PHYSICAL REVIEW B VOLUME 36, NUMBER 2 15 JULY 1987-I

Temperature shift of the absorption edge in mixed single crystals of $Zn_xCd_{1-x}Se$

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(Received 31 July 1986; revised manuscript received 16 March 1987)

The thermal dependence of the absorption-edge shift has been measured in mixed single crystals of $Zn_xCd_{1-x}Se$, in the temperature range 13–300 K. The experimental results support the argument that the energy gap shift is caused by an internal Franz-Keldysh effect which results from electric fields induced by phonons. However, the exact dependences of the energy gap shift and the increase in the absorption coefficient on the electric fields differ from those calculated by Franz and Keldysh, because of final-state interaction correction. It is shown that in mixed single crystals of $Zn_xCd_{1-x}Se$, as well as in other single crystals of pure II-VI compounds, the electric fields which determine the thermal shift of the absorption edge are dominated by the LO-phonon-induced electric fields.

INTRODUCTION

A temperature dependence of the absorption-edge energy has been observed in many crystals, both insulators and semiconductors. In most cases the absorption edge shifts to lower energies with increasing temperature. Various processes can be involved in the absorption, depending upon whether the electronic transition is direct or indirect.

The purpose of the present research is to study the thermal absorption-edge shift in mixed single hexagonal crystals of $Zn_xCd_{1-x}Se$, in order to ascertain the main processes involved.

THEORY

Various external parameters can be used to influence the optical properties of solids. One of the most commonly used techniques is electroabsorption. It is argued here that also the thermal shift of the absorption edge in the mentioned materials is due to internal electric microfields, which cause an internal Franz-Keldysh[1,2] (FK) effect.

The main features of the theoretical proof, supported by experimental results, are obtained using concepts originally introduced for absorption modulation by an external electric field and are adapted[3] to the new purpose by replacing the external field by an average effective internal field created by phonons.

Most of the theoretical procedure which is relevant here, has been introduced in Ref. 3 (in the Theory and Appendix sections).

In the present paper we define the shift of a certain high and constant value of the absorption coefficient (α_g) as the criterion for the absorption-edge shift with temperature $E_g(T)$. Since

$$\alpha_g(T)=\alpha_0\exp\left[\frac{C}{F_p(T)}[E_g(T)-E_0]\right], \tag{1}$$

where α_0 and E_0 are not temperature dependent, and $F_p(T)$ is the phonon-induced electric field (in other papers also denoted as $F_{\rm rms}$), we obtain

$$\frac{C}{F_p(0)}[E_g(0)-E_0]=\frac{C}{F_p(T)}[E_g(T)-E_0]. \tag{2}$$

When the dominant electric field is induced by LO phonons it follows that

$$F_p(T)=F_p(0)\coth\left[\frac{\hbar\omega_0}{2kT}\right]. \tag{3}$$

Hence,

$$E_g(T)=E_g(0)\coth\left[\frac{\hbar\omega_0}{2kT}\right]-E_0\left[\coth\left[\frac{\hbar\omega_0}{2kT}\right]-1\right], \tag{4}$$

$$E_g(T)\tanh\left[\frac{\hbar\omega_0}{2kT}\right]=E_g(0)-E_0\left[1-\tanh\left[\frac{\hbar\omega_0}{2kT}\right]\right]. \tag{4a}$$

We now define

$$\Theta=\frac{\hbar\omega_0}{2kT},\quad z(\Theta)=1-\tanh(\theta),$$
$$y(\Theta)=E_g(T)\tanh(\Theta).$$

A linear dependence of $y(\Theta)$ on $z(\Theta)$ of the experimental results will substantiate the validity of our assumptions and of the presented model of the absorption process.

It has to be pointed out, however, that by using the above relationships in the case of the application of an external weak electric field, the calculated energy gap shift differs from the shift calculated by Franz:

$$\Delta E_g=-PS^2F_e^2, \tag{5}$$

where

$P=e^2\hbar^2/24\mu$.

Equation (5) was obtained from calculations based on the one-electron approximation with no final-state interaction corrections. Previous published measurements of the reduced effective masses of excitons near the fundamental absorption edge of various materials rely on this calculation.[4-6]

According to the calculations in the Appendix, in the presence of a weak external electric field (F_e):

$$\Delta E_g = -\left[\frac{1}{2C^2}\right] \ln \left[\frac{\alpha_0}{\alpha_g}\right] S F_e^2 \; , \tag{6a}$$

$$\frac{\Delta\alpha}{\alpha} = \frac{1}{2C^2} \ln \left[\frac{\alpha_0}{\alpha_g}\right] S^2 F_e^2 \; , \tag{6b}$$

where α_0 and C are constant. Since $\alpha_0 > \alpha_g$, ΔE_g is negative, as required.

The difference in approach of course explains the difference in the resulting relationship. When the final-state interactions are taken into account, the resultant calculations are much more complicated. The one-electron approximation is suitable for cases where the effective mass of the hole is at least 1 order of magnitude heavier than that of the electron, and when final-state Coulombic interaction is negligible.[7] The FK approach also considers E_0 in Eq. (1) to be the energy gap[8] which is incorrect, since E_0 is in practice a fitting parameter independent of temperature,[8-10] while the energy gap is strongly temperature dependent.

The influence of the electric field is expressed through the slope parameter S, as described before.[3] The electric field creates new allowed energy states in the forbidden energy gap and thus enables the exciton to tunnel from its quasibound localized states into free ionized states. This mechanism effectively decreases the energy gap since it allows electron transitions from near the valence band to the vicinity of the conduction band at energies lower than the field-free gap. This process is of course described by the FK model, and the only controversy is about the approximation used to calculate the resultant shift of the absorption edge and the increase in the absorption coefficient.

EXPERIMENTAL PROCEDURE

The experimental apparatus and the preparation of the crystals are described in Ref. 3.

The absorption edge has been measured at an optical density of ($D=\alpha d$) 9.0, which in this case is $\alpha \simeq 900$ cm^{-1}.

RESULTS AND DISCUSSION

The temperature dependence of the absorption edge in $Zn_{0.3}Cd_{0.7}Se$ for **E**⊥**c** polarization is shown in Fig. 1. Similar curves have been obtained for all the other crystals and in both light polarization as well. In crystals where both polarizations were measured, the energy gap for **E**‖**c** was 3–4 meV larger than the energy gap for **E**⊥**c**.

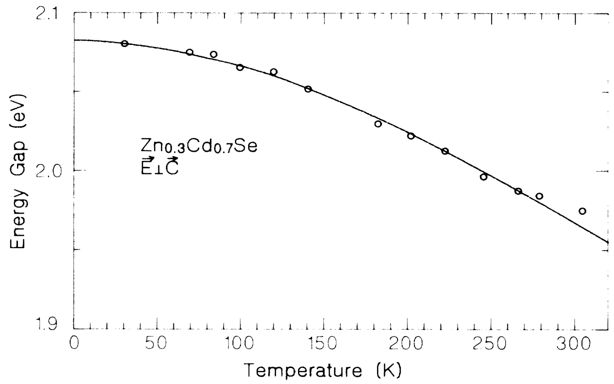

FIG. 1. Absorption-edge energy vs temperature in $Zn_{0.3}Cd_{0.7}Se$, **E**⊥**c** polarization.

For the measured hexagonal series crystals, the energy gap is linearly dependent on composition. (See Fig. 7 in Ref. 3.)

The plot of $y(\Theta)$ versus $z(\Theta)$ in $Zn_{0.3}Cd_{0.7}Se$ for the **E**⊥**c** polarization is shown in Fig. 2. For all compositions and measured polarization $y(\Theta)$ is linearly dependent on $z(\Theta)$ in a similar way. From the plot of $y(\Theta)$ versus $z(\Theta)$ the value of E_0 has been deduced, as it corresponds to the absolute value of its slope. As can be seen from Fig. 7 in Ref. 3, for the hexagonal phase crystals, E_0 is also linearly dependent on composition, i.e., on x.

The size of the energy gap, measured at room temperature, and the value of E_0, for the measured compositions with **E**⊥**c** are shown in Table I.

SUMMARY

It has been shown in the preceding paper[3] that the phonon-induced electric microfields determine the thermal dependence of the slope parameter S. The linear dependence of $y(\Theta)$ versus $z(\Theta)$ for all compositions supports the argument that those fields cause the thermal shift of the energy gap and proves that the fundamental absorption process can be described in the framework of the

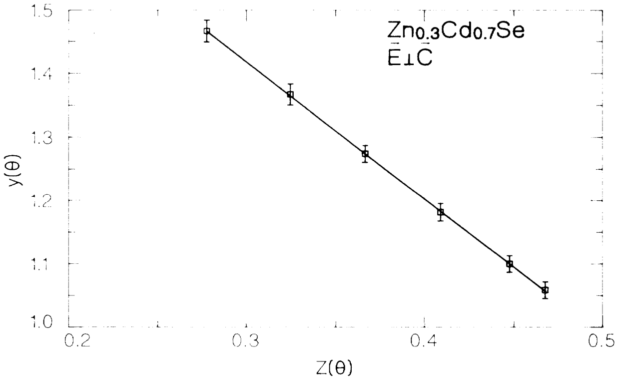

FIG. 2. $y(\Theta)$ vs $z(\Theta)$ in $Zn_{0.3}Cd_{0.7}Se$, **E**⊥**c** polarization.

Dow-Redfield theory.

In order to further confirm the validity of this model quantitively as well as qualitively, the energy gap shift due to an applied external weak electric field will be studied.

A quadratic dependence of the absorption-edge energy shift on the applied external field has been previously experimentally observed in ZnS (Ref. 11) of various crystalline structures, and the calculations carried out supported the Dow-Redfield theory. A quadratic dependence of $\Delta\alpha/\alpha F_e^2$ on S has also been experimentally observed in some crystals,[12] which proves the validity of Eq. (6b).

APPENDIX

It has been shown in Ref. 3 that in the presence of an electric field, the absorption coefficient is given by

$$\alpha(E,F)=\alpha_0\exp\left[\frac{C}{F}(E-E_0)\right] , \qquad (\mathrm{A1})$$

In the absence of an external field, F is replaced by the average field induced by the phonons. In the case of the LO phonons, it is given by

$$F_p(T)=\frac{2\epsilon_0\hbar\omega_0}{\sqrt{3}\epsilon^*\pi e a}\coth\left[\frac{\hbar\omega_0}{2kT}\right] , \qquad (\mathrm{A2})$$

where $\hbar\omega_0$ is the phonon energy, ϵ_0 and $\epsilon^*=(\epsilon_\infty^{-1}-\epsilon_0^{-1})^{-1}$ are the static and "effective" dielectric constants, and a is the exciton radius.

Hence, using Eq. (A1) and (A2) for a high and constant value of the absorption coefficient as an indicator for the absorption-edge (E_g) shift results in

$$\frac{C}{F_p(0)}[E_g(0)-E_0]=\frac{C}{F_p(T)}[E_g(T)-E_0] , \qquad (\mathrm{A3})$$

$$E_g(T)=E_g(0)\coth\left[\frac{\hbar\omega_0}{2kT}\right]-E_0\left[\coth\left[\frac{\hbar\omega_0}{2kT}\right]-1\right] , \qquad (\mathrm{A4})$$

or equivalently,

$$E_g(T)\tanh\left[\frac{\hbar\omega_0}{2kT}\right]=E_g(0)-E_0\left[1-\tanh\left[\frac{\hbar\omega_0}{2kT}\right]\right] . \qquad (\mathrm{A5})$$

TABLE I. Energy gap and its temperature dependence at room temperature (E⊥c polarization), E_0 (E⊥c polarization), and LO phonon energies versus composition.

x	E_g (eV)	$-\frac{dE_g}{dT}$ (eV/K)	$\hbar\omega_0$ (meV)	E_0 (eV)
0	1.727	5.1×10^{-4}	27.0	1.895
0.04	1.763	5.2×10^{-4}	27.5	1.957
0.3	1.975	5.35×10^{-4}	28.5	2.148
0.4	2.046	5.35×10^{-4}	29.0	2.246
1	2.664	6.09×10^{-4}	31.0	2.887

When an external electric field (F_e) is applied on the crystal it decreases the slope parameter S, by adding new allowed energy states in the forbidden energy gap, and so increases the exciton tunneling to the ionized states at lower energies.

Since the external field and the phonon-fields are not correlated, the joint field ($\bar{F}$) is

$$\bar{F}^2=F_e^2+F_p^2 , \qquad (\mathrm{A6})$$

where F_p is the phonon-induced field.

Taking the value of the absorption coefficient of the absorption edge as constant, it follows from (A1) and (A3):

$$\frac{C}{\bar{F}}(E_g'-E_0)=\frac{C}{F_p}(E_g-E_0) \qquad (\mathrm{A7})$$

where E_g' is the shifted value of the energy of constant absorption, due to the applied external field.

Assuming a weak external field, i.e., $(F_e/F_p)^2 \ll 1$, and using Eqs. (A6) and (A7) result in

$$\Delta E_g=E_g'-E_g=\frac{1}{2C^2}\ln\left[\frac{\alpha_g}{\alpha_0}\right]S_p^2F_e^2 , \qquad (\mathrm{A8})$$

where $S_p=C/F_p$ is the slope parameter which is determined only by the phonon-induced fields.

This proves that the experimentally obtained E_g depends both on the choice of α_g as well as on the square of the applied field F_e.

If we examine the increase of the absorption coefficient at a certain constant photon energy E_1, due to the weak external field

$$\ln\left[\frac{\alpha}{\alpha_0}\right]=\frac{C}{F_p}(E_1-E_0) , \qquad (\mathrm{A9})$$

$$\ln\left[\frac{\alpha'}{\alpha_0}\right]=\frac{C}{\bar{F}}(E_1-E_0) . \qquad (\mathrm{A10})$$

Assuming $\Delta\alpha \ll \alpha$,

$$\ln\left[\frac{\alpha'}{\alpha}\right]\cong\left[\frac{\Delta\alpha}{\alpha}\right]=(E_1-E_0)\left[\frac{C}{\bar{F}}-\frac{C}{F_p}\right] . \qquad (\mathrm{A11})$$

Using (A6), and the fact that $(F_e/F_p)^2 \ll 1$ yields the following:

$$\frac{\Delta\alpha}{\alpha}=\frac{1}{2C^2}\ln\left[\frac{\alpha_0}{\alpha}\right]S_p^2F_e^2 , \qquad (\mathrm{A12})$$

which does not depend on the choice of E_1.

Hence, for a constant value of the absorption coefficient (α), $\Delta\alpha/\alpha$ depends on the squares of the external-field-free slope parameter S_p and the external field F_e.

[1] L. V. Keldysh, Zh. Eksp. Teor. Fiz. **34**, 1138 (1958) [Sov. Phys.—JETP **7**, 788 (1958)].

[2] W. Franz, Naturforsch **139**, 484 (1958).

[3] L. Samuel, Y. Brada, A. Burger, and M. Roth, preceding paper, Phys. Rev. B. **36**, 1168 (1987).

[4] V. A. Sinyak, Opt. Commun. **48**, 200 (1983).

[5] V. M. Rysakov, Pis'ma Zh. Tekh. Fiz. **9**, 621 (1983) [Sov. Tech. Phys. Lett. **9**, 267 (1983)].

[6] N. Bottka, Opt. Eng. **17**, 530 (1978).

[7] A. G. Aronov and A. S. Ioselevich, in *Modern Problems in Condensed Matter Sciences,* edited by E. I. Rashba and M. D. Sturge (North-Holland, Amsterdam, 1982), Vol. 2, Chap. 7, p. 267.

[8] M. Cardona, *Modulation Spectroscopy* (Academic, New York, 1969), Suppl. 11, p. 229.

[9] M. V. Kurik, Phys. Status Solidi A **8**, 9 (1971).

[10] J. D. Dow and D. Redfield, Phys. Rev. B **5**, 594 (1972).

[11] B. G. Yacobi, Y. Brada, U. Lachish, and C. Hirsch, Phys. Rev. B **11**, 2990 (1975).

[12] E. Möhler and B. Thomas, Phys. Rev. Lett. **44**, 543 (1980).