MAGNETIC AND STRUCTURAL INVESTIGATIONS ON Nil₂ AND Col₂

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Measurements of the magnetic susceptibility of NiI₂ show an anisotropic behaviour and a magnetic ordering temperature of 75 K. The nuclear and magnetic structures are examined with X-ray and neutron diffraction. The nuclear symmetry changes at 60 K from trigonal to monoclinic. The magnetic structure of NiI₂ is an incommensurate helix of type 1, with propagation vector $Q_x = 0.1384a^*$; $Q_y = 0$; $Q_z = 1.457c^*$. The anisotropy of the magnetic susceptibility of CoI₂ is due to single-ion anisotropy. The magnetic structure is a commensurate helix of type 1, with $Q_x = \frac{1}{8}a^*$; $Q_y = 0$; $Q_z = \frac{1}{2}c^*$. ¹²⁹I-Mössbauer data of NiI₂ and CoI₂ are in good agreement with the proposed magnetic structures. The stability of magnetic structures in trigonal layer compounds is discussed. It is found that the structures of CoI₂ and NiI₂ are close to the phase boundary between helix-1 type structures and structures with ferromagnetic layers.

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 elastic [2–5] and inelastic [6, 7] neutron scattering, Raman scattering [8] and optical measurements in the visible region [3, 9, 10]. CoCl₂ and NiCl₂ have ferromagnetic layers, which are coupled antiferromagnetically. As the behaviour of the chlorides is quite simple, that of the bromides becomes more complicated, probably because the exchange interactions via the bromide ions are more long-range. The magnetic structure of NiBr₂ between 60 and 20 K is like

that of NiCl₂, but is more complex below 20 K. Recently a neutron diffraction study of NiBr₂ single crystals [4] revealed a helix-2 type magnetic structure. The results disagree with the data reported by Day et al. [3, 5].

The diiodides of nickel and cobalt have not been studied extensively. ¹²⁹I-Mössbauer experiments on NiI₂ [11] suggest the same surrounding of all iodine ions by three parallel Ni spins at 4.2 K. Accordingly, the spins of nickel would make an angle of about 63° with the *c* axis. Mössbauer experiments have been interpreted as indicating that CoI₂ consists of ferromagnetic layers of Co spins, lying in the basal ab plane, coupled antiferromagnetically in the *c* direction [11].

Billerey et al. [12, 13] recorded a neutron diffractogram of NiI₂ at 4.2 K, which revealed only one magnetic reflection. From this information alone, they claimed to have deduced the directions of 48 nickel spins in the unit cell.

In this paper we report measurements of the anisotropy and temperature dependence of the magnetic susceptibilities of single crystals of NiI_2

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and CoI₂. The crystallographic and the magnetic structures of NiI₂ and CoI₂ are studied with X-ray and neutron diffraction. In NiI₂ the trigonal symmetry is distorted. Both NiI₂ and CoI₂ have magnetic structures of a helix type. These structures are different from structures suggested earlier in the literature. It is shown that the ¹²⁹I-Mössbauer data [11] are in good agreement with the proposed magnetic structures. Finally, the stability of the magnetic structures of compounds with hexagonal layers of metal ions is discussed.

2. Growth of single crystals of NiI₂ and CoI₂

NiI₂ can 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 to promote the transport of NiI₂ to the cold side of the tube. The single crystals obtained, have an area of about 0.25 cm^2 , 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.

Large and thick single crystals of NiI₂ were grown using a Bridgman furnace. 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 furnace.

CoI₂ was synthesized from the elements in quartz tubes at about 500°C, with a temperature gradient of 75°C. CoI₂ is a black crystalline solid, and does not decompose before melting (m.p. 515°C), so that the Bridgman technique can be used without problems.

 NiI_2 is hygroscopic and CoI_2 is very hygroscopic. Extreme care has to be taken in the hand-

ling of the materials, in order to avoid hydratation and oxidation. The preparation and the mounting of crystals were performed in a glove box, flowed with dry nitrogen gas.

3. Magnetic measurements

Measurements of the magnetic susceptibilities of NiI₂ and CoI₂ were performed on a Faradaytype 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 Bridgmangrown samples and weighed 50 to 100 mg. Fig. 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. Both curves have been corrected for diamagnetism: $\chi_{dia} = -116 \times 10^{-6} \text{ cm}^3/\text{mol}$ [15].

The temperature dependence of the magnetic susceptibility agrees approximately with the



Fig. 1. Reciprocal magnetic susceptibilities of NiI₂ versus the temperature for two directions of the applied field of 8.61 kOe: the full line for $H \parallel c$ and the broken line for $H \perp c$.

powder susceptibilities reported earlier by Billerey et al. [12] and Worswick et al. [16]. However, we did not observe the sharp peak in χ at 59.5 K reported by Billerey et al. [12]. The measured difference between the susceptibilities for $H \perp c$ and $H \parallel c$ 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 а value of $\chi_{\rm VV} =$ $272 \times 10^{-6} \text{ cm}^3/\text{mol}$ is calculated from the relation $\chi_{\rm VV} = 8N\mu_{\rm B}^2/\Delta$, using a crystal-field splitting $\Delta =$ 7660 cm⁻¹ [17]. The Curie constant C = 1.37 is isotropic, the asymptotic Curie temperature θ is -60 K. From C = 1.37 one calculates a value g = 2.3. Boudewijn [18] obtained g = 2.21 from the magnetic field dependence of a zero-phonon line in the spectrum of CdI_2 : Ni²⁺.

Fig. 2 shows the temperature dependence of the susceptibilities of NiI₂ for four directions of the applied field (H = 8.61 kOe): (1) $H \parallel c$, (2) $H \perp c$, (3) the c axis makes an angle of 45° with



Fig. 2. Low-temperature magnetic susceptibilities of NiI₂ for four directions of the applied field (H = 8.61 kOe): (1) the full line: $H \parallel c$; (2) the broken line: $H \perp c$; (3) the dotted broken line: the angle between c and H is 45°; (4) the dotted line: as (3) but rotated 90° around the c axis.

the applied field, (4) as (3) but the crystal is rotated over 90° around the c axis. All four curves have a maximum at about 75 K. A strong decrease of the susceptibilities occurs between 60 and 55 K; the small anisotropy between the curves 1 and 2, and between 3 and 4 in this temperature region is not significant.

The increase of the susceptibility of curves 1 and 2, and especially 4, at low temperature is presumably due to a small paramagnetic contribution (about 5‰). Such a paramagnetic impurity is easily produced, if during the handling of the sample a slight amount of water is introduced.

The magnetization of NiI_2 at all temperatures and for the four orientations of the crystal is proportional to the field between 0 and 40 kOe.

From measurements of the heat capacity of NiI_2 Billerey et al. [12] deduced the presence of phase transitions at 76 K and at 59.5 K. The first transition corresponds to the maximum in the susceptibility at 75 K. Neutron diffraction [13] indicates that the Néel temperature is indeed 75 K. The transition at 59.5 K is due to a crystallographic distortion, and will be discussed in section 4.

A remarkable feature of the magnetic susceptibility of NiI₂ is the absence of a significant difference between the susceptibilities for $H \parallel c$ and $H \perp c$ (curves 1 and 2 in fig. 2). This behaviour strongly suggests that the spins in NiI₂ are neither parallel to the c axis nor lie in the *ab* plane.

The observed behaviour of the susceptibility can be understood in terms of the magnetic structure of NiI₂ deduced from neutron diffraction (to be discussed in section 6). The magnetic structure of NiI₂ is a helix of type 1 with a propagation vector $\mathbf{Q} = (0.1384, 0, 1.457)$ and the spins lying in a plane which makes an angle $\theta_0 = 55^\circ \pm 10^\circ$ with the *c* axis.

The linear magnetization versus field curves indicate that unwinding of the helix or redistribution of domains play no significant role in the magnetization process.

We now discuss the susceptibility data in terms of spin susceptibilities χ_{\parallel} and χ_{\perp} , for fields parallel and perpendicular to the spin, respectively. It is well known that for an antiferromagnet χ_{\perp} is independent of T for $T < T_N$, whereas χ_{\parallel} decreases rapidly at low temperature and vanishes at T = 0. For a helix (spins lying in a plane which makes an angle θ_0 with the c axis) the susceptibility for a field parallel to the plane of the spins is $\frac{1}{2}(\chi_{\perp} + \chi_{\parallel})$, that for a field perpendicular to the plane of the spins is χ_{\perp} . For $H \parallel c$ the field components parallel and perpendicular to the plane of the spins are $H \cos \theta_0$ and $H \sin \theta_0$, and the susceptibility is $\chi(H \parallel c) =$ $\frac{1}{2}(\chi_{\perp} + \chi_{\parallel}) \cos^2 \theta_0 + \chi_{\perp} \sin^2 \theta_0$. For $H \perp c$, with the field in the plane of the c axis and Q, the components of the field parallel and perpendicular to the plane of the spins are $H \sin \theta_0$ and $H \cos \theta_0$, and the susceptibility is $\chi(H \perp c) =$ $\frac{1}{2}(\chi_{\perp} + \chi_{\parallel}) \sin^2 \theta_0 + \chi_{\perp} \cos^2 \theta_0$. If θ_0 is close to 45°, the susceptibilities $\chi(H \parallel c)$ and $\chi(H \perp c)$ will be approximately equal, as is observed (curves 1 and 2 of fig. 2). The behaviour of curve 4 can be understood if the field lies in the plane of the c

axis and Q, and makes an angle of 45° with the *c* axis; in this case the field is approximately perpendicular to the plane of the spins, and the susceptibility is equal to χ_{\perp} . This explains why the susceptibility in this case does not decrease at low temperature. Finally curve 3 represents a situation in which there is an appreciable contribution of χ_{\parallel} , so that the susceptibility in this case decreases at low temperature.

Fig. 3 shows the susceptibilities of CoI₂ versus the temperature for two directions of the applied field (H = 8.61 kOe). The curves have been corrected for diamagnetism: $\chi_{dia} = -120 \times 10^{-6} \text{ cm}^3/\text{ mol}$ [15]. CoI₂ is very hygroscopic and difficult to handle; weighting errors may amount to 5-10%, so that the absolute accuracy of the measured χ values is not better than 5-10%. However, the $H \perp c$ susceptibility is certainly larger than the $H \parallel c$ susceptibility.

The susceptibilities of CoI_2 do not exhibit a Curie-Weiss behaviour between 150 and 300 K. In the temperature region from 200 to 300 K, we calculated for $H \perp c$ a Curie constant $C_{\perp} = 3.6$ and an asymptotic Curie temperature $\theta_{\perp} =$



Fig. 3. Reciprocal magnetic susceptibilities of CoI_2 versus the temperature for $H \parallel c$ (full line) and $H \perp c$ (broken line); H = 8.61 kOe.

-14 K; for $H \parallel c$ we obtained $C_{\parallel} = 2.9$ and $\theta_{\parallel} = -7$ K. These values agree approximately with values reported by Bizette [19].

Lines [20] already pointed out that $1/\chi$ versus T is not expected to be a straight line for Co^{2+} compounds. The ground state of Co²⁺ in O_h symmetry is a ${}^{4}T_{1g}(t_{2g}^{5}e_{g}^{2})$, split by spin-orbit coupling into a doublet, a quartet and a sextet. The doublet has the lowest energy [21], 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 CoI₂ (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 $CdI_2: Co^{2+}$ [22] revealed nearly isotropic g values, indicating a small trigonal field. However, the anisotropy of the magnetic susceptibilities of CoI₂ suggests that in CoI₂ the trigonal field is appreciable.

The susceptibility curves in the region of the ordering temperature at 8.2 K (fig. 4) are characteristic of antiferromagnetism. Our results differ from the results reported by Bizette et al. [19] who did not observe any critical behaviour in the $H \perp c$ susceptibility. For samples which were



Fig. 4. Low-temperature susceptibilities of CoI₂: $H \perp c$ (broken line); $H \parallel c$ (full line); H = 8.61 kOe.

partly decomposed by air or moisture, we found results similar to those obtained by Bizette. In these cases there is a large paramagnetic susceptibility contribution, which masks all anomalies at low temperature. For $H \parallel c$, Bizette et al. observed a maximum in the susceptibility at 3 K. Later, Van Uitert et al. [23] reported a value of 12 K, and we obtain a value of 9.35 K for this maximum.

If the Co²⁺ spins were oriented parallel to the *c* axis, one would expect $\chi(\mathbf{H} \| \mathbf{c}) = \chi_{\parallel}$ to decrease rapidly at low temperature. This is not observed. Thus the observed data indicate that the Co²⁺ spins are oriented (mainly) in a plane perpendicular to the *c* axis, so that $\chi(\mathbf{H} \| \mathbf{c}) \approx \chi_{\perp} - \Delta \chi$. In that case $\chi(\mathbf{H} \perp \mathbf{c}) \approx \frac{1}{2}(\chi_{\perp} + \chi_{\parallel})$ decreases more rapidly at low temperatures than $\chi(\mathbf{H} \| \mathbf{c})$, due to the contribution of χ_{\parallel} . The value of $\chi(\mathbf{H} \| \mathbf{c})$ is lowered by a contribution $\Delta \chi$, due to the out-of-plane anisotropy which is appreciable for the Co²⁺ ion. The magnetization of CoI₂ at all temperatures for $\mathbf{H} \perp \mathbf{c}$ and $\mathbf{H} \| \mathbf{c}$ is proportional to the field for fields up to 40 kOe.

4. X-ray diffraction of 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 cell. We prefer the latter description: one Ni at the origin, and two I at $\pm(0, 0, z)$ of space group R3m. The *c* axis is the uniaxial axis. A profile refinement of a neutron diffractogram of NiI₂ at 300 K yields a = 3.922(1) Å, c = 19.808(1) Å and c/3a =1.684(1) (standard deviations are given in brackets). The *z* parameters of the iodine ions are $z_I = \pm 0.2560$, which means that the octahedron NiI₆⁴ is trigonally compressed along the *c* axis.

Billerey et al. [12] discovered two anomalies in the heat capacity, indicating phase transitions at 59.5 and 76 K. The second transition was not observed by Worswick et al. [16]. We carried out a low-temperature X-ray examination of NiI_2 in order to determine the crystallographic structure at low temperature.

Small distortions are best studied using reflections with large values of h, k and especially l. Fig. 5 shows the temperature dependence of the 1016, 0114 and 1112 reflections, recorded at a few selected temperatures in the neighbourhood of 60 K. From 82.9 to 66.8 K the intensity of the hexagonal 1016 reflection strongly increases without a change in the intensity ratio 2/1 of the two peaks (α_1/α_2 ratio); this is probably due to a decrease of the z parameter of the iodine atom to the value $z_1 = 0.25$. From 66.8 to 60.5 K the peak height of the 1016 reflection decreases, and the reflection broadens. At 57.5 K we clearly see that the intensity ratio of the two peaks no longer reflects the α_1/α_2 ratio, due to a splitting of the 1016 reflection. The same behaviour is observed at lower temperatures down to 35 K. The actual transition temperature is 60 K, in good agreement with the value of 59.5 K reported by Billerey et al. [12]. The hexagonal 0114 and 1112 reflections show a similar temperature dependence.

The α_1 components of the three reflections at



Fig. 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 α_1 component only. Vertical bars give the calculated 2θ values of the monoclinic cell.



Fig. 6. Monoclinic cell of NiI₂. Closed circles are Ni atoms, open circles are I atoms. One slab I-Ni-I is drawn; + denotes the upper iodine, - the lower iodine.

35 K have been obtained by subtracting half of the intensity of the α_1 component at the corresponding α_2 scattering angle (fig. 5) [24]. The hexagonal 1016 reflection at 35 K is broadened towards larger 2 θ values, while the 0114 broadens towards lower 2 θ values. The 1112 reflection broadens in an asymmetric way.

The observed splittings can be indexed on the basis of a monoclinic cell. The axes of the nonprimitive monoclinic cell are $a_m \approx 2a + b$, $b_m \approx b$ and $c_m \approx c$, with a, b, c referring to the hexagonal cell (fig. 6). The monoclinic cell dimensions at 35 K are $a_m = 6.765(1)$ Å, $b_m = 3.919(1)$ Å, $c_m =$ 19.635(1) Å and $\beta = 90.23(2)^\circ$. The vertical lines in fig. 5 indicate the calculated position of the monoclinic cell reflections.

5. Nuclear neutron diffraction of NiI₂ at 4.2 K

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 led to better statistics. A disadvantage of these improvements is the appearance of $\lambda/2$ and $\lambda/3$ contributions above the background.

Fig. 7 gives the diffractogram of NiI₂; the dots

represent the measured diffractogram at 4.2 K, the higher order $\lambda/2$ and $\lambda/3$ contributions are indicated by B. The original hexagonal reflections are indicated by N; in the region of these reflections the full line represents the calculated profile. Furthermore, the diffractogram shows the magnetic satellites M.

Because the wavelength of neutrons (2.5861 Å) larger than the wavelength of CuK_a is (1.5418 Å), the hexagonal 0 1 14, 1 1 12 and 1 0 16 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 scatprofile angles. However, analysis tering reproduced the observed broadening of the reflections, due to the monoclinic distortion of the hexagonal cell, quite well. The observed pattern is described by a non-primitive monoclinic cell with dimensions $a_{\rm m} = 6.769(1)$ Å, $b_{\rm m} =$ 3.914(1) Å, $c_m = 19.630(1)$ Å and $\beta = 90.20(2)^\circ$. These cell constants agree with the results obtained with X-ray diffraction at 35 K. Preliminary calculations indicate small shifts (~ 0.1 Å) of the Ni atoms from the positions in the hexagonal cell.

6. Magnetic structure of NiI₂

Few attempts have been reported to solve the magnetic structure of NiI₂. Two publications of Mössbauer spectra of NiI₂ have appeared. The first paper stated that NiI₂ is a simple antiferromagnet with alternating spins in the (100) direction [25]. Billerey et al. [12] 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 shows several magnetic reflections (indicated by M in fig. 7), Billerey et al. observed only the first magnetic reflection at $2\theta = 355$ DMC. This reflection was indexed in [12] as the 013 reflection in a very large cell with dimensions a, $4a\sqrt{3}$, 2c. From the intensity of



Fig. 10. Neutron diffractogram of CoI₂ at 4.2 K. The scattering angle is given in units of DMC (10⁴ DMC \equiv 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.

this reflection the authors claimed to have deduced the directions of 48 nickel spins and they suggested that all other reflections, such as the 0 1 1 and 0 1 9, were lost in the background. In our diffractogram, however, the background is much lower. At 180 DMC, the 2θ value of the 0 1 1 reflection, no intensity is observed, so that the magnetic structure proposed by Billerey et al. does not agree with our neutron data.

Because of the confusion about the magnetic reflections, we will discuss the indexing of the reflections in some detail. First we construct the reciprocal lattice on the basis of the unit cell, 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/dvalues of the diffractogram. The first magnetic reflection is regarded as the satellite of the origin $(0, 0, 0)^{\pm}$. 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 intersection of the circles around the origin and the circles with radius |Q| around the reciprocal lattice points.

In fig. 8 a reciprocal lattice plane, containing the c^* axis, is shown. The horizontal axis can either be taken as the hexagonal [100] or $[\bar{1}20]$ 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 (~2/a $\sqrt{3}$) gives a helix-1 type structure (fig. 9), Q_y (~2/a) a helix-2 type structure [26, 27]. Attached to the circles around the origin of the reciprocal lattice are the 2θ values (in units of DMC, with $10^4 \text{ DMC} = 360^\circ$) of the first two magnetic reflections (fig. 8). The only way to explain the large gap from 367 to 967 DMC between the first and the second magnetic reflection is to add a large Q_z component to the Q_x or Q_y component of the pro-



Fig. 8. A reciprocal lattice plane perpendicular to the a^*b^* plane. The radii of the circles around the origin correspond to the observed 1/d values of the satellites, indicated by their 2θ values in units of DMC. The full arrows are the Q vectors $\pm (0.1384, 0, 1.457)$.

pagation vector, as shown in fig. 8 by the drawn arrows. The otherwise missing (003)[±] 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 correspond to the magnetic unit cell proposed by Billerey et al. [12]. The indexing of the magnetic satellites is better in our case, and our incommensurable Q values explain the observed broadenings of the first and second magnetic reflection.

In principle the two solutions $(\pm Q_x, 0, Q_z)$ are not equivalent, because the c^* axis makes an angle of $\beta \neq 90^\circ$ with the a^* axis. There are four other solutions obtained by rotating the previous ones over 120° and 240° in the hexagonal plane. The differences between the calculated 2θ 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 fig. 9 the corresponding spiral angles are shown. In table I we have listed the observed and calculated positions of the two satellites of each reflection.

The magnetic cross sections of the satellites are given by [28]

А



Fig. 9. 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 NiI₂. The broken line is the intersection with the plane of fig. 9B. B: Spiral angles in the $(1\overline{2}0)$ plane. The ellipses indicate the plane in which the Ni spins rotate.

$$\sigma_{H\pm O} = \frac{1}{4} (1 + \cos^2 \omega) \\ \times \left[\frac{e^2 \gamma}{2mc^2} \sum_{v} \mu_v f_v (\boldsymbol{H} \pm \boldsymbol{Q}) \\ \times \sin \beta_v \exp i(2\pi \boldsymbol{H} \cdot \boldsymbol{r}_v \mp \boldsymbol{\phi}_v) \right]^2, \quad (1)$$

where H is the nuclear reflection, ω the angle between the cone axis and the scattering vector, $e^2\gamma/2mc^2 = 0.2695 \times 10^{-12}$ cm, μ_v the magnetic moment of the vth Ni atom, $f_v(H \pm Q)$ the form factor for magnetic scattering [29], β_v the opening angle of the cone, r_v the relative position of the vth Ni atom in the cell and ϕ_v is an arbitrary phase angle of the vth Ni atom. For a simple helix, as we assume for NiI₂, $\beta_v = 90^\circ$ and $\phi_v =$ 0°. In eq. (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 eq. (1) is the same for all satellites. The variation of this part, due to the small displacements of the nickel atoms is neglected.

The observed profile of the first magnetic reflection was compared with the profile calculated for the cone axis lying in the ab plane parallel to the x direction (fig. 9A) and for a case with the spins in a plane making an angle $\theta = 55^{\circ}$ with the c axis (fig. 9B). In the latter case a much better agreement is obtained, and we conclude that this case with $\theta = 55^{\circ} \pm 10^{\circ}$ describes the orientation of the spins in Nil₂ at 4.2 K quite well. The magnetic moment of Ni²⁺, calculated from the observed intensities of the first two magnetic satellites, is $1.6 \mu_{\rm B}$. The intensities of the satellites, calculated for the proposed magnetic structure of NiI₂ (fig. 9) are listed in table I. The observed intensities are not very accurate, because of overlap with nuclear reflections and background peaks.

7. The crystallographic and magnetic structure of CoI₂

 CoI_2 crystallizes in the $Cd(OH)_2$ -structure, which has a hexagonal close packing of anions

Table I

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

Hexagonal	+O satel	lites			-O sate			
reflection	2θ obs (DMC)	2θ calc (DMC)	intensity obs	intensity calc	2θ obs (DMC)	2θ calc (DMC)	intensity obs	intensity calc
000	350	350	10800	10624	350	350	10800	10624
003	965	965	1800	2286	365	365	11300	11538
111	N	1285	800	661	1358	1351	1000	659
011	1358	1351	1000	659	Ν	1285	800	661
101	Ν	1538	?	700	1068	1072	1000	1285
006	1653	1646	850	636	983	982	1400	1790
102	1448	1436	530	615	В	1308	?	623
ī12	В	1172	?	873	Ν	1557	?	609
012	Ν	1558	?	609	В	1172	?	873
ī 14	Ν	1693	?	394	1458	1461	410	475
014	1458	1462	410	475	Ν	1693	?	394
104	-	1912	~0	459	1198	1206	2000	1347
105	1638	1640	500	364	В	1803	?	308
115	1408	1407	600	732	Ν	2016	~0	354
015	Ν	2017	~0	354	1408	1407	600	732

[1]. The hexagonal unit cell contains one CoI_2 unit; the uniaxial axis is the *c* axis. Fig. 10 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 some broadening. These phenomena are well known and are caused by stacking faults, which are easily introduced, because 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 Å and c = 6.664 Å at 4.2 K. Also from these reflections the scaling factor, the preferred orientation parameter G, induced by the platelet form of CoI₂ 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:

$$I_{\text{corrected}} = I_{\text{calc}} e^{G\alpha^2}, \qquad (2)$$

where α is the angle between the scattering vector and the *c* axis. We found G = 0.186. The *z* parameters of the iodine ions are close to ± 0.25 .

The only data available on the magnetic structure of CoI_2 are the ¹²⁹I-Mössbauer measurements of Friedt et al. [11]. From these data the authors concluded that CoI_2 is an antiferromagnet, consisting of ferromagnetic layers with the spins in the *ab* plane.

Not only nuclear reflections are broadened, the magnetic satellites are broadened too. In fig. 10^* the magnetic satellites of CoI₂ are indicated with the letter M. The first magnetic reflection at

^{*} See p. 238.



Fig.11. Orthorhombic magnetic unit cell $(4a\sqrt{3}, a, 2c)$ of CoI₂ (*ab* plane). Attached to the Co²⁺ ions are the spiral angles.

341 DMC can be described as the $(000)^{\pm}$ and $(001)^{-}$ satellites, the second magnetic reflection at 948 DMC as the $(001)^+$ and $(002)^-$ satellites. The indexing scheme is the same as used in the case of NiI₂ (fig. 8). For CoI₂ the 2θ values of the magnetic satellites are explained using $Q_x = \frac{1}{8}a^*$ and $Q_z = \frac{1}{2}c^*$. The magnetic unit cell is commensurable with the nuclear unit cell, within the experimental errors introduced by the stacking faults. The magnetic unit cell has dimensions $4a\sqrt{3}$, a and 2c. The ab plane of this cell has the same dimensions as Billerey et al. suggested for NiI_2 [12] (see fig. 11). There is an antitranslation of the spins along the c axis. 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 (fig. 11). The magnetic moments lie in the ab plane as indicated by the magnetic susceptibility data. Further evidence for this structure is obtained from ¹²⁹I-Mössbauer spectra (section 8).

The calculated profile of the neutron diffractogram of CoI₂ up to 1000 DMC agrees quite well with the observed profile. The magnetic moment of Co²⁺ in CoI₂ is $1.67 \mu_B$. For the lowest Kramers doublet E'_g of the ground state of Co²⁺ in an octahedral coordination one calculates a value of $2.16 \mu_B$. The difference could be due to covalency, or to the presence of stacking faults.

8. Transferred hyperfine fields in CoI₂ and NiI₂

In this section we reinterpret the available ¹²⁹I-Mössbauer data [11] in terms of the magnetic structures proposed in previous sections.

The hyperfine fields at the iodine site in the magnetically ordered phases of CoI_2 and NiI_2

arise from the spin polarization of the valence electrons of the nominally diamagnetic ligands [30]. The hyperfine field at the iodine nucleus is written as

$$\boldsymbol{H}_{\rm hf} = \boldsymbol{H}_{\rm FC} + \boldsymbol{H}_{\rm SD} + \boldsymbol{H}_{\rm d} \,, \tag{3}$$

where H_{FC} is the isotropic contact field provided by both the core polarization mechanism and the finite spin density (f_s) in the 5s orbital. H_{SD} is the spin dipolar term arising from an unpaired spin density (f_{σ}, f_{π}) transferred into the 5p valence orbital of iodine. H_d is the regular dipolar field induced by the metal magnetic moments at the iodine site.

Considering only the three nearest neighbour M ions (i, j, k) of an iodine atom, the hyperfine field components along the three equivalent M-I bonds are [31]

$$H_{\alpha} = -\left\{ (H_{iso} + H_{an}) \frac{\langle S_{\alpha}^{i} \rangle}{S} + (H_{iso} - \frac{1}{2}H_{an}) \frac{\langle S_{\alpha}^{j} \rangle}{S} \right. \\ \left. + (H_{iso} - \frac{1}{2}H_{an}) \frac{\langle S_{\alpha}^{k} \rangle}{S} \right\}, \\ H_{\beta} = -\left\{ (H_{iso} - \frac{1}{2}H_{an}) \frac{\langle S_{\beta}^{j} \rangle}{S} + (H_{iso} + H_{an}) \frac{\langle S_{\beta}^{j} \rangle}{S} \right. \\ \left. + (H_{iso} - \frac{1}{2}H_{an}) \frac{\langle S_{\beta}^{k} \rangle}{S} \right\}, \\ H_{\gamma} = -\left\{ (H_{iso} - \frac{1}{2}H_{an}) \frac{\langle S_{\gamma}^{i} \rangle}{S} + (H_{iso} - \frac{1}{2}H_{an}) \frac{\langle S_{\gamma}^{j} \rangle}{S} \right. \\ \left. + (H_{iso} + H_{an}) \frac{\langle S_{\gamma}^{k} \rangle}{S} \right\},$$

$$(4)$$

where

$$H_{\rm iso} = (8\pi/3)f_{\rm s}\rho(0)\mu_{\rm B} - \kappa (f_{\sigma} + 2f_{\pi})\langle r^{-3}\rangle\mu_{\rm B} ,$$

$$H_{\rm an} = (4/5)(f_{\sigma} - f_{\pi})\langle r^{-3}\rangle\mu_{\rm B} + 2gS\mu_{\rm B}R^{-3} .$$
(5)

The 5s electron density at the iodine nucleus, taken from free ion calculations, is $\rho(0) = 150 \times 10^{24} \text{ cm}^{-3}$. The radial average over the 5p electronic charge distribution is $\langle r^{-3} \rangle = 121.5 \times 10^{24} \text{ cm}^{-3}$. The core polarization field per unpaired p electron $\kappa \langle r^{-3} \rangle \mu_B$ is small and can be neglected. *R* is the *M*-*I* distance and $gS\mu_B$ the magnetic moment of Co²⁺ or Ni²⁺. Note that expressions (4) do not take into account the effects of the non-spherical electronic structure and unquenched orbital moments of Co²⁺. For a complete discussion of these effects see the detailed theory developed by Thornley et al. [32].

First we discuss the magnetic structure of CoI₂. A collinear magnetic structure of CoI₂, similar to the structure proposed by Billerey et al. for NiI₂ [12], gives rise to two non-equivalent iodine sites: one with three parallel neighbour cobalt moments (a), the other with two parallel moments and one antiparallel (b). Their relative occupation number is in the ratio a:b=3. In case (a) the transferred field obtained from eq. (4) is isotropic, i.e. the field is collinear with the spin direction and given by $H_{hf}(a) = 3H_{iso}$. In case (b) the transferred field has an anisotropic contribution. However, if we neglect the small dipolar term, and if $f_{\sigma} \simeq f_{\pi}$ (a reasonable approximation for Mn²⁺ and Co²⁺ ions) the anisotropic contribution can be neglected, and the hyperfine field at the b site is $H_{hf}(b) = H_{iso}$. Therefore the ratio of the hyperfine fields at sites a and b of the collinear structure must be approximately equal to 3. This is not consistent with the observed ¹²⁹I-Mössbauer spectra of CoI₂ at 4.2 K. Indeed, it has been shown by Friedt et al. [11] that the Mössbauer data could be interpreted in terms of a single magnetic site and a transferred field $H_{hf} = 130 \pm 3 \text{ kOe}$, making an angle $\theta = 90^{\circ} \pm 5^{\circ}$ with the crystallographic c axis.

Let us now examine the helix-1 magnetic structure of CoI_2 , described in fig. 11, with the spins lying in the *ab* plane. This structure gives rise to four non-equivalent iodine sites, labelled a, b, c, d. Their relative occupation number is a:b:c:d = 1. However, assuming again that the anisotropic field can be neglected, it is found that the transferred field at all four sites is the same and is given by

$$H_{\rm hf} = H_{\rm iso} \{5 + 4\cos 45^\circ\}^{1/2} \tag{6}$$

and makes an angle of 90° with the c axis. From the observed hyperfine field a value of $f_s = 0.4 \times 10^{-2}$ is deduced. Calculations taking into account a small anisotropic contribution $f_{\sigma} - f_{\pi} = 1.5 \times 10^{-2}$ show that the magnitude of the transferred field as well as its orientation with respect to the c axis remain unchanged within the experimental errors (table II). The conclusion is that the helix-1 structure of CoI₂ is in good agreement with the Mössbauer data.

The interpretation of the transferred hyperfine field in CoI₂ is complicated by the fact that the ground state of Co²⁺ in an octahedral crystal field is orbitally degenerate. This makes it difficult to obtain accurate values for the spin transfer coefficients. From the Mössbauer measurements we deduce $f_s = 0.4 \times 10^{-2}$, to be compared with the value of 0.386×10^{-2} obtained from zero-field NMR experiments at the chlorine nucleus in CoCl₂ [33]. From EPR data of CdI₂: Co²⁺ a value of $f_s = (0.54 \pm 0.1) \times 10^{-2}$ was obtained [34].

The ¹²⁹I Mössbauer data of NiI₂ at 4.2 K were interpreted by Friedt et al. in terms of a single magnetic site and a transferred field $H_{hf} =$ 263 ± 3 kOe, making an angle of $63^{\circ} \pm 5^{\circ}$ with the *c* axis [11]. In the magnetic structure of NiI₂ proposed by Billerey et al. [12] there are two non-equivalent magnetic sites giving rise to quite different hyperfine fields. Therefore, the Mössbauer data are not consistent with the magnetic structure proposed by Billerey et al.

Strictly speaking the helix-1 magnetic structure of NiI_2 gives rise to an infinite number of iodine

Table II

Values of the hyperfine field $H_{\rm hf}$ and its orientation with respect to the c axis (angle θ) for CoI₂, calculated from eq. (4), using $f_{\rm s} = 0.4 \times 10^{-2}$ and $f_{\sigma} - f_{\pi} = 1.5 \times 10^{-2}$

Site	H _{hf} (kOe)	θ					
a	133.8	87.1					
b	134.6	88.8					
c	127.4	88.7					
d	126.5	86.9					

magnetic sites. In order to estimate the distribution of H_{hf} and θ (angle between H_{hf} and the *c* axis), we can neglect in a first step the anisotropic contribution to the field. Within this approximation the field has a unique value

$$H_{\rm hf} = H_{\rm iso}(5 + 4\cos\epsilon)^{1/2}, \qquad (7)$$

where ϵ is the spiral angle ($\epsilon = 49.8^{\circ}$), and the angle θ is distributed uniformly between $\theta =$ $55^{\circ} \pm 10^{\circ}$ and 90°. Calculations taking into account a small anisotropic contribution $f_{\sigma} =$ 5×10^{-2} (estimated from a comparison with data for other nickel dihalides) show that the hyperfine fields at the various iodine sites are approximately the same, and that the values of θ are distributed uniformly between $\theta = 55^{\circ} \pm 10^{\circ}$ and $85 \pm 5^{\circ}$ (table III). Computer simulations of Mössbauer spectra as a function of θ show that the shape of the spectra is not very sensitive to variations of θ in the range of interest $55^\circ < \theta <$ 85°. Therefore, the Mössbauer spectra can be well represented by a single set of hyperfine parameters with an average angle 68.5° (calculated from $(\cos^2 \theta)$, in good agreement with the experimentally determined value of $63^{\circ} \pm 5^{\circ}$. The value of $f_s = 0.82 \times 10^{-2}$ deduced from Mössbauer spectra of NiI₂, is to be compared with the value $f_s = 0.64 \times 10^{-2}$ for NiCl₂ [33].

9. Stability of the magnetic structures of NiI₂ and CoI₂

For layered compounds complicated magnetic

structures have been reported [3, 4, 35–39]. The stability of magnetic structures in compounds with hexagonal layers of magnetic ions has been studied by several authors [26, 27, 36, 40]. In this section we review some of the results, and discuss the stability of the observed magnetic structures of NiI₂ and CoI₂.

For the discussion the following Hamiltonian is used [27]:

$$H = -\sum_{\alpha} J_{\alpha} \sum_{i,\boldsymbol{\delta}_{\alpha}} \{ \boldsymbol{S}_{i}^{(\mathbf{a})} \cdot \boldsymbol{S}_{i+\boldsymbol{\delta}_{\alpha}}^{(\mathbf{a})} + \boldsymbol{S}_{i}^{(\mathbf{b})} \cdot \boldsymbol{S}_{i+\boldsymbol{\delta}_{\alpha}}^{(\mathbf{b})} \}$$
$$-2J' \sum_{i,\boldsymbol{\delta}'} \boldsymbol{S}_{i}^{(\mathbf{a})} \cdot \boldsymbol{S}_{i+\boldsymbol{\delta}'}^{(\mathbf{b})}, \qquad (8)$$

where a and b refer to spins in even and odd layers perpendicular to the c axis, δ_{α} are the vectors from the atom at site *i* in the *ab* plane to its neighbours of type α in the same plane, δ' is the vector to the atom in the adjacent layers. In the calculations reduced exchange parameters $j_{\alpha} = Z_{\alpha}J_{\alpha}/(Z_1|J_1|)$ are used, where Z_{α} denotes the number of neighbours interacting via J_{α} . Rastelli [27] has shown that canted spin structures are not stable; only in exceptional cases quantum effects may lead to canted spin structures. We discuss only helical structures with a single propagation vector Q. If the spins rotate in a plane (ξ, η) , the spin components along two orthogonal directions ξ and η in this plane are given by $S_{i\xi} = S \cos \mathbf{Q} \cdot \mathbf{r}_i$ and $S_{i\eta} = S \sin \mathbf{Q} \cdot \mathbf{r}_i$, where \mathbf{r}_i is the position of atom i with spin S_i . The ground state energy in the mean field approximation is

$$E_0 = -2Z_1 |J_1| NS^2 \left\{ \sum_{\alpha} j_{\alpha} \gamma^{\alpha} + j' \gamma' \right\}, \qquad (9)$$

Table	III
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Values of the hyperfine field H_{hf} and its orientation with respect to the *c* axis (angle θ), calculated from eq. (4), using $f_s = 0.82 \times 10^{-2}$ and $f_{\sigma} = 5 \times 10^{-2}$ ($f_{\pi} = 0$ for Ni²⁺). The iodine ions 1 and *n* are surrounded by three Ni²⁺ spins with spin angles of 0°, 49.8°; 49.8° and (*n* - 1) × 49.8°; *n* × 49.8°, respectively

odine	1	2	3	4	5	6	7	8
$H_{\rm hf}$ (kOe)	263.4	264.8	269.2	266.4	262.9	258.7	269.2	264.3
θ	67.0	54.4	64.1	83.5	59.1	51.5	79.0	72.8

with

$$\gamma^{\alpha} = \frac{1}{Z_{\alpha}} \sum_{\boldsymbol{\delta}_{\alpha}} e^{i\boldsymbol{Q}\cdot\boldsymbol{\delta}_{\alpha}}; \qquad \gamma' = \frac{1}{Z'} \sum_{\boldsymbol{\delta}'} e^{i\boldsymbol{Q}\cdot\boldsymbol{\delta}'}. \tag{10}$$

The strongest interaction J_1 ($Z_1 = 6$) is between nearest neighbours (distance a). J_1 contains contributions of a direct exchange interaction between metal ions and a 90° superexchange along, for instance, AKB (fig. 12). This superexchange is between t_{2g} and e_{g} orbitals via σ and π overlap with anion p orbitals. Because of the large radius of iodine the metal-metal distance is large and the direct exchange is expected to be small. According to the Goodenough-Kanamori rules [41, 42], the 90° superexchange for Ni^{2+} and Co^{2+} is ferromagnetic. Indeed it is observed that CoCl₂, CoBr₂, NiCl₂ and NiBr₂ have a dominant ferromagnetic interaction $(J_1 > 0)$ in the *ab* plane. Therefore we consider for NiI₂ and CoI₂ only the case $J_1 > 0$ ($j_1 = +1$).

The interactions J_2 and J_3 are expected to be much weaker, as they involve superexchange via at least two anions; J_2 ($Z_2 = 6$) is via an exchange path over a distance $a\sqrt{3}$ (AKRC in fig. 12), J_3 ($Z_3 = 6$) over a distance 2a.

First we take into account only the intralayer interactions J_1 , J_2 and J_3 . Minimizing the energy with respect to Q_x and Q_y leads to five types of magnetic structures: I – ferromagnetic layers, II – antiferromagnetic order, III – helix 1, IV – helix 2, V – special case of helix 2: 120° structure. The stability regions of these magnetic structures are sketched in fig. 13. For helix 1 the Q vector is parallel to a^* , and is given by

$$Q_x = \frac{2}{a\sqrt{3}} \arccos \frac{-1-j_2}{2(j_2+2j_3)}; \qquad Q_y = 0.$$
 (11)

Substituting the observed value $Q_x = 0.1384a^*$ of NiI₂, we obtain a linear relation between j_2 and j_3 , which corresponds to a straight line in region III of the stability diagram (fig. 13). For CoI₂ we substitute $Q_x = 0.1250a^*$. These solutions for NiI₂ and CoI₂ are close to the phase boundary between ferromagnetic layers and helix 1.

For helix 2 the propagation vector Q is

$$Q_{x} = 0;$$

$$Q_{y} = \frac{2}{a} \arccos \frac{2j_{3} - 3j_{2} - \sqrt{(3j_{2} + 2j_{3})^{2} - 8j_{3}}}{8j_{3}}.$$
 (12)

The broken line in region IV of fig. 13 represents the relation between j_2 and j_3 for helix 2 with a spiral angle of 9.72°, as observed for NiBr₂ at T < 22.5 K [4]. This line is very near to the phase boundary between helix 2 and a structure with ferromagnetic layers (region I). It is of interest to remark that NiBr₂ undergoes at 22.5 K a first-order phase transition to an antiferromagnetic structure with ferromagnetic layers [4].

In order to understand the component Q_z of



Fig. 12. A: Two unit cells of the Cd(OH₂) structure. The closed circles denote the anions, the open circles the iodine ions. B: (110) plane of the Cd(OH₂ structure. C: 1/3 part of the CdCl₂ structure.



Fig. 13. Stability diagram as a function of j_2 and j_3 ($j_1 = 1$). The solutions of NiI₂, CoI₂ and NiBr₂ are indicated by broken lines.

the propagation vector along the c^* axis, we have to consider also the interlayer interactions. These are different for the CdCl₂ and Cd(OH)₂ structure types, due to the different stacking of the hexagonal layers. In this discussion we neglect j_3 which is presumably small.

In NiI₂ (CdCl₂ structure) the main interlayer interaction j' (Z' = 6) is the two-anion superexchange over a distance $[a^2/3 + c^2/9]^{1/2}$ (exchange path AKLE in fig. 12). If the interlayer interaction j' and the intralayer interactions j_1 and j_2 are considered, only two types of magnetic structures are stable, a structure with ferromagnetic layers and a helix-1 type structure. These two structures are separated by the line $|j'| = -9j_2 - 3$ [27]. For helix 1 in the CdCl₂ structure the following relation exists between Q_x and Q_z (obtained by minimizing the energy with respect to Q_z):

$$\tan \frac{1}{3} cQ_z = \frac{2 \sin(aQ_x/2\sqrt{3}) - \sin(aQ_x/\sqrt{3})}{2 \cos(aQ_x/2\sqrt{3}) + \cos(aQ_x/\sqrt{3})}.$$
 (13)

For finite j', the spiral angle $\frac{1}{3}cQ_z$ differs from 180°. Substituting the observed value $Q_x = 0.1384a^*$ for NiI₂ in eq. (13), we calculate $Q_z =$

1.496 c^* , which is close to the observed value $Q_z = 1.457c^*$. The difference can be accounted for by the contribution of weak exchange interactions with more distant neighbours.

In CoI₂ (with the Cd(OH)₂ structure) three types of two-anion superexchange interactions are important, an interaction j' (Z' = 2) over a distance c, j'' (Z'' = 12) over a distance $\sqrt{a^2 + c^2}$ and j''' (Z''' = 12) over a distance $(3a^2 + c^2)^{1/2}$. Rastelli [27] considered only interaction j'. However, as pointed out by Van Erk [26], the interaction j''' is probably important, because it is close to 180° superexchange via two anions, involving $e_g - e_g$ interactions via both anion s and p orbitals. The interaction j''' is necessary to explain the observed collinear magnetic structures of FeI₂ [37] and MnBr₂ [38].

If only j''' is considered (and j' and j'' are neglected) we obtain the following relation between Q_x and Q_z for helix 1 in the Cd(OH)₂ structure:

$$\tan cQ_{z} = \frac{2\sin(\frac{1}{2}aQ_{x}\sqrt{3}) - \sin(aQ_{x}\sqrt{3})}{2\cos(\frac{1}{2}aQ_{x}\sqrt{3}) + \cos(aQ_{x}\sqrt{3})}.$$
 (14)

Substituting the spiral angle $\frac{1}{2}aQ_x\sqrt{3} = 45^\circ$ of CoI₂ we obtain $cQ_z = 164^\circ$ or 196°. This is close, but not equal, to the observed value $cQ_z = 180^\circ$, and it indicates that the interactions j' and j'' play an important role in CoI₂.

Within the mean field approximation it is possible to calculate J_1 and J_2 from the observed Néel temperatures of CoI₂ ($T_N = 8.2$ K) and NiI₂ ($T_N = 75$ K). For CoI₂ we obtain $J_1 = 4.5$ K and $J_2 = -1.9$ K, for NiI₂ $J_1 = 15.6$ K and $J_2 = -6.8$ K. These values are not very accurate. The mean field theory can be used to compare the stability of magnetic structures at low temperatures, but especially for layered compounds it does not lead to good results for the transition temperatures.

We conclude that the stability of the observed complicated magnetic structures of CoI_2 and NiI_2 can be explained in terms of superexchange interactions. The strongest interaction is the intralayer 90° superexchange via one intermediate anion. However, the stability of the observed structures can be understood only if several types of exchange interactions via two anions are taken into account. The importance of long-range superexchange interactions is expected to increase rapidly with increasing covalency [43, 44], and indeed the superexchange via two anions plays a more important role in the more covalent transition metal dibromides and diiodides than in the more ionic dichlorides.

Rastelli [27] also discussed the influence of the single-ion anisotropy D on the magnetic structure. It was found that for CoI₂, with the spins in the *ab* plane, D must be positive and $j_2 < -1/3$. The plane of the spins for NiI₂ cannot be explained in terms of the single-ion anisotropy; the influence of dipolar anisotropy has not been investigated.

10. Conclusions

NiI₂ undergoes a structural phase transition at 60 K and a magnetic phase transition at 75 K. The structural phase transition was investigated with X-ray and neutron diffraction. It was found that the low-temperature structure corresponds to a monoclinic distortion of the hexagonal cell, with small shifts of the Ni atoms. This distortion is presumably of an antiferroelectric nature, with the large polarizability of iodine and the small size of the Ni²⁺ favouring an asymmetric coordination of the iodine ions.

The low-temperature magnetic structure of NiI₂ was studied with neutron diffraction. The observed reflections were interpreted in terms of a helix-1 type structure with propagation vector Q = (0.1384, 0, 1.457), with spins lying in a plane which makes an angle of about 55° with the *c* axis. This spin structure explains the observed anisotropy of the magnetic susceptibility, and also the Mössbauer data.

A remarkable feature of the transition metal dihalides with layered structures, is that the ordering of the magnetic moments leads to very complex magnetic structures, especially for the dibromides and the diiodides. In section 9 we attempted to understand the observed helix structures of CoI_2 and NiI_2 in terms of a few magnetic interactions between nearest and nextnearest magnetic neighbours. The stability diagrams for trigonal layer compounds were calculated with the help of the theory of Rastelli [27]. It was found that the magnetic structures of CoI_2 and NiI_2 are close to the phase boundary between the regions of ferromagnetic and helix-1 type structures. In order to explain the observed spiral angles in NiI_2 and CoI_2 , it was necessary to take into account also interlayer exchange interactions.

A comparison with the dichlorides and the dibromides of cobalt and nickel shows that J_2 is more important in the diiodides than in the other dihalides. In NiBr₂ a different type of helix (helix 2) with a spiral angle of only 9.72° was found, indicating that the intralayer interaction j_3 in this compound is more important than the interlayer interaction j'. Thus, whereas the nickel chlorides and bromides can be regarded as two-dimensional magnetic systems, nickel diiodide has a more three-dimensional character.

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