

ISOTOPE SHIFT OF EMISSION AND ABSORPTION LINES AT CdS:Ni²⁺: INTERPRETATION BY A DYNAMIC JAHN-TELLER EFFECT

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Isotope effects of the emission and absorption lines of the $3T_1(P) \rightarrow 3T_1(F)$ and $3A_2(P) \rightarrow 3T_1(F)$ -Ni²⁺ transitions in CdS are investigated. The fine structures of these lines are interpreted by an intermediate Jahn-Teller effect at the $3T_1(P)$ and $3T_1(F)$ state. The calculated isotope shifts agree with the theory and the experiment.

The incorporation of Ni²⁺ ions in a concentration smaller than 10⁻² ppm into perfect CdS crystals gives rise to several series of extremely narrow absorption, emission and excitation lines ¹⁾ in the infrared spectral region. Different kinds of fine-structures become detectable. At the ICL 81 ²⁾, we reported on isotope effects in this fine-structure spectra of Ni doped CdS. These effects are not only an excellent tool for the identification of the defect but give valuable additional information about electron phonon coupling. Therefore, we used this system to describe the observed fine structures and isotope effects in a model calculation of the Jahn-Teller coupling. In fig. 1, the zero phonon lines of the $3A_2(F) \rightarrow 3T_1(F)$ Ni²⁺ emissions (lower part) are compared with those of the $3T_1(P) \rightarrow 3T_1(F)$ (upper part). The clearly resolved isotope shifts of the Ni²⁺-transitions are given in the table. The isotope shifts of the $3A_2(F) \rightarrow 3T_1(F)$ Ni²⁺ emissions are four times larger than that of the $3T_1(P) \rightarrow 3T_1(F)$ emissions.

The emission and absorption lines are interpreted in terms of a dynamic Jahn-Teller effect by the energy level scheme of fig. 2. The coupling of the electronic states to local vibrational modes gives rise to shifts of the vibronic energy levels depending on the impurity mass. The isotope splittings obtained from the experi-

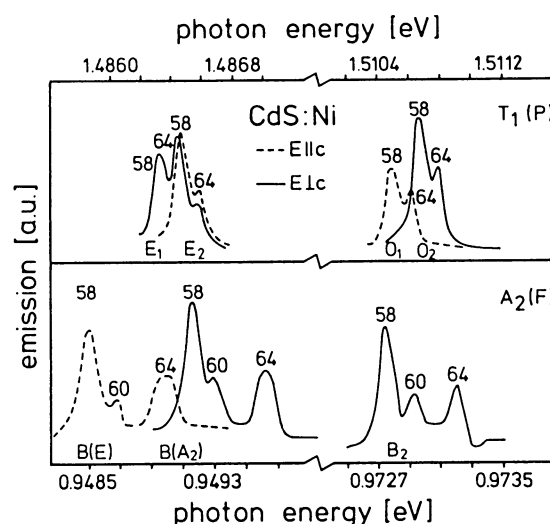


FIGURE 1
 Isotope shifts of the $3T_1(P) \rightarrow 3T_1(F)$ -Ni²⁺ emissions (top) and of the $3A_2(F) \rightarrow 3T_1(F)$ Ni²⁺ transition (bottom)

ment are explained by our model with different shifts of the initial and final states. The impurity is coupled to a radial T₂ mode which only moves the impurity and its nearest neighbours only. We obtain different phonon energies and Huang Rhys factors for the ground state $3T_1(F)$ and the excited state $3T_1(P)$. The excited state $3A_2(F)$ shows no isotope shift. We set the spin orbit coupling parameter equal to 250 cm⁻¹ and

take a trigonal field parameter of $K = -1.2\text{cm}^{-1}$. The phonon energies $\hbar\omega$ and the Huang Rhys factor S were fitted separately to the fine structure of the ${}^3T_1(P)$ and ${}^3T_1(F)$ states. Taking into account up to $N = 7$ excited phonon states, we found $\hbar\omega = 450\text{ cm}^{-1}$ and $S = 0.44$ for the ${}^3T_1(F)$ ground state and $\hbar\omega = 375\text{ cm}^{-1}$, $S = 1.0$ for the excited ${}^3T_1(P)$ state. First results with $N = 3$ were reported earlier by Nestler et al ³⁾. The isotope shifts of the vibronic states are obtained, if the dependence of the phonon energy on the impurity mass is calculated (see fig. 3). The table shows that the calculated energy differences ΔE between the lines of Ni^{58} and Ni^{64} agree with the experiment.

The Zeeman splitting has also been determined. We used an orbital reduction factor of $K = 0.78$, so that the calculation of the Zeeman effect contains no fitting parameter. We can show that the Zeeman splittings sensitively depends on the Huang Rhys factors.

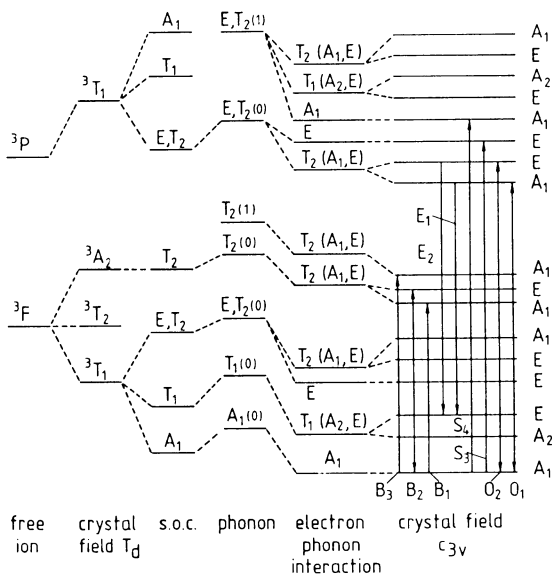


FIGURE 2
Energy level scheme of a Ni^{2+} ion at metal site in CdS . The splitting of the levels for successive interactions is shown from left to right. The observed transitions from a single Ni ion is shown on the right

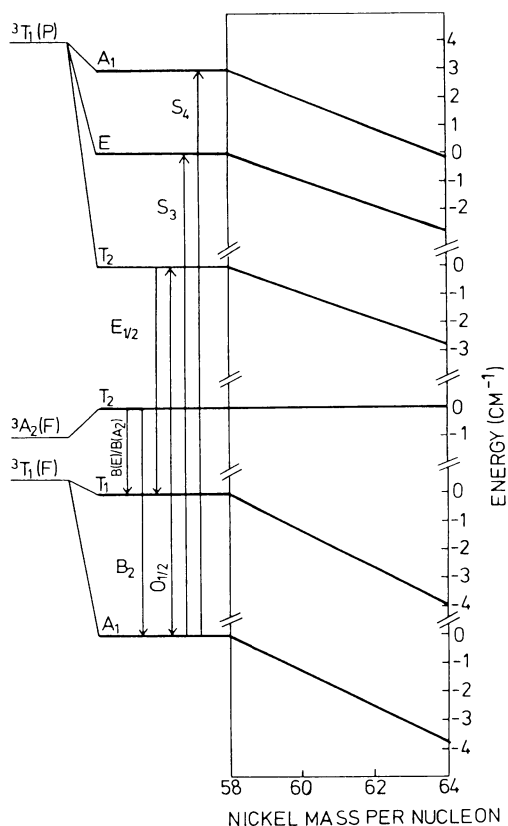


FIGURE 3
Calculated isotope shifts of tetrahedral fine-structure energy levels of the ${}^3T_1(F)$ ground state and ${}^3A_2(F)$, ${}^3T_1(P)$ excited states

	$0_{1/2}$	S_3	S_4	$E_{1/2}$	B_2	$B(A_2)$	Transition
ΔE	1.10	1.13	0.77	1.33	3.92	3.62	Calculated
	1.06	0.89	1.01	0.98	3.95	3.95	Observed

TABLE
Comparison of the calculated and observed isotope shift ΔE (in cm^{-1}) of the fine-structure transitions between the ground state ${}^3T_1(F)$ and the excited ${}^3T_1(P)$ state

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