CHAPTER II
MAGNETIC AND STRUCTURAL INVESTIGATIONS ON NiI₂ AND CoI₂

ABSTRACT

In this chapter we discuss the magnetic and structural properties of NiI₂ and CoI₂. Measurements of the susceptibilities of NiI₂ reveal two phase transitions, a magnetic ordering temperature and a structural phase transition, which is investigated with X-ray diffraction. The nuclear and magnetic structures are examined with neutron diffraction. It is found that the nuclear symmetry is lowered from trigonal to monoclinic or triclinic. The magnetic structure of NiI₂ is of helix-1 type. The anisotropy of the susceptibilities of CoI₂ for \( H \perp c \) and \( H//c \) is explained in terms of a single-ion anisotropy, which forces the spins in the ab-plane. Neutron diffraction on CoI₂ shows a similar magnetic ordering as NiI₂ (helix 1). The stability diagrams for trigonal layer compounds are calculated with the help of the theory of Rastelli. It is found that the solutions for CoI₂ and NiI₂ are close to the phase boundary between regions where ferromagnetic layer and helix-1 type structures, respectively, are stable. The observed spiral angles are explained in terms of intra- and interlayer exchange interactions.
II.1 INTRODUCTION

The dihalides of Ni and Co are layer compounds, crystallizing in the CdCl_2 and Cd(OH)_2 structure [1]. These structures consist of slabs of A-M-A (A is the anion, M is the metal ion), which are weakly interacting. The metal ion is octahedrally surrounded by six halogen ions.

Most of the magnetic investigations of the dihalides of nickel and cobalt concern the chlorides and the bromides. Experiments performed are neutron scattering, both elastic [2-4] as well as inelastic [5,6], Raman experiments [7] and optical measurements in the visible region [3,8,9]. CoCl_2 and NiCl_2 have ferromagnetic layers, which are coupled antiferromagnetically. Both compounds have relatively simple two-sublattice interactions. As the behaviour of the chlorides is quite simple, that of the bromides becomes more complicated. The reason is perhaps that the exchange interactions via the bromine ions are more long-range. The magnetic structure of NiBr_2 between 60 K and 20 K is simply that of NiCl_2, but becomes puzzling below 20 K. Many suggestions have been made on the low-temperature structure including canted spins. Very recently a neutron diffraction study of NiBr_2 single crystals [4] revealed a helix-2 type magnetic structure. The results disagree with the data obtained by Day [3]. The stability of the magnetic structure of NiBr_2 is discussed in Section II.8.

The diiodides of nickel and cobalt have not been studied extensively. Mössbauer experiments on NiI_2 [10] suggest the same surrounding of all iodine ions by three parallel Ni spins at 4.2 K. According to these data the spins of nickel would make an angle of about 63 degrees with the direction of the field gradient, parallel to the c-direction. In the case of CoI_2 [10] Mössbauer experiments indicated that CoI_2 too would consist of ferromagnetic layers of Co spins, lying in the basal ab-plane, coupled antiferromagnetically in the c-direction.

Billerey et al. [11,12] recorded a neutron diffractogram of NiI_2 at 4.2 K. Their diffractogram only revealed one magnetic reflection. From this information only, they claimed to have deduced the direction of 48 nickel spins. These authors excluded the possibility of ferromagnetic Ni^{2+} layers.

In this chapter we report the growth of single crystals of NiI_2 and CoI_2, and measurements of the anisotropy and temperature dependence of the magnetic susceptibilities. The crystallographic and the magnetic structures of NiI_2 and CoI_2 are studied with X-ray and neutron diffraction. In NiI_2 the trigonal symmetry is distorted. Both NiI_2 and CoI_2 have a magnetic structure of a helix type. These proposed structures are different from structures proposed earlier.
in the literature. Finally, the stability of the magnetic structures of compounds with hexagonal layers of metal ions is discussed.

II.2 GROWTH OF SINGLE CRYSTALS OF NiI₂ AND CoI₂

NiI₂ can easily be synthesized from the elements at a temperature of 750°C. Preparation and growth of single crystals (black shiny platelets) were carried out in the same quartz tube. A temperature gradient of about 50°C was applied. A small excess of iodine was used, which promoted the transport of NiI₂ to the cold side of the tube. The single crystals obtained, have an area of about 0.25 cm², but are only 0.01 cm thick. For neutron and X-ray experiments, we preferred much smaller crystals, which were grown using a temperature gradient of 500°C; each day small crystals were moved to the coldest point in the tube. Before filling the sample holder the crystals were passed through a 0.05 cm sieve.

Because the magnetic effect of a single thin crystal of NiI₂ is small, we have also grown thick single crystals using a Bridgman oven. Care should be taken, because just before melting NiI₂ partially decomposes at 760°C into metallic nickel and an iodine-rich phase. We have evidence that this process is reversible; still some metallic nickel formed must be removed by moving the tube slowly through the temperature gradient of the oven.

CoI₂ was synthesized from the elements in quartz tubes at about 500°C. The temperature gradient applied to the tube was about 75°C. CoI₂ is a black crystalline solid, and resembles NiI₂. A second modification of CoI₂, called β-CoI₂, which was reported to form by sublimation of black α-CoI₂ at 570°C in high vacuum, has not been found [13]. CoI₂ does not decompose before melting (m.p. 515°C), so that the Bridgman technique can be used without problems.

NiI₂ is hygroscopic and CoI₂ is very hygroscopic. Extreme care has to be taken in the handling of the materials, in order to avoid hydration and oxidation. The preparation and the mounting of crystals were performed in a glove box, flowed with dry nitrogen gas.

II.3 MAGNETIC MEASUREMENTS

Measurements of the magnetic susceptibilities of NiI₂ and CoI₂ have been performed on a Faraday-type system (Oxford Instruments), equipped with a Mettler ME 21 electronic vacuum microbalance, described elsewhere [14].
The crystals of NiI₂, used for the magnetic measurements, were cut from the Bridgman-grown samples and weighed 50 to 100 mg. Figure II.1 shows the reciprocal susceptibilities of NiI₂ for two directions of the applied field (H = 8.61 kOe): for the broken curve H is perpendicular to the c-axis, the full curve has been measured with H parallel to the c-axis. The c-axis is the trigonal axis perpendicular to the layers (see Section II.4). Both curves have been corrected for diamagnetism: \( \chi_{\text{dia}} = -116 \times 10^{-6} \text{ cm}^3/\text{mol} \) [15].

![Figure II.1: Reciprocal magnetic susceptibilities of NiI₂ versus the temperature for two directions of the applied field of 8.61 kOe: the full line for H//c and the broken line for H\perp c.](image)

The obtained values of the susceptibilities compare well with the powder susceptibility of NiI₂, measured by Billerey et al. [11]. The measured anisotropy for H\perp c and H//c is very small over the whole temperature range. From 200 to 300 K a Curie-Weiss behaviour of the reciprocal susceptibilities is observed. In order to analyze the susceptibilities in terms of a Curie-Weiss Law, the contribution of Van Vleck temperature-independent paramagnetism should be taken into account. For NiI₂ a value of \( \chi_{VV} = 272 \times 10^{-6} \text{ cm}^3/\text{mol} \) is calculated from the relation \( \chi_{VV} = 8N\mu_B^2/\Delta \), using a crystal-field splitting \( \Delta = 7660 \text{ cm}^{-1} \) (see Chapter V). The Curie constant is isotropic, \( C = 1.37 \). For the asymptotic
Curie temperature \( \theta \) we calculated -60 K. The values reported in the literature are \( C = 1.06 \) and \( \theta = -56 \) K [16]. From our value, \( C = 1.37 \), one calculates with the formula \( C = \frac{N g^2 \mu_B^2 S(S+1)}{3 k} \) a value of \( g = 2.3 \). Boudewijn [17] obtained \( g = 2.2 \) from the magnetic-field dependence of a zero-phonon line in the spectrum of CdI\(_2\):Ni\(^{2+}\).

**Figure II.2**: Low-temperature magnetic susceptibilities of NiI\(_2\) for four directions of the applied field \( (H = 8.61 \) kOe); 
1) the full line: \( H//c \); 
2) the broken line: \( H\perp c \); 
3) the dotted broken line: the angle between \( c \) and \( H \) is 45\(^\circ\); 
4) the dotted line: as 3) but rotated 90\(^\circ\) around the \( c \)-axis.

Figure II.2 shows the detailed temperature dependence of the susceptibilities of NiI\(_2\) for four directions of the applied field \( (H = 8.61 \) kOe) with respect to the \( c \)-axis: 1\(^\circ\) \( H//c \), 2\(^\circ\) \( H\perp c \), 3\(^\circ\) the \( c \)-axis makes an angle of 45 degrees with the applied field, 4\(^\circ\) as 3\(^\circ\), but the crystal is rotated over 90 degrees around the \( c \)-axis. All four curves have a maximum at about 75 K. By lowering the temperature down to 60 K the susceptibilities of NiI\(_2\) are still isotropic. A strong decrease of the susceptibilities occurs between 60 and 55 K;
the anisotropy between the curves 1 and 2, and between 3 and 4 is not significant, and could be due to the smaller number of measuring points in the first set. At about 52 K the curves labelled 3 and 4, which represent measurements on the same crystal, become anisotropic. The increase of curve 4 at low temperature is presumably due to a small paramagnetic contribution (about 5°/oo). Such a paramagnetic impurity is easily produced, if during the handling of the sample a slight amount of water is introduced. Applying a paramagnetic correction to curves 3 and 4 leads to an appreciable anisotropy at 5 K. Curve 4 then becomes almost horizontal from 40 to 5 K; curve 3 then tends to go to zero, indicating the well-known perpendicular and parallel spin susceptibilities for an antiferromagnet. We remark that we do not know the directions of the hexagonal a- and b-axis in the crystal.

Measuring the heat capacities of NiI₂ versus the temperature, Billerey et al. [11] discovered two transitions: one at 76 K, the other at 59.5 K. The first transition corresponds to the maximum in the susceptibility at 75 K. Neutron diffraction [12] indicates that the Neel temperature is indeed 75 K. The transition at 55 K in our susceptibilities is due to a crystallographic distortion, and will be discussed in Section II.4. We emphasize that the steepest descent in the susceptibility does not correspond to the critical temperature of NiI₂.

The magnetizations of NiI₂ at all temperatures and for the four orientations of the crystals show straight lines, varying the field from 0 to 40 kOe; no flops are observed up to 40 kOe.

Figure II.3 shows the susceptibilities of CoI₂ versus the temperature for two directions of the applied field (H = 8.61 kOe): H/c and H⊥c. The curves have been corrected for diamagnetism: \( X_{\text{dia}} = -120 \times 10^{-6} \text{ cm}^3/\text{mol} \) [15]. It was difficult to measure the susceptibilities of CoI₂ in a reproducible way. CoI₂ is a very hygroscopic compound. The ampoules used for our Faraday system are not completely air-tight, so that an unknown quantity of vacuum grease must be on the screw of the ampoule. Although we managed several times to tighten the holder using this grease, we are aware that weighing errors of 5-10% are introduced. However, the H⊥c susceptibility is certainly larger than the H/c susceptibility.

The susceptibilities of CoI₂ do not exhibit a Curie-Weiss behaviour between 150 and 300 K. Contrary to NiI₂, the susceptibilities are anisotropic. In the temperature region from 200 to 300 K, we calculated for H⊥c a Curie constant \( C_\perp = 3.6 \) and a Curie temperature \( \Theta_\perp = -14 \text{ K} \); for H/c \( C_{//} = 2.9 \) and \( \Theta_{//} = -7 \text{ K} \). From the susceptibilities given by Bizette [18], we deduced values
of $C_\perp = 3.6$, $\Theta_\perp = -36$ K and $C_\parallel = 3.3$ and $\Theta_\parallel = -43$ K. The anisotropy of the susceptibilities we found, agrees with the anisotropy reported by Bizette et al., although these authors did not observe deviations from the Curie-Weiss Law.

Lines [19] already pointed out that $1/\chi$ versus $T$ is not expected to be a straight line for Co$^{2+}$ compounds. One expects different values of $C$, obtained from different temperature regions. The ground state of Co$^{2+}$ in $O_h$ symmetry is $a^4_1 t_2^5 e^2_g$. This state is split by spin-orbit coupling into a doublet, a quartet and a sextet, characterized by $J = 1/2$, $J = 3/2$ and $J = 5/2$, respectively. The doublet has the lowest energy [20]. The quartet lies about 400 cm$^{-1}$, and the sextet about 1000 cm$^{-1}$ above the ground state. The lower trigonal symmetry of the site in CoI$_2$ ($D_{3d}$ instead of $O_h$) will lead to a shift of the lowest level and a shift and further splitting of the other levels. This leads to anisotropic magnetic susceptibilities. Electron paramagnetic resonance data of CdI$_2$:Co$^{2+}$ [17] revealed nearly isotropic $g$ values indicating a small trigonal field. However, the anisotropy of the magnetic susceptibilities of CoI$_2$ suggests that in CoI$_2$ the trigonal field is appreciable.

The susceptibility curves in the region of the ordering temperature at 8.2 K (Figure II.4) are characteristic of antiferromagnetism. Our results dif-
Figure II.4: Low-temperature part of the susceptibilities of CoI₂: H⊥c (broken line); H∥c (full line). H = 8.61 kOe.

From the results of Bizette [18] who did not observe any critical behaviour in the H⊥c susceptibility. We have results similar to those obtained by Bizette for samples which have been partly destroyed by air or moisture. In such a case there is a large paramagnetic susceptibility contribution, which covers any anomaly. For H∥c Bizette [18] observed a maximum in the susceptibility at 3 K. Later Van Viltert et al. [21] found 12 K. We find 9.35 K for this maximum. As $X_{⊥c}$ is larger than $X_{∥c}$, we assume that the Co²⁺ spins are lying in the basal plane. The difference ($X_{⊥c} - X_{∥c}$) is due to out-of-plane anisotropy, and the absence or small value of in-plane anisotropy. The anisotropy of the susceptibilities of CoI₂ is further discussed in Section II.8.

The magnetizations of CoI₂ for H⊥c and H∥c are straight lines up to 40 kOe at various temperatures and no spin flops are observed.

II.4 X-RAY DIFFRACTION ON NiI₂

NiI₂ crystallizes in the CdCl₂ structure. The unit cell of NiI₂ can be described in two ways: rhombohedrally with one formula unit NiI₂ or hexagonally with three NiI₂ units per unit cell. We prefer the latter description: one
Ni at the origin, and two I at ± (0,0,z) of space group R̅3m. The c-axis is the uniaxial axis. A profile refinement of a neutron diffractogram of NiI₂ at 300 K yields a = 3.922 Å, c = 19.808 Å and c/3a = 1.684. The z-parameters of the iodine ions are: z_I = ± 0.2560, which means that the octahedron NiI₆⁴⁻ is trigonally compressed along the c-axis.

Billerey et al. [11] discovered two anomalies in the heat capacity: one at 59.5 K and one at 76 K, indicating phase transitions. Worsswick et al. did not observe the second transition [16]. Also small peaks in our neutron diffractogram of NiI₂ at 4.2 K, which we could not ascribe to magnetic satellites, made a low-temperature X-ray examination of NiI₂ necessary.

Small crystals of NiI₂ were sifted through a 0.05 cm sieve and then spread on vacuum grease on the copper block of the cold-finger cryostat. Only temperatures down to 35 K can be achieved with this cryostat. Because of the large preferred orientation of the platelet-like crystals of NiI₂ only 00l reflections and hkl reflections with a large ℓ had reasonable intensities. Small distortions of the lattice of NiI₂ are best studied, using reflections with large values of h, k and especially, ℓ. Three reflections of NiI₂ appeared to be particularly suitable for studying the change of the structure with the temperature: the hexagonal 10 16, 0 114 and the 1112 reflections.

Figure II.5 shows the temperature dependence of 10 16, 0 114 and 1112 reflections, recorded at a few selected temperatures in the neighbourhood of 60 K. From 82.9 K to 66.8 K the intensity of the hexagonal 10 16 reflection strongly increases without a change in the α₁/α₂ ratio of 2/1, most likely due to a decrease of the z-parameter of the iodine atom to the ideal octahedron value of z = 0.25. Also from 100 K to 300 K, the intensities of the three reflections change continuously, due to the variation of the z-coordinate of the iodine atom. From 66.8 to 60.5 K the intensity of the 10 16 reflection decreases again. At 57.5 K we clearly see that the intensity ratio of the two peaks no longer reflects the α₁/α₂ ratio, because of a splitting of the 10 16 reflection. It looks as if some intensity of the α₁ component has been transferred to the intensity of the α₂ component. This process is continued by lowering the temperature down to 35 K. The actual transition temperature is 60 K, in good agreement with the temperature of 59.5 K Billerey found. The hexagonal 0 114 and 1112 reflections show a similar temperature dependence, but contrary to the 10 16, some intensity of the 0 114 has been removed to a lower scattering angle.

The α₁ component of the three reflections at 35 K has been obtained by substracting half of the intensity of the α₁ component at the corresponding
Figure II.5: Temperature dependence of the hexagonal 1016, 1112 and 0114 reflections of NiI₂, denoted with A, B and C, respectively. The peaks at the extreme right-hand side show the intensity profiles of the α₁ component only. Vertical bars give the calculated 2θ values of the monoclinic cell.

α₂ scattering angle (Figure II.5) [22]. The hexagonal 1016 reflection at 35 K is broadened towards larger 2θ values, while the 0114 broadens towards lower 2θ values. The 1112 is split into three components.

The observed splittings can be indexed either on the basis of a monoclinic or a triclinic cell. The axes of the monoclinic cell are \( a_m = 2a + b \), \( b_m = b \) and \( c_m = c \) with \( a \), \( b \) and \( c \) referring to the hexagonal cell. The axes of the triclinic cell are \( a_t = a \), \( b_t = 2b \) and \( c_t = c \). Both cells are shown in Figure II.6. The monoclinic cell dimensions are at 35 K: \( a_m = 6.765 \ \text{Å} \), \( b_m = 3.919 \ \text{Å} \), \( c_m = 19.635 \ \text{Å} \) and \( β = 90.23^0 \). Especially, the deviation of angle \( β \) from 90° is significant. The triclinic cell dimensions are \( a_t = 3.909 \ \text{Å} \), \( b_t = 7.839 \ \text{Å} \), \( c = 19.635 \ \text{Å} \), \( α = 90.00^0 \), \( β = 90.20^0 \) and \( γ = 120.09^0 \).
Figure II.8: The monoclinic and triclinic unit cells. Closed circles are Ni atoms, open circles are I atoms. One slab I-Ni-I is drawn; + denotes the upper iodine, — the lower iodine.

TABLE II.1: Observed and calculated 2θ values, multiplicities and the observed relative intensities of the components of the reflections 0 1 14, 1 1 12 and 1 0 16.

<table>
<thead>
<tr>
<th>Hexagonal</th>
<th>Monoclinic</th>
<th>2θ</th>
<th>Multi-</th>
<th>Tri-</th>
<th>2θ</th>
<th>Multi-</th>
<th>2θ</th>
<th>Obs.</th>
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<td>4</td>
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<td></td>
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Table II.1 gives the calculated and observed positions of the components of the hexagonal 0 1 14, 1 1 12 and 1 0 16 reflections in the monoclinic and the
triclinic cell. The vertical lines in Figure II.5 indicate the calculated positions of the monoclinic cell reflections. The observed 2θ values are obtained from a Gaussian fit of the $a_1$ profiles at 35 K. Such a fit shows that the ratio of the multiplicities is not maintained in the intensities. This is possible if not only the cell dimensions have changed, but also the relative positions of the atoms in the cells. As the scattering factors of the iodine atoms are much larger than those of nickel, the positions of the iodines mainly determine the observed relative intensities of the components. However, as we only have a few rather reliably changed ratios, it is not possible to determine the coordinates of the atoms in the distorted unit cell.

II.5 NUCLEAR NEUTRON DIFFRACTION AT 4.2 K ON NiI$_2$

Neutron diffractograms were recorded at the high-flux reactor in Petten. A neutron wavelength of 2.5861 Å was obtained from the (111) plane of a copper crystal. Pyrolytic graphite was used as a higher-order filter. Improvements of the counter system have lead to better statistics of the diffractograms. A disadvantage of these improvements is the appearance of $\lambda/2$ and $\lambda/3$ contributions above the background. Especially if the intensities of reflections of a compound are not too large, extra high-order peaks are visible in the diagram. The diagram of NiI$_2$ at 4.2 K (Figure II.7) shows these high-order contributions, indicated by B.

Neutron diffraction is a nice complementary method to X-ray diffraction, because usually the scattering lengths of the atoms differ considerably in neutron and X-ray diffraction. The scattering length of nickel is 1.03, that of iodine 0.53 x 10$^{-12}$ cm. A problem in neutron experiments is the possible appearance of magnetic satellites at low-scattering angles. In principal one has to solve both the nuclear and the magnetic structure in order to know the origin of an observed peak.

In Figure II.7 the dots represent the measured diffractogram of NiI$_2$ at 4.2 K. This diffractogram includes the contributions of the background; the peaks of the background are indicated in the figure with the letter B. In calculating the profile of this diagram the background has been represented by a series of straight lines, the peaks thus being described as triangles. The original hexagonal reflections are indicated by N in Figure II.7. In the 2θ region of these reflections and in the regions where nuclear, triclinic superreflections, indicated with vertical bars, are present, the full line represents the
Figure II.7: Neutron diffractogram of NiI₂ at 4.2 K. The scattering angle 2θ is in units of DMC (10⁴ DMC = 380°).

N = nuclear, original hexagonal reflection;
M = magnetic satellites;
B = peaks of the background due to high-order contributions;
vertical bars indicate the strongest calculated nuclear superreflections of the triclinic cell (see text).
calculated profile. Furthermore, the diffractogram contains the magnetic satellites (M), discussed in Section II.6.

Because the wavelength of the neutrons (2.5861 Å) is larger than the wavelength of Cu Kα (1.5418 Å), the hexagonal 0114, 1112 and 1016 reflections cannot be observed in the neutron diffractogram. Neither do we observe a clear splitting of the hexagonal reflections due to the severe broadening of the reflections at high-scattering angles. However, a profile analysis reproduced the observed broadenings of the reflections, due to the distortion of the hexagonal cell, quite well. The observed pattern can be described either with a non-primitive monoclinic cell with cell dimensions of \( a = 6.769 \text{ Å}, b = 3.914 \text{ Å}, c = 19.630 \text{ Å} \) and \( \beta = 90.20^\circ \), or with a non-primitive triclinic cell with \( a_t = 3.912 \text{ Å}, b_t = 7.827 \text{ Å}, c_t = 19.629 \text{ Å}, \alpha = 90.02^\circ, \beta = 90.18^\circ \) and \( \gamma = 120.05^\circ \). The cell constants agree with the data, obtained with X-ray diffraction at 35 K.

We have tried to refine the coordinates of two nickel and four iodine atoms in one slab. The translation from one slab to another within the unit cell was retained. Thus, only reflections with \( h + l = 3n \), \( n \) is an integer number, are used in the refinement for the monoclinic cell. The results of this refinement are listed in Table II.2; the atom numbers are shown in Figure II.8. A few

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<thead>
<tr>
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<tbody>
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<td>-.025 (4)</td>
<td>-.003 (1)</td>
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<td>0.003 (1)</td>
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<td>0.075 (1)</td>
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estimated errors are between brackets.

constraints were added to the refinement procedure: Ni 1 and Ni 2, I 1 and I 2, and I 3 and I 4 were supposed to have opposite shifts. In the structure factor of the superreflections this leads to sine terms only, so that relatively small displacements of the atoms can lead to appreciable intensities of these reflections. The calculated standard deviations (Table II.2) are rather large, except
Figure II.2: Displacements of the Ni ions (closed circles) and I ions (open circles) in a slab of the monoclinic cell. The arrows indicate the direction of the displacement.

for the z-coordinates of nickel and iodine. The correlation between the z-coordinates of I1 or I2, and I3 or I4 is 93%. The residual R-factor of this structure is not lower than 8%, due to the presence of magnetic satellites and the complicated background. The shifts of the iodine atoms are tentatively given in Table II.2. Although the reflections could be indexed on basis of a monoclinic cell, the atomic positions do not correspond to a monoclinic space group.

The results of the refinement of the coordinates of the atoms in the triclinic cell are listed in Table II.3; the atom numbers are shown in Figure II.9.

TABLE II.3: Atomic coordinates of Ni and I in the triclinic cell. The atom numbers are shown in Figure II.9. Estimated errors are between brackets.

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<th>z</th>
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</thead>
<tbody>
<tr>
<td>Ni 1</td>
<td>-.028 (3)</td>
<td>-.006 (2)</td>
<td>-.002 (1)</td>
</tr>
<tr>
<td>Ni 2</td>
<td>0.028 (3)</td>
<td>0.506 (2)</td>
<td>0.002 (1)</td>
</tr>
<tr>
<td>I 1</td>
<td>0.667 (6)</td>
<td>0.167 (4)</td>
<td>0.082 (1)</td>
</tr>
<tr>
<td>I 2</td>
<td>0.321 (7)</td>
<td>0.815 (3)</td>
<td>-.075 (1)</td>
</tr>
<tr>
<td>I 3</td>
<td>0.679 (7)</td>
<td>0.685 (3)</td>
<td>0.075 (1)</td>
</tr>
<tr>
<td>I 4</td>
<td>0.333 (6)</td>
<td>0.333 (4)</td>
<td>-.082 (1)</td>
</tr>
</tbody>
</table>

Again the packing of the slabs is assumed to be unchanged; reflections with \( h + k - l = 3n \) are used in the refinement. The constraints used in the proce-
Figure II.9: Displacements of Ni and I ions in a slab in the triclinic cell.

dure are: Ni 1 and Ni 2, I 1 and I 4, and I 2 and I 3 have opposite shifts. The R-factor is 8% for this structure. The calculated profile is shown in Figure II.7.

In the monoclinic cell the displacements of the nickel atoms approximately lie in the hexagonal (210) plane, in the triclinic cell the displacements are in the (120) plane. The absolute value of the nickel displacements in both cells amounts 0.1 Å, mainly due to displacements in the ab-plane. Also the displacements of the iodine atoms amount 0.1 Å. The iodine shifts in the unit cells are similar: the iodine ions with the z-parameter close to the ideal cubic close packing value, 1/12, are not displaced in the ab-plane. The direction of the displacements of the other iodine ions is quite different in both cells. The displacements of the iodine atoms calculated from the neutron diffraction data, are not accurate enough to permit a quantitative comparison with the observed X-ray intensities.

II.6 THE MAGNETIC STRUCTURE OF NiI₂

There have been a few attempts to solve the magnetic structure of NiI₂. Two publications on Mössbauer spectra of NiI₂ have appeared. The first stated that NiI₂ is simple antiferromagnetic with alternating spins in the [100]-direction [23]. In the second paper the authors concluded that the magnetic structure of NiI₂ consists of a ferromagnetic order in the ab-plane, the nickel sheets being coupled antiferromagnetically [10]. A paper by Billerey et al. [11] reported a neutron-diffraction study using neutrons with a wavelength of 1.140 Å, which gave rise to a very high background. Our neutron diffractogram of NiI₂ at 4.2 K (Figure II.7) shows magnetic reflections indicated with the letter M. Billerey et al. only observed the first magnetic reflection, at 2θ = 355 DMC in Figure II.7. This reflection was indexed as the 013 reflection in an extremely large cell with dimensions a, 4a√3 and 2c. From the intensity of
this reflection the authors claimed to have deduced the directions of 48 nickel spins and suggested that other reflections, such as the 0 11 and 0 19, were lost in the background. In our diffractogram, however, the background is much lower. At 180 DMC, the 2θ value of the 0 11, no intensity is observed, so that the model of Billerey does not agree with our neutron data. Friedt et al. [10] concluded from the Mössbauer data that all iodine ions have the same type of surrounding by nickel magnetic moments, and that all magnetic moments make an angle of 63° with the c-axis. This is not compatible with Billerey's magnetic structure, where the spins would be aligned along the 4a\sqrt{3} axis.

Because there has been confusion about the origin of the magnetic reflections, we will consider carefully all possible ways of indexing of the reflections. First we construct the reciprocal lattice on the basis of the unit cells, discussed in the previous sections. The magnetic reflections are described as satellites of the reciprocal lattice points of the nuclear cell. In a reciprocal lattice plane the scattering vectors of the magnetic reflections lie on circles around the origin of the reciprocal space, with the radii of the circles corresponding to the observed 1/d values of the diffractogram. The first magnetic reflection is regarded as the satellite of the origin, (0,0,0). The length of this scattering vector, which is the propagation vector Q, is circled around each reciprocal lattice point. The direction of the vector Q is obtained from the intersections of the circles around the origin and the circles with radius |Q| around the reciprocal lattice points.

In Figure II.10 a reciprocal lattice plane, containing the c*-axis is shown. The horizontal axis can either be taken as the hexagonal [100] or [120] direction, or any other direction perpendicular to c*. The [100] and [120] directions correspond to two orthogonal vectors, Q_x and Q_y, respectively. A propagation vector Q_x (\sqrt{2}/(a\sqrt{3})) gives a helix-1 type structure (Figure II.12A), Q_y (\sqrt{2}/a) a helix-2 type structure (Figure II.11), in the ab-plane. Attached to the circles around the origin of the reciprocal lattice are the 2θ values (in units of DMC, 10^4 DMC = 360°) of the first two magnetic reflections (Figure II.10). On the axes a number of Q vectors are indicated. The first magnetic reflection could be indexed with a Q vector [0,1/6,0], corresponding to a helix-2 type structure with a spiral angle of 60° (Figure II.11). However, from Figure II.10 we see that in that case the (0 0 3)\textsuperscript{±} satellites fall in the gap between the first and second magnetic reflection. Also more complicated Q vectors, for instance Q \approx [0,1/6,1/4], only explain the intensity of the first magnetic reflection. The intensities of the (0 0 3)\textsuperscript{±} satellites cannot be reduced to zero. The only way to explain the large gap between the first and
second magnetic reflections is to add a large $Q_z$ component to the $Q_x$ or $Q_y$ component of the propagation vector, as shown in Figure II.10 by the drawn arrows. The missing $(003)^\pm$ satellites now nearly coincide with the $(000)^\pm$ satellites and the $(006)^-$ satellite, respectively. Whether we are dealing with $Q_x$ or $Q_y$ in the $a^*b^*$ plane, can be distinguished by calculating the positions of the satellites of the nuclear reflections, except of course the 001 set. We find better agreement of the calculated positions with the observed ones for $Q_x$. The calculated components of the propagation vector are $Q_x = 0.1384a^*$ and $Q_z = 1.457c^*$. These values give an incommensurable magnetic structure of helix-1 type. The values are close to the commensurable values, $Q_x = 1/8$ and $Q_z = 3/2$, which lead to the magnetic unit cell proposed by Billerey et al. [11]. The indexing of the magnetic satellites is much better, and our incommensurable $Q$ values explain the observed broadenings of the first and second magnetic reflection (Figure II.10).
Figure II.11: Commensurable helix of type 2, drawn with a spiral angle of $60^\circ$; $Q_y = 1/6(2/a)$. The arrows indicate the orientation of the spins.

Figure II.12: Spin orientations for helix 1 with $Q = (0.1384, 0, 1.457)$.
A: Spiral angles of the Ni spins in the hexagonal $ab$-plane of NiI$_2$. The broken line is the intersection with the plane of Figure II.12B.
B: Spiral angles in the $(1 \bar{2} 0)$ plane. The ellipses indicate the plane in which the Ni spins rotate.
TABLE II.4: Observed and calculated positions and intensities of the magnetic satellites of NiI₂, using \( Q_x = 0.1384a^* \) and \( Q_z = 1.457c^* \). \( N \) and \( B \) denote an overlap with a nuclear or background peak, respectively.

<table>
<thead>
<tr>
<th>Hexagonal reflection</th>
<th>+Q satellites</th>
<th>-Q satellites</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \theta )</td>
<td>( \theta )</td>
</tr>
<tr>
<td></td>
<td>obs. (DMC)</td>
<td>calc.</td>
</tr>
<tr>
<td>0 0 0</td>
<td>350</td>
<td>350</td>
</tr>
<tr>
<td>0 0 3</td>
<td>965</td>
<td>965</td>
</tr>
<tr>
<td>T11</td>
<td>N</td>
<td>1285</td>
</tr>
<tr>
<td>0 1 T</td>
<td>1358</td>
<td>1351</td>
</tr>
<tr>
<td>1 0 1</td>
<td>N</td>
<td>1538</td>
</tr>
<tr>
<td>0 0 6</td>
<td>1653</td>
<td>1646</td>
</tr>
<tr>
<td>1 0 2</td>
<td>1448</td>
<td>1436</td>
</tr>
<tr>
<td>T1 2</td>
<td>B</td>
<td>1172</td>
</tr>
<tr>
<td>0 1 2</td>
<td>N</td>
<td>1558</td>
</tr>
<tr>
<td>T1 4</td>
<td>N</td>
<td>1693</td>
</tr>
<tr>
<td>0 1 4</td>
<td>1458</td>
<td>1462</td>
</tr>
<tr>
<td>1 0 4</td>
<td>-</td>
<td>1912</td>
</tr>
<tr>
<td>1 0 5</td>
<td>1638</td>
<td>1640</td>
</tr>
<tr>
<td>T1 5</td>
<td>1408</td>
<td>1407</td>
</tr>
<tr>
<td>0 1 5</td>
<td>N</td>
<td>2017</td>
</tr>
</tbody>
</table>

In principle the two solutions \((\pm Q_{a^*}, 0, Q_{c^*})\) are not equivalent, because the \( c^* \) axis makes an angle of \( \beta \neq 90^\circ \) with the \( a^* \) axis. It is also possible to take \((0, \pm Q_{b^*}, Q_{c^*})\) or \((\pm Q_{a^*}, \pm Q_{b^*}, Q_{c^*})\). The differences between the calculated \( \theta \) values of the satellites for these six directions of \( Q \), however, are very small, and it is not possible to distinguish these solutions. For the sake of simplicity we take \( Q_x = 0.1384a^* \) and \( Q_z = 1.457c^* \). In Figure II.12 the corresponding spiral angles are shown. In Table II.4 we have listed the observed and
calculated positions of the two satellites of each reflection of a hexagonal set.

The magnetic cross sections of the satellites are given by [24]:

\[
\sigma_{H \pm Q} = \frac{1 + \cos^2 \omega}{4} \left[ \sum_v \frac{e^{2 \gamma}}{2mc^2} \mu_v f_v(H \pm Q) \sin \beta_v \exp \left(i(2mH \cdot r_v + \phi_v)\right) \right]^2
\]

where \(H\) is the nuclear reflection, \(\omega\) the angle between the cone axis and the scattering vector, \(e^{2 \gamma}/2mc^2 = 0.2695 \times 10^{-12}\) cm, \(\mu_v\) the magnetic moment of the \(v\)-th Ni atom, \(f_v(H \pm Q)\) the form factor for magnetic scattering [25], \(\beta_v\) the opening angle of the cone, \(r_v\) the relative position of the \(v\)-th Ni atom in the cell and \(\phi_v\) an arbitrary phase angle of the \(v\)-th Ni atom. For a simple helix, as we assume for Ni\(\text{I}_2\), \(\beta_v = 90^0\) and \(\phi_v = 0^0\). In equation (1) the factor \((1 + \cos^2 \omega)/4\) has a maximum value of 1/2 and a minimum value of 1/4. The exponential part of equation (1) is the same for all satellites. The variation of this part, due to the small displacements of the nickel atoms is neglected. The intensities of satellites arising from superreflections are expected to be too weak to be observable.

The profile of the first magnetic reflection has been calculated for two directions of the cone axis of the helix of Ni\(\text{I}_2\). In Figure II.13A the profile of the first magnetic reflection is calculated with the cone axis in the ab-plane parallel to the \(x\)-direction. In Figure II.13B the calculated profile is in much better agreement with the observed profile: we assumed the spins in a plane making an angle of 55.4° with \(c\) (Figure II.12B), as indicated by the ellipses in this picture. The magnetic moment of Ni\(\text{I}^{2+}\), calculated from the ob-

---

**Figure II.13:**

A: Observed (dotted) and calculated (full) profile of the first magnetic reflections with the cone axis along the \(x\) axis, defined in Figure II.12A.

B: Observed and calculated profile with the spins rotating in a plane making an angle of 55.4° with the \(c\)-axis.
served intensities of the first two magnetic satellites, is 1.56 \mu_B. The intensities of the satellites, calculated for the proposed magnetic structure of NiI_2 (Figure II.12) are listed in Table II.4. The observed intensities are not very accurate, because of overlap with nuclear reflections and background peaks.

As shown in Figure II.12, in the magnetic structure of NiI_2 each iodine ion is surrounded by two parallel spins and one spin making an angle of 49.8° with the two others. The plane in which the magnetic moments of nickel rotate, makes an angle of 55.4° with the c-axis. In principle the surroundings of the ions by three nickel spins are all different. Preliminary calculations of the hyperfine field at the iodine ions in CoI_2 (Section II.7) give an unique value of the field, assuming that anisotropic parts of the field are neglectable.

II.7 THE CRYSTALLOGRAPHIC AND MAGNETIC STRUCTURE OF CoI_2

CoI_2 crystallizes mainly in the Cd(OH)_2-structure, which has a hexagonal close packing of anions [1]. The hexagonal unit cell contains one CoI_2 unit; the uniaxial axis is the c-axis. Figure II.14 shows the neutron diffractogram of CoI_2, recorded at 4.2 K. The room-temperature diffractogram is very similar. We see that reflections with h-k = 3n are narrow. Other reflections with h-k \neq 3n are severely broadened. Guinier-Hägg films of CoI_2 taken at room temperature show the same broadening. These phenomena are well known and are caused by stacking faults, which are easily introduced, because the Van der Waals interactions between the slabs I-Co-I are very weak. As the faults in the packing do not affect the octahedral surrounding of the cobalt ion, we do not further examine this phenomenon.

From the h-k = 3n reflections we have calculated the cell parameters: a = 3.985 \AA and c = 6.664 \AA at 4.2 K. Also from these reflections the scaling factor, preferred orientation parameter G, induced by the platelet form of CoI_2 crystals, and the z-parameters of the iodine ions were estimated. The preferred orientation parameter is a measure for the assumed Gaussian distribution of the normals of the platelets about the preferred orientation direction (c-axis). The intensity of the reflections is corrected in the following way:

\[ I_{\text{corrected}} = I_{\text{calc}} e^{\alpha^2} \]

where \( \alpha \) is the angle between the scattering vector and the c-axis. We found
Figure II.14: Neutron diffractogram of CoI₂ at 4.2 K. The scattering angle is given in units of DMC (10^4 DMC = 360°). Up to 1000 DMC the dots represent the observed pattern, the full line is the calculated pattern. Above 1000 DMC only the observed profile is given; the full line is only a guide line for the eye. Nuclear reflections (N), magnetic satellites (M) and background peaks (B) are indicated.
G = 0.186. The z-parameters of the iodine ions are close to ±0.25, the value for an ideal uncompressed octahedron CoI$_6$.

The only data available on the magnetic structure of CoI$_2$ are the $^{129}$I-Mössbauer measurements of Friedt et al. [10]. From these data the authors concluded that CoI$_2$ is an in-plane ferromagnet with an antiferromagnetic coupling between the layers; the spins lie in the ab-plane. There is only one type of coordination of the iodine ions by three cobalt spins.

Not only nuclear reflections are broadened, the magnetic satellites are broadened too. In Figure II.14 the magnetic satellites of CoI$_2$ are indicated with the letter M. The first magnetic reflection at 341 DMC can be described as the ±Q satellite of the 000 and the -Q satellite of the 001 reflection. The second magnetic reflection at 948 DMC can be described as the +Q satellite of the 001 and -Q of the 002 reflection of CoI$_2$. The indexing scheme is the same as used in the case of NiI$_2$, illustrated in Figure II.10. For CoI$_2$ the 2θ values of the magnetic satellites are explained using $Q_x = 1/8 a^*$ and $Q_z = 1/2 c^*$. The magnetic unit cell is commensurable with the nuclear unit cell, within the experimental errors introduced by the stacking faults. The magnetic cell has dimensions 4a$\sqrt{3}$, a and 2c. The ab-plane of this cell is the same as Billerey suggested for NiI$_2$ [11] (see Figure II.15). There is an antitranslation of the spins along the c-axis.

One might think that along the magnetic a-axis the spins of cobalt align like + - + - , but such a collinear structure gives rise to two types of coordination of iodine ions by the spins of cobalt, in contradiction to the Mössbauer conclusions [10]. If the iodine ion is surrounded by three parallel spins (site a), the transferred hyperfine field $H_{hf}$ is given by $H_{hf}(a) = 3H_{iso}$, where $H_{iso}$ is the isotropic part of the transferred field (Section III.7). The anisotropic part is small and is neglected. In the case the iodine ion is surrounded by two parallel and one antiparallel spin (site b), the hyperfine field is given by $H_{hf}(b) = H_{iso}$. Therefore, we suggest that the magnetic structure of CoI$_2$ is a helix of type 1 with a spiral angle of 45° in the ab-plane. In Figure II.15

![Figure II.15: Orthorhombic magnetic unit cell (4a$\sqrt{3}$,a,2c) of CoI$_2$ (ab-plane). Attached to the Co$^{2+}$ ions are the spiral angles.](image_url)
the spiral angles are indicated at each cobalt position. The magnetic moments lie in the ab-plane as shown by our magnetic-susceptibility measurements as well as by the Mössbauer experiments. With respect to the latter, each iodine is surrounded by two parallel spins and one spin which makes an angle of 45° with the two others. The structure of Figure II.16 gives rise to four non-equivalent iodine sites. Preliminary calculations show that the transferred field at each iodine site has an unique value, $H_{hf} = H_{iso} \{ (2 + \cos 45^0)^2 + (\sin 45^0)^2 \}$, neglecting the anisotropic field. If the core-polarization field can be neglected, a finite spin density ($f_\text{s}$) in the 5s orbital can be estimated. One deduces $f_\text{s} = 0.4\%$, a reasonable value in comparison with a value of $f_\text{s} = 0.54\%$ obtained from ESR measurements on CdI$_2$:Co$^{2+}$ [36].

The calculated profile of the neutron diffractogram of CoI$_2$ up to 1000 DMC (Figure II.14) agrees well with the observed profile. The magnetic moment of Co$^{2+}$ in CoI$_2$ is 1.67 $\mu_B$. For the lowest Kramers doublet $E'_g$ ($J = \frac{1}{2}$) of the $4^2T_{1g}$ ground state of Co$^{2+}$ in an octahedral coordination one calculates a value of 2.16 $\mu_B$. The difference is reasonably well accounted for by a covalent reduction. The calculated positions and intensities of the magnetic reflections are listed in Table II.5. It is difficult to compare most of these values with observed data, because of background high-order contributions and the extreme broadening of the 101 reflections.

**TABLE II.5:** Calculated positions and intensities in the magnetic cell 4a/3, a and 2c of CoI$_2$ using a magnetic moment of Co$^{2+}$ of 1.67 $\mu_B$ and a preferred orientation parameter of $G = 0.186$.

<table>
<thead>
<tr>
<th>Magn. reflection</th>
<th>$2\theta$ (DMC)</th>
<th>Calc. intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>101</td>
<td>341</td>
<td>15468</td>
</tr>
<tr>
<td>103</td>
<td>948</td>
<td>1862</td>
</tr>
<tr>
<td>701</td>
<td>1105</td>
<td>938</td>
</tr>
<tr>
<td>311</td>
<td>1189</td>
<td>1576</td>
</tr>
<tr>
<td>511</td>
<td>1344</td>
<td>1164</td>
</tr>
<tr>
<td>901</td>
<td>1417</td>
<td>510</td>
</tr>
<tr>
<td>703</td>
<td>1437</td>
<td>552</td>
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<tr>
<td>313</td>
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<td>1612</td>
<td>492</td>
</tr>
<tr>
<td>513</td>
<td>1639</td>
<td>748</td>
</tr>
<tr>
<td>903</td>
<td>1703</td>
<td>334</td>
</tr>
</tbody>
</table>
II.8 STABILITIES OF THE MAGNETIC STRUCTURES OF NiI₂ AND CoI₂

It is well known that in simple crystals sometimes very complicated magnetic structures, for example helical structures or structures with canted spins, are observed. Especially for compounds with layered structures complicated magnetic structures have been reported [3,4,26-30]. The stability of magnetic structures in compounds with hexagonal layers of magnetic ions has been studied by several authors [27,31-33]. In this paragraph we will review some of the results, and discuss in particular the stability of the observed magnetic structures of NiI₂ and CoI₂.

Rastelli et al. [33] have calculated the stability of magnetic structures of the dihalides of the 3d-transition metals, as a function of the exchange interactions

- $J_1$ between nearest neighbours (distance $a$),
- $J_2$ between next nearest neighbours (distance $a\sqrt{3}$), and
- $J_3$ between next next nearest neighbours (distance $2a$)

in the hexagonal ab-plane. Rastelli considered a single exchange $J'$ between the layers over a distance $c$ in the Cd(OH)₂ structure, and over a distance $\sqrt{a^2/3 + c^2/9}$ in the CdCl₂ structure. In Figure II.16 the exchange paths are illustrated. A central ion A has exchange interactions via $J_1$, $J_2$ and $J_3$ in the hexagonal ab-plane. $J_1$ contains contributions of a direct exchange between metal ions and a 90° superexchange along for instance AKB. $J_2$ describes a two-ion 90° superexchange via AKRC; contributions of direct exchange can be neglected in this case. $J_3$ is a superexchange via two anions over a distance $2a$.

**Figure II.16:**

- **A:** Two unit cells of the Cd(OH)₂ structure. The closed circles denote the cations, the open circles the iodine ions.
- **B:** (1 1 0) plane of the Cd(OH)₂ structure.
- **C:** 1/3 part of the CdCl₂ structure.
In the Cd(OH)$_2$ structure a central metal ion interacts via $J'$ with two neighbouring ions. If a 90° superexchange mechanism is assumed, the interaction goes via two anions on a screw-like path (for instance via AKNE). In the CdCl$_2$ structure (Figure II.16C) the central ion interacts with six neighbouring ions, three above and three below the ab-plane. The interaction is a two-anion 90° superexchange (path AKLE).

The following Hamiltonian has been used [33]:

$$H = -C \sum_{\alpha=1}^{3} J_{\alpha} \sum_{i,\delta_{\alpha}} \left( S_{i}^{(a)} S_{i+\delta_{\alpha}}^{(a)} + S_{i}^{(b)} S_{i+\delta_{\alpha}}^{(b)} \right) -2J' \sum_{i,\delta'} S_{i}^{(a)} S_{i+\delta'}^{(b)} + D \sum_{i} \left[ (S_{i}^{(a)})^{2} + (S_{i}^{(b)})^{2} \right]$$  

(3)

where $a$ and $b$ refer to spins in even and odd layers perpendicular to the c-axis, $\delta_{\alpha}$ ($\alpha = 1,2,3$) are the vectors from the atom at site $i$ in the ab-plane to its neighbours of type $\alpha$, $\delta'$ is the vector to the atom in the adjacent layers. $D$ is the single-ion anisotropy constant. In the calculations reduced exchange parameters $j_{\alpha} = z_{\alpha} J_{\alpha}/(|J_{1}|)$ are used, where $z_{\alpha}$ denotes the number of neighbours, interacting via exchange $J_{\alpha}$. Rastelli has shown that one expects that canted spin structures are not stable; only in exceptional cases with compensating exchange interaction and single-ion anisotropy, the presence of small quantum effects, due to zero-point spin deviations may lead to canted structures. Thus, normally one needs to consider only spin structures with all spins parallel to the uniaxial axis or structures with all spins in the basal plane. We discuss only helical structures for which the spin direction is determined by a single propagation vector $Q$, with $S_{iX} = S \cos Qr_{i}$ and $S_{iY} = S \sin Qr_{i}$, where $r_{i}$ is the position of atom $i$ with spin $S_{i}$. The reduced energy in the mean-field approximation can be expressed in terms of magnetic structure factors:

$$e_{0} = -\sum_{\alpha} j_{\alpha} \gamma_{k}^{\alpha} - j' \gamma_{k}^{'}$$  

(4)

with $\gamma_{k}^{\alpha} = \frac{1}{z_{\alpha}} \sum_{\delta_{\alpha}} e^{ik\delta_{\alpha}}$

(5)

and $\gamma_{k}^{'} = \frac{1}{z'} \sum_{\delta'} e^{ik\delta'}$

(6)

The ground state energy is $E_{0} = 2z_{1} |J_{1}| N S^{2} e_{0}$.
The exchange interaction $J_1$ is dominated by a $90^\circ$ superexchange between $t_{2g}$ and $e_g$ orbitals via $\sigma$ and $\pi$ overlap with anion $p$ orbitals. Because of the large radius of the iodine ions the metal-metal distance is large, and the direct exchange between the metal spins is expected to be small. According to the Goodenough-Kanamori rules [34,35] the $90^\circ$ superexchange interaction is ferromagnetic for Ni$^{2+}$ and Co$^{2+}$. Another interaction, contributing to $J_1$ via the $e_g$ orbitals of the metal ions and anion $s$ orbitals, is expected to be weak and antiferromagnetic. Indeed it is observed that CoCl$_2$, CoBr$_2$, NiCl$_2$ and NiBr$_2$ have a dominant ferromagnetic interaction in the ab-plane. We therefore consider only the case of $J_1 = +1$ for CoI$_2$ and NiI$_2$.

If in the Cd(OH)$_2$ structure only the interlayer interaction $J'$ is considered, the part of the structure factor which depends on $Q_z$, is completely separated from the parts which depend on $Q_x$ and $Q_y$ ($Q_x$ and $Q_y$ are defined in Figure II.11 and Figure II.12A). If $J'$ is positive the metal layers are ferromagnetically coupled; if $J'$ is negative, we predict an antiferromagnetic coupling. Other interactions between the slabs are discussed later. In the CdCl$_2$ structure the structure factor depending on $Q_z$, depends also on $Q_x$. For simplicity, we first neglect this part of the energy.

Minimization of the mean-field energy of equation (4) with respect to $k_x$ and $k_y$ (with $J' = 0$) gives five minima of the energy corresponding to five types of magnetic structures:

I  ferromagnetic layers
II simple antiferromagnetic order
III helix type 1 (Figure II.12A)
IV helix type 2 (Figure II.11)
V special case of helix 2: the $120^\circ$ structure.

The stability regions of these magnetic structures [33] are sketched in Figure II.17 as a function of the exchange parameters $J_2$ and $J_3$. For helix 1 the $Q$-vector is given by:

$$Q_x = \frac{2}{\sqrt{3}a} \arccos \frac{-1 - J_2}{2(J_2 + 2J_3)}$$

Substituting the observed value of $Q_x = 0.1384a^*$ of NiI$_2$, we obtain a linear relation between $J_2$ and $J_3$, which corresponds to a straight line in region III in the stability diagram (Figure II.17). For CoI$_2$ we substitute $Q_x = 0.1250a^*$. These solutions for NiI$_2$ and CoI$_2$ are close to the phase boundary between the ferromagnetic layers and helix 1.
Figure II.17: Stability diagram as a function of \( j_2 \) and \( j_3 \) \((j_1 = 1)\). The solutions of \( \text{NiI}_2 \) and \( \text{CoI}_2 \) are indicated by the broken lines in region III. The solution of \( \text{NiBr}_2 \) is indicated by the broken line in region IV. The other broken lines in region IV are described in the text.

In Section II.6 also helix 2 with \( Q_y = 0.0800(\frac{2}{a}) \), \( Q_z = 1.5(\frac{1}{c}) \) or \( Q_y = 0.1538(\frac{2}{c}) \), \( Q_z = 0.2500(\frac{1}{c}) \) were mentioned. In the first case the spiral angle in the hexagonal ab-plane is 28.8°, in the latter the spiral angle is 55.4°. For helix 2 the propagation vector is given by:

\[
Q_y = \frac{2}{a} \arccos \left( \frac{2j_3 - 3j_2 - \sqrt{(3j_2 + 2j_3)^2 - 8j_3}}{8j_3} \right) \tag{8}
\]

The broken curves in region IV of Figure II.17 represent the relationship between \( j_2 \) and \( j_3 \), obtained by substituting the spiral angles of 9.72°, 28.8° and 55.4° in equation (8). The spiral angle of 9.72° was obtained for \( \text{NiBr}_2 \) from neutron diffraction [4]. The calculated relationship between \( j_2 \) and \( j_3 \) is very close to the phase boundary between the region of ferromagnetic layers and helix 2. A large spiral angle of 55.4° for helix 2 is not realistic, because this corresponds to values of \( j_2 \) and \( j_3 \) which are too large with respect to \( j_1 = 1 \).
As a matter of fact helix 2 can be stable only, if we include the third interaction in the ab-plane. Also $j_3$ is expected to be small and positive, as it should have the same sign as $j_1$.

We can understand the stability of helix 1 of NiI$_2$ and CoI$_2$ only, if we consider also the interlayer interactions. The error we make, if we neglect $j_3$, is presumably small. Especially in the CdCl$_2$ structure of NiI$_2$, $j'$ plays an important role. In this structure there are three neighbouring atoms in the slab below and three in the slab above. The appropriate part of the structure factor is

$$
\gamma'_k = \frac{1}{3} \left[ \cos \frac{1}{3} ck_z \left( 2 \cos \frac{ak_x}{2\sqrt{3}} \cos \frac{ak_y}{2} + \cos \frac{ak_x}{\sqrt{3}} \right) \\
+ \sin \frac{1}{3} ck_z \left( 2 \sin \frac{ak_x}{2\sqrt{3}} \cos \frac{ak_y}{2} - \sin \frac{ak_x}{\sqrt{3}} \right) \right]
$$

From the minimization of the energy with respect to $k_y$, it follows that $\sin \frac{1}{3} aQ_y = 0$. Other solutions with $\sin \frac{1}{3} aQ_y \neq 0$ would yield helix 2 magnetic structures, but these structures are unstable with respect to helix 1 and the ferromagnetic solution. Only at the phase boundary between the regions of helix 1 and ferromagnetic layers in the stability diagram of Figure II.19, helix 2 has the same energy as the other two solutions.

Thus, we conclude that $Q_y = 0$. Maximizing $\gamma'_k$ with respect to $k_z$ yields the following relation between the propagation-vector components $Q_x$ and $Q_z$:

$$
\cos \frac{1}{3} cQ_z = \pm \frac{\cos (aQ_x/\sqrt{3}) + 2 \cos (aQ_x/2\sqrt{3})}{\sqrt{4 \cos (\sqrt{3}aQ_x/2) + 5}}
$$

This formula is equivalent with

$$
\tan \frac{1}{3} cQ_z = \frac{2 \sin (aQ_x/2\sqrt{3}) - \sin (aQ_x/\sqrt{3})}{2 \cos (aQ_x/2\sqrt{3}) + \cos (aQ_x/\sqrt{3})}
$$

Van Erk [31] deduced an equation of this type for a similar interaction $j'''$ in the Cd(OH)$_2$ structure, to be discussed later. The relation between $Q_z$ and $Q_x$ is plotted in Figure II.18. The + sign in equation (10) refers to the lower branch in Figure II.18 (ferromagnetic coupling of the layers), the - sign to the upper branch (antiferromagnetic coupling of the layers).
Figure II.18: Plot of equations (10) and (11) (see text). The upper branch refers to \( j' < 0 \), the lower branch to \( j' > 0 \).

Minimization of the mean-field energy, including \( j_1, j_2 \) and \( j' \), with respect to \( Q_x \), and substitution of equation (10) gives:

\[
1 + j_2 + 2j_2 \cos(\sqrt{3}Q_x/2) \pm \frac{j'}{\sqrt{4\cos(\sqrt{3}Q_x/2) + 5}} = 0 \quad (12)
\]

Substitution of the spiral angle of NiI\(_2\), \( \sqrt{3}Q_x/2 = 49.8^\circ \), again yields a linear dependence of \( j_2 \) and \( j' \) (Figure II.19; broken line for NiI\(_2\)). As Rastelli already concluded only two types of magnetic structures are stable in this case: the ferromagnetic layers and helix-I type structures, separated by the lines \( |j'| = -9j_2 - 3 \) (Figure II.19A). For finite \( j' \), the spiral turn angle \( \frac{1}{3}cQ_z \) differs from \( 180^\circ \). Substituting \( Q_x = -1.1384a^* \) in equation (11), we obtain a \( Q_z = 1.496c^* \), which is close to the observed value of \( Q_z = 1.457c^* \). The difference can be accounted for by the contributions of other weak exchange interactions with more distant neighbours.

In the Cd(OH)\(_2\) structure of CoI\(_2\), three interactions between the layers of Co\(^{2+}\) can be considered, an interaction

- \( j' \) with 2 neighbours (distance \( c \)),
- \( j'' \) with 12 neighbours (distance \( \sqrt{a^2 + c^2} \)) and
- \( j''' \) with 6 neighbours (distance \( \sqrt{3a^2 + c^2} \)) (Figure II.16).
Rastelli [33] only included the first interaction in his calculation. However, as pointed out by Van Erk [31], the third interaction \( j'''' \) is probably important too, because it is close to 180° superexchange via two anions, involving \( e_g \)–\( e_g \) interactions via both anion \( s \) and \( p \) orbitals. This interaction \( j'''' \) certainly plays an important role in the collinear magnetic structures of \( FeI_2 \) [28] and \( MnBr_2 \) [29].

For the time being, we consider the interaction \( j'''' \), and neglect \( j' \) and \( j'' \). The structure factor is

\[
\gamma_k'''' = \frac{1}{3} \left[ \cos k_z \left( 2 \cos \frac{\sqrt{3} k_x}{2} \cos \frac{3}{2} k_y + \cos \sqrt{3} k_x \right) \right. \\
\left. + \sin k_z \left( 2 \sin \frac{\sqrt{3} k_x}{2} \cos \frac{3}{2} k_y - \sin \sqrt{3} k_x \right) \right]
\] (13)

Minimization of the energy with respect to \( k_z \), with \( \frac{1}{2} a \Phi_y = 0 \), yields:

\[
\tan cQ_z = \frac{2 \sin (\sqrt{3} Q_x/2) - \sin (\sqrt{3} Q_x)}{2 \cos (\sqrt{3} Q_x/2) + \cos (\sqrt{3} Q_x)}
\] (14)
Substituting $\sqrt{3}Q_x/2 = 45^\circ$, the spiral angle of CoI$_2$, in this formula, we obtain $cQ_z = 164^\circ$ or $196^\circ$, taking the upper branch (j" < 0) of Figure II.18. Hence, the effect of the packing of the cations on $cQ_z$ would be much larger in the Cd(OH)$_2$ structure than in the CdCl$_2$ structure, although the interplane Ni-Ni distance in the latter is much smaller. Of course in reality we have to weigh formula (14) by factorizing with j" for CoI$_2$. This weighing can be achieved by including the parameters j' and j" of the Cd(OH)$_2$ structure.

The structure factors for j' and j" are

$$\gamma' = \cos ck_z$$

and

$$\gamma'' = \frac{1}{3}\left[\cos ck_z \left(2\cos \frac{\sqrt{3}k_x}{2} \cos \frac{ak_y}{2} + \cos ak_y\right)\right].$$

After minimization of the energy, equation (14) now becomes

$$\tan cQ_z = \frac{\{2\sin(\sqrt{3}Q_x/2) - \sin(\sqrt{3}Q_x)\}j''}{\{2\cos(\sqrt{3}Q_x/2) + \cos(\sqrt{3}Q_x)\}j'' + \{\cos(\sqrt{3}Q_x/2) + 1\}j'' + 3j'}$$

Substituting again $\sqrt{3}Q_x/2 = 45^\circ$, we see that the inclusion of j' and j" in the calculation leads to values of $cQ_z$ closer to $180^\circ$. In CoI$_2$ a value of $cQ_z = 180^\circ$ is observed. This is only compatible with the calculations, if the contributions of j' and j" are important. Therefore, we calculate the relation between intralayer and interlayer exchange interactions in a simplified model with j" = 0. We minimize the energy with respect to $k_x$ and obtain

$$1 + \{2\cos(\sqrt{3}Q_x/2) + 1\}j_2 + j'' = 0 \text{ for } cQ_z = 0^\circ,$$

and

$$1 + \{2\cos(\sqrt{3}Q_x/2) + 1\}j_2 - j'' = 0 \text{ for } cQ_z = 180^\circ.$$

Substitution of $\sqrt{3}Q_x/2 = 45^\circ$ for CoI$_2$ yields the broken line in Figure II.19B. Instead of j' for NiI$_2$, we have plotted j", the interaction with distance $\sqrt{a^2 + c^2}$. The phase boundaries between the regions where the ferromagnetic layers, respectively helix 1, are stable, are $|j'| = -3j_2 - 1$. As shown in Figures II.17 and II.19, the observed and calculated differences between CoI$_2$ and NiI$_2$ are very small. If we take into account only the first two interactions in the ab-plane, we can calculate from the Néel temperatures of CoI$_2$ and NiI$_2$, 8.2 K and 75 K, respectively, these interactions. For CoI$_2$ we deduce $J_1 = 4.5$ K and $J_2 = -1.9$ K; for NiI$_2$ $J_1 = 15.6$ K and $J_2 = -6.8$ K. Both the lines for CoI$_2$ and NiI$_2$ (broken lines in Figures II.17 and II.19) are close to the phase boundary between helix 1 and ferromagnetic layers. The chlorides and
bromides of cobalt and nickel \((\text{for NiBr}_2: T > 22.5 \text{ K} [12])\) have ferromagnetic layers. It is not clear whether \(|J_2|\) is increased or \(J_3\) is decreased, going from the chlorides to the iodides. Adam et al. [4] discussed the phase transition in \(\text{NiBr}_2\) at 22.5 K. This phase transition is of first order, due to the weak coupling between the layers. In fact, \(\text{NiBr}_2\) is a two-dimensional magnetic system, in which the in-plane \(J_3\) interaction plays a more important role than the inter-plane \(J'\). \(J_3\) stabilizes the helix-2 type structure of \(\text{NiBr}_2\), whereas \(J'\) stabilizes the helix-1 type structure of \(\text{NiI}_2\). Thus \(\text{NiI}_2\) should be regarded as a more three-dimensional system than \(\text{NiBr}_2\).

Rastelli et al. take into account a single-ion anisotropy \(d\). According to Rastelli \(d\) must be positive and \(J_2 < -1/3\) for \(\text{CoI}_2\) with the spins in the ab-plane. Indeed we found \(g_L > g//c\) in \(\text{CoI}_2\) from magnetic susceptibility measurements (Section II.5). At temperatures below the critical temperature \((T_c = 8.2\ \text{K})\) of \(\text{CoI}_2\) the out-of-plane anisotropy between \(x_Lc\) and \(x//c\) \((x_Lc > x//c\) resembles the results obtained for \(\text{CoBr}_2\) [18]. In \(\text{CoBr}_2\) and \(\text{CoI}_2\) the spins lie in the hexagonal ab-plane.

The plane in which the spins of \(\text{Ni}^{2+}\) rotate in \(\text{NiI}_2\) (Figure II.12), cannot be explained by a single-ion anisotropy. On the basis of an axial single-ion anisotropy Rastelli predicts a ferromagnetic order with the spins along the c-axis or a helix-1 with the spins in a plane perpendicular to the ab-plane. The influence of dipolar interactions has not been investigated.

**II.9 SUMMARY**

In this chapter the magnetic and structural properties of \(\text{NiI}_2\) and \(\text{CoI}_2\) were discussed. Measurements of the magnetic susceptibilities of \(\text{NiI}_2\) showed two phase transitions one at 75 K and the other near 60 K. The first transition is the antiferromagnetic ordering temperature, the second is a structural phase transition. This phase transition has been investigated with X-ray diffraction. Two possible supercells were found: a monoclinic or a triclinic one. Neutron diffraction studies at 4.2 K revealed the same possible supercells. A refinement of the atomic coordinates gave shifts of the Ni atoms of about 0.1 Å; the iodine-atom shifts were given tentatively. The low-temperature part of the susceptibility curves of \(\text{NiI}_2\) showed an anisotropy for two oblique orientations of the crystal (Figure II.2). The magnetic part of the neutron diffractogram of \(\text{NiI}_2\) was carefully indexed on the basis of a helix-1 type structure. A propagation vector \(Q = (0.1384, 0, 1.457)\) was found. The profile of the first magnetic reflection was better described with an oblique plane in which
the Ni$^{2+}$ spins rotate. This oblique plane might explain the observed anisotropy of the susceptibility measurements of NiI$_2$.

The anisotropy of the susceptibilities of CoI$_2$ for H$\perp$c and H$\parallel$c was explained in terms of a single-ion anisotropy, which forces the Co$^{2+}$ spins in the ab-plane. Neutron diffraction on CoI$_2$ showed a similar magnetic ordering as NiI$_2$ (helix 1). A propagation vector for CoI$_2$, $Q = (1/8,0,1/2)$ was found, which is commensurable with the nuclear Cd(OH)$_2$ cell, within the experimental errors.

In both CoI$_2$ and NiI$_2$ a large covalent reduction ($\sim$25%) of the magnetic moments was calculated from the neutron data.

Finally, the stability diagrams for trigonal layer compounds were calculated with help of the theory of Rastelli [33]. It was found that, including only intralayer exchange interactions, the solutions for CoI$_2$ and NiI$_2$ are close to the phase boundary between the regions where ferromagnetic layer and helix-1 type structures, respectively, are stable. In order to explain the observed spiral angles in NiI$_2$ and CoI$_2$, interlayer exchange paths were included in the calculations. From these calculations it was shown that exchange with more distant neighbours across the Van der Waals gap is important.

A comparison with the dichlorides and dibromides of cobalt and nickel shows that especially the relative magnitude of $|J_2|$ with respect to $J_1$ is more important in the diiodides than in the other dihalides. In NiBr$_2$, a different type of helix (helix 2) with a spiral angle of only 9.72° was found. In this compound the intralayer interaction $J_3$ is more important than the interlayer interaction $J'$. Thus, whereas the nickel bromides and chlorides can be regarded as simple two-dimensional magnetic systems, nickel iodide clearly has a three-dimensional character.

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II.10 REFERENCES


