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PRESSURE-DEPENDENT COUPLING OF THE $^3A_2(F)$ AND $^1T_2(D)$ STATES OF Ni^{2+} IN ZnS AND $ZnSe^*$

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We have investigated two close-lying $^3A_2(F)$ and $^1T_2(D)$ states of Ni^{2+} impurity in ZnS and $ZnSe$. These states are strongly coupled to each other via the spin-orbit interaction and therefore, small variations of their energies induced by pressure have significantly changed absorption spectra related to them. In order to give a good interpretation to the experimental results we took into account the interaction between both states, their coupling to the lattice vibrations and the pressure-dependent separation between them.

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Recently it has been shown that under hydrostatic pressure most of the absorption bands due to intracenter excitations of Ni^{2+} impurity in ZnS and $ZnSe$ shift rigidly with the pressure coefficients which have been described in the frame of the Static Crystal Field Theory (SCFT) [1, 2]. In this model it was sufficient to introduce the pressure-dependent crystal field parameter Δ and the Racah parameter B (C/B was taken as pressure-independent and the spin-orbit interaction was neglected). However, one absorption band, due to close-lying $^3A_2(F)$ and $^1T_2(D)$ states could not be described within this model. In the present paper we have undertaken the experimental and theoretical work in order to resolve this discrepancy.

We measured transmission spectra of $ZnS:Ni$ and $ZnSe:Ni$ at 5 K in the spectral range of $^3T_1(F) \rightarrow ^3A_2(F)$ and $^3T_1(F) \rightarrow ^1T_2(D)$ transitions under hydrostatic pressure up to 1 GPa. The spectra of both investigated materials revealed

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the subband structure which should be related to the coupling with optical modes. Moreover, in ZnS:Ni fine structure of these subbands with line spacing two times smaller than the acoustic TA phonon of ZnS could be resolved. Under hydrostatic pressure it appeared that the absorption bands in both ZnS and ZnSe were shifted to higher energies but: (i) in ZnSe:Ni the two first subbands significantly approached the maximum of the band while relative intensities of all the subbands were not much pressure-dependent (see Fig. 1); (ii) in ZnS:Ni the relative positions

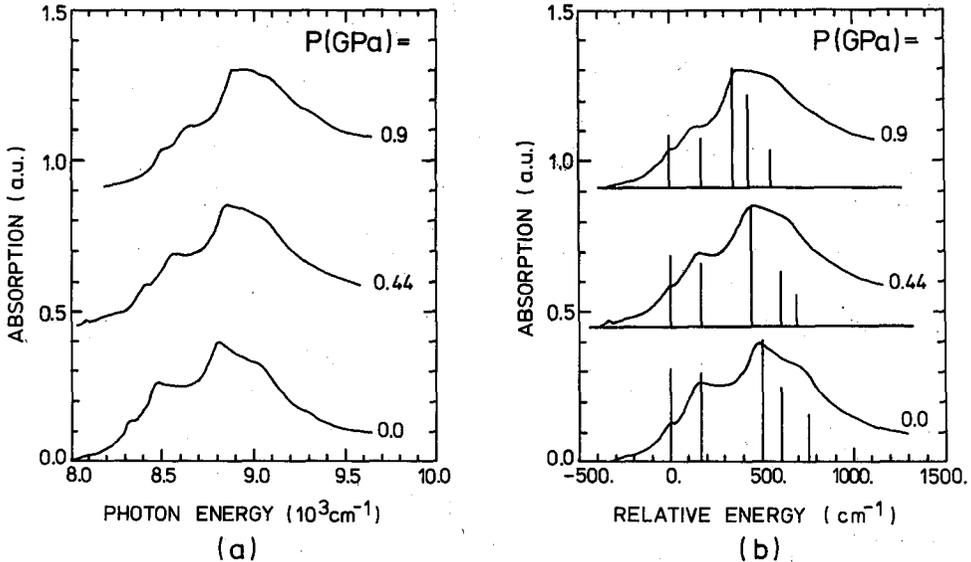


Fig. 1. Absorption spectra of ${}^3T_1(F) \rightarrow {}^3A_2(F)$ and ${}^3T_1(F) \rightarrow {}^1T_2(D)$ transitions measured at various pressures in ZnSe:Ni. Vertical lines — theoretical calculations.

of the sharp lines were almost unchanged, while their intensities strongly varied with pressure (see Fig. 2).

We used the following theoretical model. We assumed that much more complicated pressure evolution of the experimental spectra than the one predicted by SCFT was due to the intermixing of the close-lying states ${}^3A_2(F)$ and ${}^1T_2(D)$ caused by the spin-orbit interaction and the coupling of both of them to the lattice vibrations. Zero order (i.e. without spin-orbit and electron-lattice interactions) pressure coefficients, $\partial E_1/\partial P$, of both states in respect to the ground state ${}^3T_1(F)$ were predicted in the previous work [1, 2]. In the case of ZnSe:Ni we took into account the coupling of 3A_2 and 1T_2 states with totally symmetric lattice vibrations with the energy $\hbar\omega_{LO} = 210 \text{ cm}^{-1}$ corresponding to the peak of the phonon density of states (optical branch). Coupling parameters $V({}^3A_2) = 300 \text{ cm}^{-1}$ and $V({}^1T_2) = -150 \text{ cm}^{-1}$ were deduced from the formula

$$V(i) = \frac{3R}{2\kappa\alpha} \frac{\partial E_i}{\partial P},$$

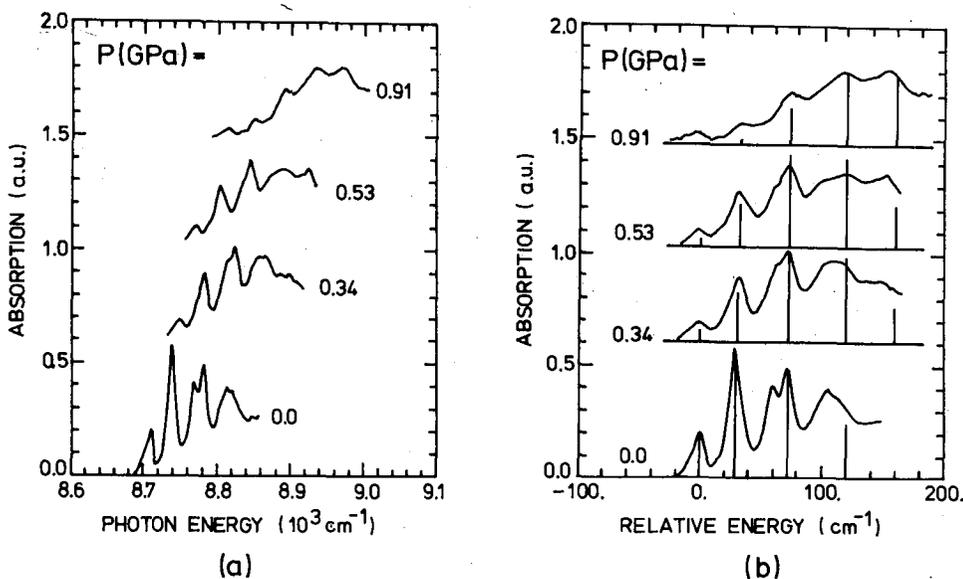


Fig. 2. Absorption spectra of ${}^3T_1(F) \rightarrow {}^3A_2(F)$ and ${}^3T_1(F) \rightarrow {}^1T_2(D)$ transitions measured at various pressures in ZnS:Ni. Vertical lines — theoretical calculations.

where $\alpha = \sqrt{\frac{\hbar}{\mu\omega}}$, κ — the bulk compressibility and R — the distance between an impurity ion and ligands and μ — the reduced mass. The zero-pressure value of the energetic separation between both interacting levels, E_0 , was the fitting parameter, while its pressure variation was determined from $\partial E_i/\partial P$ of the levels [1, 2].

TABLE
Parameters used in our theoretical calculations.

	$\partial E({}^3A_2)/\partial P$ ($\text{cm}^{-1}/\text{GPa}$)	$\partial E({}^1T_2)/\partial P$ ($\text{cm}^{-1}/\text{GPa}$)	Fitting parameters	
			E_0 (cm^{-1})	$E_{JT}(\epsilon)$ (cm^{-1})
ZnS	+154	-80	550	560
ZnSe	+167	-91	470	

In the case of ZnS:Ni, we interpreted only the low energy part of the absorption band. In order to describe this structure as well as its pressure evolution, beside the spin-orbit interaction we considered the coupling of 1T_2 state with ϵ -symmetry vibrations with the energy $\hbar\omega_{TA} = 70 \text{ cm}^{-1}$. Here, beside E_0 , we had an additional fitting parameter, namely Jahn-Teller energy $E_{JT}(\epsilon)$.

The results of the theoretical calculations (obtained with fitting parameters listed in the Table) are presented in Fig. 1b and 2b as vertical lines. The calculations very well reproduce the main features of the observed spectra: (i) relative changes of the positions of the subbands observed in ZnSe:Ni under pressure; (ii) relative changes of the line intensities observed in ZnS:Ni under pressure; (iii)

a strong reduction of the TA-mode energy (from 70 cm^{-1} to 30 cm^{-1}) observed in ZnS:Ni. So, we conclude that the observed discrepancies between SCFT and the experiment really originate from the intermixing of $^3A_2(F)$ and $^1T_2(D)$ states and their coupling to the lattice vibrations.

References

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