

## MULTIPHONON STRUCTURE OF OPTICAL TRANSITIONS TO IMPURITY RESONANCE STATES

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A theory is developed for the absorption spectrum of optical transitions to impurity resonance states accompanied by multiphonon processes. Experimental results for  $\text{CdS} : \text{Ti}^{2+}$  are presented and compared with theory.

### 1. Introduction

Deep impurity states of semiconducting or insulating crystals couple strongly to lattice vibrations. Optical transitions of electrons from and into such states are usually accompanied by multiphonon excitation or deexcitation processes which result in broad absorption and emission bands [1]. On the other hand, excited states of deep impurities are often degenerate with the continuum of conduction or valence band states. Then an auto-ionization of impurity atoms from the excited state becomes possible which may be thought to be due to a resonance interaction between band and impurity states changing the bare impurity state into an impurity resonance state [2]. For the absorption and emission spectra of optical transitions into resonance states line shapes of Fano type have to be expected under the condition that no further interaction takes place besides of the resonance interaction [2]. This holds approximately for certain excited levels of free atoms where Fano line shapes have been really observed in experiment [2]. For impurity atoms the resonance interaction has to compete with the lattice coupling and, obviously, can be neglected in several cases [3]. In other cases experimental results indicate that absorption or emission spectra can be understood only if both interactions

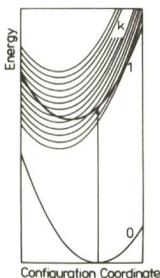


Fig. 1  
Energy level  
schema

are simultaneously taken into account. Such an example represents the  $\text{CdS} : \text{Ti}^{2+}$  system with an  ${}^3A_2$ -impurity ground state within the energy gap 0.3 eV below the conduction band minimum of  $\text{CdS}$  and two excited  ${}^3T_1$  levels within the conduction band 0.4 eV and 0.9 eV above the conduction band minimum. Anomalous absorption and electro-absorption spectra have been reported for transitions between these impurity states [4]. In this paper we present a theory for the absorption spectrum of optical transitions into impurity resonance states taking account of multiphonon processes. The model for our calculation is shown in fig. 1.

Both the impurity states, the ground state  $|0\rangle$  and the bare excited state  $|1\rangle$ , couple to lattice vibrations whereas band states  $|K\rangle$  do not. Optical transitions from  $|0\rangle$  into  $|1\rangle$  and  $|K\rangle$  are supposed to be dipole allowed. By assuming the impurity states to be non-degenerate the Jahn-Teller effect is omitted automatically.

2. Theory

The Hamiltonian H of our model is taken in the form

$$H = \sum_n E_n a_n^\dagger a_n + \sum_{\vec{k}} E_{\vec{k}} a_{\vec{k}}^\dagger a_{\vec{k}} + \sum_{\vec{q}} \hbar \omega_{\vec{q}} b_{\vec{q}}^\dagger b_{\vec{q}} + H' + H_{ep}, \quad (1)$$

$$H' = \sum_{\vec{k}} (V_{1\vec{k}} a_1^\dagger a_{\vec{k}} + V_{1\vec{k}}^* a_{\vec{k}}^\dagger a_1), \quad (2)$$

$$H_{ep} = -i \sum_n \dot{U}_n a_n^\dagger a_n, \quad (3)$$

$$U_n = \sum_{\vec{q}} (u_{n\vec{q}}^* b_{\vec{q}}^\dagger - u_{n\vec{q}} b_{\vec{q}}). \quad (4)$$

Here H' means the resonance interaction energy between the excited impurity state |1) and continuum states |k). H<sub>ep</sub> is the electron-phonon interaction Hamiltonian. The form (3) of H<sub>ep</sub> guarantees that the standard results of the multiphonon theory are obtained if H'=0. For the calculation of the absorption spectrum  $\alpha(\omega) = (\omega/n(\omega) c) \text{Im} \epsilon$  the Kubo formula will be used :

$$\text{Im} \epsilon(\omega) = \frac{4}{\hbar} \frac{e^2 N}{m^2} \text{Im} (p_{01} p_{10} G_{0110}(\omega) + \quad (5)$$

$$\sum_{\vec{k}} (p_{01} p_{\vec{k}0} G_{01\vec{k}0}(\omega) + p_{0\vec{k}} p_{10} G_{0\vec{k}10}(\omega)) + \sum_{\vec{k}\vec{k}'} p_{0\vec{k}} p_{\vec{k}'0} G_{0\vec{k}\vec{k}'0}(\omega)).$$

G<sub>orr'o</sub>(ω) with r = 1, k, r' = 1, k' represents the two particle Green's function; p<sub>or</sub>, p<sub>r'o</sub> are the matrix elements of the momentum operator component parallel to the light polarization direction, N is the density of impurity atoms. Without electron-phonon interaction but in the presence of resonance interaction, the four Green's functions on the right hand side of eq. (5) can be calculated exactly and the result can be comprehended into the closed expression [2]

$$\text{Im} \epsilon^{\text{Fano}}(\omega) = F(\omega) \text{Im} \epsilon^{\text{cont}}(\omega), \quad (6)$$

$$F(\omega) = (q + (\omega - \omega_{10}/\Gamma))^2 / (1 + (\omega - \omega_{10}/\Gamma)^2). \quad (7)$$

Here  $\epsilon^{\text{cont}}(\omega)$  means the dielectric function for transitions from the localized ground state into the continuum of conduction band states. F(ω) represents the Fano curve with q and Γ as parameters closely related to V<sub>1k</sub>, in particular,  $\Gamma \sim |V_{1\vec{k}}|^2$  [2]. In deriving eq. (6) V<sub>1k</sub> and momentum matrix elements have been assumed to be independent of k. If the electron-phonon interaction is taken into account but the resonance interaction is neglected, Imε is given by the well-known result of the multiphonon theory [1]. The inclusion of both the interactions requires additional approximations. The approximate Green's functions we use obey the following relations

$$\sum_{\vec{r}} G_{orr'o}(t) = \Phi(t) \sum_{\vec{r}} g_{orr'o}(t), \quad (8)$$

$$\Phi(t) = \left\langle e^{u_1(t) - u_0(t) + \gamma^2 [u_1 - u_0, \dot{u}_1 - \dot{u}_0] t - (u_1(0) - u_0(0))} \right\rangle. \quad (9)$$

Here g<sub>orr'o</sub>(t) means the two particle Green's function without electron-phonon coupling,  $\sum_{\vec{r}}$  acts only for r=k. Relation (8) inclu-

des the approximation that  $\epsilon^{\text{cont}}(\omega)$  is a slowly varying function as compared to  $\Phi(\omega)$ . It follows

$$\text{Im} \epsilon(\omega) = \frac{1}{\omega^2} \int_{-\infty}^{\infty} d\omega' \Phi(\omega - \omega') \omega'^2 \text{Im} \epsilon^{\text{Fano}}(\omega'). \quad (10)$$

For certain simplified models of lattice vibrations and electron-phonon coupling  $\Phi(\omega)$  can be represented in an analytical form. The Einstein model yields

$$\Phi(\omega) = \sum_{l=-\infty}^{\infty} \delta(\omega - l\omega_0) e^{-S(2N_0+1)} (N_0+1/N_0)^{1/2} I_{|l|} (2S(N_0+1/N_0)^{1/2}) \quad (11)$$

( $\omega_0$ ,  $N_0$ -oscillator frequency and mean occupation number,  $S=|u_{10}-u_{00}|^2$  - multiphonon factor,  $I_l$  - Bessel function). The line shape from eq. (10) is calculated by using expression (11) for  $\Phi(\omega)$  with the following modification : Phonon dispersion and other phonon branches are taken into account in an effective way by smoothing out the  $\delta$ -functions in expression (11) with the exception of the zero phonon line. After performing the convolution integral in eq. (10) the zero phonon line exhibits a pure Fano shape. The zero phonon

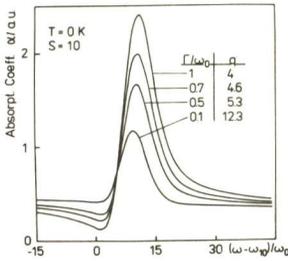


Fig. 2 Calculated absorption spectrum for various values of Fano parameters

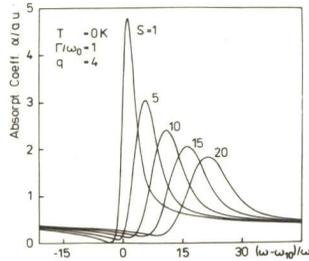


Fig. 3 Calculated absorption spectrum for various values of S

line is omitted in fig. 2 and 3 where we have plotted line shapes at  $T = 0\text{K}$  for various sets of parameters  $q$ ,  $\Gamma$ , and  $S$ . In fig. 2  $q$  and  $\Gamma$  have been varied simultaneously keeping the product  $(q^2-1)\Gamma$  constant. For small interaction matrix elements  $V_{1k}$  this corresponds to a change of  $V_{1k}$  only. Therefore, it can be seen from fig. 2 how the multiphonon line shape changes if the Fano effect is turned on. In fig. 3 it is shown how the Fano line shape changes with increasing electron-phonon coupling.

### 3. Experiment and Comparison with Theory

Fig. 4 shows the absorption spectrum of  $\text{CdS}:\text{Ti}^{2+}$  at 10 and 77 K with the two bands due to the  ${}^3A_2 \rightarrow {}^3T_1(F)$  and  ${}^3A_2 \rightarrow {}^3T_1(P)$  transitions. The bands are polarised as a consequence of the axial crystal-field component. The temperature-dependent triplet structure which is seen in the  ${}^3T_1(F)$  band and, less distinctly, also in the  ${}^3T_1(P)$  band was shown to be due to  $T \otimes \tau_2$  Jahn-Teller coupling in [5]. Note some features in the low-temperature shape especially of the  ${}^3T_1(P)$  band (dip on the low energy side at 10 K, asymmetry) which may be related to the presence of resonance inter-

action. These features were not clearly visible in the spectra analysed in [5], because those spectra were measured on samples of worse crystallographic quality. The high perfection on the present crystals arising from improved growth-conditions manifests itself

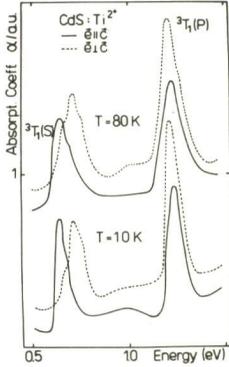


Fig. 4 Exp. abs. spectra of CdS:Ti<sup>2+</sup> single crystals (vert. shifted)

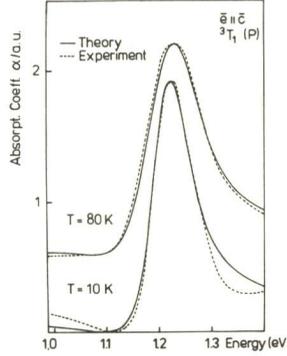


Fig. 5 Exp. and calculated abs. spectra of CdS:Ti<sup>2+</sup> single crystals (vert. Shifted)

in the pronounced dependence on light polarization as well as on somewhat smaller band widths at the lowest temperatures. We have calculated the shape of the  ${}^3T_1(P)$  band ( $\vec{e} \parallel \vec{c}$ ) for 10 and 80 K on the basis of equ. (10) using the parameters values  $\hbar\omega_{10} = 1.14$  eV,  $\hbar\omega_0 = 5$  meV,  $S = 15$ ,  $q = 3.8$ ,  $\Gamma/\omega = 6$ . The results are presented in fig. 5 together with the experimental band shapes. The agreement between theory and experiment is good, apart from some deviation in the

background of the 10 K curve. It should be emphasized that T-independent Fano parameters  $q$  and  $\Gamma$  were used in our fit. The values of  $\hbar\omega_0$  and  $S$  have been estimated from the temperature dependence of

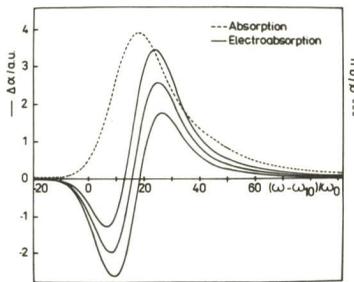


Fig. 6 Calculated electroabsorption spectra of CdS:Ti<sup>2+</sup> single crystals for various sets of field coefficients

band width. They somewhat deviate from the data given in [5] due to better accuracy of the present study. Fig. 6 shows theoretical electroabsorption spectra. In addition to the Stark effect an additional field dependence of the Fano parameters is assumed. The curves show the characteristic features of the experimental observations [4], in particular, a shift of the energy where the electroabsorption signal vanishes relative to the absorption band maximum.

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