CHAPTER IV

A FAR-INFRARED STUDY OF THE LATTICE DYNAMICS OF NiI₂ AND CoI₂

ABSTRACT

We have measured the far-infrared reflection spectra of the layered compounds NiI₂ and CoI₂ in the wave-number region from 50 to 650 cm⁻¹. An oscillator parameter fit and a Kramers Kronig analysis showed transverse optical frequencies of 178 cm⁻¹ and 156 cm⁻¹ for the A₂u mode (E//c) and the E_u mode (E⊥c) of NiI₂, and 185 cm⁻¹ and 152 cm⁻¹ for the A₂u and E_u modes of CoI₂, respectively. The oscillator strength of the E_u modes is much larger than that of the A₂u modes. The observed anisotropy of the parameters is caused by the presence of large static and oscillating dipoles induced in the highly polarizable iodine ions.
IV. 1 INTRODUCTION

The far-infrared and Raman spectra of the layered compounds CdI\(_2\) and PbI\(_2\) have been widely studied during the last few years [1-5]. In a detailed paper on the lattice dynamics of the dichlorides and dibromides of 3d-transition metals Benedek and Frey discussed the microscopic parameters of these compounds, obtained from calculations with the Extended Shell Model [6]. Only two publications have appeared on the far-infrared spectra of the diiodides of the 3d-transition metals [7,8]. The first [7] is a preliminary report on the far-infrared spectra of NiI\(_2\). The second article by Frey and Benedek [8] deals with VI\(_2\). By adjusting the ionicity, the iodine shell charge and the static shell-core displacement, these authors obtained a good agreement between the calculated and the experimental optical frequencies. The dispersion curves for several directions in the Brillouin zone of VI\(_2\) were calculated, using the Extended Shell Model [6].

In this chapter the far-infrared reflection spectra of NiI\(_2\) and CoI\(_2\) single crystals are reported. The spectra are analyzed with an oscillator fit and a Kramers Kronig analysis. The parameters obtained from this analysis are discussed using the polarizable-ion model developed by Van der Valk [1]. Although the local environment of the cation is quite isotropic, the long-range Coulomb interactions in the crystal lead to a strong anisotropy of the infrared-active lattice vibrations. It will be shown that, just as was found for CdI\(_2\) and PbI\(_2\) [1], the static dipoles at the anions cause an anisotropy of the static dielectric constant, a higher frequency of the A\(_{2u}\) modes than of the E\(_u\) modes, and a larger oscillator strength for the E\(_u\) mode than for the A\(_{2u}\) mode.

IV. 2 CRYSTAL STRUCTURES OF CoI\(_2\) AND NiI\(_2\)

CoI\(_2\) and NiI\(_2\) are easily synthesized from the elements at temperatures of about 500°C and 700°C, respectively. The application of a temperature gradient of about 100°C to the quartz tube yields beautiful black-shiny crystal plates, which, however, are too small and too thin for far-infrared reflection spectroscopy. Large crystals are grown using the Bridgman technique. CoI\(_2\) melts at 550°C, NiI\(_2\) at 780°C. Before melting NiI\(_2\) partially decomposes at 760°C into metallic nickel and an iodine-rich phase. It is possible to remove partly the formed nickel by passing the crystal slowly through the temperature gradient of the oven.
Due to the layer structure of CoI₂ and NiI₂ it was easy to cut a thick sample with a shiny surface. The crystallographic c-axis is always perpendicular to this surface. Crystalline surfaces parallel to the c-axis were obtained by carefully cutting and polishing thick single crystals of CoI₂ and NiI₂. A small amount of metallic Ni is present in these crystals of NiI₂ in form of fine needles.

The crystal structure of CoI₂ is the Cd(OH)₂-type (C6) structure. NiI₂ crystallizes in the CdCl₂-type (C19) structure [9]. Both the Cd(OH)₂ and CdCl₂ structures can be described with a hexagonal unit cell; the uniaxial axis is the c-axis. The unit cell of CoI₂ contains one formula unit, the hexagonal unit cell of NiI₂ contains three units of NiI₂, but the primitive rhombohedral cell only one unit of NiI₂. CoI₂ and NiI₂ consist of sandwiches I-M-I; the anions are packed in a hexagonal and cubic way, respectively. The metal ions are octahedrally surrounded by six iodine ions; the octahedron is slightly compressed along the trigonal c-axis. In Chapter II it was shown that, due to stacking faults, the h-k ≠ 3n reflections in the neutron diffractogram of CoI₂ were broadened. In the reflection spectra of CoI₂ there is no evidence of such faults.

A factor-group analysis indicates that there are six fundamental optical modes at the Brillouin zone center classified as:

\[ \Gamma_0 = A_{1g} + E_g + A_{2u} + E_u \]  

The gerade (g) modes are Raman active, the ungerade (u) are infrared active. The \( A_{2u} \) is the vibration with out-of-plane atomic displacements (electric field \( E//c \)), the \( E_u \) is the vibration with in-plane displacements (electric field \( E\perp c \)). Figure IV.1 shows the normal modes of CoI₂ and NiI₂.

\[ \text{Figure IV.1: Results of a factor-group analysis: the normal coordinates of the } \]
\[ k = 0 \text{ fundamental modes of CoI}_2 \text{ and NiI}_2. \]
IV.3 REFLECTION SPECTRA OF NiI₂ AND CoI₂

Far-infrared reflection spectra of single crystals of NiI₂ and CoI₂ in the frequency region from 50 to 650 cm⁻¹ were recorded on a Bruker IFS 114 Fourier spectrometer at 300 and 4.2 K, and at 77 K on a Beckmann FS 720 spectrometer*. In both Fourier spectrometers approximately normal incidence of the light has been used. The resolution is 2 cm⁻¹.

Figure IV.2: Reflection spectrum of NiI₂ for a crystal plate perpendicular to the c-axis (E⊥c). The broken curves indicate the results of an oscillator fit for the E_u mode.

Figure IV.2 gives the reflectance at 300 K of a 0.1 cm thick crystal of NiI₂ with the c-axis perpendicular to the surface of the crystal plate. The crystal surface area is about 1 cm². The electric E vector is perpendicular to the c-axis, so that the observed "Reststrahlen" band at 160 cm⁻¹ is due to the E_u mode. The reflection spectrum, with unpolarized light, of a surface parallel to the c-axis shows both the E_u and A₂u modes (Figure IV.3). The spectrum of Figure IV.3 was corrected for the reflection of the Ni needles.

* The spectra were recorded at the "Physikalisches Institut" of the "Technischen Hochschule" in Aachen.

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Figure IV.3: Reflection spectrum of $\text{NiI}_2$, for a crystal plate parallel to the $c$-axis with unpolarized light. The broken curve is calculated from an oscillator fit for the $\Lambda_{2u}$ and $E_u$ modes.

The low-temperature spectra look quite similar; just a small increase of the transverse optical frequency and a decrease of the damping constant is observed, as the temperature is lowered. The presence of the small deformation of the unit cell at temperatures below 60 K (Chapter II) is not reflected in the spectra at 4.2 K.

$\text{NiI}_2$ is hygroscopic, but $\text{CoI}_2$ is extremely hygroscopic and difficult to handle. Crystal surfaces of $\text{CoI}_2$ exposed to air, are destroyed in a few seconds. Therefore, we covered our samples with very thin (thickness $\sim 7 \mu$) Mylar foil. The size of the crystals of $\text{CoI}_2$ is comparable with those of $\text{NiI}_2$. Figure IV.4 shows the reflectance of $\text{CoI}_2$, covered with the foil, at 4.2 K, the only temperature at which spectra of $\text{CoI}_2$ were recorded. The $c$-axis is perpendicular to the crystal surface ($E \perp c$).

The reflection spectrum of $\text{CoI}_2$ shows a strong "Reststrahlen" band at 160 cm$^{-1}$ (polar $E_u$ mode). Furthermore, an interference pattern, originating from the Mylar foil, is disturbing the spectrum. The interference of the foil is well described by a multi-beam interference with a refractive index of the foil of $n = 1.7$ and a thickness of about $7 \mu$, except for regions where the foil absorbs the incident light. The reflection and transmission spectra of the
Mylar foil show an absorption band at 135 cm\(^{-1}\), so that the band at 135 cm\(^{-1}\) in Figure IV.4 should be ignored. The spectrum of Figure IV.4 can be described as the sum of the reflection of the Mylar foil and a term, which depends on the transmission of the foil and the reflectance of the CoI\(_2\) sample. The height of the interference depends on the corrugation of the foil. From 50 to 80 cm\(^{-1}\) the spectra of Mylar are less reliable due to the noise of the pyro-electric detector.

Figure IV.5 gives the reflectance of a crystal of CoI\(_2\) with the surface parallel to the c-axis; again CoI\(_2\) is covered by a Mylar foil. The full line
is the spectrum for the electric field $E$ perpendicular to the c-axis, the broken line is the spectrum for $E$ parallel to the c-axis. The first spectrum ($E \perp c$) exhibits the same band at $160 \text{ cm}^{-1}$ ($E_u$ mode) and the Mylar absorption at $135 \text{ cm}^{-1}$. The spectrum with $E//c$ shows a small residue of the $160 \text{ cm}^{-1}$ band, a weak "Reststrahlen" band at $185 \text{ cm}^{-1}$ ($A_{2u}$ mode) and also the absorption at $135 \text{ cm}^{-1}$.

It is possible to give an estimation of the optical frequencies and the electronic dielectric constants of CoI$_2$ from the reported spectra, after application of a correction for the presence of the Mylar foil. However, the use of the Mylar foil is not a very satisfactory solution for far-infrared experiments on hygroscopic compounds. The use of a small flow cryostat, small enough to be put in a glove box, is recommendable.

IV.4 OPTICAL PARAMETERS OF THE $E_u$ AND $A_{2u}$ MODES OF NiI$_2$ AND CoI$_2$

There are two classical ways in analyzing the reflection spectra of polar modes in the far-infrared region. The first is to fit the observed data to one or more damped harmonic oscillators, the second method is the Kramers Kronig Analysis. Both methods have been used in analyzing the spectra of NiI$_2$ and CoI$_2$. The spectrum of Figure IV.2 can be described with a single damped harmonic oscillator. The complex dielectric constant is given by

$$\varepsilon = \varepsilon_\infty + \frac{\Delta \chi \omega_0^2}{\omega_0^2 - \omega^2 - i\gamma \omega} = \varepsilon_1 + i\varepsilon_2$$

where $\varepsilon_\infty$ is the electronic dielectric constant, $\Delta \chi$ the oscillator strength, $\omega_0$ the transverse optical frequency and $\gamma$ the damping constant. The reflectance is given by

$$R = \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2}$$

$n$ is the refractive index, $\kappa$ the extinction coefficient and $\varepsilon = (n-i\kappa)^2$. The reflectance $R$ can be expressed in terms of the optical parameters $\varepsilon_\infty$, $\Delta \chi$, $\gamma$ and $\omega_0$. The unpolarized spectrum of Figure IV.3 with both the $E_u$ and $A_{2u}$ mode can be described as the sum of two spectra, each characterized by a single harmonic oscillator.
About the same results should be obtained with the Kramers Kronig Analysis. A useful formulation of this analysis employs the reflection coefficient \( R \) and the phase angle \( \phi \) as related variables; \( \phi \) is the phase of the amplitude reflection coefficient \( \rho = \sqrt{R} e^{i\phi} \). It can be written as:

\[
\phi(\omega) = \frac{\omega}{i\pi} \int_0^\infty \frac{\ln R(\omega') - \ln R(\omega)}{\omega^2 - \omega'^2} \, d\omega'
\]  

(4)

The value of the integrand for \( \omega' = \omega \) can be estimated with L'Hopital's rule.

In Table IV.1 the optical parameters of NiI\(_2\) at 300 K and CoI\(_2\) at 4.2 K are listed. The parameters of the \( E_u \) mode of NiI\(_2\) are obtained, using the Kramers Kronig analysis and an oscillator fit. The parameters of the \( A_{2u} \) mode of NiI\(_2\) are calculated by a fit of two independent oscillators to the spectrum of Figure IV.3. A Kramers Kronig analysis and two-oscillator fits, applied to the spectra of CoI\(_2\), fail in the 135 cm\(^{-1}\) region. However, ignoring this wave-number region, the spectra of NiI\(_2\) and CoI\(_2\) show a great similarity. Reliable values for the static dielectric constants \( \varepsilon_0 \) of CoI\(_2\) cannot be obtained from the spectra. The values of \( \varepsilon_0 \) of CoI\(_2\) have been calculated from the Lyddane-Sachs-Teller relation

\[
\frac{\omega_{10}^2}{\omega_{to}^2} = \frac{\varepsilon_0}{\varepsilon_{\infty}}
\]

(5)

TABLE IV.1: Optical parameters of NiI\(_2\) (300 K) and CoI\(_2\) (4.2 K).

<table>
<thead>
<tr>
<th>mode ( A_{2u} )</th>
<th>( \omega_{to} ) (cm(^{-1}))</th>
<th>( \omega_{10} ) (cm(^{-1}))</th>
<th>( \varepsilon_{\infty} )</th>
<th>( \Delta \chi )</th>
<th>( \varepsilon_0 )</th>
<th>( \gamma ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiI(_2) ( E_u )</td>
<td>156</td>
<td>176</td>
<td>6.4</td>
<td>1.8</td>
<td>8.2</td>
<td>5.6</td>
</tr>
<tr>
<td>CoI(<em>2) ( A</em>{2u} )</td>
<td>185</td>
<td>191</td>
<td>5.1</td>
<td>0.3</td>
<td>5.4</td>
<td>-</td>
</tr>
<tr>
<td>CoI(_2) ( E_u )</td>
<td>152</td>
<td>175</td>
<td>5.3</td>
<td>1.7</td>
<td>7.0</td>
<td>-</td>
</tr>
</tbody>
</table>
where $\omega_{\text{lo}}$ is the longitudinal optical frequency. The optical frequencies $\omega_{\text{lo}}$ and $\omega_{\text{lo}}$ of the $E_u$ and $A_{2u}$ modes of CoI$_2$ are easily estimated from the spectra of Figures IV.4 and IV.5 (broken line), respectively. The electronic dielectric constants are calculated from the reflectances in the frequency regions from 550 to 600 cm$^{-1}$, where sharp absorption peaks of Mylar are absent. The optical parameters of CoI$_2$, especially the static dielectric constants are given with some reservation.

IV.5 MICROSCOPIC ANALYSIS OF THE FAR-INFRARED MODES

We will briefly discuss the theory for the anisotropy of lattice vibrations of layered compounds [1].

Following Huang [10] the infrared-active vibrations of polar lattices are described by a force and a polarization equation. These equations depend on the normal coordinates of the $A_{2u}$ and $E_u$ vibration and the effective electric field in anisotropic crystals. The coefficients $d_{ij}$ in these equations now become axial tensors. The principal values are given by

$$d_{22} = a_\infty = \frac{3}{4\pi} \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}$$

$$d_{12}^2 = \frac{9}{4\pi} \frac{\omega_{\text{lo}}^2}{\varepsilon_0 - \varepsilon_\infty}$$

$$d_{11} = -\frac{\omega_{\text{lo}}^2}{4\pi} \frac{\varepsilon_0 + 2}{\varepsilon_\infty + 2}$$

and can be calculated readily from the optical spectra. The values of the $d$-tensors of the polarization and force equations are now expressed in terms of the microscopic parameters. This can be achieved by use of the polarizable-ion model [1]. In this model not only the charges, the polarizabilities of the ions and resulting dipoles are included, but also the static dipoles on the anions, resulting from their asymmetric coordination in layer compounds, should be considered. Szigeti [11] has introduced an effective charge $Z^*e$, which accounts for the induced dipoles due to the deformation of the ions. Of course it would be possible to explain the observed anisotropy of the oscillator strength of the $A_{2u}$ and $E_u$ modes using very anisotropic values for
the effective charge. However, we will show that this is not necessary: the observed anisotropy is well accounted for by the permanent dipoles on the anions. The dipoles can be separated into a static and an oscillating part \( \mu_j = \mu_j^0 + \delta \mu_j \). Also the coordinates of the ions, the local fields and forces are divided into a static and an oscillating part. The local field of ion \( j \) consists of the contributions of surrounding ions within a large sphere (~100 Å) and a homogeneous polarization outside this sphere. For the calculation of the static and oscillating parts of the fields and forces three lattice sums are needed:

\[
\begin{align*}
    k_{ij} &= \sum_n \nabla_i n \frac{1}{r_n - r_{ij}^0} \\
    L_{ij} &= -\nabla_j k_{ij}, \quad M_{ij} &= -\nabla_j L_{ij}
\end{align*}
\]

(9)
i, j denote the three sublattices of the Cd(OH)\(_2\)- and CdCl\(_2\)-structure, and \( n \) specifies the lattice translations. Sublattice 1 consists of the iodine ions above the metal-ion layer (sublattice 2), sublattice 3 of the iodine ions below the metal ions. For the relations between the lattice sums the reader is referred to reference [1]. In Table IV.2 the lattice sums for CoI\(_2\) and NiI\(_2\) are given. For symmetry reasons some lattice sums are zero in the case of an ideal close packing, but they have a small value, if the lattices are trigonally distorted (\( z_1 \neq 0.25 \)).

**TABLE IV.2:** Lattice sums for CoI\(_2\): \( a = 3.977 \) Å, \( c = 6.669 \) Å and \( z_1 = 0.25 \), and NiI\(_2\): \( a = 3.922 \) Å, \( c = 19.808 \) Å for \( z_1 = 0.25 \) and \( z_1 = 0.2556 \).

<table>
<thead>
<tr>
<th>( \text{CoI}_2 )</th>
<th>( \text{NiI}_2 (z = 0.25) )</th>
<th>( \text{NiI}_2 (z = 0.2556) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N \left( 10^{21} \text{ cm}^{-3} \right) )</td>
<td>10.947</td>
<td>11.350</td>
</tr>
<tr>
<td>( k_{12}^{2} \left( 10^{15} \text{ cm}^{-2} \right) )</td>
<td>-1.69</td>
<td>-1.74</td>
</tr>
<tr>
<td>( k_{13}^{2} \left( 10^{15} \text{ cm}^{-2} \right) )</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>( L_{11}^{zz} \left( 10^{21} \text{ cm}^{-3} \right) )</td>
<td>-81.17</td>
<td>-84.72</td>
</tr>
<tr>
<td>( L_{12}^{zz} \left( 10^{21} \text{ cm}^{-3} \right) )</td>
<td>-1.04</td>
<td>0.00</td>
</tr>
<tr>
<td>( L_{13}^{zz} \left( 10^{21} \text{ cm}^{-3} \right) )</td>
<td>81.28</td>
<td>84.72</td>
</tr>
<tr>
<td>( M_{12}^{zzz} \left( 10^{30} \text{ cm}^{-4} \right) )</td>
<td>13.60</td>
<td>14.59</td>
</tr>
</tbody>
</table>
The harmonic potential energy produced by short-range forces can be described by an effective force constant for each of the polar modes $E_u$ and $A_{2u}$

$$U_{\text{short range}} = \frac{1}{2} \sum_{x,y,z} f^{\alpha\alpha} (\delta r_1 - \delta r_2)^2 + f^{\alpha\alpha} (\delta r_2 - \delta r_3)^2$$  \hspace{1cm} (10)

After an extensive calculation Van der Valk arrived at the local force equation:

$$\frac{\partial^2 S_u}{\partial t^2} = -\frac{1}{\mu} f S_u - \frac{1}{2} \left(\frac{2}{\mu}\right)^{\frac{3}{2}} \delta K_2$$  \hspace{1cm} (11)

In this equation $S_u$ is the normal coordinate of the vibration and $\mu$ is the reduced mass given by $1/\mu = (1/m) + (2/M)$ ($M$ = mass of the cation, $m$ = mass of the anion). $\delta K_2$ represents the oscillating force at the metal ions, caused by long-range electrostatic interactions of charges and dipoles in the crystal. The polarization equation reads:

$$P = -\left(\frac{2}{\mu}\right)^{\frac{3}{2}} N Z^* e S_u + N \{\alpha_1 (\delta E_1 + \delta E_3) + \alpha_2 \delta E_2\}$$  \hspace{1cm} (12)

The expression of the macroscopic properties in terms of the microscopic parameters yields quite complicated expressions for the $d$-tensors. Because $\alpha_2 L_{12}$ and $\alpha_1 (L_{11} + L_{13})$ are small with respect to one, these expressions for a CdI$_2$- or CdCl$_2$-type structure with a small trigonal distortion can be simplified to:

$$\alpha_\infty = N \{2 \alpha_1 U + \alpha_2 (U - \alpha_2 L_{11})^{-1}\}$$  \hspace{1cm} (13)

$$d_{12} = -\left(\frac{2}{\mu}\right)^{\frac{1}{2}} (Z^* e U - \alpha_2 (\mu^0 M_{12} - Z^* e L_{12})(U - \alpha_2 L_{11})^{-1})$$  \hspace{1cm} (14)

$$d_{11} = -\frac{1}{\mu} f + \left(\frac{2}{\mu}\right)^{\frac{1}{2}} d_{12} \cdot (\mu^0 M_{12} - Z^* e L_{12})$$  \hspace{1cm} (15)

where $U$ is the unit tensor, and $\alpha_1$ and $\alpha_2$ are the polarizabilities of the anion and cation, respectively.

The local parameters of the metal and iodine ions are calculated by substituting the optical values of the $d$-tensors of the $A_{2u}$ and $E_u$ modes, re-
spectively, in equations (13)-(15). The polarizability of the metal ion is calculated from the small anisotropy of the electronic dielectric constant \( \varepsilon_{\infty} \). Its value depends strongly on the quality of the reflecting surface. The obtained values of the ionic polarizability of \( I^- (a_1) \) and \( M^{2+} (a_2) \), the effective charges \( Z^*/Z \), the static dipoles \( \mu^0 \) at the iodine ions and the force constants for \( NiI_2, CoI_2, CdI_2 \) and \( PbI_2 \) are listed in Table IV.3. The dipoles on the iodine ions calculated from the purely ionic charge distribution with charges \(-Ze\) at the anion and \(+2Ze\) at the cation, are given by

\[
\mu^0_{\text{ion}} = \frac{Ze(k_{13}^Z - 2k_{12}^Z)}{L_{13}^{zz} - L_{11}^{zz} + 1/a_1}
\]  

(16)

In this equation again we neglected \( a_2^Z \) with respect to one.

**TABLE IV.3:** Ionic polarizabilities of \( I^- (a_1) \) and \( M^{2+} (a_2) \), effective charges \( (Z^*/Z) \), static dipoles \( (\mu^0) \), static dipoles calculated for \( Z = 1 \) \( (\mu^0_{\text{ion}}) \) and their ratio, and the force constants, calculated with the theory of reference [1].

<table>
<thead>
<tr>
<th>( a_1 \times 10^{-24} \text{ cm}^3 )</th>
<th>( a_2 \times 10^{-24} \text{ cm}^3 )</th>
<th>( Z^*/Z \times 10^{-18} \text{ esu} )</th>
<th>( \mu^0 \times 10^{-18} \text{ esu} )</th>
<th>( \mu^0_{\text{ion}} \times 10^{-18} \text{ esu} )</th>
<th>( \frac{\mu^0}{\mu^0_{\text{ion}}} )</th>
<th>( f(A_{2u}) \times 10^5 \text{ dyne cm}^{-1} )</th>
<th>( f(E_u) \times 10^5 \text{ dyne cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( NiI_2 )</td>
<td>5.5</td>
<td>2.2</td>
<td>0.29</td>
<td>1.5</td>
<td>5.0</td>
<td>0.29</td>
<td>0.42</td>
</tr>
<tr>
<td>( CoI_2 )</td>
<td>5.6</td>
<td>1.5</td>
<td>0.30(5)</td>
<td>1.4</td>
<td>4.8</td>
<td>0.30</td>
<td>0.46</td>
</tr>
<tr>
<td>( CdI_2 )</td>
<td>5.6</td>
<td>2.4</td>
<td>0.58</td>
<td>3.0</td>
<td>4.5</td>
<td>0.67</td>
<td>0.36</td>
</tr>
<tr>
<td>( PbI_2 )</td>
<td>8.4</td>
<td>2.0</td>
<td>0.68</td>
<td>3.8</td>
<td>5.6</td>
<td>0.68</td>
<td>0.29</td>
</tr>
</tbody>
</table>

As shown in Table IV.3 the parameters of \( NiI_2 \) and \( CoI_2 \) do not differ much. Because the analysis of the spectra of \( NiI_2 \) was more straightforward than the analysis of \( CoI_2 \), the data of \( NiI_2 \) are more reliable. In both compounds the Szigeti effective charge shows a strong reduction. A comparison can be made with the values reported for \( CdI_2 \) and \( PbI_2 \) [1]. The cations in these compounds have completely occupied d-shells. According to the Szigeti deformation dipole
model, the reduction of the charges is caused by the distortion, due to the overlap with the charge distribution of neighbouring ions [11,12]. In CoI₂ and NiI₂ there is a rather strong overlap of the 3d orbitals (3d⁷ and 3d⁸) with iodine 5p orbitals, as indicated by spectroscopic data (Chapter V) and Mössbauer experiments [13]. This leads to a larger distortion of the charge distribution of the cation and to a larger reduction of the effective charge; the covalency is larger in CoI₂ and NiI₂ than in CdI₂ and PbI₂.

The results given in Table IV.3 show that the dipole moment μ⁰ exhibits the same reduction with respect to the dipole moment μ⁰ ion calculated from an ionic charge (Z = 1) distribution, as expected. For CoI₂ the reflectance data at low frequencies were not sufficiently accurate to obtain reliable values for the anisotropy of the static dielectric constant. Therefore, we assumed for CoI₂ that μ⁰/μ⁰ ion = Z*/Z; this assumption is consistent with the data as it leads to a minor anisotropy of only ±0.05e of the effective charge Z*e.

The polarizabilities of Co²⁺ and Ni²⁺ calculated with our model are 1.5 x 10⁻²⁴ and 2.2 x 10⁻²⁴ cm³. As these values are calculated from the small difference between the electronic dielectric constants for the E_u and the A₂u modes, the error is relatively large. For the electronic polarizabilities of Co²⁺ and Ni²⁺ in the metal oxides values of 0.99 x 10⁻²⁴ and 0.89 x 10⁻²⁴ cm³, respectively, are calculated [14]. Tessman et al. [15] reported for the alkali iodides a polarizability of the iodide ion of 6.2 x 10⁻²⁴ cm³. The values of α¹ given in Table IV.3 are reasonable.

Within the experimental errors the obtained short-range force constants are equal for the A₂u and E_u modes of CoI₂ and NiI₂. This shows that the observed anisotropy is not due to short-range forces. The coordination of the metal ion by six iodine ions is nearly that of a perfect octahedron and so one expects f(A₂u) and f(E_u) to be the same. For a proper calculation of the anisotropy of the A₂u and E_u modes of CoI₂ and NiI₂ it is necessary to take into account the long-range Coulomb interactions. The most important contribution comes from the presence of the static dipoles on the easily polarizable iodine ions, directly resulting from the asymmetric coordination of these ions in the layered type structures. As a matter of fact it is the polarization energy which stabilizes the layered structures of the compounds.

We have separated the various contributions to the frequencies of the A₂u and E_u modes (Figure IV.6) of NiI₂. In the first column only the short-range force constants of Table IV.3 were taken into account. The frequency of the A₂u mode is even lower than the E_u-mode frequency. The influence of the isotropic charges gives an equal splitting of the A₂u and E_u vibration into the
transverse and longitudinal optical frequencies. If the trigonal field is switched on by means of the lattice sums in Table IV.2, all frequencies remain almost the same. The addition of the static dipoles on the iodine ions finally gives the observed anisotropy of the lattice modes.
A comparison of the parameters of CoI$_2$ and NiI$_2$ (Table IV.3), obtained with the help of the polarizable-ion model, and the parameters of CoCl$_2$, CoBr$_2$, NiCl$_2$ and NiBr$_2$, obtained with the Extended Shell Model [6], is not easily made. In the latter model the static dipole on the anion arises from a displacement of the shell charge with respect to the core of the anion. Three parameters are fitted: $-\varepsilon Z_1$ the net halogen charge, $w_0$ the static shell-core displacement and $eY_1$ the anion shell charge. One can write $Z_1 = X_1 + Y_1$, where $eX_1$ is the core charge. With the assumption $Z_1 \ll |Y_1|$ equation (12) of reference [6] reduces to our equation (16). Benedek and Frey neglect the polarizability of the cation, as we did in equation (16). The static-dipole equation reads:

$$\mu = eY_1w_0.$$  
In the first row of Table IV.4 the static dipoles of VX$_2$, CoX$_2$ and NiX$_2$ are listed; in the third row we list the ratios of $\mu^0/\mu^0_{\text{ion}}$, where $\mu^0_{\text{ion}}$ is calculated using equation (16). There is a slight increase of the dipole moment in going from CoX$_2$ to NiX$_2$, and an increase of the dipole moment from the dichlorides to the dibromides of cobalt and nickel. A strong decrease of the dipole moment $\mu^0$ is calculated in going from the dibromides to the diiodides of cobalt and nickel.

**TABLE IV.4:** Static dipoles at the anions of some 3d transition-metal halides, calculated with the extended shell model [6,8]. $\mu^0_{\text{ion}}$ is calculated with equation (16).

<table>
<thead>
<tr>
<th></th>
<th>VCl$_2$</th>
<th>VBr$_2$</th>
<th>VI$_2$</th>
<th>CoCl$_2$</th>
<th>CoBr$_2$</th>
<th>CoI$_2^*$</th>
<th>NiCl$_2$</th>
<th>NiBr$_2$</th>
<th>NiI$_2^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu^0$</td>
<td>1.25</td>
<td>1.34</td>
<td>1.67</td>
<td>1.78</td>
<td>1.97</td>
<td>1.4</td>
<td>1.92</td>
<td>2.02</td>
<td>1.5</td>
</tr>
<tr>
<td>($10^{-18}$ e.s.u. cm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\mu^0_{\text{ion}}$</td>
<td>3.564</td>
<td>4.168</td>
<td>4.950</td>
<td>3.616</td>
<td>-4.232</td>
<td>4.8</td>
<td>3.672</td>
<td>4.232</td>
<td>5.0</td>
</tr>
<tr>
<td>($10^{-18}$ e.s.u. cm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\mu^0/\mu^0_{\text{ion}}$</td>
<td>0.35</td>
<td>0.32</td>
<td>0.34</td>
<td>0.49</td>
<td>0.47</td>
<td>0.30</td>
<td>0.52</td>
<td>0.48</td>
<td>0.29</td>
</tr>
</tbody>
</table>

* The values for CoI$_2$ and NiI$_2^*$ are calculated with the polarizable-ion model [1].
The theory of Van der Valk and Haas can be applied to the optical parameters calculated by Benedek and Frey, only, if we neglect the polarizability of the cation ($\alpha_2$). However, with this assumption the calculated dielectric constants of $\text{VI}_2$ [8] are $\varepsilon_{xx} = 3.703$ and $\varepsilon_{zz} = 3.480$. These values are unrealistically low, as compared with the dielectric constants of $\text{CoI}_2$ and $\text{NiI}_2$ (Table IV.1), and clearly demonstrate that one cannot neglect the polarizability of the cation. Also the neglect of $\alpha_2$ would lead to an anisotropic Szigeti charge.

We have applied the polarizable-ion model to chlorides and bromides of Ni and Co, taking into account both the polarizabilities of the anion and cation, $\alpha_1$ and $\alpha_2$, respectively. For $\alpha_1$ we take the polarizabilities of Tessmann [15], for $\alpha_2$ the polarizabilities of Shanker [14]. From these values we obtain the slightly anisotropic tensor $\varepsilon_{\infty}$ (equation (13)), from which the $\varepsilon_{xx}$ and $\varepsilon_{zz}$ are readily calculated (equation (6)). The static dielectric constants are obtained by use of the Lyddane-Sachs-Teller relation and the (experimental) frequencies [6,8]. These experimental infrared frequencies are as yet unpublished and we do not know the accuracy of the data. The principle values of the $\varepsilon$-tensors (equations (7) and (8)) can now be calculated and the microscopic analysis is performed in the same way as for $\text{CoI}_2$ and $\text{NiI}_2$. The microscopic parameters for a number of compounds are collected in Table IV.5. The discrepancies

<table>
<thead>
<tr>
<th>TABLE IV.5: Microscopic parameters of some 3d-transition-metal halides, calculated from [1]. A comparison with Table IV.3 should be made.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1$ [15]</td>
</tr>
<tr>
<td>units</td>
</tr>
<tr>
<td>VI$_2$</td>
</tr>
<tr>
<td>CoCl$_2$</td>
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<tr>
<td>NiCl$_2$</td>
</tr>
<tr>
<td>CoBr$_2$</td>
</tr>
<tr>
<td>NiBr$_2$</td>
</tr>
</tbody>
</table>

in the series are probably due to the lack of information about the optical frequencies and dielectric constants. Benedek and Frey already complained about the lack of structural data, especially the iodine-z parameter is often unknown.
and taken as 1/4. The values of the longitudinal optical frequencies are calculated by Benedek and Frey; it is not known how large the influence of $\alpha_2$ is on this frequency. For the application of the theory of the lattice vibrations of the layered 3d-transition-metal halides accurate optical constants are required; the existing data on the Ni and Co chlorides and bromides are probably not sufficiently accurate.

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IV.7 REFERENCES