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# On the temperature dependence of the energy gap in PbSe and PbTe

M Baleva†, T Georgiev† and G Lashkarev‡

† Faculty of Physics, University of Sofia, 1126 Sofia, Bulgaria

‡ Institute for Problems of Materials Science, Academy of Science, Kiev, Ukrainian SSR, USSR

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**Abstract.** A detailed temperature dependence of the energy gap $E_0$ in PbSe and PbTe was obtained from the transmittance measurements. A non-linear change of $E_0$ in the vicinity of the Debye temperature was noticed. An attempt to find an empirical formula describing the experimental dependence $E_0(T)$ led us to the conclusion that the non-linear change can be attributed to the electron interaction with the optical phonons.

## 1. Introduction

A relatively comprehensive review of the theoretical and the experimental investigations of the energy gap $E_0$ temperature dependence in lead salts was given by Nimtz and Schlicht (1983). It is accepted that the temperature dependence of $E_0$ is linear above approximately 75 K where the temperature dependence of the expansion coefficient is linear. However, the experimental investigations of the PbSe magnetic properties imply a non-linear dependence $E_0(T)$ in the vicinity of the Debye temperature (Borodovoi *et al* 1984). Several peculiarities in the temperature behaviour of the PbSe magnetic and transport parameters have been noticed. While the behaviour of the kinetic parameters can be attributed to the change of the scattering mechanism, this is not the case with the magnetic susceptibility. The susceptibility depends on temperature because of the $E_0$ temperature dependence. The small value of $E_0$ in this narrow-gap semiconductor makes the susceptibility very sensitive to variations in $E_0$. Then it becomes important that the exact value of $E_0$ at various temperatures is known.

This work was undertaken to measure the detailed $E_0$ temperature dependences in PbSe and PbTe which are not available in the literature. The temperature coefficient, $\partial E_0/\partial T$, in PbSe is determined from the $E_0$ values at four temperatures in the range from liquid nitrogen to room temperature and that in PbTe only from two $E_0$ values (see Nimtz and Schlicht 1983).

## 2. Samples and experiment

PbSe and PbTe films, grown by laser-assisted deposition on KCl and $BaF_2$ substrates, have been investigated. A PbSe film grown by the 'hot-wall' technique was also investigated for comparison. The thicknesses of the films and their carrier concentrations and

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**Table 1.** Film parameters together with the gap temperature coefficients: $A$, the sum of the anharmonic lattice contribution and the contribution of the electron interaction with the acoustic phonons; $A_2/\theta$ the contribution of the electron interaction with the optical phonons.

| Sample | Thickness ($\mu$m) | Carrier concentration ($10^{-18}$ cm$^{-3}$) 80 K | Carrier concentration ($10^{-18}$ cm$^{-3}$) 300 K | Hall mobility (cm$^2$ V$^{-1}$ s$^{-1}$) 80 K | Hall mobility (cm$^2$ V$^{-1}$ s$^{-1}$) 300 K | $A$ (eV K$^{-1}$) | $A_2/\theta$ (eV K$^{-1}$) |
|---|---|---|---|---|---|---|---|
| PbSe | | | | | | 0.84 | −0.44 |
| B203 | 7.0 | 1.0 | 1.0 | 2500 | 600 | | |
| K191 | 3.25 | 1.0 | 1.0 | 14100 | 1030 | | |
| M43LS | 5.7 | 0.9 | 0.9 | 20000 | 950 | | |
| PbTe | | | | | | 0.96 | −0.54 |
| B228 | 3.5 | 0.06 | 0.13 | 40 | 200 | | |

mobilities are given in table 1. Our previous investigations (Baleva *et al* 1986) of the crystal structure and lattice constant of laser deposited films indicated a monocrystalline structure for the films on KCl substrates and a polycrystalline one for those on $BaF_2$ substrates. The value of the lattice constant, determined by the Bragg diffraction technique, was one and the same for both types of films with a thickness higher than 0.5 $\mu$m and very close to that of a bulk material (0.61288 nm against 0.6125 nm). Then it can be concluded that the thickness of the strained layer in the case of laser-assisted deposition is not higher than 0.5 $\mu$m. Thus the thicknesses of the films, investigated in this work, as is seen from table 1, are sufficient so that the strained-layer behaviour does not prevail.

The transmittance spectra have been taken by a double-beam UR-20 spectrometer in the energy range 0.05 to 0.5 eV at 10 K intervals in the range between 80 and 320 K. The spectral dependences of the absorption coefficient $\alpha$ have been calculated in a way described before by Baleva *et al* (1987).

The values of $E_0$ at various temperatures have been determined by fitting the experimental dependences $\alpha(\hbar\omega)$ to the calculated ones according to the appropriate relation (degenerate or non-degenerate semiconductor, Kane or Cohen model—Globuss *et al* 1981, Baleva *et al* 1987), describing the spectral dependence of the absorption coefficient in the case of direct transitions.

The values of $E_0$ for both compounds obtained in this way, are plotted against the temperature in figure 1 (points). It is seen that at temperatures well above the corresponding Debye temperature $T_\theta$ ($T_\theta$ = 140 K for PbTe and $T_\theta$ = 170 K for PbSe (Finkenrath *et al* 1979)) the dependence $E_0(T)$ is very close to a linear one. The mean-square approximation (broken lines in figure 1) of the linear portions of the curves give the following values for the temperature coefficient:

$$\frac{\partial E_0}{\partial T} = \begin{cases} 0.385 \text{ meV for PbTe} \\ 0.395 \text{ meV for PbSe.} \end{cases}$$

The deviations, $\Delta E_0$, from these linear dependences (figure 2) increase with the decrease of temperature and are of the order of 10 meV at 80 K.

## 3. Discussion

The temperature dependence of the energy gap at a constant pressure $p$ is determined by two contributions,

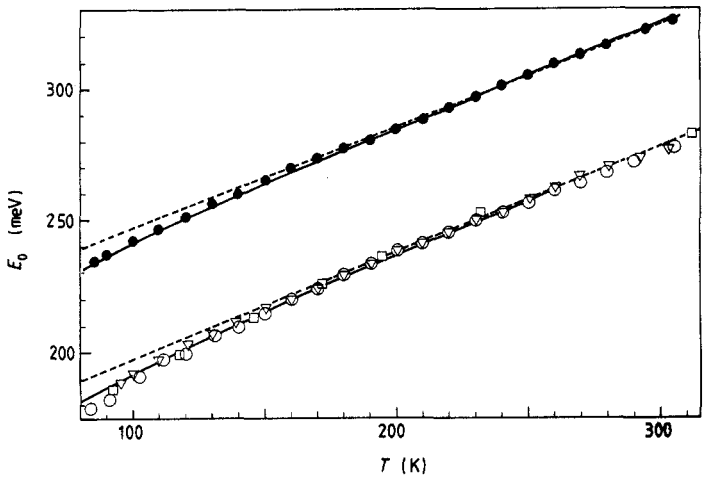


**Figure 1.** Temperature dependences of the energy gap $E_0$ for PbTe (B228, curves, full circles) and PbSe (B203, curves, open circles; K191, curves, open squares; M43LS, curves, open triangles). The full curves represent the dependences calculated according to relation (1); the broken curves represent the linear dependences at high temperature.

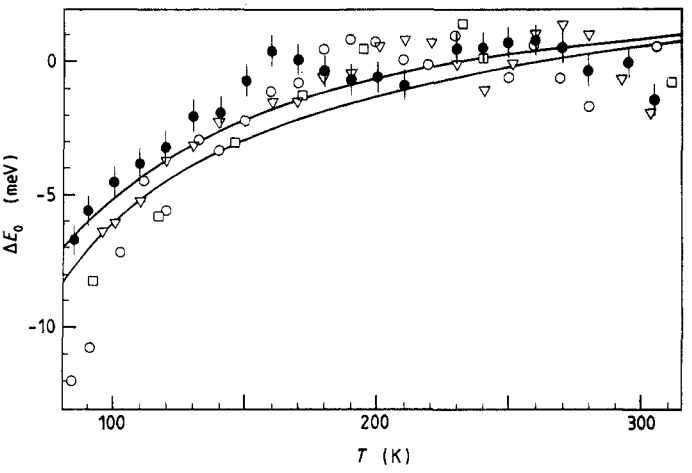


**Figure 2.** The deviations $\Delta E_0$ from the linear dependences for PbTe (B228, curves, full circles) and PbSe (B203, curves, open circles; K191, curves, open squares; M43LS, curves, open triangles). The full lines represent the dependences calculated according to relation (1).

$$(\partial E_0/\partial T)_P = (\partial E_0/\partial T)_V - 3\alpha_L\beta(\partial E_0/\partial P)_T$$

with $\alpha_L = (1/L)(\partial L/\partial T)_P$ being the linear thermal expansion coefficient and $\beta$ the bulk modulus. The term

$$(\partial E_0/\partial T)_{anh} = -3\alpha_L\beta(\partial E_0/\partial P)_T$$

is the anharmonic lattice contribution. The experimental values of the pressure coefficients $(\partial E_0/\partial P)_T$ together with the values of the linear thermal expansion coefficients and bulk modulus, obtained by various authors, are summarised by Nimtz and Schlicht (1983). From these data they have obtained

$$\left(\frac{\partial E_0}{\partial T}\right)_{\text{anh}} \cong \begin{cases} +0.24\ \text{meV K}^{-1} & \text{for PbSe} \\ +0.18\ \text{meV K}^{-1} & \text{for PbTe.} \end{cases}$$

In the case of PbSe and PbTe the dilatation term contributes about one half to the total temperature coefficient, obtained from the empirical formulae describing the linear part of the experimental dependences.

$$\left(\frac{\partial E_0}{\partial T}\right)_{P} \approx \begin{cases} +0.45\ \text{meV K}^{-1} \text{ and } 0.41\ \text{meV K}^{-1} & \text{for PbSe} \\ +0.51\ \text{meV K}^{-1} \text{ and } 0.44\ \text{meV K}^{-1} & \text{for PbTe.} \end{cases}$$

The values of $(\partial E_0/\partial T)_{\text{anh}}$ have been reproduced theoretically in several papers (Schluter *et al* 1975a, b), Martinez *et al* 1975, Tsang and Cohen 1971). The term $(\partial E_0/\partial T)_V$ describes the contribution of the electron–phonon interaction. It seems much more difficult to arrive at satisfactory quantitative calculations for the electron–phonon term. Reasonable results have been obtained in the case of PbTe (Schluter *et al* 1975a, b) by including in the electron–phonon interaction term only atomic displacements to first order, which predict the opposite sign in the temperature coefficient for PbSe. There is evidence that the addition of a term containing atomic displacements in second order might solve the problem. The interpretation of the energy shifts as a result of second-order processes, including virtual absorption and re-emission or emission and reabsorption of a phonon leads to the following expression for the shift of a conduction band state $\omega_k$ (Fan 1951)

$$\Delta\omega_k(T) = \sum_{l,\text{ph}} \frac{|M_{k,l,\text{ph}}|^2}{\omega_k - \omega_l \pm \omega_{\text{ph}}} \tag{1}$$

$M_{k,l,\text{ph}}$ is the electron–phonon interaction matrix element, with $|M_{k,l,\text{ph}}|^2$ being proportional to the phonon number. The term $\omega_k - \omega_l \pm \omega_{\text{ph}}$ corresponds to emission of a phonon. At the conduction band bottom, $\Delta\omega_k$ is negative in the case of emission and may be negative or positive in the case of absorption of a phonon. The number of states for which $\Delta\omega_k$ is negative is significantly higher. Analogously at the valence band top the $\Delta\omega_l$ have to be positive. Thus the electron–phonon interaction in general has to contribute to the energy gap narrowing. However, as was pointed out by Keffer *et al* (1970) in the lead salts, with their small band gaps, the positive interband contribution might overcompensate the negative intraband terms thus increasing the gap. The calculations of Schluter *et al* (1975a, b) for intravalley and intervalley scattering confirm this effect and also indicate that the effect is stronger in PbSe than in PbTe.

The temperature coefficient $\partial E_0/\partial T$ is positive in the narrow-gap semiconductor HgTe also, which is very unusual for a semiconductor with the zincblende structure. A number of workers tried to explain this anomalous behaviour of $\partial E_0/\partial T$, the main contributions to which are expected to result from the electron–phonon interaction. A reasonable explanation, it seems, can again be associated with the small size of the gap. Generalising Fan's approach, Guenzer and Bienenstock (1973) show that to make the sign of $\partial E_0/\partial T$ agree with the experimental result the interband contributions must be included. The interband electron–phonon interaction in the narrow-gap semiconductors leads to band mixing in addition to the Kane mixing and to an additional renormalisation of the energies of the electron bands.

Our attempt to find an empirical formula, describing the experimentally observed dependence $E_0(T)$ led us to the following conclusion. The electron interaction with the acoustic and optical phonons has to be divided and, moreover, it has to be assumed that their contributions to $\partial E_0/\partial T$ are of opposite sign. Then the gap temperature dependence, $E_0(T)$, can be written in the form

$$E_0(T) = E_0(0) + \left(\frac{\partial E_0}{\partial T}\right) T_{\text{anh}} + A_1 \left(e^{\hbar\omega_{ac}/kT} - 1\right)^{-1} - \frac{A_2}{1 - e^{-\theta/T}}$$

where $E_0(0)$ is the energy gap at 0 K, $\omega_{ac}$ is the acoustic phonon frequency, $A_1$ and $A_2$ are temperature-independent constants and $\theta$ is the Debye temperature, determined from the longitudinal optical phonon frequency $\omega_{LO}(k/\hbar)\theta$ ($k$ is the Boltzmann constant).

In the temperature range under consideration, $T > 80$ K, the thermal expansion coefficient $\alpha_T$ is linear with $T$, then $(\partial E/\partial T)_{\text{anh}}$ is a constant.

The term

$$A_1 \left(e^{\hbar\omega_{ac}/kT} - 1\right)^{-1}$$

may be written in the form $(A_1/\hbar\omega_{ac})T$ as the number of the phonons becomes proportional to $T$ when $\hbar\omega_{ac} < kT$. Then at $\hbar\omega_{ac} < kT$,

$$E_0(T) = E_0(0) + AT - A_2/(1 - e^{-\theta/T})$$

where

$$A = (\partial E_0/\partial T)_{\text{anh}} + A_1/\hbar\omega_{ac}.$$

The term $A_2(1 - e^{-\theta/T})^{-1}$, proportional to the probability for LO phonon emission, represents the contribution of the electron interaction with the LO phonons.

The relation (1) was fitted to the experimental dependences (full curves in figures 1 and 2). The adjustable parameters were $E_0(0)$, $A$ and $A_2$. The temperature-independent values of $\theta$ were: $\theta = 140$ K for PbTe and $\theta = 170$ K for PbSe (Finkenrath *et al* 1979). The best fitting (the full lines in figures 1 and 2) was obtained for the values of the adjustable parameters given in table 1. The results indicate that the increase of the energy gap is much stronger in the temperature range below the Debye temperature, where the term describing the interaction with the optical phonons is negligible. A detailed experimental $E_0(T)$ dependence in the low-temperature range is available only for PbS (Kurbatov *et al* 1970). It is obvious from that experiment that $E_0$ increases about two times stronger below the Debye temperature than above it.

The values of the other adjustable parameter $E_0(0)$ are not correct as in relation (1) the non-linear change of the terms $(\partial E_0/\partial T)_{\text{anh}}$ and

$$A_1 \left(e^{\hbar\omega_{ac}/kT} - 1\right)^{-1}$$

at lower temperature is ignored.

Taking into account the values of the terms $(\partial E_0/\partial T)_{\text{anh}}$ calculated by Nimtz and Schlicht (1983), we obtained for the contributions to the temperature coefficients, $\partial E_0/\partial T$, at high temperatures: (i) the contribution of the electron interaction with the acoustic phonons

$$\left(\frac{\partial E_0}{\partial T}\right)_{ac} = \frac{A_1}{\hbar\omega_{ac}} = \begin{cases} 0.60 \text{ meV K}^{-1} & \text{for PbSe} \\ 0.78 \text{ meV K}^{-1} & \text{for PbTe} \end{cases}$$

(ii) the contribution of the electron interaction with the LO phonons

$$\left(\frac{\partial E_0}{\partial T}\right)_0 = \frac{A_2}{\theta} = \begin{cases} -0.44 \text{ meV K}^{-1} & \text{for PbSe} \\ -0.54 \text{ meV K}^{-1} & \text{for PbTe.} \end{cases}$$

The total contribution of the electron–phonon interaction is

$$\left(\frac{\partial E_0}{\partial T}\right)_T \approx \begin{cases} 0.16 \text{ meV K}^{-1} & \text{for PbSe} \\ 0.24 \text{ meV K}^{-1} & \text{for PbTe.} \end{cases}$$

These values are really about one half of the total experimental temperature coefficients as they are usually accepted in the case of lead salts.

## 4. Conclusions

We do not claim that the formula (1) describes the temperature dependence of the energy gap well as we have ignored not only the non-linear change of the terms $(\partial E_0/\partial T)_{anh}$ and

$$A_1 (e^{\hbar\omega_{ac}/kT} - 1)^{-1}$$

but also the electron interaction with the TO phonons and the phonon frequency temperature dependences. The advantage of the formula consists in demonstrating the fact that a satisfactory explanation of the experimental temperature dependence $E_0(T)$ can be obtained when the contribution of the electron–phonon interaction to the temperature coefficient $\partial E_0/\partial T$ is divided in two parts: (i) an electron interaction with the lower energy acoustic phonons which has the main and positive contribution to $\partial E_0/\partial T$ and (ii) an electron interaction with the higher energy optical phonons which has a negative contribution to $\partial E_0/\partial T$.

The non-linear temperature change of the energy gap $E_0$ in the vicinity of the Debye temperature in PbTe and PbSe can be attributed to the electron interaction with the optical phonons.

## References

Baleva M I, Maksimov M H, Metev S M and Sendova M S 1986 *J. Mater. Sci. Lett.* **5** 533–6
Baleva M I, Maksimov M H and Sendova M S 1987 *J. Phys. C: Solid State Phys.* **20** 941–51
Borodovoi A V, Lashkarev G V, Radchenko M V and Tovstjuk K D 1984 *Sov. Phys.–Solid State* **18** 4 610–4
Fan H Y 1951 *Phys. Rev.* **145** 675
Finkenrath H, Franz G and Uhle N 1979 *Phys. Status Solidi* b **95** 179
Globuss T R, Gelmont B L, Geuman K I, Kondrashov V E and Matveenko A V 1981 *Sov. Phys.–JETP* **80** 1926
Guenzer C S and Bienenstock A 1973 *Phys. Rev.* B **3** 4655
Keffer Ch, Hayes T M and Bienenstock A 1970 *Phys. Rev.* B **2** 1966
Kurbatov L N, Britov A D and Mochalkin N N 1970 *Sov. Phys.–Semicond.* **4** 95
Martinez G, Schluter M and Cohen M L 1979 *Phys. Rev.* B **11** 651
Nimtz G and Schlicht B 1983 *Narrow-Gap Semiconductors* (Berlin: Springer) p 35
Schluter M, Martinez G and Cohen M L 1975a *Phys. Rev.* B **11** 3808
—— 1975b *Phys. Rev.* B **12** 650
Tsang Y W and Cohen M L 1971 *Phys. Rev.* B **3** 1254