Environment of iodine ions. A spectroscopic, magnetic and structural investigation on transition - metal diiodides
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SUMMARY

In this thesis the results of spectroscopic, magnetic and structural investigations on VI₂, NiI₂ and CoI₂ and solid solutions of NiI₂ and CoI₂ in CdI₂ and PbI₂ are discussed. Many of the properties are related to the layer-type structure and the partly filled d orbitals of the transition-metal ions.

In Chapter II we report investigations of the nuclear and magnetic structures of NiI₂ and CoI₂. In NiI₂ two phase transitions appear, one at 75 K attributed to the antiferromagnetic ordering and a structural phase transition near 60 K. The latter is investigated by X-ray and neutron diffraction; the symmetry is lowered from trigonal to monoclinic or triclinic. The magnetic structure is deduced from the magnetic satellites in the neutron diffraction pattern. A helix-1 type structure with propagation vector \( q_x = 0.1384a^* \) and \( q_z = 1.457c^* \) is found. The spins rotate in a plane which makes an angle of about 55.4° with the uniaxial axis. The unusual anisotropy of the susceptibilities observed for oblique orientations of the crystal with respect to the applied field is presumably related to the oblique direction of the cone.

Measurements of the susceptibility of CoI₂ show an anisotropy for H/\( c \) and H//c. The out-of-plane anisotropy is caused by the spins of Co\( ^{2+} \), which lie in the ab-plane. The in-plane order is examined by neutron diffraction. CoI₂ has the same type of magnetic order as NiI₂, hence a helix-1 type with \( q_x = 1/8 a^* \) and \( q_z = 1/2 c^* \).

Using the theory developed by Rastelli the stability of the magnetic structures of NiI₂ and CoI₂ is discussed. We found that the nearest neighbour exchange \( J_1 \) is positive, and the next-nearest neighbour exchange \( J_2 \) negative. Furthermore, the interlayer exchange interactions in the iodides play an important role in NiI₂ and CoI₂.

In Chapter III the magnetic susceptibility of single crystals of VI₂ is discussed. At 14 K an anomaly is discovered. Neutron diffraction at a few selected temperature near 14 K shows that the anomaly can be ascribed to a magnetic phase transition from a 120° structure above 14 K to a collinear structure with cell dimensions of \( a_{\text{magn}} = a\sqrt{3} \), \( b_{\text{magn}} = 2a \) and \( c_{\text{magn}} = 2c \). Several arguments make it plausible that the 120° structure is not a magnetic phase with long-range order, but rather a paramagnetic phase with a high degree of short-range order. The dipolar anisotropy and the interlayer exchange inter-
actions are most likely responsible for the phase transition. The collinear structure, in which the spins of $V^{2+}$ make an angle of about $60^\circ$ with the a-axis, is compatible with $^{129}$I-Mössbauer spectra. Calculations show that the $120^\circ$ structure is stable for $J_1 < 0$ and $J_2 > 0$ in the absence of anisotropy; the collinear structure of $VI_2$, for the same $J_1$ and $J_2$, is stabilized, if a strong anisotropy couples the spins of $V^{2+}$ to one particular direction in the lattice.

Chapter IV describes measurements of infrared reflection spectra of $NiI_2$ and $CoI_2$ from 50 to 650 cm$^{-1}$. Two infrared-active lattice vibrations of $NiI_2$ and $CoI_2$ are found: an $E_u$ mode at about 155 cm$^{-1}$ with atomic displacements in the ab-plane, and an $A_{2u}$ mode at about 180 cm$^{-1}$ with displacements parallel to the c-axis. The spectra are analyzed with an oscillator fit and a Kramers-Kronig analysis. The oscillator strength of the $E_u$ mode is much larger than that of the $A_{2u}$ mode. This anisotropy is caused by the presence of static and oscillating dipoles; the dipoles are due to the asymmetric coordination of the iodine ions. The data are analyzed in terms of the polarizable-ion model of Van der Valk, and the obtained parameters are compared with the values for the chlorides and bromides.

In Chapter V the optical transitions of d electrons of $NiI_2$, $CdI_2$:Ni$^{2+}$ and $CoI_2$ in the near-infrared wavelength region are discussed. The spectra are interpreted in terms of electron repulsion, the octahedral crystal field and spin-orbit coupling. The large covalency of the compounds makes it necessary to include the spin-orbit interaction of the 5p orbitals of the iodine ions. From the parameters of the spin-orbit coupling spin densities are deduced: $f_\sigma \approx 7\%$ and $f_\pi \approx 3\%$. These values are comparable with values calculated from Mössbauer data. A birefringence experiment on $NiI_2$ as a function of temperature confirms the presence of two phase transitions.

In Chapter VI a theoretical explanation of the vibronic coupling of the phonons of layered diiodides to isoconfigurational d-d transitions is given. In the spectra of such transitions in the solid solutions $CdI_2$:Ni$^{2+}$, $PbI_2$:Ni$^{2+}$ and $CdI_2$:Co$^{2+}$ a complicated vibronic fine structure is observed. This fine structure is discussed in terms of the coupling of a localized $t_{1u}$-type distortion, which modulates the metal-ligand distance, to the electronic transitions; the displacements of the $t_{1u}$-type distortions are decomposed into contributions of the phonons of the host lattices. The vibronic coupling in layer compounds is shown to be strongly anisotropic due to the presence of dipoles at the iodine ions.

The maxima of the vibronic fine structure in the spectra are assigned to vibrations belonging to special points in the Brillouin Zones of $CdI_2$ and $PbI_2$. 128
The dispersion of the vibrational branches of PbI$_2$ have been partly measured and calculated, so that a straightforward assignment is possible. The dispersion of the branches in the Brillouin Zone of CdI$_2$ is unknown. The experimental data for CdI$_2$ are used to deduce the dispersion of the phonon branches also for CdI$_2$. 