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ELECTRON–PHONON INTERACTION IN THE DEEP CENTRE PHOTOLUMINESCENCE OF CdS:Ag:Cl

J. KRUSTOK and J. MÄDASSON

Institute of Materials Technology, Tallinn Technical University, 5 Ehitajate tee,
Tallinn EE0026, Estonia

Abstract—The temperature dependence of the half-width of the red band in CdS:Ag:Cl upon chlorine concentration is studied. It is found that an increase in chlorine concentration ($N_{Cl} > 10^{18}$ cm^{-3}) leads to an increase in the local phonon energy ($\hbar\omega_e \sim N_{Cl}^{1/2}$) and a decrease in the number of phonons emitted. This change in the local lattice dynamics is interpreted as the result of screening by a complex neutral defect which ionizes between 80 and 150 K.

Although radiative recombination centres in wide gap semiconductors of II–VI type have been extensively studied over the past 40 years, the shape of the corresponding broad photoluminescence (PL) bands is still a matter of debate. The line shapes are of considerable importance for a correct interpretation of the Coulomb interaction between the components of the recombination centre, the Coulomb interactions with charged defects surrounding the centre and the electron–phonon coupling. Numerous papers dealing with the deep-level luminescence of II–VI materials indicate that the shape of these PL bands is extensively sensitive to the preparation conditions of the material and thus to the physical structure of the centres [1–4].

An increasing concentration of defects in a crystal increases the Coulomb interaction of the active luminescence centre with surrounding charged defects. This kind of screening also leads to a variation of the position of the energy levels of the centre, affects its recombination parameters and produces changes in the local crystal lattice dynamics. Several authors have reported the role of phonon interactions in the so-called "edge emission" band shape of II–VI materials [2, 4–6], and it is known that the strength of electron–phonon coupling (or the number of interacting phonons S) is usually a function of preparation conditions [2, 5].

The traditional method of analysis of electron–phonon interactions in the case of bands with large halfwidths and no structure is to compare the experimentally measured dependence of the luminescence band halfwidth W on temperature with the calculated one [7–8]

$$W(T) = W(0)*[\coth(\hbar\omega_e/2kT)]^{1/2}, \qquad (1)$$

where

$$W(0) = 2(2\ln 2)^{1/2}S^{1/2}\hbar\omega_e \qquad (2)$$

is the halfwidth at 0 K, $\hbar\omega_e$ is the interacting "effective" phonon energy in the excited state of the centre, and S is the mean number of phonons emitted after the transition. The use of only a single "effective" phonon to describe the temperature dependence of the band halfwidth has a certain theoretical weakness, but it has been proven to be a quite effective way to fit the experimentally observed behaviour of many II–VI compounds. The deep centres in II–VI materials are usually complexes which involve more than one charged defect, and recombination in these complexes may be characterized either as a bound-to-bound or free-to-bound recombination. The free-to-bound recombination usually dominates at higher temperatures, and in this case the free electron recombines with the hole, previously captured by the complex. The same situation is valid also at low temperatures, if the distance between components is very short. It is known that the energy levels of the complex are connected with the distance R between the components, and a decrease in the distance between charged components of the complex also affects the complex oscillations. It has been found

that these complexes are connected mainly with local phonon modes [9]. The energy of a local phonon which is related to a recombination centre is determined by the lattice force constant and by the reduced mass of the centre. If the latter is affected by a charged defect with effective charge Z_2, then the local phonon energy in the excited state of the centre will increase [9]

$$\hbar\omega_e = \hbar \left[(K_0 + 2Z_1 Z_2/\varepsilon R^3)/M\right]^{1/2} \qquad (3)$$

where Z_1 is the effective charge of the centre, K_0 is the force constant when there is no interaction between defects, and M is the reduced mass of complex. It is obvious that if we can change the distance R by varying, for instance, the concentration of the impurity, then there is the possibility of detecting a change in the phonon energy. A similar situation holds if the centre is screened by charged defects at an average distance R. In Refs [2 and 10] screening effects in CdS:Ag:Cl were considered, and it was found that an increase in chlorine concentration caused an increase in the fluctuation of the impurity potential, thus affecting the shape of the green edge emission band. These fluctuations became important for a concentration of chlorine $N_{Cl} > 4 \times 10^{17} \, cm^{-3}$ [2]. The same concentration criterion was also found to be crucial for the deep red band (R-band) [10]. The concentration dependence of the temperature quenching of the R-band indicates that the centre is screened by an ionized complex defect, and in the present paper we examine the role of this X-defect on the "effective" phonon energy of the R-centre in CdS:Ag:Cl.

CdS:Ag:Cl powders with $N_{Ag} = 10^{17} \, cm^{-3}$ and $N_{Cl} = 10^{17}$–$10^{19} \, cm^{-3}$ were used, detailed descriptions of the purification and doping process being given in [3]. The PL was excited with monochromatic u.v. emission (356 nm) from a 250 W high-pressure mercury lamp, measured with a SPM-2 monochromator by a conventional lock-in technique. Computer analysis of the measured spectra was carried out by the method of damped least squares to determine the parameters of each PL band in the temperature range 80–450 K.

The R-band in CdS:Ag:Cl is typical of the deep luminescence band. At 77 K it has an almost perfect Gaussian shape with $E_{max} \approx 1.7 \, eV$ and halfwidth $W \approx 0.26 \, eV$. The luminescence and the quasi-chemical analysis of the defect structure of CdS:Ag:Cl given in [11] indicate that the R-centre is connected with the complex defect $Ag_{Cd}Cl_S$. The temperature dependences of the R-band halfwidths are given in Fig. 1, and may be divided into two groups. In the first group with $N_{Cl} < 10^{18} \, cm^{-3}$, the
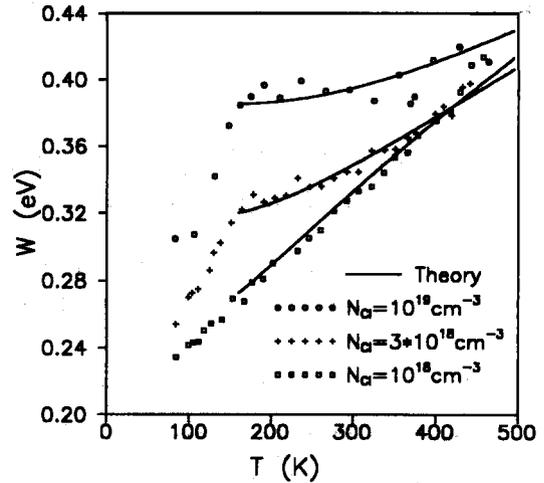
Fig. 1. The temperature dependence of the R-band halfwidth, W.

dependences may be characterized by eqn (1) over the whole temperature region, while the second group with $N_{Cl} > 10^{18} \, cm^{-3}$ shows a steep increase in halfwidth between 80 and 150 K. Above 150 K the dependences may also be described by eqn (1). The parameters obtained in the fit of eqn (1) to the experimental data are given in Table 1. As can be seen from Table 1, an increase in N_{Cl} leads to an increase in the phonon energy and to a decrease in the number of emitted phonons S. For $N_{Cl} > N_{Ag}$ the increase in phonon energy with N_{Cl} may be described by a power law (see Fig. 2):

$$\hbar\omega_e \sim N_{Cl}^{1/2}. \qquad (4)$$

All these facts indicate that the R-centre is indeed screened by the defects, which are ionized when $T > 150 \, K$. The ionization takes place between 80 and 150 K, and as a result the halfwidth of the R-band increases steeply. According to [10], the concentration of this X-defect has a linear dependence upon chlorine concentration. If we suppose that there is a random distribution of this defect, then the average distance R between the R-centre and the X-defect is

$$R \sim N_X^{-1/3} \sim N_{Cl}^{-1/3}, \qquad (5)$$

Table 1. Parameters for the electron–phonon interaction of the R-centre in CdS:Ag:Cl

$N_{Cl}(cm^{-3})$	$W_0(eV)$	$\hbar\omega_e(eV)$	S
2×10^{17}	0.236	0.0293	11.7
4×10^{17}	0.239	0.0299	11.5
10^{18}	0.247	0.0319	10.8
3×10^{18}	0.316	0.0597	5.1
10^{19}	0.385	0.0944	3.0
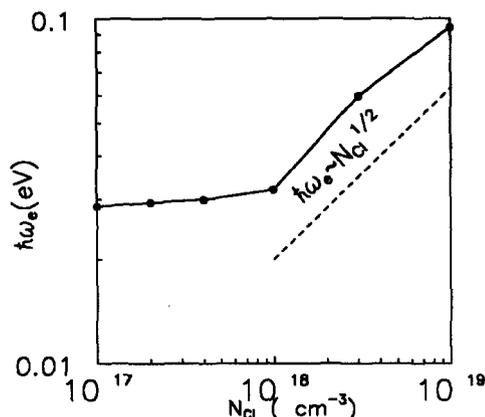
Fig. 2. The dependence of the "effective" phonon energy on the chlorine concentration.

and from (3) and (5) we get

$$\hbar\omega_e = \hbar\,[(K_0 + 2Z_1 Z_2 c^* N_{Cl}/\varepsilon)/M\,]^{1/2} \sim N_{Cl}^{1/2} \qquad (6)$$

where c^* is a constant. Equation (6) has the same form as the experimentally determined one in eqn (4). The "effective" phonon energies for $N_{Cl} > 10^{18}\,cm^{-3}$ exceed the phonon energies found in the CdS lattice ($\hbar\omega_{LO} = 0.038\,eV$ [12]) and even those for light impurities in CdS. These high values are connected with changes in the physical structure of the R-centres due to screening. As found in [10], this kind of screening also causes a decrease in the energy of the temperature quenching E_T of the R-band for $N_{Cl} > 4 \times 10^7\,cm^{-3}$, and changes in the electron and hole capture rates by the R-centre.

It is obvious that the "effective" phonon is a concept without real physical content. In the case of the deep centres in II–VI materials it includes a kind of complicated average phonon density function, and further theoretical treatment is necessary to solve the problem of the electron phonon interaction of deep centres. In this paper we have shown that the "effective" phonon energy is a parameter which can be used to characterize the interactions between centres and defects in crystals, and that these interactions fundamentally affect the phonon structure and thus the band shape of the luminescence in CdS.

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