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≪Original≫ A Mechanism of the Bound Exciton Interaction with Longitudinal Optical Lattice Vibrations in Cathodoluminescence of Cadmium-Sulphide

Kie Hyung Chung

College of Engineering, Seoul National University, Seoul, Korea

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Abstract

The exciton emission spectra of CdS single crystals excited by electrons were measured at 80°K as a function of the wave length. The measured dissociation energy of exciton bound to neutral donor was 2.0 meV, compared to the corresponding theoretical value of 2.4 to 3.2 meV. An exciton bound to neutral donor and a longitudinal optical (LO) phonon may not interact, but a free exciton dissociated from a neutral donor and a LO phonon is expected to interact each other. Therefore the origin of the spectra consisting of interaction term was located at the spectrum consisting of a free exciton dissociated from a neutral donor (I_2d). From the analysis of the spectra the LO phonon energy of CdS was found to be 40.5 meV.

요 약

80°K에서 카드미움설파이드 단결정에 펄스형 전자빔을 쪼였을 때 자연적으로 방출되는 빛의 스펙트럼을 파장의 함수로 측정하였다. 측정된 스펙트럼으로부터 중성도너에 묶인 엑사이톤의 분리에너지가 2.0 meV였으며, 계산치는 2.4~3.2 meV 였다. 이 중성도너에 구속된 엑사이톤과 세로방향 광학 음향양자와는 상호작용을 하지 않으며 분리된 자유엑사이톤과 상호작용을 한다는 결론을 얻었다. 그러므로 상호작용으로 구성되는 스펙트럼의 원점은 중성도너로부터 분리된 자유엑사이톤의 스펙트럼의 위치에 있게 되며 또한 스펙트럼의 분석으로부터 카드미움설파이드의 세로방향 광학음향양자 에너지는 40.5meV 로 밝혀졌다.

1. Introduction

The crystals with periodic structure of atomic arrangement have the periodic potential of nearly free electron of atom, and the electrons have the energy gap. The particles do not exist in the energy gap (so called the forbbiden band). But excitonic levels appear in the gap when the periodic structure of nearly free electron is locally distorted by the applied force. Because an excited electron exists *in the specified quantum state*, an excitonic level is also characterized by some quantum states. The concept of the exciton has been effectively used to explain the interactions of electron hole pairs and the optical properties of solids.

A cathodoluminescent spectra in CdS were studied by many investigators: Basov[1] and Benoit[2]. Their work utilized the electronic excitation sources capable of producing exciton of the order of 10^{16} cm^{-3}. In order to analyze these observed spectra, we had proposed a mechanism based on the excited state of excitonic molecule[3]. As it turned out this interactions was erroneous; If annihilation of an exciton assisted by phonon occurs in excited states of an exciton, the spectra should look similar to those of hydrogen atom. But this is not consistent with published results.

In ref.(2) Benoit and coworkers point out some problems for the case of I_2-lst LO phonon interaction. According to his experimental result, LO-phonon energy of the I_2-lst LO phonon interaction is 38 meV, and LO phonon energies of the 2nd and 3rd interactions with I_2 are identically 41 meV. They state that the reason for the discrepancy among I_2, I_2-LO. and I_1-LO is not clearly understood, and that it is possible that the emitted phonons in these two transitions are not lattice phonons, but localized modes associated with the impurity centers responsible for the I_1 and I_2 lines.

It seems not reasonable, however, that the excitons creating single LO mode consisting of impurity center are coupled again to two times LO mode, three times LO mode etc. But that some percentage of the bound excitons is cooperated simultaneously with single LO phonon, and some percentage of bound excitons with multiple LO phonons.

2. Experiment

The experimental apparatus has been descrived previously[3] and the essential features are as follows.

(1) The typical samples were about 0.2×5×7mm^3, clear yellow, brittle and transparant platelets.

The samples were etched 3 minutes in a 25°C conc.-HCl solution as proposed by Strehlow[4] and then washed with demineralized water. The etching conditions were connected with a dead voltage empirically. A resistivity of N-type CdS single crystal was about 2×10^8 ohm-cm at room temperature. For the resistance measurements Gillette razer blades were used for ohmic contacts.

A mixture of the Al powder and the Silicon grease is used for mounting the specimen on a cold finger. The emitted X-ray during the operation was blocked by thick plexiglass.

The fluorescence screen was set up near the path of electron beam to detect the direction of electron beam.

(2) The emitted light from CdS was collimated by a lense and a microscope lense in front of the spectrometer. The monochromator is of 0.25m every type having resolution of 2 A with 25 u slit. The dectors used were 1P28 P.M. tube and 7120 P.M. tube, for the visible and red light range, respectively. The P.M. tube output signal was plotted on a X-Y recorder. The recording system were placed in the electromagnetically shielded chamber.

3. Experimental Results.

The spontaneous emission spectrum of a pure CdS platelet excited by electrons as a function of wave length at 80°K are given in Fig.1. One essential feature of these spectra is the shift toward the long wave length when the energy of the bombarding electrons is increased.

In Fig.2. the spontaneous emission spectrum in this work is compared with Benoit's[2] data. The I_2d was interpreted the origin of I_2-LO interaction terms in Benoit's data, which is equivalent to I_2d-LO in this paper. It is evident that the origin of emission line I_2d-LO result from an nihilation

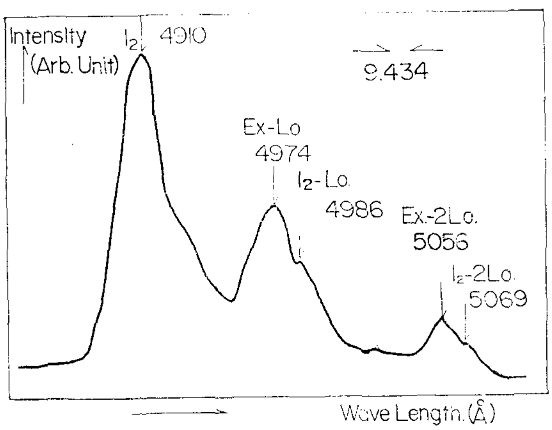

Fig. 1. 1 Spontaoeous emission spectrum of CdS excited by electrons as a function of wave length at 80°K. Energy of bombarding electron is 28 KeV.

of a free exciton dissociated from a neutral donor, simultaneously with emission of one LO phonon.

The I_2 and the spectral lines in this data are shifted about 40 A toward the long wave-length side compared to Benoit's values. It should be noted, however, that the values corresponding to the LO-phonon energy are almost identical each other. The reason for the shift of about 40 A may be due to the fact that the energy gap is due to the difference in the temperature and the excitation energy of electrons (4.2°K and 25 KeV for Benoit's data).

The difference between I_2-lst and I_2-2nd LO phonon interaction is about 3 meV in the spectrum measured by Thomas[7] *et al.* at low temperature.

Also the measure spectra of spontaneous emission by Benoit[2] showed the same result. The value obtained by Thomas[7] *et al.* of dissociation energy is 3.9 meV. Therefore the energy of free exciton E_{ex1} dissociated from neutral donor is 2.5509 eV.

Fig. 2. Comparison of data of Benoit & this experimention emission lines of CdS and measured sparations.

Benoit Experiment 4.2° K, Emission Ciaxis				This Experiment 80° K, Emissionic			
Emission line	Energy (eV)	Distance between associated lines	Origin	Emission line	Emergy (eV)	Distance between associated lines	Origin
A_f	2.5525		Annihilation of a free exciton in the triplet state	A_f	Not observed (N.O)		Annihilation of free exciton in th triplet state
I_2	2.547		Annihiation of an exciton bound to a neutral donor	I_{2d}	2.5267 (N.O)		Annihilation of a fre exciton dissociate from neatral donor
$E_x—LO$	2.514		Annihilation of a free exciton with emission of one LO phonon	I_2	2.5247		Annihilation of a exciton bound to gr ound state of donoı
$I_2—LO$	2.509		Annihilation of a free exciton bound to a neutral donor with emission of one LO phonon	$E_x—LO$	2.4922		Annihilation of free exciton wit emission of one L phonon
$E_x—2LO$	2.473		Annihilation of a free exciton with emission of two LO phonons	$I_{2d}LO$	2.4862		Annihilation of free exciton dissoci ated from neutr donor with emissio of one LO phonon
$I_2—2LO$	2.468		I_2 replica with two LO phonons	$E_x—2LO$	2.4518		Annihilation of a fre exciton with emissi on of two L phonons
$E_x—3LO$	2.432		Annihilation of a free exciton with emission of three LO phonoons	$I_{2d}—2LO$	2.4455		I_2 replica with tw LO phonons
				$E_x—3LO$	(N.O)		

Table 1. LO-phonon wave numbers in CdS

Auther	LO-phonon wave numbers(cm^{-1})
Verleur[8]	303
Poulet[9]	325
Tell[10]	305
Nusimovici[11]	308
Benoit[2]	331
Thomas[7]	304
This work	327

If the distribution of the excitons bound to neutral donor is applied to the Maxwell-Boltzmann statistics, the peak of the spectrum is broadened with increasing temperature. Accordingly the spectrum of dissociated exciton from neutral donor overlaps with I_2 at this temperature, and it does not appear in the present experiment.

From Fig. 1 we obtain 38.5 meV for the 1st interacting LO-phonon energy with I_2 and also 40.5meV for the 2LO energy, while Benoit obtained 41meV, and Thomas 37.7 meV from measurement of optical transmittance. The energy of one LO-phonon in CdS reported by various investigators are listed in Table 1.

The LO-phonon energy calculated theoretically at the Γ point in CdS contains many parameters which is the static and optical dielectric constants, effective charge, etc. These parameters may vary depending on the samples used. Also the differences in experimental values for the one LO-phonon energy arise due to differences in apparatus employed particularly the monochromater, and the measuring method. Therefore we believe that the comparison is hardly meaningful unless we know all the parameters of CdS and the characteristics of the apparatus employed by the various investigators. But the data of this work is very close to the values of Poulet[9] and Benoit[2].

The calculated value of dissociation energy of an exciton bound to a neutral donor is 3.2 or 2.4meV while this experimental value gives 2.0 meV (Benoit obtained an experimental value of 3 meV). The discrepancy between the calculated and experimental values may partly be due to the effective mass approximation which is valid only for shallow donor levels and to the temperature effect because the calculated value was obtained from ground state of hydrogen atom.

Recently Figueira[12] also observed a molecular binding energy of 3 to 4 meV for the excitonic molecule from a transmittance experiment at very low temperature in CdS.

This value is very closely agreement with present experimental and calculated one.

4. Conclusion

We believe that the origin of I_2d-LO phonon is I_2d, and that the dissociation energy of an exciton bound to neutral donor from experiment is 2.0 meV, compared to the corresponding theoretical value of 2.4 to 3.2 meV. This value agrees well with Figueira's[12] report. The LO phonon energy in CdS is 40.5 meV

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