeding from the dispersion law the spin-wave contributions to the specific heat and magnetization are obtained. The complexity of the dispersion law forces one to determine C_v and \mathbf{M} by numerical integration. As a result of carrying out these integrations it is seen that the use of the exact dispersion law has interesting consequences even for uncanted arrays. The most direct manifestation of the use of the exact dispersion law is the appearance of a small T^3 term in the spin-wave contribution to the specific heat. Since such a term would not be separable from the lattice specific heat, it could cause some difficulty in the interpretation of low-temperature specific-heat measurements. We might also observe that this work represents an extension of that of Kouvel and Brooks,⁷ who considered simple cubic lattices with finite external and anisotropy fields. These workers, however, restricted their work to the consideration of fields along a crystallographic axis.

DESCRIPTION OF SPIN SYSTEM AND HAMILTONIAN

For the purposes of this calculation it will be assumed that the system is a regular array of well-localized spins which may be divided into two sublattices. It will be assumed further that this division can be accomplished in such a way that all the nearest neighbors of a spin on one sublattice are on the other sublattice and conversely. A given spin may be subject to three distinct torques due to (a) the exchange interaction with neighboring spins, (b) the interaction with crystalline anisotropy fields and (c) interaction with an externally applied field.

The exchange interactions have the form (for the entire spin system)

$$2J \sum_i \mathbf{S}_1^{(i)} \cdot \sum_z \mathbf{S}_2^{(j)}, \quad (1)$$

where the sum on i goes over all spin sites on sublattice one and the sum on z goes over the sites on lattice two which are nearest neighbors of the i th site on lattice one. J is the negative of the exchange integral as usually defined.⁸

The anisotropy energy, i.e., the energy responsible for easy and hard directions of magnetization, is the result of some complicated combination of the effects of spin-orbit coupling and the interaction of orbital angular momentum with inhomogeneous electric fields.⁹ As a result of this anisotropy energy there are certain directions, fixed with respect to the crystallographic axes, in which the spins prefer to align. We assume that

there is such a direction for each of the two sublattices but do not insist that they be parallel. We do require, however, that the direction be the same for all spins on a given sublattice. The symmetry properties of various crystal structures lead to relatively general expressions for the anisotropy energy; however, for our purposes the expression

$$\begin{aligned} & - \sum_i g_1 \beta \mathbf{H}_1 \cdot \mathbf{S}_1^{(i)} - \sum_j g_2 \beta \mathbf{H}_2 \cdot \mathbf{S}_2^{(j)} \\ & + \sum_i \frac{(\mathbf{K}_1 \times \mathbf{S}_1^{(i)}) \cdot (\mathbf{K}_1 \times \mathbf{S}_1^{(i)})}{K_1 S_1} \\ & + \sum_j \frac{(\mathbf{K}_2 \times \mathbf{S}_2^{(j)}) \cdot (\mathbf{K}_2 \times \mathbf{S}_2^{(j)})}{K_2 S_2} \end{aligned} \quad (2)$$

will suffice. \mathbf{H}_1 and \mathbf{H}_2 are vectors in the easy direction of magnetization as are \mathbf{K}_1 and \mathbf{K}_2 . It will be assumed that the \mathbf{H} 's and \mathbf{K} 's are temperature independent.¹⁰ This expression at best is valid only for small deviations from the preferred directions. However, it does lead to tractable problems and contains both of the forms commonly used for the anisotropy energy. Thus the results of this calculation can be compared readily with previous less general calculations.

The third term of interest is simply the Zeeman energy of the spins in the external field \mathbf{H}_0 ,

$$- \sum_i g_1 \beta \mathbf{S}_1^{(i)} \cdot \mathbf{H}_0 - \sum_j g_2 \beta \mathbf{S}_2^{(j)} \cdot \mathbf{H}_0. \quad (3)$$

By introducing new fields $\mathbf{H}_1' = \mathbf{H}_1 + \mathbf{H}_0$ and $\mathbf{H}_2' = \mathbf{H}_2 + \mathbf{H}_0$, the Zeeman energy can be included with the first two terms in the anisotropy energy. It is well to note that the exchange energy is about 10^3 times the Zeeman energy while the anisotropy energy is about 10 times the Zeeman energy.¹¹

The expressions given above can be combined to give the Hamiltonian \mathcal{H} for the spin system:

$$\begin{aligned} \mathcal{H} = & - \sum_i g_1 \beta \mathbf{S}_1^{(i)} \cdot \mathbf{H}_1' - \sum_j g_2 \beta \mathbf{S}_2^{(j)} \cdot \mathbf{H}_2' \\ & + \sum_i \frac{(\mathbf{K}_1 \times \mathbf{S}_1^{(i)}) \cdot (\mathbf{K}_1 \times \mathbf{S}_1^{(i)})}{K_1 S_1} \\ & + \sum_j \frac{(\mathbf{K}_2 \times \mathbf{S}_2^{(j)}) \cdot (\mathbf{K}_2 \times \mathbf{S}_2^{(j)})}{K_2 S_2} \\ & + 2J \sum_i \mathbf{S}_1^{(i)} \cdot \sum_z \mathbf{S}_2^{(j)}. \end{aligned} \quad (4)$$

This Hamiltonian can be treated as a classical energy expression and used to compute torques exerted on the various spins or alternatively may be considered as a quantum-mechanical Hamiltonian. In the latter case, equations of motion for the individual spins may be

⁷ J. S. Kouvel and H. Brooks, Technical Report 198, Cruft Laboratory, Harvard University, 1954 (unpublished).

⁸ J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932).

⁹ C. Kittel and J. K. Galt, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1956), Vol. 3, p. 437.

¹⁰ The temperature dependence is discussed by C. Zener, *Phys. Rev.* **96**, 1335 (1954); and F. Keffer, *Phys. Rev.* **100**, 1692 (1955).

¹¹ J. H. Van Vleck, *Proc. Inst. Radio Engrs.* **44**, 1270 (1956).

obtained from

$$\frac{i}{\hbar}[\mathcal{H}, \mathbf{S}_1^{(i)}] = \frac{d\mathbf{S}_1^{(i)}}{dt}; \quad \frac{i}{\hbar}[\mathcal{H}, \mathbf{S}_2^{(j)}] = \frac{d\mathbf{S}_2^{(j)}}{dt}. \quad (5)$$

The result of evaluating the commutator for \mathbf{S}_1 is the exact quantum-mechanical equation of motion

$$\begin{aligned} \hbar d\mathbf{S}_1^{(i)}/dt &= g_1\beta\mathbf{S}_1^{(i)} \times \mathbf{H}_1' \\ &+ \frac{(\mathbf{S}_1^{(i)} \times \mathbf{K}_1)(\mathbf{S}_1^{(i)} \cdot \mathbf{K}_1) + (\mathbf{S}_1^{(i)} \cdot \mathbf{K}_1)(\mathbf{S}_1^{(i)} \times \mathbf{K}_1)}{K_1 S_1} \\ &- 2J\mathbf{S}_1^{(i)} \times \sum_z \mathbf{S}_2^{(j)}. \end{aligned} \quad (6)$$

The corresponding equation for \mathbf{S}_2 is obtained by simply interchanging the appropriate subscripts and superscripts. Equation (6) is equivalent to the equations of motions used by Kouvel and Brooks⁷ and by Orbach,⁶ among others, when the appropriate restrictions are imposed.

DISPERSION RELATION

As noted earlier, the central problem in spin-wave theory is the deduction of the appropriate dispersion relation or dependence of frequency on wave vector. Obtaining this dispersion relation is essentially equivalent to solving Eq. (6). We have accomplished this in two ways; first by treating the \mathbf{S} 's as classical vectors and solving Eq. (6) for small deviations from equilibrium and second by making appropriate transformations to reduce the Hamiltonian (4) to one which describes a set of uncoupled harmonic oscillators. Since the same result was obtained in each case, only the first will be considered here.¹²

The classical equivalents of (6) are

$$\begin{aligned} \hbar \frac{d\mathbf{S}_1^{(i)}}{dt} &= g_1\beta\mathbf{S}_1^{(i)} \times \mathbf{H}_1' + \frac{2(\mathbf{S}_1^{(i)} \times \mathbf{K}_1)(\mathbf{S}_1^{(i)} \cdot \mathbf{K}_1)}{K_1 S_1} \\ &- 2J\mathbf{S}_1^{(i)} \times \sum_z \mathbf{S}_2^{(j)}, \\ \hbar \frac{d\mathbf{S}_2^{(j)}}{dt} &= g_2\beta\mathbf{S}_2^{(j)} \times \mathbf{H}_2' + \frac{2(\mathbf{S}_2^{(j)} \times \mathbf{K}_2)(\mathbf{S}_2^{(j)} \cdot \mathbf{K}_2)}{K_2 S_2} \\ &- 2J\mathbf{S}_2^{(j)} \times \sum_z \mathbf{S}_1^{(i)}. \end{aligned} \quad (7)$$

The lowest energy equilibrium configuration of the spins must now be found. As long as the anisotropy fields are not both zero for both lattices, this ground state is the configuration in which all spins on sublattice one are parallel to a vector which is fixed with respect

to the crystallographic axes and all spins on sublattice two are parallel to another such vector.¹³ From (7) it is clear that this may be phrased

$$\begin{aligned} \lambda_1 \mathbf{S}_1^{(i)} \Big|_{\text{eq}} &= \left\{ g_1\beta\mathbf{H}_1' + \frac{2\mathbf{K}_1(\mathbf{S}_1^{(i)} \cdot \mathbf{K}_1)}{K_1 S_1} - 2J \sum_z \mathbf{S}_2^{(j)} \right\} \Big|_{\text{eq}} \\ &= M_1 \mathbf{k}_1, \\ \lambda_2 \mathbf{S}_2^{(j)} \Big|_{\text{eq}} &= \left\{ g_2\beta\mathbf{H}_2' + \frac{2\mathbf{K}_2(\mathbf{S}_2^{(j)} \cdot \mathbf{K}_2)}{K_2 S_2} - 2J \sum_z \mathbf{S}_1^{(i)} \right\} \Big|_{\text{eq}} \\ &= -M_2 \mathbf{k}_2. \end{aligned} \quad (8)$$

In (8) the subscript eq means that the quantity to which it is attached is to be evaluated for the equilibrium configuration of the spins. The λ 's are simply proportionality constants. Thus M_1 and M_2 are constants and \mathbf{k}_1 and \mathbf{k}_2 constant unit vectors.

Classical spin waves are phase-coherent displacements of the spins from their equilibrium positions such that the termini of the spin vectors describe ellipses about their equilibrium positions. The im-

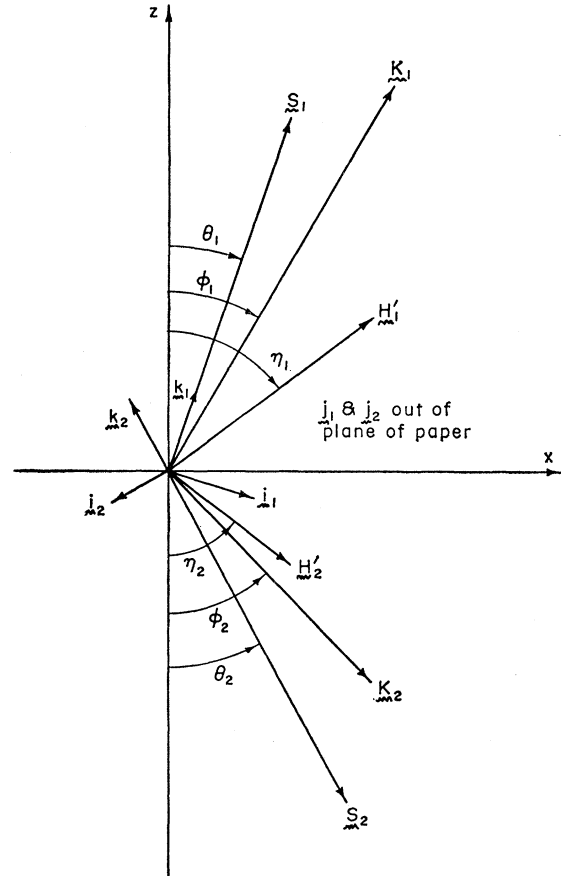


FIG. 1. Canted spin orientations.

¹² H. Unruh, Jr., Technical Report No. 3, Case Institute of Technology, 1959 (unpublished).

¹³ The validity of this approximation has been discussed by P. W. Anderson, Phys. Rev. **83**, 1260 (1951), and others.

mediate problem is the determination of such solutions. To do this we introduce new variables $\mathbf{r}^{(i)}$ and $\mathbf{p}^{(j)}$ by

$$\mathbf{S}_1^{(i)} = S_1 \mathbf{k}_1 + \mathbf{r}^{(i)}; \quad \mathbf{S}_2^{(j)} = -S_2 \mathbf{k}_2 + \mathbf{p}^{(j)}, \quad (9)$$

and treat $\mathbf{r}^{(i)}$ and $\mathbf{p}^{(j)}$ as small. That is to say only small deviations of the spin system from its equilibrium configuration will be considered.

It is convenient at this point to define two coordinate systems by using \mathbf{k}_1 and \mathbf{k}_2 as unit vectors in the z_1 and z_2 directions and taking \mathbf{j}_1 and \mathbf{j}_2 to be unit vectors perpendicular to the z_1, z_2 plane. The remaining unit vectors, \mathbf{i}_1 and \mathbf{i}_2 , lie in the z_1, z_2 plane and complete the appropriate right-handed coordinate systems as indicated in Fig. 1. In these coordinates the spin deviations \mathbf{p} and \mathbf{r} may be described by standing waves of the form

$$\begin{aligned} \mathbf{S}_1^{(i)} &= \mathbf{i}_1 r_x \cos \mathbf{k} \cdot \mathbf{R}^{(i)} \sin \omega t \\ &\quad + \mathbf{j}_1 r_y \cos \mathbf{k} \cdot \mathbf{R}^{(i)} \cos \omega t + \mathbf{k}_1 S_1, \\ \mathbf{S}_2^{(j)} &= \mathbf{i}_2 p_x \cos \mathbf{k} \cdot \mathbf{R}^{(j)} \sin \omega t \\ &\quad + \mathbf{j}_2 p_y \cos \mathbf{k} \cdot \mathbf{R}^{(j)} \cos \omega t + \mathbf{k}_2 S_2, \end{aligned} \quad (10)$$

where \mathbf{k} is the wave vector and $\mathbf{R}^{(i)}, \mathbf{R}^{(j)}$ are the position vectors of the i th spin on sublattice one and the j th spin on sublattice two, respectively. Arbitrary waves of the form (10) do not satisfy the equations of motion. However, substituting (10) into the equations of motion leads to a set of four simultaneous, homogeneous, linear algebraic equations whose secular equation gives ω as a function of \mathbf{k} . This procedure is discussed in more detail later. Before doing this it is convenient to express the sum over neighboring spins in each equation of motion in a slightly different form. The pertinent sums all have the form $\sum_z \cos(\mathbf{k} \cdot \mathbf{R}^{(j)})$ with

$$\begin{aligned} AF(B^2 + \frac{1}{4}) &= \{M_1[M_1 - 2K_1 \sin^2(\theta_1 - \varphi_1)] + M_2[M_2 - 2K_2 \sin^2(\theta_2 - \varphi_2)] - 8J^2 z^2 S_1 S_2 \cos(\theta_1 + \theta_2)\} / 2(\kappa T)^2, \\ F &= \left\{ M_1[M_1 - 2K_1 \sin^2(\theta_1 - \varphi_1)] - \frac{[M_1 - 2K_1 \sin^2(\theta_1 - \varphi_1)][M_2 - 2K_2 \sin^2(\theta_2 - \varphi_2)]}{\cos(\theta_1 + \theta_2)} \right. \\ &\quad \left. - \cos(\theta_1 + \theta_2) M_1 M_2 + M_2[M_2 - 2K_2 \sin^2(\theta_2 - \varphi_2)] \right\} / (\kappa T)^2, \\ (BF)^2 &= \{[M_1 M_1 - 2K_1 \sin^2(\theta_1 - \varphi_1) - M_2 M_2 - 2K_2 \sin^2(\theta_2 - \varphi_2)]^2 - 16J^2 z^2 S_1 S_2 (\kappa T)^2 F \cos(\theta_1 + \theta_2)\} / 4(\kappa T)^4, \\ x^2 &= \frac{4J^2 z^2 S_1 S_2 \cos(\theta_1 + \theta_2)}{(\kappa T)^2} (1 - \gamma^2). \end{aligned}$$

The seemingly awkward notation has been introduced for subsequent convenience of numerical work. The variable x is actually proportional to k in the approximation $ka \ll 1$; thus (13) gives the dispersion law for spin waves in a useful form.

The dispersion law (13) reduces in the proper way to those obtained by Kouvel and Brooks,⁷ and to those obtained by Orbach⁶ when the appropriate restrictions are introduced.

This dispersion law gives directly the so-called spin-

the sum extending over the $\mathbf{R}^{(j)}$'s corresponding to the nearest neighbors of $\mathbf{R}^{(i)}$. Thus sum can be rewritten

$$\begin{aligned} \sum_z \cos(\mathbf{k} \cdot \mathbf{R}^{(j)}) &= z\gamma \cos(\mathbf{k} \cdot \mathbf{R}^{(i)}) \\ &\quad - \sum_z \sin \mathbf{k} \cdot (\mathbf{R}^{(j)} - \mathbf{R}^{(i)}) \sin \mathbf{k} \cdot \mathbf{R}^{(i)}, \end{aligned} \quad (11)$$

with $\gamma = (1/z) \sum_z \cos \mathbf{k} \cdot (\mathbf{R}^{(j)} - \mathbf{R}^{(i)})$. The sum in the last term vanishes if the lattice has cubic symmetry. For noncubic symmetry the last term is not generally zero but is small if the nearest neighbors are approximately evenly distributed. We will assume that this smallness is of such order as to justify neglecting the last term of (11).

Within the framework of the approximation noted above and maintaining only linear terms in \mathbf{p} and \mathbf{r} , the equations of motion, (7), become

$$\begin{aligned} \hbar \omega r_x &= M_1 r_y - 2Jz S_1 p_y, \\ \hbar \omega r_y &= [M_1 - 2K_1 \sin^2(\theta_1 - \varphi_1)] r_x \\ &\quad - 2Jz S_1 \gamma \cos(\theta_1 + \theta_2) p_x, \\ \hbar \omega p_x &= -M_2 p_y + 2Jz S_2 \gamma r_y, \\ \hbar \omega p_y &= -[M_2 - 2K_2 \sin^2(\theta_2 - \varphi_2)] p_x \\ &\quad + 2Jz S_2 \gamma \cos(\theta_1 + \theta_2) r_y, \end{aligned} \quad (12)$$

where the angles are defined in Fig. 1. These four equations are a set of simultaneous linear homogeneous equations for p_x, p_y, r_x , and r_y . As such, they have a nontrivial solution only if the determinant of the coefficients vanishes. The solution of this secular equation has the form

$$(\hbar \omega / \kappa T)^2 = AF(B^2 + \frac{1}{4}) + x^2 \pm \{(BF)^2 + Fx^2\}^{\frac{1}{2}}, \quad (13)$$

where κ has been used for the Boltzmann constant and

wave spectrum of the material. This is important in considerations of ferro-, ferri-, and antiferromagnetic resonance¹⁴ as well as in connection with recent experiments² on the direct observation of spin waves. These aspects of the spin wave spectrum have been considered by other authors both for parallel and for canted arrays⁶ and will not be further considered here except to note that the spectrum is now available in Eq. (13) for an array of great generality.

¹⁴ F. Keffer and C. Kittel, Phys. Rev. **85**, 329 (1952).

A second thing which can be done with the dispersion law is to obtain the partition function for the spin system and from it the spin-wave contribution to the specific heat and the low-temperature magnetization. These aspects are considered in detail in the next section.

SPECIFIC HEAT AND MAGNETIZATION

In the quantized spin-wave theory (13) gives the classical frequencies of the normal modes of the spin system. One may follow Van Kranendonk and Van Vleck³ and relate these normal modes to spin deviations from which the low-temperature magnetization can be computed directly. Alternatively, one may follow the traditional approach and calculate the partition function for the system from which the magnetization and specific heat follow through simple operations. We will follow this latter approach.

It is well known that the partition function for a system of harmonic oscillators of frequencies ω_λ is given by

$$Z = e^{-E_0/\kappa T} \prod_{\lambda=1}^N [(1 - e^{-\hbar\omega_\lambda/\kappa T})]^{-1}, \quad (14)$$

where E_0 is the ground-state energy at absolute zero and the zero-point energy has been suppressed.¹⁵ From this partition function one readily obtains

$$C_v = \frac{\partial}{\partial T} \left(\kappa T^2 \frac{\partial \ln Z}{\partial T} \right) = \sum_{\lambda=1}^N \left(\frac{\hbar\omega_\lambda}{\kappa T} \right)^2 e^{\hbar\omega_\lambda/\kappa T} (e^{\hbar\omega_\lambda/\kappa T} - 1)^{-2} \quad (15)$$

and

$$M = \kappa T \nabla_H (\ln Z) = -\nabla_H E_0 - \kappa T \nabla_H \sum_{\lambda=1}^N \ln(1 - e^{-\hbar\omega_\lambda/\kappa T}), \quad (16)$$

in (16) the gradient operator is

$$\nabla_H = \mathbf{i} \frac{\partial}{\partial H_x} + \mathbf{j} \frac{\partial}{\partial H_y} + \mathbf{k} \frac{\partial}{\partial H_z}. \quad (17)$$

The quantity $-\nabla_H E_0 = \mathbf{M}_0$ is just the magnetization at absolute zero.

The summations which appear in (15) and (16) can

$$\begin{aligned} \mathbf{M} - \mathbf{M}_0 = & -\frac{1}{2} \kappa T \nabla_H [AF(B^2 + \frac{1}{4})] \int_0^\infty \frac{g(k)dk}{(\hbar\omega/\kappa T)(e^{\hbar\omega/\kappa T} - 1)} + \frac{1}{2} \kappa T \tan(\theta_1 + \theta_2) \nabla_H(\theta_1 + \theta_2) \int_0^\infty \frac{x^2 g(k)dk}{(\hbar\omega/\kappa T)(e^{\hbar\omega/\kappa T} - 1)} \\ & - \frac{1}{4} \kappa T \nabla_H (BF)^2 \int_0^\infty \frac{g(k)dk}{(\hbar\omega/\kappa T) \{ (\hbar\omega/\kappa T)^2 - AF(B^2 + \frac{1}{4}) - x^2 \} (e^{\hbar\omega/\kappa T} - 1)} \\ & - \frac{\kappa T}{4} [\nabla_H F - F \tan(\theta_1 + \theta_2) \nabla_H(\theta_1 + \theta_2)] \int_0^\infty \frac{g(k)dk}{(\hbar\omega/\kappa T) \{ (\hbar\omega/\kappa T)^2 - AF(B^2 + \frac{1}{4}) - x^2 \} (e^{\hbar\omega/\kappa T} - 1)}. \end{aligned} \quad (24)$$

This is also amenable to numerical treatment.

be transformed to integrals by introducing a density function $g(\omega)$. This density function $g(\omega)$ can be obtained from

$$g(\mathbf{k})d^3k = [V/(2\pi)^3]d^3k,$$

with V the crystal volume, by methods which are well known in the theory of the electronic structure of solids.¹⁶ If ω is not an isotropic function of k some complexity may be involved in this procedure; however, in the simple case where x^2 in (13) is proportional to k^2 one may write

$$g(\omega)d\omega = [4\pi k^2 V / (2\pi)^3] dk. \quad (18)$$

The specific heat (per unit volume) and magnetization then have the form

$$C_v = \int_0^\infty \kappa \left(\frac{\hbar\omega}{\kappa T} \right)^2 \frac{e^{\hbar\omega/\kappa T}}{(e^{\hbar\omega/\kappa T} - 1)^2} \frac{4\pi k^2}{(2\pi)^3} dk \quad (19)$$

and

$$\mathbf{M} - \mathbf{M}_0 = -\kappa T \nabla_H \int_0^\infty \ln(1 - e^{-\hbar\omega/\kappa T}) \frac{4\pi k^2}{(2\pi)^3} dk. \quad (20)$$

The substitution

$$\gamma = 1 - \alpha k^2 a^2, \quad (21)$$

which follows from the definition of γ in the approximation $k^2 a^2 \ll 1$ and which essentially defines α , gives

$$x^2 = \frac{4J^2 z^2 S_1 S_2 \cos(\theta_1 + \theta_2)}{(\kappa T)^2} 2\alpha k^2 a^2. \quad (22)$$

Using (22) to change the variable of integration in (19) to x gives

$$C_v = \frac{1}{2\pi^2} \frac{\kappa(\kappa T)^3}{[8J^2 z^2 S_1 S_2 \cos(\theta_1 + \theta_2) \alpha a^2]^{\frac{3}{2}}} \times \int_0^\infty \left(\frac{\hbar\omega}{\kappa T} \right)^2 \frac{e^{\hbar\omega/\kappa T}}{(e^{\hbar\omega/\kappa T} - 1)^2} x^2 dx. \quad (23)$$

Using the dispersion law,

$$(\hbar\omega/\kappa T)^2 = AF(B^2 + \frac{1}{4}) + x^2 \pm \{ (BF)^2 + Fx^2 \}^{\frac{1}{2}}, \quad (13)$$

it is now possible to evaluate C_v by numerical integration. A similar procedure can be applied to (20); however, because of the complicated dependence of ω on the external field the final result is not as simple as that for the specific heat. It is

¹⁵ M. J. Klein and R. S. Smith, Phys. Rev. **80**, 1111 (1950).

¹⁶ J. R. Reitz, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1955), Vol. 1, p. 2.

It is perhaps worth noting explicitly that both the optical and acoustical modes should be included when (23) and (24) are evaluated. The specific heat [and each term of (24)] is then given as the sum of two integrals, one for each mode. Furthermore, for some values of the parameters ω^2 may vanish for finite x in the acoustical mode; in this case the lower limit on the integration over the acoustical mode should be the value of x for which $\omega=0$.¹⁷ Both of the points have been properly taken into account in our subsequent evaluation of C_v and M .

To summarize then, a straightforward but somewhat tedious application of statistical mechanics to a set of harmonic oscillators with frequencies given by (13) leads to the expressions (23) and (24) for the spin-wave contribution to the specific heat and the deviation of the magnetization from saturation. In the next section the numerical treatment of these results will be described.

NUMERICAL RESULTS FOR C_v AND M

The detailed evaluation of the integrals in (23) and (24) for an extensive range of the parameter A does not

TABLE I. The specific heat integral, $R = \int_0^\infty (\hbar\omega/\kappa T)^2 e^{\hbar\omega/\kappa T} (e^{\hbar\omega/\kappa T} - 1)^{-2} x^2 dx$.

| F/B | 0.1 | 0.4 | 1 | 4 | 10 | 40 | 100 |
|-------|-------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|--------|
| 0.501 | 52.5 | 52.4 | 53.0 | 55.6 | 60.8 | | 130.0 |
| 0.51 | 52.5 | 52.7 | 53.3 | 55.9 | 61.0 | 86.6 | 127.0 |
| 0.54 | 52.3 | 52.7 | 53.0 | 55.1 | 60.0 | 82.1 | 117.0 |
| 0.58 | 52.5 | 52.5 | 53.0 | 54.8 | 58.8 | 77.5 | 104.0 |
| 1.0 | 52.1 | | | | | | |
| 1.5 | 51.7 | 49.9 | 47.1 | 34.4 | 23.9 | 2.11 | 0.511 |
| 2.0 | 51.1 | 48.1 | 42.5 | 25.2 | 11.1 | 0.626 | 0.0104 |
| 4.0 | 47.3 | 36.9 | 21.7 | 3.02 | 0.377 | 2.35×10^{-5} | |
| 8.0 | 35.7 | 13.0 | 2.47 | 8.94×10^{-3} | 5.78×10^{-6} | | |
| 16.0 | 12.2 | 0.566 | 6.94×10^{-3} | | | | |
| 32.0 | 0.522 | 2.02×10^{-4} | | | | | |

TABLE II. The magnetization integral, $\int_0^\infty x^2 dx / [(\hbar\omega/\kappa T)(e^{\hbar\omega/\kappa T} - 1)]$.

| F/B | 0.1 | 0.4 | 1 | 4 | 10 | 40 | 100 |
|-------|-----------------------|-----------------------|-----------------------|-----------------------|------------------------|-----------------------|-----------------------|
| 0.501 | 11.0 | 18.6 | 27.3 | 50.6 | 76.7 | | 218.0 |
| 0.51 | 5.60 | 7.80 | 10.2 | 16.4 | 22.8 | 37.6 | 51.1 |
| 0.54 | 4.25 | 5.12 | 6.05 | 8.21 | 10.2 | 13.6 | 15.5 |
| 0.58 | 3.80 | 4.24 | 4.70 | 5.65 | 6.37 | 7.07 | 6.74 |
| 1.0 | 2.80 | | | | | | |
| 1.5 | 2.34 | 1.60 | 1.20 | 0.352 | 0.175 | 2.19×10^{-3} | 3.25×10^{-4} |
| 2.0 | 2.00 | 1.26 | 0.745 | 0.186 | 0.0377 | 4.55×10^{-4} | 2.28×10^{-6} |
| 4.0 | 1.14 | 0.404 | 0.120 | 4.20×10^{-3} | 8.34×10^{-6} | 1.77×10^{-9} | |
| 8.0 | 0.379 | 0.0411 | 2.89×10^{-3} | 1.87×10^{-6} | 3.53×10^{-10} | | |
| 16.0 | 0.0391 | 3.53×10^{-4} | 1.32×10^{-6} | | | | |
| 32.0 | 3.38×10^{-4} | 1.97×10^{-8} | | | | | |

TABLE III. The magnetization integral, $\int_0^\infty x^4 dx / [(\hbar\omega/\kappa T)(e^{\hbar\omega/\kappa T} - 1)]$.

| F/B | 0.1 | 0.4 | 1 | 4 | 10 | 40 | 100 |
|-------|--------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| 0.501 | 13.4 | 14.5 | 16.7 | 27.6 | 50.0 | | 416.0 |
| 0.51 | 13.4 | 14.4 | 16.5 | 26.3 | 45.0 | 131.0 | 293.0 |
| 0.54 | 13.3 | 14.3 | 16.1 | 24.2 | 38.0 | 90.8 | 166.0 |
| 0.58 | 13.3 | 14.2 | 15.8 | 22.4 | 32.7 | 64.7 | 97.6 |
| 1.0 | 12.0 | | | | | | |
| 1.5 | 12.5 | 11.3 | 10.0 | 5.19 | 3.14 | 0.0984 | 0.0157 |
| 2.0 | 12.0 | 9.98 | 7.56 | 3.00 | 0.868 | 0.0190 | 1.45×10^{-4} |
| 4.0 | 9.30 | 4.89 | 1.98 | 0.108 | 3.52×10^{-3} | 1.41×10^{-7} | |
| 8.0 | 4.64 | 0.821 | 0.0828 | 9.80×10^{-5} | 2.81×10^{-8} | | |
| 16.0 | 0.708 | 0.0124 | 6.94×10^{-5} | | | | |
| 32.0 | 0.0119 | 1.29×10^{-7} | | | | | |

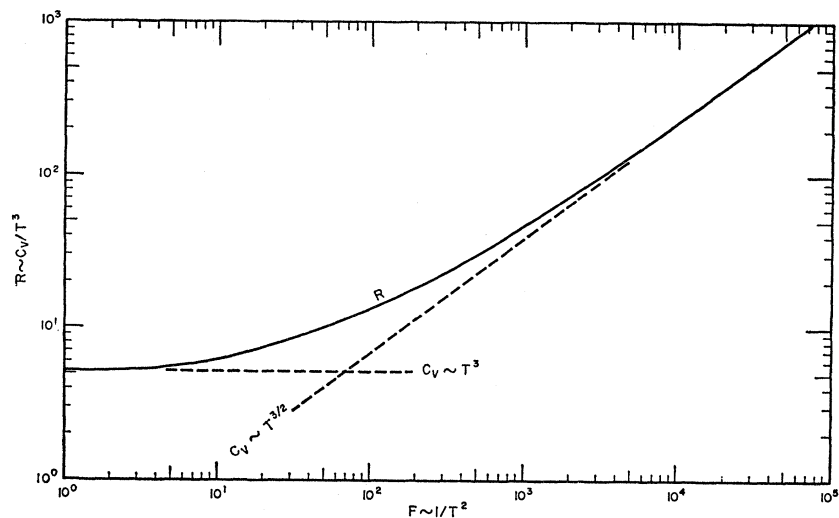
¹⁷ The nonzero lower limit is responsible for the "exponential" low-temperature behavior found by Kouvel and Brooks, reference 7.

TABLE IV. The magnetization integral, $-\int_0^\infty \frac{x^2 dx}{(\hbar\omega/\kappa T)\{(\hbar\omega/\kappa T)^2 - AF(B^2 + \frac{1}{4}) - x^2\}(e^{\hbar\omega/\kappa T} - 1)}$.

| F/B | 0.1 | 0.4 | 1 | 4 | 10 | 40 | 100 |
|-------|-----------------------|------------------------|-----------------------|-----------------------|------------------------|------------------------|-----------------------|
| 0.501 | 154 | 76.2 | 47.7 | 23.4 | 14.5 | | 4.23 |
| 0.51 | 47.7 | 22.8 | 13.6 | 6.48 | 3.82 | 1.66 | 0.925 |
| 0.54 | 22.2 | 10.4 | 6.16 | 2.65 | 1.45 | 0.531 | 0.252 |
| 0.58 | 14.9 | 6.78 | 3.90 | 1.57 | 0.799 | 0.249 | 0.100 |
| 1.0 | 4.14 | | | | | | |
| 1.5 | 2.14 | 0.663 | 0.301 | 0.0387 | 8.74×10^{-3} | 4.52×10^{-5} | 1.98×10^{-6} |
| 2.0 | 1.35 | 0.401 | 0.141 | 0.0147 | 1.47×10^{-3} | 5.05×10^{-6} | 1.06×10^{-8} |
| 4.0 | 0.378 | 0.0662 | 0.0121 | 1.80×10^{-4} | 1.75×10^{-5} | 1.04×10^{-11} | |
| 8.0 | 0.0645 | 3.56×10^{-3} | 1.54×10^{-4} | 4.20×10^{-8} | 3.88×10^{-12} | | |
| 16.0 | 3.50×10^{-3} | 1.60×10^{-5} | 3.67×10^{-8} | | | | |
| 32.0 | 1.58×10^{-5} | 4.59×10^{-10} | | | | | |

TABLE V. The magnetization integral, $-\int_0^\infty \frac{x^4 dx}{(\hbar\omega/\kappa T)\{(\hbar\omega/\kappa T)^2 - AF(B^2 + \frac{1}{4}) - x^2\}(e^{\hbar\omega/\kappa T} - 1)}$.

| F/B | 0.1 | 0.4 | 1 | 4 | 10 | 40 | 100 |
|-------|-----------------------|-----------------------|-----------------------|-----------------------|------------------------|------------------------|-----------------------|
| 0.501 | 4.91 | 4.92 | 4.95 | 5.10 | 5.35 | | 6.84 |
| 0.51 | 4.81 | 4.72 | 4.65 | 4.58 | 4.48 | 4.50 | 4.51 |
| 0.54 | 4.67 | 4.45 | 4.23 | 3.79 | 3.43 | 2.81 | 2.33 |
| 0.58 | 4.54 | 4.23 | 3.91 | 3.25 | 2.72 | 1.84 | 1.26 |
| 1.0 | 3.87 | | | | | | |
| 1.5 | 3.33 | 2.24 | 1.50 | 0.421 | 0.132 | 1.68×10^{-3} | 9.04×10^{-5} |
| 2.0 | 2.89 | 1.73 | 0.959 | 0.197 | 0.0296 | 1.98×10^{-4} | 6.46×10^{-7} |
| 4.0 | 0.167 | 0.573 | 0.161 | 4.56×10^{-3} | 6.88×10^{-5} | 8.01×10^{-10} | |
| 8.0 | 0.563 | 0.0593 | 3.94×10^{-3} | 2.08×10^{-6} | 2.99×10^{-10} | | |
| 16.0 | 0.0580 | 5.12×10^{-4} | 1.82×10^{-6} | | | | |
| 32.0 | 5.05×10^{-4} | 2.86×10^{-8} | | | | | |

FIG. 2. The specific-heat integral as a function of the parameter F .

appear to be warranted at this time. Instead A has been fixed at unity, giving the simpler dispersion law

$$\hbar\omega/\kappa T = (B^2 F + x^2)^{1/2} \mp \frac{1}{2} F^{1/2}. \quad (25)$$

This general form is obtained in the conventional treatment of ferrimagnetic and antiferromagnetic arrays; however, an approximation to (25) is usually made which appears to destroy some interesting features.

Using (25) the integrals in (23) and (24) have been

evaluated for $0.5 < B \leq 32$ and $0.1 \leq F \leq 100$. These calculations were accomplished by relatively straightforward numerical integration using an IBM 650 computer. The results are given in Tables I-V.

The specific heat integral, R , defined by

$$R = \int_0^\infty \left(\frac{\hbar\omega}{\kappa T} \right)^2 \frac{e^{\hbar\omega/\kappa T}}{[e^{\hbar\omega/\kappa T} - 1]^2} x^2 dx, \quad (26)$$

is plotted as a function of F for $A=1$, $B=0.5$ in Fig. 2. In this figure the range of F extends to 10^5 , the extension having been accomplished by hand calculation and, for large F , use of the approximation

$$R = \frac{1}{2}\Gamma\left(\frac{7}{2}\right)\zeta\left(\frac{5}{2}\right)F^{\frac{1}{2}}, \quad (27)$$

with Γ the gamma function and ζ the Riemann zeta function, which is easily derived.

DISCUSSION

A conventional antiferromagnetic material is described by $F=0$. The dispersion law, (25), then takes the form $\hbar\omega/\kappa T = \mp x$. Such a linear dispersion law leads, as is well known, to a T^3 dependence of the specific heat on temperature. The usual ferrimagnetic result is obtained by taking $B=\frac{1}{2}$ and $\frac{1}{4}F \gg x^2$. This gives $\hbar\omega/\kappa T = x^2/\sqrt{F}$ for the acoustic mode. This simple quadratic dispersion law gives a $T^{\frac{3}{2}}$ temperature dependence of the specific heat, again a well-known result. For finite F and $B > \frac{1}{2}$, one obtains the results of Kouvel and Brooks,⁷ which they have described as an exponential low-temperature behavior.

One very interesting feature of our calculation is that it explicitly shows the transition from the T^3 behavior of the specific heat at relatively high temperatures to the $T^{\frac{3}{2}}$ behavior at low temperatures in weakly ferrimagnetic materials. This change in behavior occurs as a function of temperature in spite of the fact that the dispersion law is actually temperature independent (F contains $1/T^2$ as a factor; x contains $1/T$ as a factor; B does not depend on T). This is easily understood when it is remarked that the values of x which contribute to C_v increase as the temperature increases. The change in behavior is thus due to the factor $e^{\hbar\omega/\kappa T}/[e^{\hbar\omega/\kappa T}-1]^2$ which occurs in R .

To further explore this change in behavior of C_v it may be noted that to a good approximation

$$R = 52 + 2.15F^{\frac{1}{2}},$$

and that the middle of the transition region occurs at $F=70$. A simple (uncanted) ferrimagnetic material can be described within the restrictions

$$2K_1 \sin^2(\theta_1 - \varphi_1) = 2K_2 \sin^2(\theta_2 - \varphi_2) = 0; \quad \cos(\theta_1 + \theta_2) = 0,$$

which are consistent with $A=1$, $B=0.5$ and give

$$F = (M_1 - M_2)^2/(\kappa T)^2. \quad (28)$$

Introducing the further restrictions $H_1' = H_2' = K_1 = K_2 = 0$ gives $M_1 = 2JzS_1$, $M_2 = 2JzS_2$, from which

$$F = 4J^2z^2(S_1 - S_2)^2/(\kappa T)^2. \quad (29)$$

Taking $J/\kappa = 18^\circ\text{K}$, $z=6$, and $S_1 - S_2 = 1.5$, which are typical values for nickel-zinc ferrites, gives $F = 1.05 \times 10^5/T^2$ and $R = 52 + 1.25 \times 10^4 T^{-\frac{1}{2}}$. The coefficient of T^3 in C_v is therefore about 4×10^{-3} of the coefficient $T^{\frac{3}{2}}$. This result has been obtained using ferrite data in formulas which were derived on the assumption of cubic symmetry. This of course casts some doubt on its validity; however, it is interesting to proceed assuming that the relative importance of the T^3 term compared to the $T^{\frac{3}{2}}$ term is correctly given by our analysis. Considering Kouvel's¹⁸ data on magnetite which shows an experimental ratio of the coefficient of T^3 to the coefficient of $T^{\frac{3}{2}}$ of about 0.01 one readily sees that the spin-wave contribution to the T^3 dependence may indeed be significant. In fact if one used Kouvel's values 5.15°K for J_{AB}/κ and $S_1 - S_2 = 0.25$ in (29) one finds that our spin-wave calculations give a contribution which is much larger than the entire experimental T^3 term. The use of $J_{AB}/\kappa = 19^\circ\text{K}$ as obtained from $T_c = 848^\circ\text{K}$ improves matters but still leads to a contribution larger than that which is observed experimentally.

These comments must be taken as preliminary since they are based on a comparison between experiments on a material with a slightly distorted spinel structure (magnetite) and a theory which assumes a simpler cubic symmetry. In spite of this obvious deficiency the surprising importance of the T^3 portion of the specific heat due to spin waves seems to merit further consideration. A careful consideration of the implications of the canting of the spins and comparison with available experimental data would also be desirable.

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¹⁸ J. S. Kouvel, Phys. Rev. **102**, 1489 (1956).