Quantum size effects in luminescence of thin lead sulfide films and PbS-EuS superlattices

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(Submitted 9 October 1987)
Zh. Eksp. Teor. Fiz. **94**, 239–246 (July 1988)

The luminescence of very thin (down to 4 nm) PbS films and of EuS-PbS superlattices with PbS potential wells and EuS barriers is investigated for the first time ever. It is observed that the luminescence band of lead sulfide can shift at 80 K by 240 to 440 meV, depending on the thickness of the PbS layers and on their deformation by a KCl substrate and by EuS layers. The greater part of the shift is attributed to a 20–200 meV change of the first size-quantization level upward in energy relative to the edge of the conduction band.

INTRODUCTION

The interest in superlattices (SL) based on IV-VI compounds is due to the need of verifying in experiment whether the general ideas on the electric spectrum of electrons in two-dimensional systems are applicable to new superconducting materials. It is also due to the possibility of developing on their basis new IR-band photoreceivers and emitters. The bulk of the research is devoted to systems such as PbTe-PbSnTe (Refs. 1–7) with low potential barriers. The use of the wide-gap semiconductor PbEuTeSe as a barrier in PbTe-PbEuTeSe systems with quantum wells[8] makes it possible to construct semiconductor lasers operating at relatively high temperatures (up to 240 K at 4 μm wavelength).

Progress in the production of multilayer films and superlattice structures based on lead and europium chalcogenides[9,10] have made relevant the problem of creating composite PbS-EuS superlattices with high potential barriers and very thin layers, in which quantum size effects should be manifested. Research into the electric properties of such systems encounters difficulties connected with the production of ohmic contacts for the individual layers. Our task in the present study was the investigation of such superlattices by contactless luminescence methods. A procedure previously developed for the investigation of thin layers and heterostructures of IV-VI compounds excited by pulsed Nd-laser luminescence[11,12] was improved and used to investigated PbS-EuS superlattices. The present work was first reported in Ref. 13.

1. EXPERIMENT

The specimens were prepared in a vacuum installation with an oil-free exhaust system ($P_{\rm res} = 10^{-4}$–10^{-5} Pa) by thermal evaporation of lead sulfide from a tungsten "boat" and by electron-beam evaporation of the europium sulfide. The vapors were subsequently condensed on a (001) surface of KCl at a temperature 520–570 K. The layer thickness and the condensation rate were monitored against the lowering of the frequency of a calibrated quartz resonator placed alongside the substrate. A batch of single-layer PbS films was produced, ranging in thickness from 150 to 4 nm, as were also Pbs-EuS SL of two types: a) With constant barrier (EuS) thickness $b = 14$ nm and with quantum-well (PbS) thickness in the range $a = 0.5$–15 nm; in this case the number of the superlattice periods ranged from 100 to 4, so that the total thickness of the PbS layers remained constant at ≈ 150 nm. b) with constant layer-thickness ratio $a/b = 1.5$ and with a variable period $(a + b)$ ranging from 1 to 16 nm.

The EuS band gap ($E_g = 1.63$) is substantially wider than that of PbS ($E_g = 0.31$ eV). A hypothetical energy diagram of the PbS-EuS superlattice, based on data on the work functions and electron-affinity energies of the compounds, is shown in Fig. 1. This diagram shows that luminescence excitation with an Nd laser having a quantum energy $\hbar\omega_0 = 1.18$ eV permits excitation of PbS layers without laser-beam absorption in wide-gap SL layers. The emission of the narrow-gap PbS layers should leave the sample without being absorbed by the europium sulfide.

2. STRUCTURE OF FILMS

For the structure investigations, the films were floated off the substrates by dissolving KCl in distilled water and brought out on glass slides or electron-microscope object nets. The x-ray reflection photographs were obtained by the standard θ-2θ scanning scheme with a DRON-2 diffractometer in Cu-Kα radiation, using a graphite crystal (200) as the secondary monochromator. The electron microscope investigations of the film structure were carried out with an EMV electron microscope at an accelerating voltage 100 kV. The microscope resolution was 1 nm, and the magnification ranged from 10 000 to 90 000.

These investigations have shown that lead sulfide grows on KCl substrates in the form single-crystal films with (001) orientation and a growth dislocation density not higher than 10^7–10^8 cm^{-2}.

Owing to the high density of the PbS nuclei, the films become solid at very low thicknesses (~ 4 nm). This makes it possible to grow isolated single-crystal lead-sulfide layers of thickness $a = 4$–150 nm.

Investigation of the features of the epitaxial growth of europium sulfide on lead sulfide has shown that, notwithstanding the low substrate temperatures ($T_s = 520$ K) compared with the EuS melting point (2833 K), the films grow on one another layer by layer, by the Frank–van der Merwe mechanism. This results in single-crystal layers of high degree of crystal-structure perfection (Fig. 2). The slight disparity of their lattice periods ($f = 0.5\%$) ensures a pseudomorphous state of the PbS/EuS bicrystals over a layer

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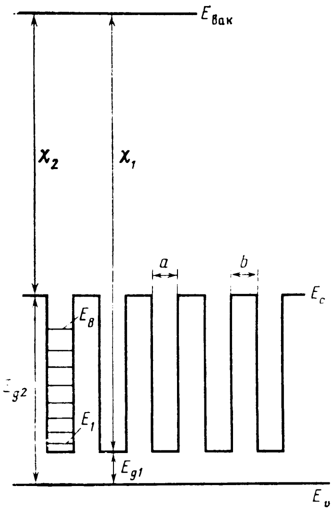

FIG. 1. Model of energy diagram of PbS-EuS superlattice: E_{g1} (PbS) = 0.31, E_{g2} (EuS) = 1.63 eV, $\chi_1 = 3.8 - 4.2$ eV, $\chi_2 = 2.7$ eV. The size-quantization levels $E_1 - E_8$ are shown for $a = 5.5$ nm and $b = 14$ nm.

thickness 200 nm, with their interface free of disparity dislocations.

Investigations of x-ray diffraction of multilayer films have shown that they are periodic with abrupt separation boundaries (boundary width not larger than 1 nm), as attested by the distinct satellite reflections around the Bragg reflections (Fig. 3) and near the primary beam. The superlattice period is determined with high accuracy by the distance between the satellite reflections.[14]

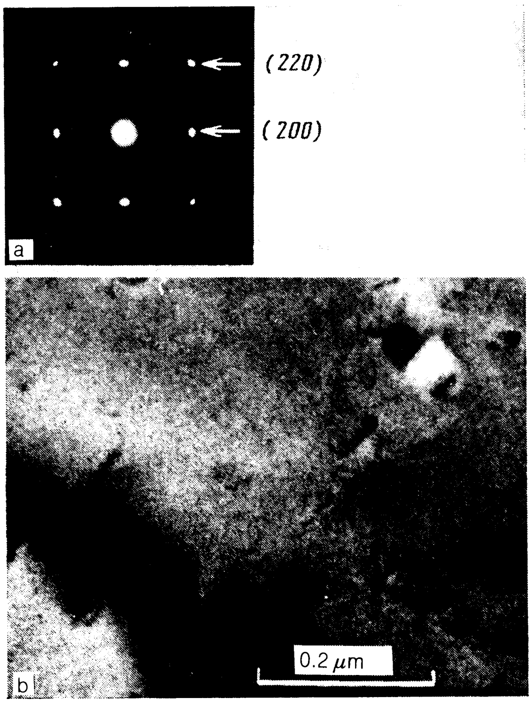

FIG. 2. Electron-microgram (b) and electron-diffraction pattern (a) of a two-layer EuS/(001)PbS film grown on (001) KCl.

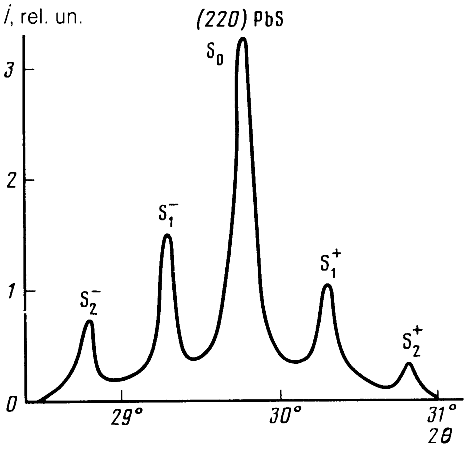

FIG. 3. Reflection diffraction pattern of a PbS-EuS SL with period $(a + b) = 18$ nm; $S_n^\pm$-satellite reflections.

3. PHOTOLUMINESCENCE SPECTRA OF SINGLE-LAYER PbS FILMS

Figure 4a shows typical spontaneous photoluminescence (PL) spectra, at 80 K, for PbS films on KCl substrates. The arrows mark the positions of the maximum $\hbar\omega_m$, the edges of the spectrum $\hbar\omega_e$ at the noise level, and the width $\Delta(\hbar\omega)_{1/2}$ at half intensity. These parameters depend, within certain limits, on the excitation level $W_0 = 5 \cdot 10^3 - 5 \cdot 10^5$ W/cm^2 (see also Fig. 5).

The main result of the experiments is shown in Fig. 4b, viz., the position of the spectral line ($\hbar\omega_e$, to be specific) was shifted upward in energy as the film thickness decreased by an amount on the order of half the band gap of the lead sulfide. These shifts were much larger than the shifts due to the change of W_0. For large film thickness, however, the PL lines were located 60–70 MeV lower than tha PbS band gap (E_g (80 K) = 0.308 eV) marked on the figure. This can be attributed to the influence of thermal stresses induced in the PbS by the KCl substrate on cooling to 80 K, owing to the difference between their thermal-expansion coefficients. The band gap change (ΔE_p) due to deformation of the films by the KCl substrate was determined experimentally by comparing the positions of the PL film spectra before and after separation from the substrates. The position of the PL line of a 150-nm PbS film floated off the KCl and raised on a plate agrees with E_g of lead sulfide.

Thus, that part of the PL specrum shift which is due to deformation by thermal stresses amounts to $\Delta E_p = -80$ meV.

Let us estimate the size-quantization level shift in a thin lead-sulfide film, i.e., the position of the first discrete level E_1 determined by electron motion in a well of width a. For an infinitely high barrier, in the case when the effective mass m_c^* should depend on the energy E measured from the bottom of the conduction band, the energy of the level E_1 is determined by solving the equations

$$(2m_c^*(E)E)^{1/2}a/\hbar=\pi n, \quad n=1, \tag{1}$$

$$m_c^*(E)=m_{c0}^*(1+2E/E_g), \tag{2}$$

where the $m_c^*(E)$ dependence is assumed for simplicity in

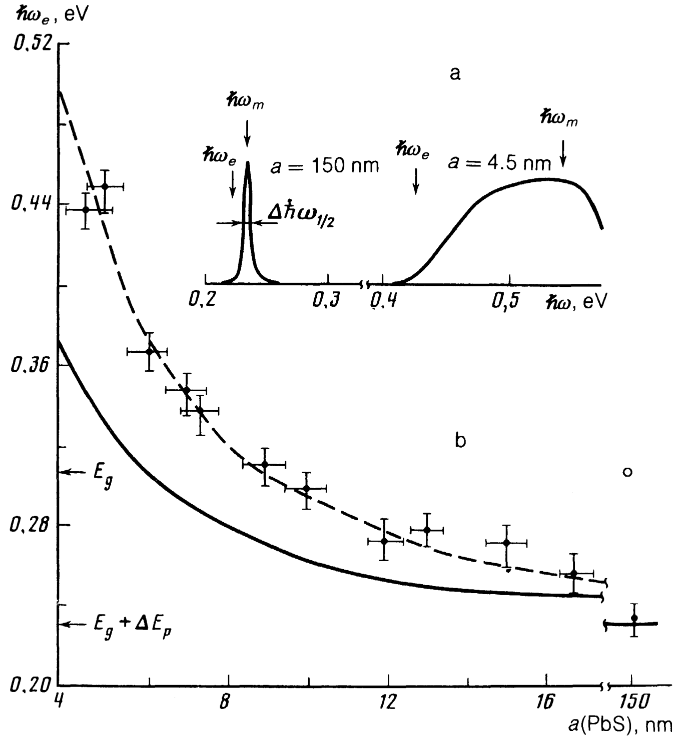

FIG. 4. PL spectra of thin epitaxial PbS films on KCl substrates for $a = 150$ and 4.5 nm (a), and dependence of the position of the spectrum edge $\hbar\omega_e$ on the film thickness at $T = 80$ K (b). Solid line—calculated from Eq. (2) with allowance for quantization only in the conduction band; dashed line—with allowance for quantization in both the valence and conduction bands; ●—PbS on KCl; O—PbS on metal.

Kane's two-band approximation. The solution of the quadratic equation with effective mass on the bottom of the PbS conduction band, averaged over three directions

$$\frac{1}{m_{c0}^{*}}=\frac{1}{3}\left(\frac{1}{m^{*}_{c0\parallel}}+\frac{2}{m^{*}_{c0\perp}}\right)=\frac{1}{0.093m_0}, \qquad (3)$$

is shown in Fig. 4b by a solid line corresponding to the quantity $E_g + \Delta E_p + E_1$. It can be seen that the $\hbar\omega_e(a)$ dependence is qualitatively described by the shift of the first size-quantization level $E_1(a)$ under the assumption that the influence of the strain remains constant ($\Delta E_p = \text{const}$).

Film-thickness inhomogeneities ($\Delta a \approx 1$ nm) can produce in E_1 a scatter on the order of 40 meV at $a = 4.5$ nm, which accords with the experimentally observed PL line broadening of a thin film (Fig. 4a).

Similar hole-energy quantization phenomena can undoubtedly take place in the valence band. Optical transitions are allowed between the levels E_1^c and E_1^v of the conduction and valence band. The calculation of $\hbar\omega_e$ in this case (for $m_c^* = m_v^*$) is also shown in Fig. 4b by a dashed line that lies closer to the experimental points. It can thus be stated that the observed PL spectrum shift due to the decrease of the PbS film thickness is due to quantum size effects.

Figure 5 shows the changes of the positions of the maximum and of the edge of the spectrum ($\hbar\omega_m$ and $\hbar\omega_e$) with change of the excitation level W_0. It should be noted that for films 150 nm thick the change, up to $W_0 = 5 \cdot 10^5$ W/cm^2, does not exceed the experimental error ~ 10 meV (the spectral gap width is comparatively large for low excitation level). For a thin film ($a = 4.5$ nm) the shift of the maximum with change of W_0 reaches 40 meV. This can be qualitatively attributed to the fact that in a thin film the density of states in the conduction band is low on the first size-quantization level, and the shifts of the Fermi level due to density changes should be much larger than in the bulk.

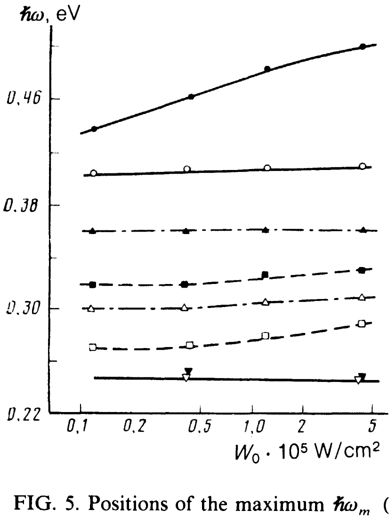

FIG. 5. Positions of the maximum $\hbar\omega_m$ (dark symbols) and edge $\hbar\omega_e$ (light) of PL spectra of PbS films of different thicknesses: a—4 nm (●, O), 9 nm (▲, △), 15 nm (■, □), 150 nm (▼, ▽) as functions of the excitation level W.

4. PHOTOLUMINESCENCE SPECTRA OF PbS-EuS SUPERLATTICES

Figure 6 shows the measured PL spectra of a number of SL of constant thickness b(EuS) = 14 nm and of thicknesses a(PbS) = 1-15 nm. These SL were grown on KCl substrates with a PbS buffer layer 20 nm thick. For each SL sample there was produced simultaneously, by the same technological process, a satellite sample without the EuS layers, but with an equal total PbS thickness. The spectra of the SL and of the satellite sample were compared and the difference effects due to the SL were separated.

Figure 6a shows the dependence of $\hbar\omega_e$ on the thickness

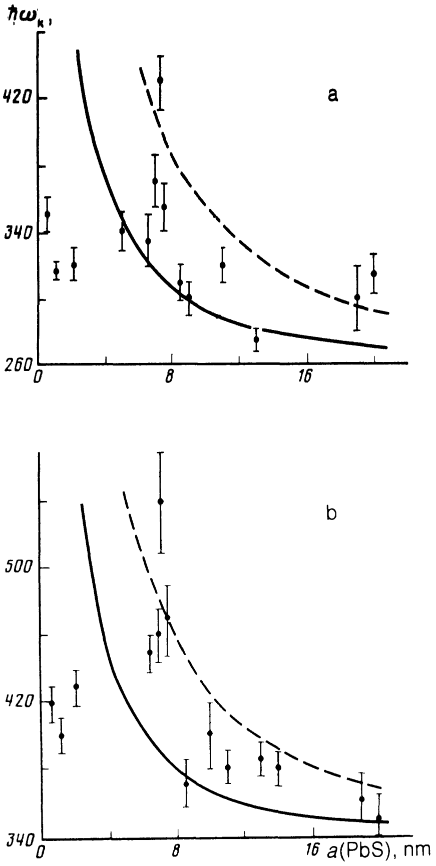

FIG. 6. Values of $\hbar\omega_e$ (SL)—$\hbar\omega_e$ (PbS) vs PbS layer thickness in SL on KCl at a thickness $n_{\rm EUS} = 14$ nm, $T = 80$ K, $W_0 = 4 \cdot 10^5$ W/cm^2 (a), and position of the PL line edge for the same SL samples floated off KCl substrates (b). Solid curve—solution of Eq. (4) for the first size-quantization level, dashed—for the second.

a. It is seen that $\hbar\omega_e$ increases with decreasing a and reaches for $a = 7$ nm a value 430 meV close to the change of $\hbar\omega_e$ in single-layer lead-sulfide samples (Fig. 4b). This quantity decreases, however, with further decrease of a. To explain the causes of the nonmonotonic dependence of $\hbar\omega_e\,(\text{SL}) - \hbar\omega_e\,(\text{PbS})$ on a, the SL films were transferred from the KCl substrate to a copper plate, and the spectrum investigation was repeated. Figure 6b shows that after the SL are separated from the substrates the form of $\hbar\omega_e\,(a)$ dependence remains unchanged. It can thus be concluded that the deformation of the films by the KCl susbtrate is not the reason why $\hbar\omega_e$ decreases at very small thicknesses a. A probable cause of this decrease may be luminescence of the PbS buffer layer; this should be verified with a sample having no such layer.

A similar effect was observed in a number of samples with variable SL period $(a + b)$, viz., when $(a + b)$ was decreased from 20 to 6 nm the value of $\hbar\omega_e$ increased to 500–400 meV, after which it decreased to 230 meV when $(a + b)$ was further decreased to 1 nm.

The lattice periods of PbS-EuS SL exhibit a small disparity ($f = 0.5\%$) that leads to the onset of pseudomorphous stresses in the layers and to a change of the band gap. A pseudomorphous increase of the films produces a planar elastically deformed state in which only normal stresses act along the layer interface $(\sigma_{11}\sigma_{22})$. Estimates show that at a disparity $f = 0.5\%$ the tensile stresses in the PbS layers should not exceed $\sigma_{11} \approx 4 \cdot 10^8$ Pa, and the increase of the PbS bandgap under the influence of these stresses is $\Delta E_g^\sigma \approx 30$ meV. Thus the pseudomorphous stresses in the PbS-EuS SL should shift the PL lines upward in energy by ≈ 30 meV, much less than the shifts observed in experiment (Fig. 6).

If the valence-band ceilings in PbS and EuS are on the same energy level, as in Fig. 1, the potential barriers on the boundaries in the conduction band are determined by the band gap difference $E_{g2} - E_{g1}$. We calculate the energy spectrum of the PbS-EuS SL in accordance with the Kronig-Penney model, following Refs. 15 and 16, assuming for simplicity that the dependence of the effective mass $m_1^*(E)$ in PbS is given by Eq. (2), and that the effective mass m_2^* in EuS is constant and spin-averaged: $m_2^* = 0.42m_0$ (Ref. 13). The equation

$$\begin{gathered}-1 \leqslant \cos[(2m_1^*(E)E)^{1/2}a/\hbar]\,\text{ch}[(2m_2^*(V-E))^{1/2}b/\hbar] \\ +0.5\{[m_2^*(V-E)/m_1^*(E)E]^{1/2} - [m_1^*(E)E/m_2^*(V-E)]^{1/2}\} \\ \times\sin[(2m_1^*(E)E)^{1/2}a/\hbar]\,\text{sh}[(2m_2^*(V-E))^{1/2}b/\hbar] \leqslant 1, \\ V = E_{g2} - E_{g1}, \qquad (4)\end{gathered}$$

was solved numerically with a computer. Figure 1 shows the size-quantization levels E_n for $a = 5.5$ nm and $b = 14$ nm. At $b \leqslant 4$ nm the levels broaden into minibands, i.e., the tunneling percolation of the electrons between the wells comes into play. At the given calculation parameters the level spacings $E_2 - E_1$ are larger than kT for $T = 80$ K, so that they should not be manifested in the luminescence. It is important that for $a \geqslant 6$ nm the calculated curve agrees with some of the experimental points if account is taken of the strain shift (Fig. 6a).

Thus, with decrease of the layer thicknesses, the luminescence-spectrum shift of the PbS-EuS SL is determined principally by the shift of the first size-quantization level.

5. DISCUSSION OF RESULTS

The observed shifts in the PL spectra reach values on the order of E_g. No such large PL line shifts were observed earlier in other systems with SL. Analysis of close systems of type PbTe-PbSnTe (Ref. 3) shows that to describe the $E(a + b)$ dependences for large shifts $\hbar\omega_e$ it is necessary to consider a six-band approximation in the entire Brillouin band with allowance for deformations and hybridization of the bands in the potential well and in the barrier. In our case such an analysis would call for allowance for the difference between the band structures of PbS and EuS: the valence band in EuS is made up of Eu f-electrons, and the minimum of the conduction band is located at point X of the Brillouin zone. In PbS, E_v is made up of the S p-electrons, and the minimum of E_c lies at the point L. These differences can lead apparently only to an increase of the effective potential barrier for the electrons.

It must be recognized that absorption of an exciting photon with $\hbar\omega_0 = 1.18$ eV can decrease noticeably in thin ($a \leqslant 4$ nm) layers, owing to the shift of the excited levels and to the decrease of the effective density of the compounds. A quantitative estimate of this effect calls for an investigation of the absorption spectra of the PbS-E superlattice. A decrease of the density of states at an energy noticeably higher than the bottom of the conduction band should lead also to a possible heating of the electron gas in thin layers.[15] This assumption can be verified by measuring the PL spectra at lower temperatures.

The calculations were compared above with experiment on the basis of the model of Fig. 1, with no sufficient justification of the assumption that the top of the valence-band is on the same level E_v as the PbS-EuS heteroboundary. Favoring the assumption that E_v in PbS is not lower than E_v in EuS is the very fact that the emission from the investigated SL is quite intense. In the opposite case, i.e., in the case of an SL of the second kind, the probability of radiative recombination would be substantially lowered by the spatial separation of the electrons and holes.

The investigated structures were grown without meeting the conditions of Ref. 17, which are optimal for a large quantum yield of the radiative recombination in lead sulfide. Preliminary experiments have shown that if the initial charge and the evaporation temperature of the PbS are made close to optimal the SL radiation intensity can be increased by two orders of magnitude.

The results, which demonstrate a substantial quantization of the carrier energy spectrum in narrow-gap SL layers and the possibility of decreasing the density of their intrinsic defects, give grounds for using similar structure in IR-emitting devices.

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Translated by J. G. Adashko