

HIGH RESOLUTION SPECTROSCOPY OF Ni^{2+} AND M-CENTERS IN POLYTYPIC ZnS -CRYSTALS

I. BROSER, R. BROSER, and E. BIRKICHT

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin-Dahlem

A. HOFFMANN

Institut für Festkörperphysik II, Technische Universität Berlin, Germany

Highly resolved near infrared emission, excitation, and magneto-absorption spectra of ZnS polytypic crystals doped with Ni isotopes in low concentrations are presented. The detection of luminescence coinciding with the absorption allows to explain the entire structure in the high energy part of the spectrum as zero-phonon transitions within the Ni^{2+} center in three differently symmetric environments. The correlation of the low energy part of the spectrum to a defect M-center has to be questioned. At least part of the transitions seem to be connected with Ni-centers, either by phonon coupling or by formation of complexes.

It is well known¹ that ZnS-Ni crystals exhibit at low temperatures several narrow absorption lines in the spectral region of 800 to 810 nm. They have been attributed¹ to the crystal field transitions ${}^3T_1(F) \rightarrow {}^3T_1(P)$ in Ni^{2+} . These structures are influenced by Jahn-Teller distortions² and show distinct isotope shifts³ and splittings.

In weakly doped polytypic crystals three main groups of very narrow transmission lines have been observed (Fig.1). They are linked with Ni-ions in three different crystal fields and consist each of two differently polarized pairs of lines. The doublet structure of most of the lines is due to an isotope effect with a splitting constant of about $\delta = 16 \mu\text{eV}/\text{neutron}$.

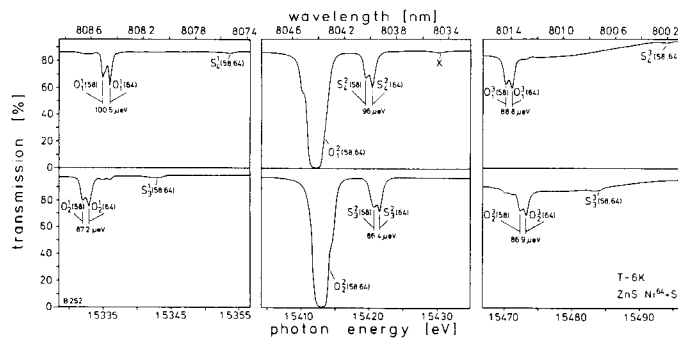


Fig.1: Transmission spectra of polytypic ZnS doped with Ni isotopes 58/64. Upper spectra $E \parallel c$, lower spectra $E \perp c$. In the cubic structure c corresponds to the $\langle 111 \rangle$ direction.

While the strong lines around 804.4 nm can be attributed to a slightly disturbed quasi-cubic environment² the two other groups belong to two different axial symmetric polytypes. All structures can only be explained by assuming a Jahn-Teller interaction of the crystal field levels involved. This interpretation is supported by Zeeman effect measurements (Fig.2). The four most intense line-pairs shown in Fig.1 all are split threefold. For the "cubic" transitions thus two levels of the final state with T₂-symmetry has to be assumed. They might result from the known T₂ and E crystal field levels subject to a dynamical Jahn-Teller effect. The axial pairs are then composed by two A₁ and E terms (only the intense pairs could be measured in a magnetic field). Our experimental results and interpretations are in accordance with those of a similar structure in hexagonal CdS-Ni²⁺ crystals^{3,4}, but contradicts former explanations⁵.

For the first time luminescence lines could be detected coinciding in energy to the transmission lines (Fig.3). At longer wavelengths the emission spectrum additionally shows a variety of lines, placed onto a broad band. The three line groups nearest in energy to the zero-phonon lines are attributed⁶ to electronic transitions from the ³T₁(P) ground level to the first excited level of the ³T₁(F) term, shifted from the ground level by about 170 cm⁻¹. The line group between 820 and 835 nm can be interpreted as phonon replicas (125 cm⁻¹) of the first high energy zero-phonon line group. Like this it is

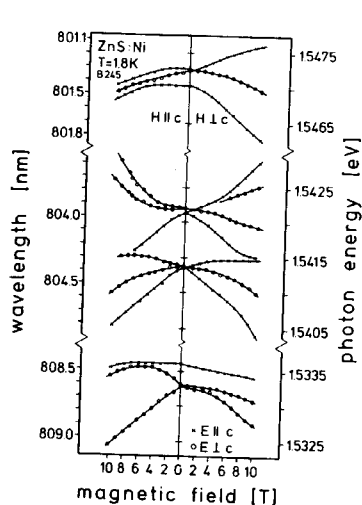


Fig.2: Zeeman splitting of the main absorption lines represented in Fig.1.

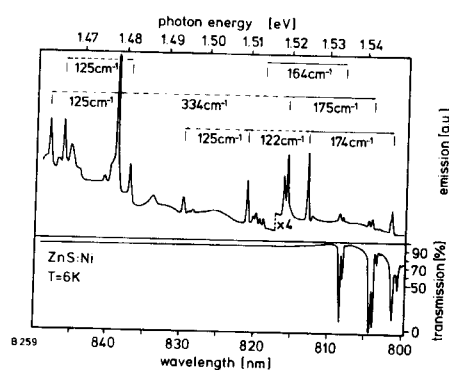


Fig.3: Absorption and emission spectrum of polytypic ZnS-Ni. Electronic (solid lines) and phononic (dashed lines) energy shifts are indicated. Excitation source: high-intensity 458 nm Ar-line.

strongly polarized. The unpolarized main line at 838.5 nm and all the other low energy lines could then be explained as phonon satellites of the cubic Ni^{2+} -lines. This observation is supported by the fact that only those crystals showed this emission, which also exhibit Ni-luminescence. A higher efficiency in all emission regions could be obtained by annealing the crystals in a sulfur atmosphere. The postulated existence of a M-center⁷ with two missing sulfur atoms must thus be questioned.

Further insight in the origin of the emission has been obtained by excitation spectroscopy (Fig.4). In the excitation spectrum of the Ni emission a fine structure occurs very similar to that found by Noras et al.⁸ in absorption. The excitation mechanism can be explained by a charge transfer process into a loosely bound hole on a Ni^{2+} -center involving several phonon replicas. In contrast, the excitation spectrum for the "M-band" starts about 20 nm at lower photon energies and has another maximum around 600 nm. This indicates a different excitation process. If the "M-band" is not connected with a defect, it cannot just consist of phonon replicas of the Ni^{2+} zero-phonon transitions. A Ni-pair can be a plausible explanation.

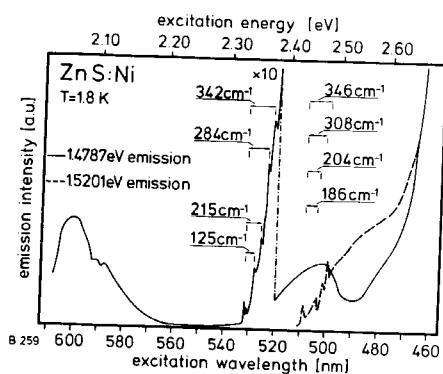


Fig.4: Excitation spectra of a Ni^{2+} -emission-line (dashed curve) and a M-band-emission line (solid curve) in the charge transfer spectral region. Excitation source: Excimer laser pumped tunable dye laser.

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