

## Spin-wave theory of the paramagnetic phase boundary in transversally anisotropic antiferromagnets\*

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Existent spin-wave theories of antiferromagnets predict the  $T^{3/2}$  behavior of the paramagnetic-spin-flop boundary in the  $(H, T)$  plane. This prediction has been confirmed by experiments on  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ . However in several compounds such dependence has not been observed. This failure is explained as arising from transversally ( $J^x \neq J^y$ ) anisotropic exchange interactions, as in  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , or from single-ion orthorhombic anisotropy field, as in  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ . In both these instances a  $T^2$  law is proposed.

### I. INTRODUCTION

A static magnetic field applied along a preferred  $z$  direction in an antiferromagnet below its Néel temperature can induce two phase transitions: a first-order transition between the antiferromagnetic phase and the spin-flop phase, and, at a higher field, a second-order transition between the spin-flop and paramagnetic states. In the paramagnetic phase the sublattices are forced to be aligned along the preferred axis, whereas in the spin-flop state the sublattices are canted.

A first theoretical description of these transitions was supplied by Falk<sup>1</sup> and it was based on a variational approach. A more detailed treatment, which employed the Green's-function method with the Callen decoupling scheme, was worked out by Anderson and Callen.<sup>2</sup> These authors discussed the properties of an antiferromagnet in the low-temperature region and in the vicinities of critical and bicritical points. Falk considered an antiferromagnet with isotropic exchange interactions and Anderson-Callen added uniaxial single-ion anisotropy. Feder and Pytte<sup>3</sup> allowed, in addition, that the coupling between the  $z$  components of the spins be different from that between the transverse components (Ising-Heisenberg model). Their theory was based on the Holstein-Primakoff<sup>4</sup> spin representation. The boundaries between the phases on the  $H$ - $T$  diagram were derived in the framework of soft-mode transitions concepts.

All of these three theories predicted that in the low-temperature region, the critical field, at which the spin-flop phase becomes unstable and transforms into the paramagnetic phase, has the form

$$H_c(T) = h(1 - c_1 T^{3/2} - c_2 T^{5/2}) + \dots$$

This prediction was confirmed experimentally by Oliveira *et al.*<sup>5</sup> in  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in the range of temperatures from 0.45 to 1.3 °K ( $T_N = 5.34$  °K). How-

ever, in the experiments by Rives and Benedict<sup>6</sup> on  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  ( $T_N = 1.62$  °K) in the range 0.3 to 1.6 °K and of Rives and Bhatia<sup>7</sup> on  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  ( $T_N = 2.29$  °K) in the range 0.33 to 2.0 °K the lack of  $T^{3/2}$  dependence was established. The authors reported the  $T^{5/2}$  law as better fitting the data, although some slight departures from the  $T^{5/2}$  curve were still present. The direction of these departures seems not to exclude the possibility that the  $T^2$  curve was actually obtained.

In this work we will show that the discrepancies between the existing theories and the results of Rives and his collaborators are due for  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  to transversally anisotropic exchange interactions, whereas for  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  they are mostly due to single-ion orthorhombic anisotropy. In the presence of transversally anisotropic exchange interactions and (or) orthorhombic crystal-field anisotropy, an antiferromagnet in its paramagnetic phase behaves as a generalized  $X$ - $Y$  system,<sup>8</sup> since its magnon frequency begins as a linear, and not quadratic, function of wave vector. This leads to the  $T^2$  shape of the coexistence curve.

### II. SPIN WAVES IN $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$

Consider first  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ . X-ray studies of Mizuno<sup>9</sup> indicated that this material has a monoclinic face-centered structure with  $a = 10.34$  Å,  $b = 7.06$  Å,  $c = 6.67$  Å,  $\beta = 122^\circ 20'$ . The magnetic ordering scheme in the antiferromagnetic phase was settled by Kleinberg<sup>10</sup> by means of neutron diffraction techniques. The ordering consists of antiferromagnetic  $ab$  planes with an antiferromagnetic coupling between adjacent planes, as shown in Fig. 1.

Now each  $\text{Co}^{2+}$  ion is surrounded by an elongated octahedron formed of four water molecules in a plane, which is inclined by  $9^\circ 20'$  from the  $cb$  plane, and by two chlorine ions along the axis perpendicular to the plane. Haseda's<sup>11</sup> empirical analysis of

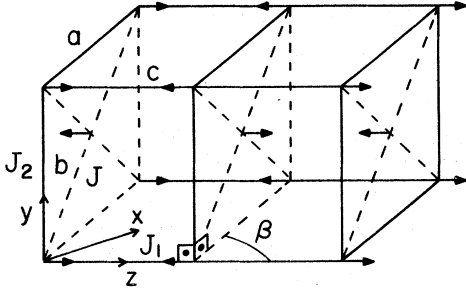


FIG. 1. Model of the ferromagnetic ordering in  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ . Cobalt ions are shown only.  $J$  denotes the antiferromagnetic coupling between the nearest neighbors,  $J_1$  the coupling between the planes (next neighbors) and  $J_2$  denotes the interaction between the next-next neighbors.

possible linkages of atoms which may carry through the superexchange interaction between two adjacent  $\text{Co}^{2+}$  ions leads to the conclusion that the coupling  $J_1$  between the planes is weaker than the coupling  $J$  in the planes, and that the  $J_2$  coupling is almost negligible. This leads several authors<sup>12-14</sup> to believe that  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  has some two-dimensional characteristics. However, even an approximate two-dimensionality of the system would not be the source of the different temperature dependence of the critical field since the magnetization in two dimensions is divergent at any nonzero temperature, unless the system is of the Ising-Heisenberg type.

It is the anisotropy of the exchange interactions that matters. Now how does this anisotropy come about? According to Date,<sup>15</sup> Metselaar *et al.*<sup>13</sup> and authors cited therein, this is due to a strong crystal field acting on the  $\text{Co}^{2+}$  ions. In the cubic (octahedral) crystal field the ground state  $^4F$  of the single ion gets split into three levels. The lowest orbital triplet  $\Gamma_4$  is subsequently split into six Kramers doublets by mainly tetragonal and slightly orthorhombic components of the field. The orthorhombic component appears because the  $\text{H}_2\text{O}$  ring surrounding  $\text{Co}^{2+}$  is not completely quadratic and, moreover, the other two waters, which do not belong to the cobalt octahedral unit, produce some contribution to the field. Since the distance between the lowest Kramers doublet and the nearest-higher energy level is about  $10^\circ\text{K}$ , whereas the Néel temperature is  $2.29^\circ\text{K}$ , the exchange energy is smaller than the doublet's separation and the spin degrees of freedom of the  $\text{CO}^{2+}$  ion are effectively reduced to two, instead of  $2 \times \frac{3}{2} + 1$ . The

magnetic properties of the system have to be described in terms of an effective fictitious spin  $s' = \frac{1}{2}$  with anisotropic exchange interactions and anisotropic Landé factors. Kimura<sup>16</sup> estimates that

$$J^x = 0.61 \times 1.19k_B, \quad J^y = 0.61 \times 3.59k_B,$$

$$J^z = 0.61 \times 3.81k_B;$$

$$J_1^x = 0.46 \times 1.19k_B, \quad J_1^y = 0.46 \times 3.59k_B,$$

$$J_1^z = 0.46 \times 3.81k_B;$$

$$J_2^x = 0.08 \times 1.19k_B, \quad J_2^y = 0.08 \times 3.59k_B,$$

$$J_2^z = 0.08 \times 3.81k_B.$$

Two conclusions are to be drawn from inspection of these numbers: The first one is that the approximate two dimensionality of the compound is not justified as  $J_1/J \approx \frac{3}{4}$ , the second is that  $J_2$  can be treated as a small correction to  $J$  and  $J_1$ . There are also known some data on the Landé factors. Haseda<sup>11</sup> reports  $g_y = g_z = 4.9$ ,  $g_x = 2.9$ , Date<sup>15</sup> gives  $g_y = 5.0$ ,  $g_z = 4.0$ ,  $g_x = 2.9$ , whereas Flippen and Friedberg<sup>17</sup> have measured  $g_x = 2.7$ ,  $g_y = 5.0$ ,  $g_z = 4.9$ . These results are not too consistent with the above exchange constants since  $J^z > J^y$ .

Spin-wave theory for  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  in all its three phases has already been worked out by Iwashita and Uryû,<sup>18</sup> with the use of Kimura's exchange constants, for the purpose of numerical analysis of the susceptibilities. The authors did not explicitly find the temperature-renormalized magnon frequencies and they did not reach the important conclusion about the power law describing the coexistence curve. They did, however, claim to achieve a good theoretical fit to that curve.

We will slightly generalize their Hamiltonian in order to be able to discuss a wider class of systems. First of all, we will not assume any relations among the nine exchange constants. However,  $J_2$  is still considered as much weaker than  $J$ . Moreover we introduce some extra, not included yet in the values of the effective exchange constants, single-ion uniaxial  $D$  and orthorhombic  $E$  anisotropies. These single-ion anisotropies are considered as much weaker than the exchange field. Otherwise, we would have to modify<sup>19</sup> the Holstein-Primakoff<sup>4</sup> representation of the spin operators. The spin can attain any value. In the case of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , it is the fictitious spin of  $\frac{1}{2}$ .

In the paramagnetic phase, the division of spins into sublattices disappears and the the Hamiltonian for the model reads (for applied field along the  $c$  axis)

$$\begin{aligned} \mathcal{H} = & \sum_{\langle i, j \rangle} (J^x S_i^x S_j^x + J^y S_i^y S_j^y + J^z S_i^z S_j^z) + \sum_{\langle i, \nu \rangle} (J_1^x S_i^x S_\nu^x + J_1^y S_i^y S_\nu^y + J_1^z S_i^z S_\nu^z) \\ & + \sum_{\langle i, \nu \rangle} (J_2^x S_i^x S_\nu^x + J_2^y S_i^y S_\nu^y + J_2^z S_i^z S_\nu^z) - H \sum_i S_i^z - D \sum_i (S_i^z)^2 + \frac{1}{2} E \sum_i [(S_i^+)^2 + (S_i^-)^2]. \end{aligned} \quad (1)$$

$H$  denotes the magnetic field multiplied by the Bohr magneton and the appropriate Landé factor.

With the use of the Holstein-Primakoff representation ( $\hbar = 1$ )

$$S_i^x = (\frac{1}{2}s)^{1/2}(a_i^\dagger + a_i) - (\frac{1}{4})(2s)^{-1/2}[a_i^\dagger a_i^2 + (a_i^\dagger)^2 a_i] + \dots, \quad (2a)$$

$$S_i^y = i\frac{1}{2}s(a_i^\dagger - a_i) + (i/4)(2s)^{-1/2}[a_i^\dagger a_i^2 - (a_i^\dagger)^2 a_i] + \dots, \quad (2b)$$

$$S_i^z = s - a_i^\dagger a_i, \quad (2c)$$

$$(S_i^+)^2 = (2s - \frac{1}{2})a_i^2 - a_i^\dagger a_i^3 + \dots, \quad (2d)$$

$$(S_i^-)^2 = (2s - \frac{1}{2})(a_i^\dagger)^2 - (a_i^\dagger)^3 a_i + \dots, \quad (2e)$$

and the Fourier transformations  $a_i = N^{-1/2} \sum_k a_k e^{ikr}$ , etc., we transform (1) into

$$\mathcal{H}C = E_0 + \mathcal{H}C_0 + \delta\mathcal{H}C + \dots,$$

$$\mathcal{H}C_0 = \sum_k \alpha(k) a_k^\dagger a_k + \frac{1}{2} \sum_k \mathfrak{G}(k) (a_k^\dagger a_{-k}^\dagger + a_k a_{-k}), \quad (3)$$

$$\delta\mathcal{H}C = \frac{1}{N} \sum_{1234} \delta(k_1 + k_2 - k_3 - k_4) \mathfrak{C}(1, 4) a_{k_1}^\dagger a_{k_2}^\dagger a_{k_3} a_{k_4} + \frac{1}{N} \sum_{1234} \delta(k_1 + k_2 + k_3 - k_4) \mathfrak{G}(1) (a_{k_1}^\dagger a_{k_2}^\dagger a_{k_3}^\dagger a_{k_4} + a_{k_4}^\dagger a_{k_3}^\dagger a_{k_2}^\dagger a_{k_1}),$$

where

$$E_0 = Ns[s(2J^z + J_1^z + J_2^z) - H - Ds], \quad (4a)$$

$$\mathfrak{G}(k) = -2s(2J^z + J_1^z + J_2^z) + H - D(2s - 1) + \frac{1}{2}s(J^x + J^y)\gamma(k) + \frac{1}{2}s(J_1^x + J_1^y)\gamma_1(k^x) + \frac{1}{2}s(J_2^x + J_2^y)\gamma_2(k^y), \quad (4b)$$

$$\mathfrak{G}(k) = E(2s - \frac{1}{2}) + \frac{1}{2}s(J^x - J^y)\gamma(k) + \frac{1}{2}s(J_1^x - J_1^y)\gamma_1(k^x) + \frac{1}{2}s(J_2^x - J_2^y)\gamma_2(k^y), \quad (4c)$$

$$\begin{aligned} \mathfrak{C}(1, 4) = & -D + \frac{1}{2}J^z\gamma(k_4 - k_1) + \frac{1}{2}J_1^z\gamma_1(k_4^x - k_1^x) + \frac{1}{2}J_2^z\gamma_2(k_4^y - k_1^y) - \frac{1}{8}(J^x + J^y)[\gamma(k_1) + \gamma(k_4)] \\ & - \frac{1}{8}(J_1^x + J_1^y)[\gamma_1(k_1^x) + \gamma_1(k_4^x)] - \frac{1}{8}(J_2^x + J_2^y)[\gamma_2(k_1^y) + \gamma_2(k_4^y)], \end{aligned} \quad (4d)$$

$$\mathfrak{G}(1) = \frac{1}{2}E + \frac{1}{8}(J^y - J^x)\gamma(k_1) + \frac{1}{8}(J_1^y - J_1^x)\gamma_1(k_1^x) + \frac{1}{8}(J_2^y - J_2^x)\gamma_2(k_1^y). \quad (4e)$$

In Eq. (4) the following definitions were adopted:

$$\begin{aligned} \gamma(k) &= \sum_{j(a,b)}^{mn} e^{ik\delta_j} \\ &= 4 \cos(k^y \frac{1}{2}b) \cos(\frac{1}{2}a) [k^x \cos(\beta - 90^\circ) \\ &\quad - k^y \sin(\beta - 90^\circ)], \end{aligned} \quad (5a)$$

$$\gamma_1(k^x) = 2 \cos k^x c, \quad (5b)$$

$$\gamma_2(k^y) = 2 \cos k^y b. \quad (5c)$$

Due to transverse anisotropy in the exchange interactions in any of the three couplings, or due to presence of an orthorhombic anisotropy, the Holstein-Primakoff bosons  $a_k^\dagger, a_k$  no longer describe the eigenmodes of the system of spins forced to be aligned in one direction. This is seen from the occurrence of the nondiagonal term  $B(k)$  in the Hamiltonian (3). Such a term was absent in the previous theories.<sup>1-3</sup>

In the harmonic approximation, the magnon frequency is no longer equal to the coefficient  $\alpha(k)a_k^\dagger a_k$  in (3), but becomes

$$\omega_0(k) = [\alpha^2(k) - \mathfrak{G}^2(k)]^{1/2}. \quad (6)$$

If we assume that the  $J_2$  coupling has only a perturbational influence and put  $J_2 = 0$ , this frequency is minimal at wave vectors  $\vec{k}_0$  for which  $\gamma(k_0) = -4$

and  $\gamma_1(k_0^x) = -2$ . There are eight such vectors:

$$\vec{k}_0^{(1)} = \hat{x} \frac{\pi}{c} \tan(\beta - 90^\circ) + \hat{y} \frac{2\pi}{b} + \hat{z} \frac{\pi}{c}, \quad (7a)$$

$$\vec{k}_0^{(2)} = \hat{x} \frac{\pi}{c} \tan(\beta - 90^\circ) - \hat{y} \frac{2\pi}{b} + \hat{z} \frac{\pi}{c}, \quad (7b)$$

$$\vec{k}_0^{(3)} = \hat{x} \left( \frac{\pi}{c} \tan(\beta - 90^\circ) + \frac{2\pi}{a \cos(\beta - 90^\circ)} \right) + \hat{z} \frac{\pi}{c}, \quad (7c)$$

$$\vec{k}_0^{(4)} = \hat{x} \left( -\frac{\pi}{c} \tan(\beta - 90^\circ) + \frac{2\pi}{a \cos(\beta - 90^\circ)} \right) - \hat{z} \frac{\pi}{c}, \quad (7d)$$

and  $-\vec{k}_0^{(1)}, -\vec{k}_0^{(2)}, -\vec{k}_0^{(3)}, -\vec{k}_0^{(4)}$ . Now, the direct magnetic lattice is spanned by the primitive vectors

$$\begin{aligned} \vec{a}_1 &= \hat{x} (\frac{1}{2}a) \cos(\beta - 90^\circ) - \hat{y} b/2 \\ &\quad - \hat{z} (\frac{1}{2}a) \sin(\beta - 90^\circ), \end{aligned} \quad (8a)$$

$$\begin{aligned} \vec{a}_2 &= \hat{x} (\frac{1}{2}a) \cos(\beta - 90^\circ) + \hat{y} b/2 \\ &\quad - \hat{z} (\frac{1}{2}a) \sin(\beta - 90^\circ), \end{aligned} \quad (8b)$$

$$\vec{a}_3 = \hat{z} c. \quad (8c)$$

If we construct the reciprocal lattice primitive vectors  $\vec{b}_1, \vec{b}_2, \vec{b}_3$  out of the appropriate products of  $\vec{a}_1,$

$\vec{a}_2, \vec{a}_3$  we will find that

$$\vec{k}_0^{(1)} = \frac{1}{2}(\vec{b}_3 + \vec{b}_2 - \vec{b}_1), \quad (9a)$$

$$\vec{k}_0^{(2)} = \frac{1}{2}(\vec{b}_3 + \vec{b}_1 - \vec{b}_2), \quad (9b)$$

$$\vec{k}_0^{(3)} = \frac{1}{2}(\vec{b}_3 + \vec{b}_1 + \vec{b}_2), \quad (9c)$$

$$\vec{k}_0^{(4)} = \frac{1}{2}(\vec{b}_1 + \vec{b}_2 - \vec{b}_3). \quad (9d)$$

This means that all  $\vec{k}_0$ 's lie at the corners of the Brillouin zone.

Since the expression under the root sign in Eq. (6) does not form a perfect square,  $\omega_0(k)$  is linear in  $|\vec{k}_0 - \vec{k}|$  in the vicinity of any  $\vec{k}_0$ . Moreover  $\omega_0(k)$  is the same function of the variable  $\vec{k}_0 - \vec{k}$  for any  $\vec{k}_0$ .

The paramagnetic phase becomes unstable when  $\omega_0(k_0) = 0$ , which happens if

$$\alpha(k_0) = \pm \mathfrak{B}(k_0). \quad (10)$$

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$$i \frac{da_k}{dt} = [\alpha(k) + \bar{\alpha}(k)]a_k + [\mathfrak{B}(k) + \bar{\mathfrak{B}}(k)]a_k^\dagger, \quad (13)$$

where

$$\alpha(k) = \frac{1}{N} \sum_{k_1} \{ \mathfrak{C}(1, 1) + \mathfrak{C}(k_1, k) + 2\mathfrak{C}(k, 1) \} \langle a_{k_1}^\dagger a_{k_1} \rangle + 2[\mathfrak{G}(k) + 2\mathfrak{G}(1)] \langle a_{k_1} a_{-k_1} \rangle, \quad (14)$$

$$\bar{\alpha}(k) = \frac{1}{N} \sum_{k_1} \{ 2\mathfrak{C}(k_1, 1) \langle a_{k_1} a_{-k_1} \rangle + 2[2\mathfrak{G}(k) + \mathfrak{G}(1)] \langle a_{k_1}^\dagger a_{k_1} \rangle \}. \quad (15)$$

The temperature-dependent averages are to be evaluated with respect to  $\mathcal{H}_0$ . The temperature-dependent frequency becomes

$$\omega(k, T) = \{ [\alpha(k) + \bar{\alpha}(k)]^2 - [\mathfrak{B}(k) + \bar{\mathfrak{B}}(k)] \}^{1/2}. \quad (16)$$

This frequency vanishes at  $\vec{k}_0$  when

$$\begin{aligned} H_c^\pm &= H_{c0}^\pm \pm \mathfrak{B}(k_0) - \bar{\alpha}(k_0) \\ &= H_{c0}^\pm - \frac{1}{N} \sum_{k_1} [W_\pm(1) \langle a_{k_1}^\dagger a_{k_1} \rangle |_{H_{c0}^\pm} + V_\pm(1) \langle a_{k_1} a_{-k_1} \rangle |_{H_{c0}^\pm}], \end{aligned} \quad (17)$$

with

$$W_\pm(1) = \pm 3E - 4D + J^z [4 - \gamma(k_1)] + J_1^z [2 - \gamma_1(k_1^z)] + 4J^{y,x} + 2J_1^{y,x} - \gamma(k_1) (\frac{3}{4}J^{y,x} + \frac{1}{4}J^{x,y}) - \gamma_1(k_1^z) (\frac{3}{4}J_1^{y,x} + \frac{1}{4}J_1^{x,y}), \quad (18a)$$

$$V_\pm(1) = -3E \mp \{ -2D + 2J^{y,x} + J_1^{y,x} - \gamma(k_1) (J^z + \frac{3}{4}J^{y,x} - \frac{1}{4}J^{x,y}) - \gamma_1(k_1^z) (J_1^z + \frac{3}{4}J_1^{y,x} - \frac{1}{4}J_1^{x,y}) \}. \quad (18b)$$

Since the harmonic Hamiltonian is diagonalized<sup>4,21</sup> under the transformation

$$a_k = (1/\sqrt{2}) [\alpha^2(k) - \mathfrak{B}^2(k)]^{-1/4} \{ \alpha(k) + [\alpha^2(k) - \mathfrak{B}^2(k)]^{1/2} \}^{1/2} b_k - \{ \alpha(k) - [\alpha^2(k) - \mathfrak{B}^2(k)]^{1/2} \}^{1/2} b_{-k}^\dagger, \quad (19)$$

where  $b_k$ 's are again Bose operators, we get

$$\langle a_k^\dagger a_k \rangle = \frac{1}{2} \left( \frac{\alpha(k)}{\omega_0(k)} - 1 \right) + \frac{\mathfrak{B}(k)}{\omega_0(k)} \langle b_k^\dagger b_k \rangle, \quad (20)$$

$$\langle a_k a_{-k} \rangle = \langle a_k^\dagger a_{-k}^\dagger \rangle = -\frac{\mathfrak{B}(k)}{2\omega_0(k)} - \frac{\mathfrak{B}(k)}{\omega_0(k)} \langle b_k^\dagger b_k \rangle. \quad (21)$$

This allows us to bring (17) to the form

$$H_c^\pm = H_{c0}^\pm - \Delta H^\pm(0) - \Delta H^\pm(T), \quad (22)$$

where

The upper sign yields

$$\begin{aligned} H_{c0}^+ &= -D(2s - 1) + E(2s - \frac{1}{2}) \\ &\quad + 4s(J^z + J^y) + 2s(J_1^z + J_1^y), \end{aligned} \quad (11a)$$

and the lower one

$$\begin{aligned} H_{c0}^- &= -D(2s - 1) - E(2s - \frac{1}{2}) \\ &\quad + 4s(J^z + J^x) + 2s(J_1^z + J_1^x). \end{aligned} \quad (11b)$$

The critical field  $H_{c0}^+$  is bigger than  $H_{c0}^-$  when

$$2J^y + J_1^y \geq -E(2 - 1/2s) + 2J^x + J_1^x. \quad (12)$$

Therefore the first solution holds when (12) is satisfied, whereas the second one holds when the inequality (12) is reversed.

Now we will include the effects of renormalization. In the random-phase approximation employed, for instance, by Feder and Pytte<sup>3</sup> (see also Ref. 20), the equation of motion for  $a_k$  reads

$$\Delta H^\pm(0) = \frac{1}{2N} \sum_{\mathbf{k}_1} \left[ W_\pm(1) \left( \frac{k_1}{\omega_0(k_1)} \Big|_{H_{c0}^\pm} - 1 \right) - V_\pm(1) \frac{\mathfrak{B}(k_1)}{\omega_0(k_1)} \Big|_{H_{c0}^\pm} \right] \quad (23)$$

$$\Delta H^\pm(T) = \frac{1}{N} \sum_{\mathbf{k}_1} \frac{\langle b_{\mathbf{k}_1}^\dagger b_{\mathbf{k}_1} \rangle}{\omega_0(k_1)} \Big|_{H_{c0}^\pm} [W_\pm(1) \mathfrak{A}(k_1) \Big|_{H_{c0}^\pm} - V_\pm(1) \mathfrak{B}(k_1)]. \quad (24)$$

$\Delta H^\pm(0)$  represents the zero-point correction. The physical origin of this correction is the nonoptimal choice of the eigenmodes of the system resulting from the fact that the real ground state is unknown. Mathematically,  $\Delta H^\pm(0)$  comes from commutators arising when the normal order in the quartic terms of the Hamiltonian is introduced. For the transversally isotropic exchange and for  $E=0$ ,  $\Delta H^\pm(0)$  vanishes. The experimental value of  $H_{c0}^\dagger - \Delta H^\dagger(0)$  (divided by the  $g$  factor and the Bohr magneton) for  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  is 41.15 kOe.<sup>7</sup>

We will be concerned with the temperature-dependent correction only. The dominant contributors to  $\Delta H^\pm(T)$  are those wave vectors which are close to any of the  $\vec{k}_0$  vectors. This allows us to replace the quantities in the curly brackets in Eq. (24) by their values at  $\vec{k}_0$ , which leaves out terms quadratic in  $(\vec{k}_0 - \vec{k})$ .

In order to find the dominant term in the frequency, we make the expansion

$$\mathfrak{A}(k) = \mathfrak{A}(k_0) + s(J^x + J^y) \left( \frac{1}{2} b \right)^2 (k_0^y - k^y)^2 + \left( \frac{1}{2} s \right) (J_1^x + J_1^y) c^2 (k_0^z - k^z)^2 + s(J^x + J^y) \left( \frac{1}{2} a \right)^2 [(k_0^x - k^x) \cos(\beta - 90^\circ) - (k_0^z - k^z) \sin(\beta - 90^\circ)]^2 + \dots, \quad (25a)$$

$$\mathfrak{B}(k) = \mathfrak{B}(k_0) + s(J^x - J^y) \left( \frac{1}{2} b \right)^2 (k_0^y - k^y)^2 + \left( \frac{1}{2} s \right) (J_1^x - J_1^y) c^2 (k_0^z - k^z)^2 + s(J^x - J^y) \left( \frac{1}{2} a \right)^2 [(k_0^x - k^x) \cos(\beta - 90^\circ) - (k_0^z - k^z) \sin(\beta - 90^\circ)]^2 + \dots. \quad (25b)$$

Since at the critical field Eq. (10) holds, we get

$$\omega_0(k) \Big|_{H_{c0}^\pm} = [sJ^{y,x} \mathfrak{A}(k_0) \Big|_{H_{c0}^\pm}]^{1/2} [b |k_0^y - k^y| + a |(k_0^x - k^x) \cos(\beta - 90^\circ) - (k_0^z - k^z) \sin(\beta - 90^\circ)| + c(2J_1^{y,x})^{1/2} |k_0^z - k^z|] + \dots, \quad (26)$$

where the quadratic and higher-order terms have been omitted. Now we select one of the wave vectors  $\vec{k}_0$ , say  $\vec{k}_0^{(1)}$ , introduce the variable  $\vec{q} = \vec{k}_0^{(1)} - \vec{k}$ , and transform (24) into

$$\Delta H(T) = 6(J^{y,x})^{-1/2} \left[ 2(J^{y,x} - J^{x,y}) + (J_1^{y,x} - J_1^{x,y}) \pm E(2 - 1/2s) \right]^{1/2} (2J^z + J_1^z + 2J^{y,x} + J_1^{y,x} - D \pm E) f(T) + \dots, \quad (27)$$

where

$$f(T) = \frac{1}{N} \sum_{\mathbf{q}} \frac{\{\exp[\omega_0(k_0^{(1)} - q)/k_B T] - 1\}^{-1}}{b |q^y| + a |q^x \cos(\beta - 90^\circ) - q^z \sin(\beta - 90^\circ)| + c(2J_1^{y,x}/J^{y,x})^{1/2} |q^z|} \quad (28)$$

The sum in (28) is not restricted to such directions of the wave vectors which do not cross Brillouin zone walls, intersecting at the corner  $\vec{k}_0^{(1)}$ . This is because the contributions from the vicinities of the other seven vectors  $\vec{k}_0$  make up for the whole space summation.

When the summation is replaced by the integration, simple change of variables shows that  $f(T)$  is proportional to  $(T/s)^2$  and not to  $(1/s)(T/s)^{3/2}$ . In particular, for an orthorhombic lattice, where  $\beta = 90^\circ$ ,  $f(T)$  becomes

$$f(T) = \frac{1}{\sqrt{2}} \left( \frac{k_B T}{s} \right)^2 \frac{\xi(2)}{(2\pi)^2} \frac{V}{Nabc} (J^{y,x} J_1^{y,x})^{-1/2} \left[ 2(J^{y,x} - J^{x,y}) + J_1^{y,x} - J_1^{x,y} \pm E(2 - 1/2s) \right]^{1/2}. \quad (29)$$

Expression (29) was derived by means of the following steps. First,  $q^y$  was rescaled by introduction of the variable  $\tilde{q}^y = q^y b/a$ , then it was noted that for small  $q$ ,  $|q^x| + |\tilde{q}^y| \approx [(q^x)^2 + (\tilde{q}^y)^2]^{1/2}$ ; finally, integration in spherical coordinates was performed.

In the case when  $E = D = 0$  Eq. (27) gives

$$\Delta H(T) = \frac{3\sqrt{2} \xi(2)}{(2\pi)^2} \left( \frac{k_B T}{s} \right)^2 \frac{V}{Nabc} \frac{2J^z + J_1^z + 2J^{y,x} + J_1^{y,x}}{J^{y,x} [J_1^{y,x} \{ 2(J^{y,x} - J^{x,y}) + J_1^{y,x} - J_1^{x,y} \}]^{1/2}}. \quad (30)$$

This formula, although derived for  $\beta = 90^\circ$  and  $J_2 = 0$ , gives quite satisfactory agreement with the experiment<sup>7</sup> on  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ . If we take Kimura's<sup>16</sup> exchange constants and Haseda's<sup>11</sup>  $g_z$ -factor, and put  $V/Nabc = \frac{1}{2}$ , as there are two spins per elementary crystallographic cell, we obtain 2.35 kOe for  $\Delta H(T)$  at  $T = 1^\circ\text{K}$ , whereas the measured value is 1.93 kOe.

The  $T^2$  dependence is not surprising in the light of the following heuristic argument due to Keffer and Loudon<sup>22</sup> and its extension by Anderson and Callen.<sup>2</sup> Consider first a ferromagnet at a low temperature and imagine an extra spin wave is being generated there. The new wave will move in the background of already existing spin waves, which have predominantly long wavelengths. This extra excitation constitutes a deviation from the previous instantaneous positions of spins. Therefore, the energy required to excite the new wave drops proportionally to an average angle made by one of the neighboring spins with the resultant spin of the pair. This leads to the conclusion that the temperature renormalization of the frequency goes like the energy.

On the other hand, in isotropic antiferromagnets in their paramagnetic phase, short wavelengths are dominant at low temperatures. In such modes, spins oscillate essentially in antiphase. An additional wave now sees not instantaneous but average positions of the already present motions. It means that a given spin detects only the  $z$  component of the spin of its neighbor, so renormalization goes like magnetization. More specifically, the exchange energy appears to be multiplied by  $1 - 2\Delta M(T)/M_0$  in the renormalized frequency, where  $M_0$  is a magnetization at  $T=0^\circ\text{K}$  and  $\Delta M(T)$  is  $M_0 - M(T)$ . The factor of 2 follows from the self-energy considerations. This leads to the relation

$$H_c(T) = H_{c0} [1 - 2\Delta M(T)/M_0]. \quad (31)$$

In the case of the anisotropic antiferromagnet, we still expect the renormalized frequency to behave roughly like magnetization. However, since the magnetization is no longer a constant of the motion, as it precesses elliptically, the amplitude of the temperature correction is only approximately reproduced by Eq. (31). Namely, (31) yields (if the zero-point corrections are neglected)

$$H_c^\pm(T) = H_{c0}^\pm \left( 1 - \frac{2}{Ns} \sum_{k_1} \frac{1}{e^{\omega_0(k_1)/k_B T} - 1} \frac{\alpha(k_1)}{\omega_0(k_1)} \right) \Big|_{H_{c0}^\pm}. \quad (32)$$

When the small- $k$  expansion is employed we arrive at a formula which reproduces Eq. (27) except for the factor of 6 which is replaced by 4, and except for some additional  $E$  and  $D$  terms which are proportional to  $1/s$ . It turns out also that the zero-temperature corrections are not right in this picture.

Consider now an antiferromagnet with small exchange and orthorhombic anisotropies. Then  $\mathfrak{B}(k)$  can give some contribution in the immediate vicinity of  $\vec{k}_0$ . In this case,  $\omega_0$  is linear at very small wave vectors ( $\vec{k}_0 - \vec{k}$ ) and then becomes quadratic. In this situation, we expect to find the coexistence curve to behave as  $T^2$  at extremely low tempera-

tures. For somewhat higher temperatures, when an effectively quadratic dispersion relation has to be used, the curve should exhibit the  $T^{3/2}$  law. Such behavior seems to have to be more common, since even in perfectly isotropic antiferromagnets there are always present dipole-dipole interactions which produce the off-diagonal terms  $a_k^\dagger a_{-k}^\dagger + a_k a_{-k}$ . If a transition between  $T^2$  and  $T^{3/2}$  laws can at all be detected, this could be possibly done for an antiferromagnet with high Néel temperature. Unfortunately, this involves very large magnetic fields.

Note that in substances which exhibit a  $T^2$  coexistence curve, a parallel pumping experiment should be very efficient due to strong ellipticity of the spin precession.

Consider finally the effect of the magnetic field applied along a transverse direction, say along the  $x$  axis. For a nonzero field in such a configuration, only spin-flop and paramagnetic phases are allowed. In the paramagnetic phase, the  $x$  direction forms the proper quantization axis for the Holstein-Primakoff excitations.  $\alpha(k)$ , as given by Eq. (4b), is replaced by

$$\alpha^x(k) = -4sJ^x - 2sJ_1^x + (\frac{1}{2}s)(J^y + J^z)\gamma(k) + (\frac{1}{2}s)(J_1^y + J_1^z)\gamma_1(k^x) + H - D(s - \frac{1}{2}) - 3E(s - \frac{1}{2}), \quad (33)$$

and  $\mathfrak{B}(k)$  by

$$\mathfrak{B}^x(k) = (\frac{1}{2}s)(J^x - J^y)\gamma(k) + (\frac{1}{2}s)(J_1^x - J_1^y)\gamma_1(k^x) + E(s - \frac{1}{4}) - D(s - \frac{1}{4}). \quad (34)$$

The frequency is again linear around  $\vec{k}_0$ . Now the uniaxial and orthorhombic anisotropies together with the difference between the exchange constants for  $y$  and  $z$  directions contribute to the off-diagonal term  $\mathfrak{B}^x(k)$ . If

$$2J^y + J_1^y \geq 2J^z + J_1^z + (D - E)(1 - 1/4s) \quad (35)$$

then, in the harmonic approximation, the critical field is given by

$$H_{c0}^{x+} = -\frac{1}{4}D + E(4s - \frac{7}{4}) + 2s(2J^x + J_1^x) + 2s(2J^y + J_1^y). \quad (36)$$

If the opposite condition holds we get

$$H_{c0}^{x-} = D(2s - \frac{3}{4}) + E(2s - \frac{5}{4}) + 2s(2J^x + J_1^x) + 2s(2J^z + J_1^z). \quad (37)$$

The temperature-dependent corrections again go like  $T^2$ . This is in qualitative agreement with Rives and Bhatia,<sup>7</sup> who observe that the shape of the coexistence curve does not depend on the direction of the applied field.

### III. CRITICAL FIELD IN $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ AND $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$

Crystallographically  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  is isomorphic to  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ .<sup>15,23</sup> It is a monoclinic crystal with

$a = 10.23 \text{ \AA}$ ,  $b = 7.05 \text{ \AA}$ ,  $c = 6.57 \text{ \AA}$ , and  $\beta = 122^\circ 10'$ . The neutron diffraction studies by Kleinberg<sup>24</sup> and the susceptibility measurements by Hamburger-Friedberg<sup>25</sup> show that the preferred direction  $a_{\parallel}$  lies in the  $ac$  plane and is tilted from the  $a$  axis by roughly  $10^\circ$ . This direction defines the new  $z$  axis. The new  $y$  axis lies in the  $ca$  plane and is perpendicular to  $a_{\parallel}$ . Finally, the new  $x$  axis is parallel to the  $b$  direction. The spin has the value  $s = 1$ . According to Kimura,<sup>26</sup> the exchange interactions in  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  are isotropic and  $J = (2.4 \pm 0.1)k_B$ ,  $J_1 = (0.5 \pm 0.2)k_B$ . The Landé factor is also isotropic<sup>25,27</sup> and is equal to 2.22. The anisotropy is of single-ion origin and it is mostly uniaxial<sup>25</sup> with  $D = (-1.5 \pm 0.5)k_B$ . It has also an orthorhombic contribution which is equal to  $E = (0.26 \pm 0.40)k_B$ .

Since in the experiment of Oliveira *et al.*<sup>5</sup> not a  $T^2$  but a  $T^{3/2}$  curve was obtained, we conclude that probably the actual value of the orthorhombic anisotropy is too small to give a  $T^2$  law in the measured range of temperatures, or perhaps the experiment was not accurate enough. For instance, a nonspherical sample was used there and a correction for the demagnetizing factor was not considered.

The magnetic structure of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  was in-

vestigated by Spence-Nagarajan<sup>28</sup> and Altman.<sup>29</sup> This compound has a monoclinic structure with  $\beta = 99^\circ 74'$  and the preferred spin direction is tilted by  $7^\circ$  from the  $c$  axis or by  $2.8^\circ$  from the axis which is perpendicular to the  $ab$  plane. The spin has the value of  $\frac{5}{2}$ . The exchange interactions seem to Rives and Benedict,<sup>6</sup> at least in the transverse directions, to be isotropic. On the other hand, some evidence against this view is presented in the paper by Abkowitz and Honig<sup>30</sup> in which observation of slightly transversally anisotropic  $g$  factor is reported.

Anyway, the orthorhombic anisotropy appears to be substantial in this material. Rives and Benedict estimate the exchange field to be  $10.375 \pm 0.03$  kOe, but the anisotropy fields in two perpendicular-to-the-preferred-axis directions to be  $2.20 \pm 0.05$  kOe and  $3.80 \pm 0.05$  kOe. This orthorhombic anisotropy seems to us mainly responsible for the lack of the  $T^{3/2}$  dependence in  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ .

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