

Antiferromagnetism in a Layer Structure by Green Function Techniques

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(Received 15 February 1963)

A Green function method has been used to investigate antiferromagnetic ordering in a layer structure. Taking a lattice with an in-plane ferromagnetic exchange interaction and a between-plane antiferromagnetic interaction, the method is used to consider a Hamiltonian which there is reason to believe is applicable to the 'metamagnetic' salts CoCl_2 and NiCl_2 and which includes a uniaxial anisotropy. It is shown that the Green function techniques are well able to deal with Hamiltonians of this more complex type, and an expression is derived for the sublattice magnetization as a function of temperature. In particular, the antiferromagnetic transition temperature is calculated as a function of the exchange parameters. In the following paper these results are used to assist in the calculation of the actual exchange interactions which are present in CoCl_2 and NiCl_2 .

1. INTRODUCTION

IN the paper which follows the present one (we shall refer to it as paper B), we consider the magnetic properties of the metamagnetic substances CoCl_2 and NiCl_2 . These salts have the CdCl_2 crystal structure, in which the cations are arranged in hexagonal layers, and they become antiferromagnetically ordered at low temperatures. The order is one in which the hexagonal layers are ferromagnetic with alternate layers oriented in opposite directions. In both salts the preferred direction of ordering is contained in the hexagonal layers. The magnetic properties of these salts indicate that there exists a strong intraplane ferromagnetic exchange interaction J_1 together with a much weaker interplane antiferromagnetic exchange J_2 . In paper B we examine, in some detail, the origin of anisotropy in the salts; and we find, to a reasonable approximation, that the exchange Hamiltonian may be written

$$\mathcal{H} = \sum_{nn} [-J_1 \mathbf{S}_i \cdot \mathbf{S}_j + D_1 S_{ix} S_{jx}] + \sum_{nnn} [J_2 \mathbf{S}_i \cdot \mathbf{S}_j - D_2 S_{ix} S_{jx}], \quad (1.1)$$

where \sum_{nn} (\sum_{nnn}) is the summation over all pairs of spins S_i and S_j which are nearest neighbors (next-nearest neighbors), where x is the hexagonal (c_0) axis, where D_1 and D_2 are positive anisotropy parameters, and where the 'effective' spin quantum number is $\frac{1}{2}$ for the cobalt salt and 1 for the nickel salt. We also find that we are able to estimate the magnitudes of both isotropic and anisotropic exchange parameters provided only that we can obtain, by some approximate method, a theoretical expression for the antiferromagnetic transition temperature T_N in terms of the exchange parameters. Finding a suitable approximate method is not, however, a simple matter since most of the well-tried methods are unable to deal with a Hamiltonian as complex as (1.1) in a simple way. The molecular field theory may, of course, be applied and quickly gives

$$kT_N = \frac{1}{3}(z_1 J_1 + z_2 J_2)S(S+1), \quad (1.2)$$

where z_1 and z_2 are the number of nearest and next-nearest neighbor spins, respectively, for the salts in question $z_1 = z_2 = 6$. We note that in the molecular field approximation the Néel temperature is independent of the anisotropy.

It is well known, however, that the molecular field theory is at best only semiquantitative giving values for transition temperatures which are too high. Moreover, for the present case we should expect it to be particularly poor since we are concerned primarily with the problem of weakly interacting layers of spins and it is known from spin-wave theory¹ that for the case of isolated two-dimensional arrays no long-range order is possible at nonzero temperatures, whereas the molecular field theory predicts a finite transition temperature for this case [see (1.2) with $J_2 = 0$].

The use of a cluster theory such as the Bethe-Peierls method^{2,3} is extremely difficult for Heisenberg-type Hamiltonians with more than one exchange parameter even excluding anisotropy, so that it is not convenient to attempt such an approximation with a Hamiltonian as complex as (1.1). Similar difficulties would also be encountered in a high-temperature expansion method, and moreover, such approximations are not suited for the calculation of antiferromagnetic transition temperatures (see for example Brown and Luttinger⁴). Spin-wave theories, on the other hand, are well suited to deal with the more complex Hamiltonians,⁵ but since they are only valid for temperatures well below T_N it is difficult to draw from them more than qualitative conclusions concerning the value of the transition temperature.

Recently, the cooperative problems in magnetism have been attacked by making use of the properties of the double-time temperature-dependent Green functions.⁶⁻¹⁰ In particular, Tahir-Kheli and ter Haar¹¹

¹ J. Van Kranendonk and J. H. Van Vleck, *Rev. Mod. Phys.* **30**, 1 (1958).

² P. R. Weiss, *Phys. Rev.* **74**, 1493 (1948).

³ Yin-Yuan Li, *Phys. Rev.* **84**, 721 (1951).

⁴ H. A. Brown and J. M. Luttinger, *Phys. Rev.* **100**, 685 (1955).

⁵ D. ter Haar and M. E. Lines, *Trans. Roy. Soc. (London)* **A255**, 1 (1962).

⁶ N. N. Bogolyubov and S. V. Tyablikov, *Dokl. Akad. Nauk SSSR* **1**, 53 (1959) [translation: *Soviet Phys.—Doklady* **4**, 589 (1959)].

⁷ K. Kawasaki and H. Mori, *Progr. Theoret. Phys. (Kyoto)* **25**, 1045 (1961).

⁸ N. A. Potapkov and S. V. Tyablikov, *Fiz. Tverd. Tela* **2**, 2733 (1960) [translation: *Soviet Phys.—Solid State* **2**, 2433 (1961)].

⁹ B. G. S. Doman and D. ter Haar, *Phys. Letters* **2**, 15 (1962).

¹⁰ D. ter Haar, in *Fluctuation, Relaxation and Resonance in Magnetic Systems* (Oliver and Boyd, Edinburgh, 1962), p. 119.

¹¹ R. A. Tahir-Kheli and D. ter Haar, *Phys. Rev.* **127**, 88 and 95 (1962).

have used this method to investigate the properties of the Heisenberg ferromagnet extending the work of Bogolyubov and Tyablikov⁶ to higher spin values. They find that a formula may be obtained which is valid over the whole temperature range and which is in reasonable agreement both at low temperatures with spin-wave theory, and at high temperatures with the results of high-temperature expansion methods. The method of Green functions has also been applied to the Heisenberg antiferromagnet, though only for the case of spin half, by Fu-Cho Pu,¹² who also finds that the method gives reasonable results. In the above papers, however, the calculations have been performed with only the simplest of Heisenberg Hamiltonians. We shall show in the present paper that the method is well able to cope both with more remote exchange interactions and with anisotropy.

In this paper we shall use the Green function method to treat the Hamiltonian (1.1). Since the low-temperature results of Green function methods show reasonable agreement with spin-wave approximations we may anticipate a theoretical value for T_N which goes to zero as $J_2 \rightarrow 0$, at least for the isotropic case.

2. THE THEORY

The double-time temperature-dependent Green functions have been discussed in detail by Zubarev¹³ and by

Bonch-Bruевич and Tyablikov.¹⁴ For the present work we shall need only one or two of the relations concerning them and we shall write these down without discussion, referring the reader to the paper by Zubarev¹³ for their derivation. If we denote the Fourier transform of the Green function involving the Heisenberg operators $A(t)$ and $B(t')$ by $\langle\langle A(t); B(t') \rangle\rangle$ then it satisfies the equation of motion

$$E\langle\langle A(t); B(t') \rangle\rangle = (1/2\pi)\langle[A(t), B(t')]_-\rangle + \langle\langle [A(t), \mathcal{H}\mathcal{C}]_-; B(t') \rangle\rangle, \quad (2.1)$$

where the double-pointed brackets indicate Fourier transforms of the Green functions, where the single-pointed brackets indicate averages over a canonical ensemble

$$\langle \dots \rangle = \text{Tr}[\exp(-\mathcal{H}\mathcal{C}/kT) \dots] / \text{Tr}[\exp(-\mathcal{H}\mathcal{C}/kT)], \quad (2.2)$$

and where $[A, B]_-$ is the comutator ($AB - BA$). We work throughout with a system of units in which $\hbar = 1$. From the analytical properties of the Green functions, through the intermediary of spectral functions, the correlation functions $\langle B(t')A(t) \rangle$ and $\langle A(t)B(t') \rangle$ may be shown to be

$$\langle B(t')A(t) \rangle = \lim_{\epsilon \rightarrow +0} i \int_{-\infty}^{\infty} \frac{\langle\langle A(t); B(t') \rangle\rangle_{E=\omega+i\epsilon} - \langle\langle A(t); B(t') \rangle\rangle_{E=\omega-i\epsilon}}{e^{\omega/kT} - 1} e^{-i\omega(t-t')} d\omega, \quad (2.3)$$

$$\langle A(t)B(t') \rangle = \lim_{\epsilon \rightarrow +0} i \int_{-\infty}^{\infty} \frac{\langle\langle A(t); B(t') \rangle\rangle_{E=\omega+i\epsilon} - \langle\langle A(t); B(t') \rangle\rangle_{E=\omega-i\epsilon}}{1 - e^{-\omega/kT}} e^{-i\omega(t-t')} d\omega. \quad (2.4)$$

In the present work we shall investigate the motion of the functions $\langle\langle S_{gx}; f(S_h) \rangle\rangle$ and $\langle\langle S_{gy}; f(S_h) \rangle\rangle$, where S_{gx}, S_{gy} refer to the x, y components of spin on a lattice site g at time t , where $f(S_h)$ means any function of S_{hx}, S_{hy}, S_{hz} where these operators refer to spin components on a site h at time t' , and where we have defined an orthogonal coordinate system x, y, z , in which x is the hexagonal (c_0) axis and z is the direction of spin alignment in the ordered state. We note that (1.1) does not fix absolutely the direction of z but simply constrains it to be in the c_0 plane. We shall be interested only in the case $t - t' \rightarrow 0$ (the retarded and advanced Green functions are not defined for the case $t = t'$ although the correlation functions, of course, are).

Using the Hamiltonian (1.1) together with the familiar commutation relationships for the components of spin, we may write down the equations of motion for these two Fourier transforms. They are [compare (2.1)]

$$E\langle\langle S_{gx}; f(S_h) \rangle\rangle = \frac{\delta_{gh}}{2\pi} \langle F_1 \rangle + i \langle\langle (\sum_{\text{nnn}}^j J_2 - \sum_{\text{nn}}^j J_1) (S_{gz} S_{jy} - S_{gy} S_{jz}); f(S_h) \rangle\rangle, \quad (2.5)$$

$$E\langle\langle S_{gy}; f(S_h) \rangle\rangle = \frac{\delta_{gh}}{2\pi} \langle F_2 \rangle + i \langle\langle (\sum_{\text{nnn}}^j J_2 - \sum_{\text{nn}}^j J_1) (S_{gz} S_{jz} - S_{gz} S_{jx}); f(S_h) \rangle\rangle + i \langle\langle (\sum_{\text{nnn}}^j D_2 - \sum_{\text{nn}}^j D_1) S_{gz} S_{jx}; f(S_h) \rangle\rangle, \quad (2.6)$$

where $\sum_{\text{nn}}^j (\sum_{\text{nnn}}^j)$ means that j is to be summed over all nearest (next-nearest) neighbors of g , and where

$$F_1 = [S_{gz}, f(S_g)]_-, \quad \text{and} \quad F_2 = [S_{gy}, f(S_g)]_-. \quad (2.7)$$

¹² Fu-Cho Pu, Dokl. Akad. Nauk SSSR **130**, 1244 (1960); *ibid.* **131**, 546 (1960) [translation: Soviet Phys.—Doklady **5**, 128 and 321 (1960)].

¹³ D. N. Zubarev, Usp. Fiz. Nauk **71**, 71 (1960) [translation: Soviet Phys.—Usp. **3**, 320 (1960)].

¹⁴ V. L. Bonch-Bruевич and S. V. Tyablikov, *The Green Function Method in Statistical Mechanics* (North-Holland Publishing Company, Amsterdam, 1961).

In an exactly similar way we could generate equations of motion for the more complex Green function transforms which appear on the right-hand side of (2.5) and (2.6). These equations in turn would involve more complex functions still. We, therefore, need to decouple this set of equations and, following Tahir-Kheli and ter Haar,¹¹ we do so at the first stage. We write

$$\begin{aligned}\langle\langle S_{gy}S_{jz}; f(S_h)\rangle\rangle &= \langle S_{jz}\rangle\langle\langle S_{gy}; f(S_h)\rangle\rangle, \\ \langle\langle S_{gz}S_{jy}; f(S_h)\rangle\rangle &= \langle S_{gz}\rangle\langle\langle S_{jy}; f(S_h)\rangle\rangle,\end{aligned}\quad g \neq j \quad (2.8)$$

and similar equations for the functions containing x components of spin. In this way we find

$$E\langle\langle S_{gx}; f(S_h)\rangle\rangle = \frac{\delta_{gh}}{2\pi}\langle F_1\rangle + i\left(\sum_{\text{nnn}}^j J_2 - \sum_{\text{nn}}^j J_1\right)\left[\langle S_{gz}\rangle\langle\langle S_{jy}; f(S_h)\rangle\rangle - \langle S_{jz}\rangle\langle\langle S_{gy}; f(S_h)\rangle\rangle\right], \quad (2.9)$$

$$\begin{aligned}E\langle\langle S_{gy}; f(S_h)\rangle\rangle &= \frac{\delta_{gh}}{2\pi}\langle F_2\rangle + i\left(\sum_{\text{nnn}}^j J_2 - \sum_{\text{nn}}^j J_1\right)\left[\langle S_{jz}\rangle\langle\langle S_{gx}; f(S_h)\rangle\rangle\right] - i\left[\sum_{\text{nnn}}^j (J_2 - D_2) - \sum_{\text{nn}}^j (J_1 - D_1)\right] \\ &\quad \times \left[\langle S_{gz}\rangle\langle\langle S_{jz}; f(S_h)\rangle\rangle\right].\end{aligned}\quad (2.10)$$

In the antiferromagnetic state the spins align ferromagnetically within the hexagonal layers, but adjacent layers are aligned in opposite directions. We are, therefore, led to introduce two sublattices into the problem, the 'up' sublattice and the 'down' sublattice. In this way we are able to distinguish four different Green function transforms. Using the translational invariance of the lattice we can Fourier transform our Green functions with respect to the reciprocal lattice when we may define the functions $G_{i\mathbf{K}}$ ($i=1, 2, 3, 4$) as follows:

(a) when g and h , whose sites we represent by position vectors \mathbf{g} and \mathbf{h} , are both on the same sublattice

$$\begin{aligned}\langle\langle S_{gx}; f(S_h)\rangle\rangle &= \frac{2}{N} \sum_{\mathbf{K}} G_{1\mathbf{K}} e^{i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})}; \\ G_{1\mathbf{K}} &= \sum_{\mathbf{g}-\mathbf{h}} \langle\langle S_{gx}; f(S_h)\rangle\rangle e^{-i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})};\end{aligned}\quad (2.11)$$

$$\begin{aligned}\langle\langle S_{gy}; f(S_h)\rangle\rangle &= \frac{2}{N} \sum_{\mathbf{K}} G_{3\mathbf{K}} e^{i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})}; \\ G_{3\mathbf{K}} &= \sum_{\mathbf{g}-\mathbf{h}} \langle\langle S_{gy}; f(S_h)\rangle\rangle e^{-i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})};\end{aligned}\quad (2.12)$$

(b) when g and h are on different sublattices

$$\begin{aligned}\langle\langle S_{gx}; f(S_h)\rangle\rangle &= \frac{2}{N} \sum_{\mathbf{K}} G_{2\mathbf{K}} e^{i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})}; \\ G_{2\mathbf{K}} &= \sum_{\mathbf{g}-\mathbf{h}} \langle\langle S_{gx}; f(S_h)\rangle\rangle e^{-i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})};\end{aligned}\quad (2.13)$$

$$\begin{aligned}\langle\langle S_{gy}; f(S_h)\rangle\rangle &= \frac{2}{N} \sum_{\mathbf{K}} G_{4\mathbf{K}} e^{i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})}; \\ G_{4\mathbf{K}} &= \sum_{\mathbf{g}-\mathbf{h}} \langle\langle S_{gy}; f(S_h)\rangle\rangle e^{-i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})};\end{aligned}\quad (2.14)$$

where N is the total number of spins in the lattice, and where \mathbf{K} is a reciprocal lattice vector and runs over

$N/2$ points in the first Brillouin zone of the reciprocal lattice (or sublattice).

Noting that the Kronecker delta may be written

$$\delta_{gh} = \frac{2}{N} \sum_{\mathbf{K}} e^{i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})} \quad (2.15)$$

and writing the average value of S_z on an 'up' site as \bar{S} and on a 'down' site as $-\bar{S}$, we may rewrite the equations of motion (2.9) and (2.10) in terms of $G_{i\mathbf{K}}$. They are

$$EG_{1\mathbf{K}} = (1/2\pi)\langle F_1\rangle + i\bar{S}(\lambda G_{4\mathbf{K}} + \mu G_{3\mathbf{K}}), \quad (2.16)$$

$$EG_{2\mathbf{K}} = -\bar{S}(\lambda G_{3\mathbf{K}} + \mu G_{4\mathbf{K}}), \quad (2.17)$$

$$EG_{3\mathbf{K}} = (1/2\pi)\langle F_2\rangle - i\bar{S}[(\lambda - \rho_2)G_{2\mathbf{K}} + (\mu + \rho_1)G_{1\mathbf{K}}], \quad (2.18)$$

$$EG_{4\mathbf{K}} = i\bar{S}[(\lambda - \rho_2)G_{1\mathbf{K}} + (\mu + \rho_1)G_{2\mathbf{K}}], \quad (2.19)$$

where we have considered S_h to be on the 'up' sublattice; and where

$$\lambda = \sum_{\text{nnn}} J_2 e^{i\mathbf{K}\cdot\mathbf{l}}, \quad (2.20)$$

$$\mu = z_1 J_1 + z_2 J_2 - \sum_{\text{nn}} J_1 e^{i\mathbf{K}\cdot\mathbf{l}}, \quad (2.21)$$

$$\rho_1 = \sum_{\text{nn}} D_1 e^{i\mathbf{K}\cdot\mathbf{l}}, \quad (2.22)$$

$$\rho_2 = \sum_{\text{nnn}} D_2 e^{i\mathbf{K}\cdot\mathbf{l}}, \quad (2.23)$$

where \mathbf{l} is the vector joining nearest or next-nearest neighbors over which is summed.

Solving Eqs. (2.16) to (2.19) for $G_{1\mathbf{K}}$ we find

$$\begin{aligned}8\pi G_{1\mathbf{K}} &= \frac{\langle F_1\rangle + iA_1\langle F_2\rangle}{E - E_1} + \frac{\langle F_1\rangle - iA_1\langle F_2\rangle}{E + E_1} \\ &\quad + \frac{\langle F_1\rangle + iA_2\langle F_2\rangle}{E - E_2} + \frac{\langle F_1\rangle - iA_2\langle F_2\rangle}{E + E_2},\end{aligned}\quad (2.24)$$

where

$$A_1^2 = \frac{\mu + \lambda}{\mu - \lambda + \rho_1 + \rho_2}, \quad A_2^2 = \frac{\mu - \lambda}{\mu + \lambda + \rho_1 - \rho_2}, \quad (2.25)$$

$$\begin{aligned} E_1^2 &= (\bar{S})^2(\mu + \lambda)(\mu - \lambda + \rho_1 + \rho_2), \\ E_2^2 &= (\bar{S})^2(\mu - \lambda)(\mu + \lambda + \rho_1 - \rho_2). \end{aligned} \quad (2.26)$$

From Eqs. (2.3) and (2.11) we have

$$\langle f(S_h)S_{gz} \rangle = \frac{2}{N} \lim_{\epsilon \rightarrow +0} \sum_{\mathbf{K}} i \int_{-\infty}^{\infty} \frac{G_{1\mathbf{K}E=\omega+i\epsilon} - G_{1\mathbf{K}E=\omega-i\epsilon}}{e^{\omega/kT} - 1} e^{i\mathbf{K} \cdot (\mathbf{g}-\mathbf{h})} d\omega, \quad (2.27)$$

and using the fact that

$$\lim_{\epsilon \rightarrow +0} \left[\frac{1}{\omega + i\epsilon - E_{\mathbf{K}}} - \frac{1}{\omega - i\epsilon - E_{\mathbf{K}}} \right] = -2\pi i \delta(\omega - E_{\mathbf{K}}) \quad (2.28)$$

together with (2.24), we obtain, for the case where g and h are on the same 'up' sublattice

$$\langle f(S_h)S_{gz} \rangle = \frac{1}{2N} \sum_{\mathbf{K}} \{i\langle F_2 \rangle [A_1 \coth(E_1/2kT) + A_2 \coth(E_2/2kT)] - 2\langle F_1 \rangle\} e^{i\mathbf{K} \cdot (\mathbf{g}-\mathbf{h})}. \quad (2.29)$$

For the case $g=h$ it, therefore, follows that

$$\langle f(S_g)S_{gz} \rangle = \frac{1}{2N} \sum_{\mathbf{K}} \{i\langle F_2 \rangle [A_1 \coth(E_1/2kT) + A_2 \coth(E_2/2kT)] - 2\langle F_1 \rangle\}. \quad (2.30)$$

In a similar manner, solving the equations of motion for $G_{2\mathbf{K}}$, $G_{3\mathbf{K}}$, and $G_{4\mathbf{K}}$ we may derive the relations

$$\langle f(S_g)S_{gy} \rangle = \frac{1}{2N} \sum_{\mathbf{K}} \{-i\langle F_1 \rangle [A_1^{-1} \coth(E_1/2kT) + A_2^{-1} \coth(E_2/2kT)] - 2\langle F_2 \rangle\} \quad (2.31)$$

and, for g and h on different sublattices,

$$\langle f(S_h)S_{gz} \rangle = \frac{1}{2N} \sum_{\mathbf{K}} \{i\langle F_2 \rangle [A_2 \coth(E_2/2kT) - A_1 \coth(E_1/2kT)] e^{i\mathbf{K} \cdot (\mathbf{g}-\mathbf{h})}\}, \quad (2.32)$$

$$\langle f(S_h)S_{gy} \rangle = \frac{1}{2N} \sum_{\mathbf{K}} \{i\langle F_1 \rangle [A_2^{-1} \coth(E_2/2kT) - A_1^{-1} \coth(E_1/2kT)] e^{i\mathbf{K} \cdot (\mathbf{g}-\mathbf{h})}\}. \quad (2.33)$$

Using Eq. (2.4) in place of (2.3) in the above analysis we may also deduce expressions for $\langle S_{gz}f(S_g) \rangle$ and $\langle S_{gy}f(S_g) \rangle$. We find that the former is obtained from (2.30) by replacing $\langle F_1 \rangle$ by $-\langle F_1 \rangle$, and the latter from (2.31) by replacing $\langle F_2 \rangle$ by $-\langle F_2 \rangle$. For $g \neq h$ we can, of course, reverse the order of the operators in the ensemble average since they will commute.

We may now choose specific functions to insert into the theory in place of $f(S)$. Putting $f(S) = S_x$ we have, from (2.7), $\langle F_1 \rangle = 0$ and $\langle F_2 \rangle = -i\bar{S}$. Similarly, putting $f(S) = S_y$ gives $\langle F_1 \rangle = i\bar{S}$, $\langle F_2 \rangle = 0$. It follows from (2.30), (2.31) that

$$\langle S_x^2 \rangle = (\bar{S}/4) \langle A_1 \coth(E_1/2kT) + A_2 \coth(E_2/2kT) \rangle_{\mathbf{K}}, \quad (2.34)$$

$$\langle S_y^2 \rangle = (\bar{S}/4) \langle A_1^{-1} \coth(E_1/2kT) + A_2^{-1} \coth(E_2/2kT) \rangle_{\mathbf{K}}, \quad (2.35)$$

$$\langle S_x S_y - S_y S_x \rangle = i\bar{S}, \quad (2.36)$$

where $\langle \dots \rangle_{\mathbf{K}}$ indicates an average for values of \mathbf{K} running over the $N/2$ allowed values in the first

Brillouin zone of the reciprocal lattice. We shall write for brevity

$$\langle A_1 \coth(E_1/2kT) + A_2 \coth(E_2/2kT) \rangle_{\mathbf{K}} = P, \quad (2.37)$$

and

$$\langle A_1^{-1} \coth(E_1/2kT) + A_2^{-1} \coth(E_2/2kT) \rangle_{\mathbf{K}} = Q. \quad (2.38)$$

With this notation, since $S_x^2 + S_y^2 + S_z^2 = S(S+1)$, we have

$$\langle S_z^2 \rangle = S(S+1) - (\bar{S}/4)(P+Q). \quad (2.39)$$

Since for the case of spin half $S_z^2 = \frac{1}{4}$, it follows that

$$\bar{S} = 2/(P+Q). \quad (S = \frac{1}{2}). \quad (2.40)$$

For higher values of spin we may proceed as follows.

Since $S_z^3 = S_z[S(S+1) - S_x^2 - S_y^2]$, it follows that

$$\langle S_z^3 \rangle = \bar{S}S(S+1) - \langle S_x S_x^2 \rangle - \langle S_y S_y^2 \rangle. \quad (2.41)$$

The last two terms may be calculated from (2.30), (2.31) by putting $f(S)$ equal in turn to $S_x S_x$ and $S_x S_y$. We find

$$\langle S_x S_x^2 \rangle = \frac{1}{16} [4S(S+1)P + 4\bar{S} - 2\bar{S}P^2 - \bar{S}PQ] \quad (2.42)$$

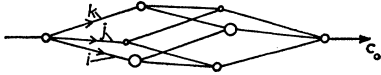


FIG. 1. The unit cell and basic vectors for the cations in the CdCl_2 crystal structure.

$$\langle S_x S_y^2 \rangle = \frac{1}{16} [4S(S+1)Q + 4\bar{S} - 2\bar{S}Q^2 - \bar{S}PQ], \quad (2.43)$$

and, therefore, from (2.41)

$$\langle S_z^3 \rangle = \frac{1}{8} [S(S+1)(8\bar{S} - 2P - 2Q) - 4\bar{S} + \bar{S}(P^2 + Q^2 + PQ)]. \quad (2.44)$$

For spin one, however, $(S_z - 1)S_z(S_z + 1) = 0$ and, therefore,

$$\bar{S} = 4(P + Q)/(4 + P^2 + Q^2 + PQ). \quad (S=1). \quad (2.45)$$

Since we are here primarily interested in the salts CoCl_2 and NiCl_2 with spins half and one, respectively, we have already generated the results which will be of use in paper B. We could, however, proceed to derive an expression for \bar{S} in terms of P and Q for any value of spin, although the labor involved rapidly increases. In this paper we have gone only as far as spin $\frac{3}{2}$ for which we find

$$\bar{S} = \frac{32 + 5(3P^2 + 3Q^2 + 2PQ)}{16(P + Q) + 2[P^3 + Q^3 + PQ(P + Q)]}. \quad (S = \frac{3}{2}). \quad (2.46)$$

In order to derive this expression it is necessary to calculate $\langle S_x^2 S_y^2 \rangle$ and $\langle S_y^2 S_x^2 \rangle$ which we do by putting $f(S) = S_x^2 S_y$ in (2.31) (for the former) and by putting $f(S) = S_y^2 S_x$ in (2.30) (for the latter). From these results we find that

$$\langle S_y^2 S_x^2 - S_x^2 S_y^2 \rangle = \frac{1}{64} \bar{S} (Q - P)(4 - PQ). \quad (2.47)$$

However, application of the simple spin commutation relations quickly shows that $S_y^2 S_x^2 = S_x^2 S_y^2$ so that we have here a demonstration of the kind of error which is introduced by the decoupling procedure.

3. THE ANTIFERROMAGNETIC TRANSITION TEMPERATURE

As the temperature nears T_N from below, \bar{S} becomes progressively smaller until, very close to T_N , we can replace $\coth(E_i/2kT)$ by $2kT/E_i$ ($i=1, 2$). It follows that

$$P_{T \rightarrow T_N} = 2kT \langle (A_1/E_1) + (A_2/E_2) \rangle_{\mathbf{K}}, \quad (3.1)$$

$$Q_{T \rightarrow T_N} = 2kT \langle (1/A_1 E_1) + (1/A_2 E_2) \rangle_{\mathbf{K}}. \quad (3.2)$$

Let us first consider the case of spin half. Using (2.40) together with (3.1) and (3.2), we find

$$kT_N = 1/(U + V), \quad (3.3)$$

where

$$U = \bar{S} \langle (A_1/E_1) + (A_2/E_2) \rangle_{\mathbf{K}} \\ = \langle 1/(\mu - \lambda + \rho_1 + \rho_2) + 1/(\mu + \lambda + \rho_1 - \rho_2) \rangle_{\mathbf{K}}, \quad (3.4)$$

$$V = \bar{S} \langle (1/A_1 E_1) + (1/A_2 E_2) \rangle_{\mathbf{K}} \\ = \langle 1/(\mu - \lambda) + 1/(\mu + \lambda) \rangle_{\mathbf{K}}. \quad (3.5)$$

In a similar manner we find for the higher spin values

$$kT_N = 2(U + V)/(U^2 + UV + V^2) \quad (S=1) \quad (3.6)$$

$$kT_N = (15U^2 + 10UV + 15V^2)/4[U^3 + V^3 + UV(U + V)] \\ (S = \frac{3}{2}). \quad (3.7)$$

In order to evaluate U and V we must now consider the magnetic lattice of CoCl_2 (or NiCl_2) specifically. The unit cell of this structure is a rhombohedron (see Fig. 1). It is essentially a face-centered-cubic lattice which has been drawn out along a body diagonal. We shall describe the lattice by the basic vectors \mathbf{i} , \mathbf{j} , \mathbf{k} , and we shall assume that our crystal has dimensions L^3 measured in lattice spacings along the basic vectors. The allowed values of the reciprocal lattice vector are then, using periodic boundary conditions,

$$\mathbf{K} = (2\pi/L)(n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2 + n_3 \mathbf{b}_3), \quad (3.8)$$

where n_i are integers $-\frac{1}{2}L \leq n_i < \frac{1}{2}L$ and where \mathbf{b}_i are vectors reciprocal to \mathbf{i} , \mathbf{j} , \mathbf{k} . If we define

$$K_i = 2\pi n_i/L, \quad (3.9)$$

it follows that

$$\sum_{\mathbf{nn}} e^{i\mathbf{K} \cdot \mathbf{1}} = 2[\cos(K_1 - K_2) + \cos(K_2 - K_3) \\ + \cos(K_3 - K_1)], \quad (3.10)$$

$$\sum_{\mathbf{nnn}} e^{i\mathbf{K} \cdot \mathbf{1}} = 2[\cos(K_1) + \cos(K_2) + \cos(K_3)], \quad (3.11)$$

where $-\pi \leq K_i < \pi$ ($i=1, 2, 3$) is the allowed range for K_i . Putting $\cos(K_i) = c_i$ and $\sin(K_i) = s_i$ we may write

$$\sum_{\mathbf{nn}} e^{i\mathbf{K} \cdot \mathbf{1}} = (c_1 + c_2 + c_3)^2 + (s_1 + s_2 + s_3)^2 - 3, \quad (3.12)$$

$$\sum_{\mathbf{nnn}} e^{i\mathbf{K} \cdot \mathbf{1}} = 2(c_1 + c_2 + c_3). \quad (3.13)$$

Consider any octant of \mathbf{K} space in the first Brillouin zone. By comparing the contributions to U and V from the points (c_1, c_2, c_3) and $(-c_1, -c_2, -c_3)$ we see that

$$\langle 1/(\mu - \lambda + \rho_1 + \rho_2) \rangle_{\mathbf{K}} = \langle 1/(\mu + \lambda + \rho_1 - \rho_2) \rangle_{\mathbf{K}}, \quad (3.14)$$

$$\langle 1/(\mu - \lambda) \rangle_{\mathbf{K}} = \langle 1/(\mu + \lambda) \rangle_{\mathbf{K}}, \quad (3.15)$$

and hence, from (2.20) to (2.23), together with (3.4), (3.5), (3.12), and (3.13)

$$U = \langle 2/\{6(J_1 + J_2) - (J_1 - D_1)[(\sum_i c_i)^2 + (\sum_i s_i)^2 - 3] \\ \pm 2(J_2 - D_2)(\sum_i c_i)\} \rangle_{\mathbf{K}}, \quad (3.16)$$

$$V = \langle 2/\{6(J_1 + J_2) - J_1[(\sum_i c_i)^2 + (\sum_i s_i)^2 - 3] \\ \pm 2J_2(\sum_i c_i)\} \rangle_{\mathbf{K}}. \quad (3.17)$$

From (3.3), (3.6), and (3.7), we see that $T_N=0$ when either U or V diverges, and in such a case we shall interpret this as meaning that no long-range order is possible for nonzero temperatures. From the above expressions for U and V we find that such is the situation for the case when $J_2=0$ when the denominator inside the pointed brackets in (3.17) is zero along the line $(\sum_i c_i)^2 + (\sum_i s_i)^2 = 9$ and, thus, V diverges logarithmically. This is the case of isolated layers of spins and we observe that no anisotropy of the form D_1, D_2 can stabilize the order.

In paper B we show that for CoCl_2 the anisotropy is such that $D_1/J_1 = D_2/J_2$ [see Eq. (3.8) of paper B] and we also find that for NiCl_2 the anisotropy is very small and to a fair approximation may be neglected in the calculation for T_N . In this paper we shall, therefore, compute U and V only for the case

$$D_1/J_1 = D_2/J_2 = D/J. \quad (3.18)$$

With this restriction we have computed U and V for a range of values of J_1, J_2 , and D/J using the Oxford University Mercury computer. From (3.3), (3.6), and (3.7) we have calculated the Néel temperature for the cases $S=\frac{1}{2}, S=1, S=\frac{3}{2}$, and the results are shown graphically as kT_N/J_1 versus J_2/J_1 for various values of anisotropy D/J in Figs. 2 and 3. Also shown in these figures is the molecular field result

$$kT_N = 2(J_1 + J_2)S(S+1). \quad (3.19)$$

We see that the Green function transition temperature is always less than the corresponding molecular field one, the factor being close to 0.7 in the isotropic case except for very small values of $J_2/J_1 (< 0.1)$ when it decreases rapidly to zero as $J_2/J_1 \rightarrow 0$. We also see that, whereas the molecular field result is independent of D/J , the method of Green functions indicates that

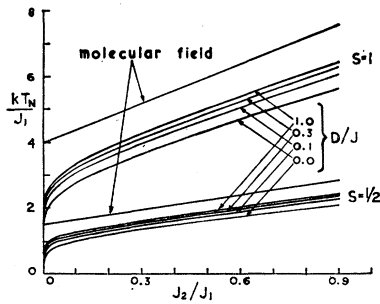


FIG. 2. The Néel temperature plotted as a function of the exchange parameters for the cases, $S=\frac{1}{2}$ and $S=1$.

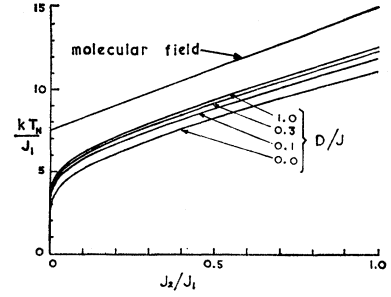


FIG. 3. The Néel temperature plotted as a function of the exchange parameters for the case, $S=\frac{3}{2}$.

the presence of anisotropy will increase T_N , a value of D/J of 0.1 increasing T_N by nearly 10%. Finally, we note that the Néel temperatures for spin 1 and spin $\frac{3}{2}$ are very closely, though not exactly (except in the isotropic case) equal to $4S(S+1)/3$ times the equivalent spin $\frac{1}{2}$ temperatures.

In closing we may deduce from the general equations above, the transition temperatures for the simple isotropic Heisenberg ferromagnet and antiferromagnet showing that we obtain the results previously derived by Tahir-Kheli and ter Haar¹¹ for the former, and by Fu-Cho Pu¹² for the latter.

Consider the case where $D_1 = D_2 = J_2 = 0$. Using Eqs. (2.20) to (2.23) and (3.3) to (3.7), we find that for this case, which is equivalent to the Heisenberg ferromagnet with nearest neighbor isotropic exchange interactions only, we obtain

$$(kT_N)_{\text{ferro}} = S(S+1)J_1/3\Phi, \quad (3.20)$$

where

$$\Phi = \langle 1/(z - \sum e^{i\mathbf{K}\cdot\mathbf{l}}) \rangle_{\mathbf{K}}, \quad (3.21)$$

where \sum runs over all nearest neighbors \mathbf{l} , and z is the number of nearest neighbors. This is the result obtained by Tahir-Kheli and ter Haar¹¹.

In a similar way, putting $D_1 = D_2 = J_1 = 0$ gives us the result for the simple isotropic Heisenberg antiferromagnet; it is

$$(kT_N)_{\text{antiferro}} = S(S+1)zJ_2/3\Psi, \quad (3.22)$$

where

$$\Psi = \langle z^2/[z^2 - (\sum e^{i\mathbf{K}\cdot\mathbf{l}})^2] \rangle_{\mathbf{K}} \quad (3.23)$$

which for the case of spin half reduces to the result obtained by Fu-Cho Pu¹² and also by Ginzburg and Fain.¹⁵

¹⁵ V. L. Ginzburg and V. M. Fain, Zh. Eksperim. i Teor. Fiz. 39, 1323 (1960) [translation: Soviet Phys.—JETP 12, 923 (1961)].