

## Theory of Antiferromagnetic Spin Waves in some Metamagnetic Crystals\*

AKIO YOSHIMORI†

*The Ohio State University, Columbus, Ohio*

(Received 25 October 1962)

The spin waves of metamagnetic hexagonal layer crystals, in particular,  $\text{NiCl}_2$  and  $\text{CoCl}_2$ , are calculated in a semicontinuum model. Temperature variations of the specific heat and of the sublattice magnetization due to the spin-wave excitations are derived and discussed.

### 1. INTRODUCTION

THE purpose of this paper is to calculate spin waves with low frequency in the hexagonal layer crystals which are called metamagnetics, in particular  $\text{NiCl}_2$  (and  $\text{CoCl}_2$ ) and to discuss a particular type of temperature variations of the specific heat and the sublattice magnetization due to the spin-wave excitations.

The anhydrous chlorides of the iron-group elements are sometimes called metamagnetics because of the field-dependence of their susceptibility. They have been a subject of numerous investigations.<sup>1-5</sup> It is assumed here that, in metamagnetic crystals, a ferromagnetic interaction makes spins parallel in the layer and a relatively much weaker antiferromagnetic interaction makes spins of adjacent layers antiparallel as Landau assumed.<sup>1</sup> This type of spin superstructure has been confirmed in  $\text{CoCl}_2$ ,  $\text{CrCl}_3$ , and  $\text{FeCl}_2$  by neutron diffraction experiments.<sup>3,4</sup> The spins in  $\text{CoCl}_2$  and  $\text{CrCl}_3$  are found to be oriented parallel to the layer.

We take two types of Hamiltonian in the spin-wave approximation, based on a theoretical discussion of  $\text{NiCl}_2$  and  $\text{CoCl}_2$  by Kanamori.<sup>2</sup> In these Hamiltonians an anisotropy energy, which makes the layer an easy plane for the spins, will also be considered in addition to these exchange interactions, and no anisotropy energy will be assumed in the layer. Therefore, we assume that spins in  $\text{NiCl}_2$  are also oriented parallel to the layer.

A semicontinuum model, analogous to that for the lattice vibrations of graphite,<sup>6</sup> will be used, namely, each layer is regarded as a ferromagnetic continuum<sup>7</sup> in two dimensions while discreteness along the threefold axis is taken into account. Since only the spin waves with very small components of the wave vector in the layer will be discussed here, the effects of the discreteness of the atomic arrangement in the layer are very

small. Consequently, a semicontinuum model, which is much simpler, is sufficient for the present discussion.

### 2. HAMILTONIAN IN THE SPIN-WAVE APPROXIMATION

We take two types of spin-wave Hamiltonian in the semicontinuum model. The first, with spin unity, is for  $\text{NiCl}_2$  and the second, with anisotropic exchange interactions with spin one-half, is for  $\text{CoCl}_2$ , a Kramers' doublet being assumed for  $\text{Co}^{++}$

$$\mathcal{H} = \sum_n \int d^2\rho [A |\text{grad}_\rho \mathbf{S}_n(\boldsymbol{\rho})|^2 + B \mathbf{S}_n(\boldsymbol{\rho}) \cdot \mathbf{S}_{n+1}(\boldsymbol{\rho}) + D S_{n,z}^2(\boldsymbol{\rho})], \quad (1)$$

$$\mathcal{H} = \sum_n \int d^2\rho \{A [\alpha_1 |\text{grad}_\rho \mathbf{S}_n(\boldsymbol{\rho})|^2 + \alpha_{11} |\text{grad}_\rho S_{n,z}(\boldsymbol{\rho})|^2] + B [\alpha_1 \mathbf{S}_n'(\boldsymbol{\rho}) \cdot \mathbf{S}_{n+1}'(\boldsymbol{\rho}) + \alpha_{11} S_{n,z}(\boldsymbol{\rho}) S_{n+1,z}(\boldsymbol{\rho})]\}, \quad (2)$$

with

$$[S_{n,x}(\boldsymbol{\rho}), S_{n',y}(\boldsymbol{\rho}')] = i\delta_{n,n'} \delta(\boldsymbol{\rho} - \boldsymbol{\rho}') S_{n,z}(\boldsymbol{\rho}), \quad (3)$$

(and cyclic permutation of  $x$ ,  $y$ , and  $z$ ). Here,  $A$  is the exchange stiffness in the layer,  $B$  is an exchange coupling constant,  $D$  is an anisotropy constant,  $\mathbf{S}_n(\boldsymbol{\rho})$  is the spin-density operator of the  $n$ th layer,  $\boldsymbol{\rho}$  is a positional vector in the layer in units of square root of area per spin of the layer (the spin density of the layer is also in units of the reciprocal of this area),  $\mathbf{S}_n'(\boldsymbol{\rho})$  is the projection of the spin-density operator onto the layer, and  $\alpha_1$  and  $\alpha_{11}$  are numerical constants with order of magnitude unity and with  $\alpha_1 > \alpha_{11}$ .

The Hamiltonians (1) and (2) are derived from spin Hamiltonians for  $\text{NiCl}_2$  and  $\text{CoCl}_2$  suggested by Kanamori<sup>2</sup> by taking

$$\mathbf{S}_n(\boldsymbol{\rho}) = \sum_m \mathbf{S}_{n,m} \delta(\boldsymbol{\rho} - \boldsymbol{\rho}_m), \quad (4)$$

where  $\mathbf{S}_{n,m}$  is the spin at the  $m$ th lattice point of the  $n$ th layer,  $\boldsymbol{\rho}_m$  being the position of the  $m$ th lattice point. Then we have

$$A = 2J_1 z_1 a / 2, \quad a = \frac{1}{4} z_1^{-1} \sum_\delta \delta_x^2, \\ B = 2J_2 z_2 / 2, \quad (5)$$

where  $J_1$  is the exchange integral between the nearest neighboring spins in the layer,  $z_1$  is the number of the neighbors in the layer,  $\delta$  is a distance between these

\* This research was supported in part by the AFOSR through a contract with The Ohio State University Research Foundation.

† Present address: Department of Physics, University of Osaka Prefecture, Mozu-Ume, Sakai, Osaka, Japan.

<sup>1</sup> L. Landau, Phys. Z. Sowjetunion 4, 675 (1933).

<sup>2</sup> J. Kanamori, Progr. Theoret. Phys. (Kyoto) 20, 890 (1958).

<sup>3</sup> M. K. Wilkinson, J. W. Cable, E. O. Wollan, and W. C. Koehler, Phys. Rev. 113, 497 (1959). References 2 and 3 contain other references of work in this field.

<sup>4</sup> J. W. Cable, M. K. Wilkinson, and E. O. Wollan, J. Phys. Chem. Solids 19, 29 (1961).

<sup>5</sup> A. Narath, Phys. Rev. Letters 7, 410 (1961).

<sup>6</sup> K. Komatsu and T. Nagamiya, J. Phys. Soc. Japan 6, 438 (1951), K. Komatsu, *ibid.* 10, 346 (1955).

<sup>7</sup> C. Herring and C. Kittel, Phys. Rev. 81, 869 (1951).

neighbors,  $\delta_x$  is the  $x$  component of  $\delta$ ,  $J_2$  is the exchange integral between nearest neighbors of adjacent layers, and  $z_2$  is the number of these neighbors.

The interlayer exchange interaction is not necessarily between neighboring spins along the threefold axis but it can be between neighboring spins along a direction having a finite angle to the threefold axis. Such an interaction will add another term to the Hamiltonian, but it can be incorporated in  $B$  because the wave vector component in the layer is assumed to be small.

The following approximations will be used:

$$\begin{aligned} S_{2l,x}(\mathbf{\rho}) &= S - a_{2l}^\dagger(\mathbf{\rho})a_{2l}(\mathbf{\rho}), \\ S_{2l+1,x}(\mathbf{\rho}) &= -S + a_{2l+1}^\dagger(\mathbf{\rho})a_{2l+1}(\mathbf{\rho}), \\ S_{2l}^\dagger(\mathbf{\rho}) &= S_{2l,y}(\mathbf{\rho}) + iS_{2l,z}(\mathbf{\rho}) \cong (2S)^{1/2}a_{2l}(\mathbf{\rho}), \\ S_{2l+1}^\dagger(\mathbf{\rho}) &= S_{2l+1,y}(\mathbf{\rho}) - iS_{2l+1,z}(\mathbf{\rho}) \cong (2S)^{1/2}a_{2l+1}(\mathbf{\rho}), \end{aligned} \quad (6)$$

with

$$\begin{aligned} [a_n(\mathbf{\rho}), a_{n'}^\dagger(\mathbf{\rho}')] &= \delta_{n,n'}\delta(\mathbf{\rho}-\mathbf{\rho}'), \\ [a_n(\mathbf{\rho}), a_{n'}(\mathbf{\rho}')] &= 0. \end{aligned} \quad (7)$$

The part of the Hamiltonian quadratic in  $a$  (there is no linear part) can be diagonalized by a transformation,

$$\begin{aligned} a_{2l+j}(\mathbf{\rho}) &= (2/N)^{1/2} \sum_{\mathbf{k}} \exp[ik_z(2l+j) + i\mathbf{k}' \cdot \mathbf{\rho}] \alpha_{\mathbf{k},j}, \\ \alpha_{\mathbf{k},j} &= 2^{-1/2} [A_{\mathbf{k},0} \cosh \theta_{\mathbf{k}}^{(+)} + A_{-\mathbf{k},0}^\dagger \sinh \theta_{\mathbf{k}}^{(+)} \\ &\quad + (-1)^j (A_{\mathbf{k},1} \cosh \theta_{\mathbf{k}}^{(-)} + A_{-\mathbf{k},1}^\dagger \sinh \theta_{\mathbf{k}}^{(-)})], \end{aligned} \quad (8)$$

$$|k_z| \leq \pi/2, \quad j=0, 1, \quad (9)$$

with

$$\tanh 2\theta_{\mathbf{k}}^{(\pm)} = (\pm b \cos k_z - \frac{1}{2}d)(k'^2 + b + \frac{1}{2}d)^{-1}, \quad (10)$$

(for the  $\text{NiCl}_2$  type),

$$\begin{aligned} \tanh 2\theta_{\mathbf{k}}^{(\pm)} &= [(1-r)k'^2 \mp b(1+r) \cos k_z - (1-r)a^{-1}] \\ &\quad \times \{ (1+r)k'^2 + b[2 \mp (1-r) \cos k_z] + (1+r)a^{-1} \}^{-1}, \end{aligned} \quad (11)$$

(for the  $\text{CoCl}_2$  type), where

$$b = B/A, \quad d = D/2A, \quad r = \alpha_{11}/\alpha_1,$$

and  $a$  was given in Eq. (5). From the fundamental assumption,  $b$  is much smaller than unity.

The resulting approximate Hamiltonian is as follows:

$$\mathfrak{H} = \sum_{\mathbf{k}} \sum_{j=0,1} \hbar\omega_{\mathbf{k},j} A_{\mathbf{k},j}^\dagger A_{\mathbf{k},j}, \quad (12)$$

with

$$\begin{aligned} (\hbar\omega_{\mathbf{k},j}/2AS)^2 &= \{k'^2 + b[1 - (-1)^j \cos k_z]\} \\ &\quad \times \{k'^2 + b[1 + (-1)^j \cos k_z] + d\}, \\ &\quad j=0, 1 \end{aligned} \quad (13)$$

(for the  $\text{NiCl}_2$  type), while the expression of  $\hbar\omega_{\mathbf{k},j}$  for the  $\text{CoCl}_2$  type is that of Eq. (13) in which  $2AS$  and  $d$  are replaced by  $2AS(\alpha_1\alpha_{11})^{1/2}$  and  $a^{-1}(1+b)(1-r)/r$ , respectively. Therefore, discussions based on Eq. (13), which will be given in the remainder of this section and in the next section, apply to both the types of spin waves.

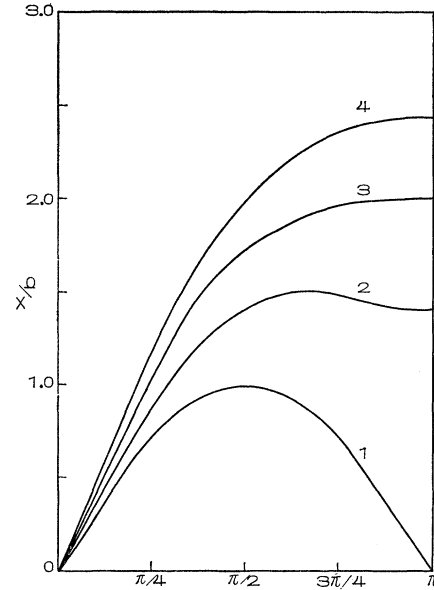


FIG. 1. The curves of  $x/b$  vs  $k_z$ . [ $x \equiv \hbar\omega/2AS$ .] (1)  $d/2b=0$ ; (2)  $d/2b=\frac{1}{2}$ ; (3)  $d/2b=1$ ; (4)  $d/2b=\frac{3}{2}$ .

There are two branches of the spin waves  $\hbar\omega_{\mathbf{k},0}$  and  $\hbar\omega_{\mathbf{k},1}$ . When  $d$  is finite, these two branches are not degenerate. The two modes with  $\mathbf{k}=0$  have frequencies 0 and  $(\hbar\omega/2AS) = (2bd)^{1/2}$ . These are the antiferromagnetic resonance modes. Since no anisotropy energy in the layer is considered, one of them has zero frequency.

It can be seen easily from Eq. (13) that, if the range of the  $k_z$  values is taken from  $-\pi$  to  $\pi$  instead of from  $-\pi/2$  to  $\pi/2$ , Eq. (13) with  $j=0$  represents both Eqs. (13) with  $j=0$  and with  $j=1$  in the enlarged reciprocal space. Hereafter, this Eq. (13) in the enlarged reciprocal space will be used.

The frequency at very small  $k_z$  and  $\mathbf{k}'$  is given approximately by

$$(\hbar\omega_{\mathbf{k}}/2AS)^2 \cong (2b+d)[(k'/k)^2 + b(k_z/k)^2]k^2. \quad (14)$$

The frequency, in this limit, is proportional to  $k$ , as for isotropic antiferromagnetic spin waves, but its proportionality constant varies rapidly with the direction of  $\mathbf{k}$  because of the very small value of  $b$ . Therefore, contours of constant frequency in the vicinity of the origin of the reciprocal space are very prolate ellipsoids.

With increasing  $k_z$  ( $\mathbf{k}'=0$ ), the following two cases will be distinguished with regard to the variation of  $\hbar\omega_{\mathbf{k}}$  vs  $k_z$ : (I)  $b > \frac{1}{2}d$  and (II)  $b \leq \frac{1}{2}d$ . There is a maximum of  $\hbar\omega_{\mathbf{k}}$  at  $k_z < \pi$  in case (I) and a maximum at  $k_z = \pi$  in case (II), as is shown in Fig. 1. The aspects of the contours of constant frequency in both cases, shown in Fig. 2, are different, though both the contours have a prolate shape along the  $k_z$  axis. The contour connects, finally, the zone boundaries in the  $\pm k_z$  direction at  $\hbar\omega = 2AS(b + \frac{1}{2}d)$  in case (I) and at  $\hbar\omega = 2AS(2bd)^{1/2}$  in case (II).

For  $\hbar\omega \gg 2AS(b + \frac{1}{2}d)$  in case (I) or  $\hbar\omega \gg 2AS(2bd)^{1/2}$

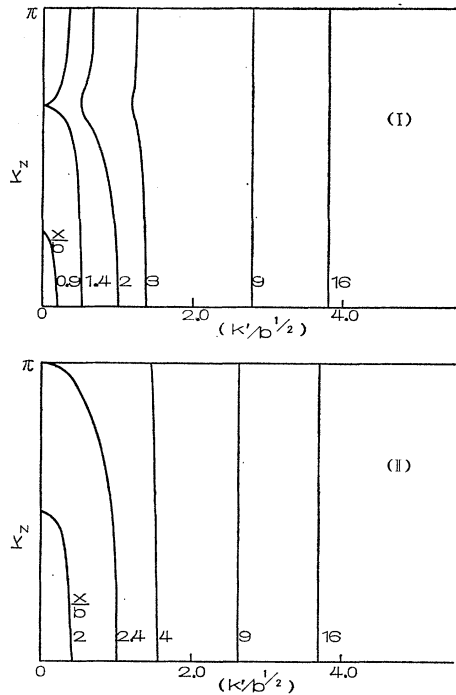


Fig. 2. The contour of constant frequency in the enlarged reciprocal space: (I)  $d/2b = \frac{1}{2}$ ; (II)  $d/2b = \frac{2}{3}$ .

in case (II), we can neglect terms with  $b$  in Eq. (13); we then have

$$(\hbar\omega_{\mathbf{k}}/2AS)^2 \cong k^4 + 2(b + \frac{1}{2}d)k^2. \quad (15)$$

This frequency expression is similar to that of a two-dimensional ferromagnetic system with the anisotropy in Eq. (1).

### 3. SPECIFIC HEAT

The frequency distribution function  $f(x)$  ( $x = \hbar\omega/2AS$ ) is calculated from a formula,

$$f(x) = \sum_{\mathbf{k}} \delta[x - (\hbar\omega_{\mathbf{k}}/2AS)], \quad (16)$$

where  $\delta(x)$  is the delta function. The summation in Eq. (16) is replaced by an integration, and one of the integration variables  $\mathbf{k}'$  is changed to  $(\hbar\omega_{\mathbf{k}}/2AS)$ . This gives

$$f(x) = \frac{N}{(2\pi)^2} \int_{-\pi}^{\pi} dk_z \int_0^{x_0} \frac{\partial k^2}{\partial(\hbar\omega_{\mathbf{k}}/2AS)} \times d(\hbar\omega_{\mathbf{k}}/2AS) \delta\left(x - \frac{\hbar\omega_{\mathbf{k}}}{2AS}\right), \quad (17)$$

where  $2ASx_0/\hbar$  is a cutoff frequency. This cutoff frequency is determined by the normalization of  $f(x)$ ,

$$\int_0^{x_0} f(x) dx = N. \quad (18)$$

A calculation of the function  $f(x)$  in cases (I) and (II) gives the following result:

Case (I):  $b > \frac{1}{2}d$

$$f(x) = N(2\pi)^{-2} \times \left[ \int_0^{k_{z,1}} I(k_z; x) dk_z + \int_{k_{z,2}}^{\pi} I(k_z; x) dk_z \right], \quad (19)$$

with

$$\begin{aligned} k_{z,1} &= \kappa_+, & k_{z,2} &= \pi & \text{for } 0 \leq x^2 \leq 2bd, \\ k_{z,1} &= \kappa_+, & k_{z,2} &= \kappa_- & \text{for } 2bd \leq x^2 \leq (b + \frac{1}{2}d)^2, \\ k_{z,1} &= k_{z,2} & & & \text{for } (b + \frac{1}{2}d)^2 \leq x^2. \end{aligned} \quad (20)$$

Case (II):  $b \leq \frac{1}{2}d$

$$f(x) = N(2\pi)^{-2} \int_0^{k_{z,1}} I(k_z; x) dk_z, \quad (21)$$

with

$$\begin{aligned} k_{z,1} &= \kappa_+ & \text{for } 0 \leq x^2 \leq 2bd, \\ k_{z,1} &= \pi & \text{for } 2bd \leq x^2, \end{aligned} \quad (22)$$

where

$$I(k_z; x) = x \left[ (b + \frac{1}{2}d)^2 + x^2 - b^2 \sin^2 k_z - 2bd \sin^2(\frac{1}{2}k_z) \right]^{-1/2}, \quad (23)$$

$$\kappa_{\pm} = \cos^{-1} \left\{ -d/2b \pm [(d/2b + 1)^2 - (x/b)^2]^{1/2} \right\}. \quad (24)$$

The function  $f(x)$  becomes simpler in several limiting cases depending on the values of  $x$  or  $d$ . Firstly, we have approximate expressions for  $f(x)$  at small or large  $x$  values, as shown in Table I. Case (I) and case (II) will be further differentiated in two and three subcases, respectively, with respect to the behavior of  $f(x)$  at small and large  $x$  values depending on the value of  $d$ : (Ia)  $(\frac{1}{2}d)^{1/2} \ll b^{1/2}$ , (Ib)  $(\frac{1}{2}d)^{1/2} \lesssim b^{1/2}$ , (IIa)  $(\frac{1}{2}d)^{1/2} \gtrsim b^{1/2}$ , (IIb)  $(\frac{1}{2}d)^{1/2} \gg b^{1/2}$  and  $d \sim x_0$ , and (IIc)  $d \gg x_0$ .

Secondly, if  $d \cong 0$ , i.e., case (Ia), we have for any value of  $x$ ,

$$f(x) = N(2\pi)^{-2} 2y(1+y^2)^{-1/2} F[(1+y^2)^{-1/2}, \sin^{-1}y], \quad y \leq 1, \quad (25)$$

$$f(x) = N(2\pi)^{-2} 2y(1+y^2)^{-1/2} K[(1+y^2)^{-1/2}], \quad y > 1,$$

with

$$y = x/b,$$

where  $F(k, \varphi)$  and  $K(k)$  are, respectively, the incomplete and complete elliptic integrals of the first kind. Thirdly, if  $d \gg b$  [case (IIb) and a part of case (IIa)], we have

$$f(x) = N(2\pi)^{-2} 2x(\frac{1}{4}d^2 + x^2)^{-1/2} \sin^{-1}[x(2bd)^{-1/2}], \quad x \leq (2bd)^{1/2}, \quad (26)$$

$$f(x) = N(2\pi)^{-2} \pi x(\frac{1}{4}d^2 + x^2)^{-1/2}, \quad x > (2bd)^{1/2}.$$

TABLE I. Approximate expressions for  $4\pi^2 N^{-1} f(x)$ .

Case	Lower frequency expression	Case	Higher frequency expression
(Ia)	$2b^{-2}x^2, x \ll b$	(I) (IIa)	$\pi, x \gg b + \frac{1}{2}d$
(Ib) (II)	$b^{-1/2}(b + \frac{1}{2}d)^{-3/2}x^2, x \ll (2bd)^{1/2}$	(IIb)	$\pi x(\frac{1}{4}d^2 + x^2)^{-1/2}, x \geq (2bd)^{1/2}$
		(IIc)	$2\pi d^{-1}x, x \geq (2bd)^{1/2}$

TABLE II. Lower temperature and higher temperature expressions for  $C_V/R$ .

Case	Lower temperature expression	Case	Higher temperature expression*
(Ia)	$1.316(T/\Theta_{1a})^3, T \ll \Theta_{1a}'$	(I) (IIa)	$0.262T/\Theta_2, T \gg \Theta_2'$
(Ib) (II)	$0.658(T/\Theta_1)^3, T \ll \Theta_1'$	(IIc)	$1.148(T/\Theta_{IIc})^2, T \gg \Theta_1'$

\* The corresponding expression in case (IIb) is not simple.

The approximate expressions of  $f(x)$  for cases (Ia) and (IIb, c) in Table I can, of course, also be obtained from Eqs. (25) and (26).

The function  $f(x)$  in cases (Ib) and (IIa) is complicated at intermediate  $x$  values. In order to know the values of  $f(x)$  in this range of  $x$ , a numerical evaluation is required of the integrals in Eqs. (18) and (20) with a given value of  $b/d$ .

In evaluating the integral in Eq. (18) in order to determine  $x_0$ , one may replace  $f(x)$  in the integral by the approximate expressions at the larger  $x$  values given in Table I. This follows from our fundamental assumption which makes  $(b+\frac{1}{2}d)$  in cases (I) and (IIa) and  $(2bd)^{1/2}$  in cases (IIb, c) very small. We have, for cases (I) and (IIa)

$$x_0 = 4\pi, \quad (27)$$

and for case (IIb, c),

$$x_0 = [4\pi(4\pi+d)]^{1/2}. \quad (28)$$

The specific heat due to the spin-wave excitation is given by the equation,

$$C_V = k_B \int_0^{x_0} E(2ASx/k_B T) f(x) dx, \quad (29)$$

with

$$E(x) = (\exp x) [(\exp x) - 1]^{-2} x^2. \quad (30)$$

One can obtain expressions of  $C_V$  at lower temperatures and also at higher temperatures, by using the approximate expressions for  $f(x)$  given in Table I. Low-temperature expressions are derived in the same way as one derives the  $T^3$  law due to ordinary antiferromagnetic spin waves.

High-temperature expressions are obtained as follows: Let us take case (Ib) as an example. Using the expression of  $f(x)$  for case (Ib), given in Table I, one has, from Eq. (29),

$$\begin{aligned} C_V/R \cong & \int_0^{b+\frac{1}{2}d} E(2ASx/k_B T) N^{-1} f(x) dx \\ & + (2\pi)^{-2} \int_{b+\frac{1}{2}d}^{x_0} E(2ASx/k_B T) \\ & \times \{ \pi + O[x/(b+\frac{1}{2}d)] \} dx. \quad (31) \end{aligned}$$

This gives, with  $y = 2ASx/k_B T$ ,  $y_0 = 2ASx_0/k_B T$ , and

$$y_1 = 2AS(b+\frac{1}{2}d)/k_B T,$$

$$\begin{aligned} C_V/R \cong & (k_B T/2AS) \left[ (2AS/k_B T) \int_0^{b+\frac{1}{2}d} E(y) N^{-1} f(x) dx \right. \\ & \left. + (4\pi)^{-1} \int_{y_1}^{y_0} E(y) dy + O(y_1^2 \ln y_1) \right]. \quad (32) \end{aligned}$$

The first term in the right-hand side of this equation has at most the order of magnitude of  $y_1$ , therefore, if  $y_1 \ll 1$ ,  $y_0 \gg 1$ , one obtains

$$C_V \cong R(k_B T/2AS) (4\pi)^{-1} \int_0^{y_0} E(y) dy. \quad (33)$$

The expressions for  $C_V$  obtained in cases (Ia)–(IIc) are given in Table II, where the  $\Theta$ 's are defined as follows:

$$\begin{aligned} k_B \Theta_{Ia}' &= 2ASb, & k_B \Theta_{Ia} &= 2ASb^{2/3}, \\ k_B \Theta_{I1}' &= 2AS(2bd)^{1/2}, & k_B \Theta_{I1} &= 2ASb^{1/6}(b+\frac{1}{2}d)^{1/2}, \\ k_B \Theta_{I2}' &= 2AS(b+\frac{1}{2}d), & k_B \Theta_{I2} &= 2AS, \\ k_B \Theta_{IIc} &= 2ASd^{1/2}. \end{aligned} \quad (34)$$

In this calculation, the following values of the integrals are used:

$$T_v = \int_0^{y_0} E(y) y^v dy, \quad (35)$$

$$T_0 = \frac{1}{3}\pi^2, \quad T_1 \cong 0.233\pi^2,$$

$$T_2 = (4/15)\pi^4.$$

#### 4. SUBLATTICE MAGNETIZATION

The sublattice magnetization is calculated, with Eqs. (6), (8), and (9), to be

$$\begin{aligned} M/g\mu &= \left\langle \sum_l \int d^2\rho S_{2l,x}(\rho) \right\rangle \\ &= \frac{1}{2}NS + \frac{1}{4} \sum_{\mathbf{k}} (1 - \cosh 2\theta_{\mathbf{k}}) \\ &\quad - \frac{1}{2} \sum_{\mathbf{k}} [\exp(2ASx/k_B T) - 1]^{-1} \cosh 2\theta_{\mathbf{k}}, \quad (36) \end{aligned}$$

where  $\theta_{\mathbf{k}}$  is  $\theta_{\mathbf{k}}^{(+)}$  in Eqs. (10) and (11) and the summation is over  $\mathbf{k}$  in the enlarged reciprocal space introduced in Sec. 2. The decrease of the sublattice magnetization from the value at absolute zero with increasing temperature is given by the third term of the right-hand side in Eq. (36).

TABLE III. Approximate expressions for  $4\pi^2N^{-1}G(x)$ . When  $4\pi^2N^{-1}G(x)$  for the  $\text{CoCl}_2$  type is different from that for the  $\text{NiCl}_2$  type, it is shown in curly brackets.

Case	Lower frequency expression	Case	Higher frequency expression
(Ia)	$2b^{-1}x, x \ll b$	(I) (IIa)	$\pi/2, x \geq b + \frac{1}{2}d$ $\{(1+r)r^{-1}\pi/4, x \gg b + \frac{1}{2}d\}$
(Ib) (II)	$b^{-1/2}(b + \frac{1}{2}d)^{-1/2}x, x \ll (2bd)^{1/2}$	(IIb) <sup>a</sup>	$\{(1+r)r^{-1}\pi/4 - \frac{1}{2}(1-r)r^{-1}[1 + (2x/d)^2]^{-1/2},$ $x \geq (2bd)^{1/2}\}$
		(IIc) <sup>a</sup>	$\{\pi/2, x \geq (2bd)^{1/2}\}$

\* In cases (IIb, c)  $G(x)$  for the  $\text{NiCl}_2$  type is not given, because the present spin-wave calculation is not valid as is discussed in Sec. 5.

If the summation in this term is replaced by an integration and when one of the integration variable  $\mathbf{k}'$  is changed to  $x$ , one finds

$$\Delta M/g\mu = N(2\pi)^{-2} \int_0^{x_0} [\exp(2ASx/k_B T) - 1]^{-1} G(x) dx. \quad (37)$$

Here,  $G(x)$  for the  $\text{NiCl}_2$ -type spin waves is given by

$$G_{\text{Ni}}(x) = \frac{1}{8}N\pi^2(k_{z,1} + \pi - k_{z,2}), \quad (38)$$

where  $k_{z,1}$  and  $k_{z,2}$  are given in Eq. (20) in case (I) and, in case (II),  $k_{z,1}$  is given in Eq. (22) and  $k_{z,2} = \pi$ . The function  $G_{\text{Co}}(x)$  for the  $\text{CoCl}_2$  type, is somewhat different, because of the difference in the expressions of  $\tanh 2\theta_{\mathbf{k}}$  [Eqs. (10) and (11)]. One has

$$G_{\text{Co}}(x) = (1+r)(2r)^{-1}G_{\text{Ni}}(x) - \left[\frac{1}{4}N\pi^{-2}(1-r)(4r)^{-1}\right] \times \left[ \int_0^{k_{z,1}} J(k_z; x) dk_z + \int_{k_{z,2}}^{\pi} J(k_z; x) dk_z \right], \quad (39)$$

with

$$J(k_z; x) = (\frac{1}{2}d + b \cos k_z) x^{-1} I(k_z; x), \quad (40)$$

where  $k_{z,1}$  and  $k_{z,2}$  are the same as in Eq. (38), and  $I(k_z; x)$  is given in Eq. (23). As was mentioned in Sec. 2, we have for the  $\text{CoCl}_2$  type

$$d = a^{-1}(1+b)(1-r)r^{-1} \cong a^{-1}(1-r)r^{-1},$$

and  $A$  in Eq. (37) should be replaced by  $A(\alpha_{11}\alpha_1)^{1/2}$ .

Approximate expressions of  $G(x)$  at small  $x$  and at large  $x$ , corresponding to those of  $f(x)$  in Table I, are shown in Table III. Quantities in curly brackets in Table III and also in Table IV are for the  $\text{CoCl}_2$  type. The function  $G(x)$  at arbitrary value of  $x$  is simple in cases (Ia) and (IIb). In case (Ia), we have

$$G_{\text{Ni}}(x) = N(2\pi)^{-2} \sin^{-1}(x/b),$$

$$G_{\text{Co}}(x) = N(2\pi)^{-2} \{ (1+r)(2r)^{-1} \sin^{-1}(x/b) - (1-r)(2r)^{-1} \sin^{-1}[x(b^2+x^2)^{-1/2}] \}, \quad x \leq b, \quad (41)$$

$$G_{\text{Ni}}(x) = N(2\pi)^{-2}(\pi/2),$$

$$G_{\text{Co}}(x) = N(2\pi)^{-2} \{ (1+r)(2r)^{-1}(\pi/2) - (1-r)(2r)^{-1} \sin^{-1}[b(b^2+x^2)^{-1/2}] \}, \quad x > b,$$

and, in case (IIb),

$$G_{\text{Co}}(x) = N(2\pi)^{-2} \sin^{-1}[x(2bd)^{-1/2}], \quad x \leq (2bd)^{1/2},$$

$$G_{\text{Co}}(x) = N(2\pi)^{-2}(\pi/2) \{ (1+r)r^{-1} - (1-r)r^{-1} \frac{1}{2} d (\frac{1}{4}d^2 + x^2)^{-1/2} \}, \quad x > (2bd)^{1/2}. \quad (42)$$

The function  $G_{\text{Ni}}(x)$  in case (IIb) is not given, because the present spin-wave approximation is not valid for the  $\text{NiCl}_2$ -type Hamiltonian in this case, as we discuss later.

Using the expressions given in Table III we can derive expressions of  $\Delta M/g\mu$  at lower temperatures and also at higher temperatures in a similar manner to that for the calculation of the specific heat in Sec. 3. Results are given in Table IV, where

$$k_B \Theta_{\text{Ia}}^{(m)} = 2ASb^{1/2}, \quad (43)$$

$$k_B \Theta_1^{(m)} = 2ASb^{1/4}(b + \frac{1}{2}d)^{1/4},$$

$$v_1 = \int_0^{b+\frac{1}{2}d} 4\pi^2 N^{-1} G(x) x^{-1} dx, \quad (44)$$

$$v_2 = \int_0^{(2bd)^{1/2}} 4\pi^2 N^{-1} G(x) x^{-1} dx.$$

## 5. DISCUSSION

As is seen from Tables II and IV, the specific heat and the sublattice magnetization have a different tem-

TABLE IV. Lower temperature and higher temperature expressions for  $\Delta M/\frac{1}{2}N g\mu$ . When  $\Delta M/\frac{1}{2}N g\mu$  for the  $\text{CoCl}_2$  type is different from that for the  $\text{NiCl}_2$  type, it is shown in curly brackets.

Case	Lower frequency expression	Case	Higher frequency expression <sup>a</sup>
(Ia)	$0.0833(T/\Theta_{\text{Ia}}^{(m)})^2, T \ll \Theta_{\text{Ia}}'$	(I) (IIa)	$0.0796(T/\Theta_2) \ln(T/\Theta_2) + 0.0505v_1 T/\Theta_2, T \gg \Theta_2'$
(Ib) (II)	$0.0417(T/\Theta_1^{(m)})^2, T \ll \Theta_1'$	(IIc) <sup>b</sup>	$\{0.0796\frac{1}{2}(1+r)r^{-1}(T/\Theta_2) \ln(T/\Theta_2) + 0.0505v_1 T/\Theta_2\}$ $\{0.0796(T/\Theta_2) \ln(T/\Theta_1') + 0.0505v_2 T/\Theta_2, T \gg \Theta_1'\}$

<sup>a</sup> The corresponding expression in case (IIb) is not simple.

<sup>b</sup> In cases (IIb, c), expressions for the  $\text{NiCl}_2$  type are not given, because the present spin wave calculation is not valid as is discussed in Sec. 5.

perature dependence at lower temperatures as well as at higher temperatures. An interpretation of this result is rather simple. As is mentioned in Sec. 2, the lower frequency spin waves are similar to those of an ordinary three-dimensional antiferromagnetic system and the higher frequency spin waves [ $\hbar\omega \gg 2AS(b + \frac{1}{2}d)$  or  $2AS(2bd)^{1/2}$ ] are similar to those of a two-dimensional ferromagnetic system. Since  $(b + \frac{1}{2}d)$  in case (I) and  $(2bd)^{1/2}$  in case (II) are much smaller than  $x_0$ , almost all modes of spin waves in this model are of the latter type. Therefore, at temperatures so low that only the low-frequency modes are excited, we have the  $T^3$  law for the specific heat and the  $T^2$  law for the sublattice magnetization, which are derived for an ordinary three-dimensional antiferromagnetic system. At temperatures so high that all modes are excited, specific heat obeys a  $T$  law if  $d \ll x_0$  and a  $T^2$  law if  $d \gg x_0$ , which can, for this two-dimensional system, be derived with the frequency expression (15). The magnetization of this two-dimensional system is divergent due to the very lowest frequency modes, as is known. However, the lower frequency modes in the present case have a three-dimensional character and we have convergent results for the higher temperature expressions of  $\Delta M$  shown in Table IV.

We may regard this change in the nature of spin waves with increasing frequency as a zone boundary effect in the  $k_z$  direction due to the high anisotropy in the magnitudes of the exchange interactions.

According to the estimation and discussion by Kanamori,<sup>2</sup>  $2J_{2z_2}$  is  $7 \text{ cm}^{-1}$  in  $\text{NiCl}_2$  and  $3 \text{ cm}^{-1}$  in  $\text{CoCl}_2$  from the susceptibility,  $D$  in  $\text{NiCl}_2$  may be fairly much smaller than  $2J_{2z_2}$ , and the quantity  $2ASa^{-1}(1-r)r^{-1} = 2J_{1z_1}(\alpha_1 - \alpha_{11})$  in  $\text{CoCl}_2$ , corresponding to  $D$  in  $\text{NiCl}_2$ , may have an order of magnitude of  $2J_{1z_1}$ . Therefore, case (I) would be realized in  $\text{NiCl}_2$  and case (II) in  $\text{CoCl}_2$ .

If we assume arbitrarily  $D = \frac{1}{2} \text{ cm}^{-1}$  in  $\text{NiCl}_2$  in order to obtain orders of magnitude of the characteristic temperatures in Tables II and IV,  $\Theta_1'$  and  $\Theta_2'$  defined in Eq. (36) are estimated to be, respectively, 4 and  $10^\circ\text{K}$ . If we assume the limiting case of the large orbital separation<sup>2</sup> in  $\text{CoCl}_2$ , that is,  $\alpha_1 = 2$  and  $\alpha_{11} = 1$ , and if we use a value of  $2J_{1z_1} = 68 \text{ cm}^{-1}$  from the Néel temperature  $25^\circ\text{K}$  on the molecular field approximation, then  $\Theta_2'$  is estimated to be  $10^\circ\text{K}$ .

The characteristic temperatures, particularly for  $\text{CoCl}_2$ , are so high, according to this rough estimation, that the higher temperature behavior might not be very clearly observed even if the semicontinuum model would be a good approximation up to one-third of the Néel temperature which is  $50^\circ\text{K}$  in  $\text{NiCl}_2$  and  $25^\circ\text{K}$  in  $\text{CoCl}_2$ . In the case of  $\text{CrCl}_3$ , which is discussed below, the semicontinuum model seems to be valid up to the highest temperature, i.e., about one-fourth of  $T_N$ , in the experiment. However, the effect of the zone boundary in the present model could still be observed. In order to obtain a full theoretical curve, a numerical

calculation with a suitable choice of the value of  $b/d$  in Eqs. (19), (38), or (39) is required. If both the lower and higher temperature behavior is observed, we can determine the value of  $b/d$  from the  $\Theta$ 's of the approximate expressions in Table II or IV.

The temperature variation of the sublattice magnetization of  $\text{CrCl}_3$ , observed in the nuclear magnetic resonance experiment of  $\text{Cr}^{53}$  by Narath,<sup>5</sup> is proportional to  $T \ln T$  at the higher temperatures in the experiment. Since the anisotropy energy is comparable to the interlayer exchange energy, as can be seen from the observed anisotropy of the critical field for the transition from the antiferromagnetic state to the ferromagnetic state,<sup>4</sup> this case corresponds to case (Ib) or (IIa). Therefore, we expect the  $T$  law for the magnetic specific heat in that temperature range. If in this case a large part of the anisotropy energy originates from the dipolar interaction, the lower frequency spin-wave modes have to be treated more carefully. The dipolar interaction would give an extra  $k$  dependence to  $\hbar\omega$ , which would not be negligible compared with that from the interlayer exchange interaction. This  $k$  dependence is, however, negligible compared with that from the larger intralayer exchange interaction when  $\hbar\omega_k$  is much larger than  $b + \frac{1}{2}d$  or  $(2bd)^{1/2}$ .

Narath explained the sublattice magnetization successfully in the temperature range of the experiment by a model which is also a semicontinuum model, but in which the interlayer exchange interaction is replaced by an effective field. The higher frequency spin wave in the present model is almost identical to that in his.

The anisotropy term,  $DS_z^2$  in the  $\text{NiCl}_2$ -type Hamiltonian has matrix elements between states with difference  $\Delta S_z = \pm 2$ . This has the effect of reducing the expectation value  $\langle S_x \rangle$ , as is seen easily in the molecular field approximation. This effect is also considered, in a fairly good approximation, in such a simple spin-wave theory as the present calculation, insofar as  $D$  is much smaller than  $2J_{1z_1}$ . When  $D$  becomes larger and comparable to  $2J_{1z_1}$ , the simple spin-wave theory cannot be a good approximation, because the ground state would be very far from the classical ground state assumed in the spin-wave theory. The excited state will not be described well by such a spin-wave theory, either.

Since  $D/2J_{1z_1}$  is believed to be much smaller than unity in  $\text{NiCl}_2$ , the present calculation will be a good approximation. The quantity, corresponding to  $D/2J_{1z_1}$ , in  $\text{CoCl}_2$  has come, fortunately, from the anisotropic exchange interaction. Therefore, the above-mentioned danger does not exist.

#### ACKNOWLEDGMENTS

The author would like to express his cordial thanks to Professor T. Nagamiya of Osaka University for suggesting this problem some years ago, to Professor J. Koringa of Ohio State University for his advice and encouragement, and to Dr. J. Kanamori of Osaka University for his helpful discussion.