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Electron–Optical-Polaron Coupling Constant in PbS, PbSe, and PbTe

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Values of the electron–optical-polaron coupling constant α have been calculated, in the weak-coupling approximation, for PbS, PbSe, and PbTe at 77 °K. Experimental values of the high-frequency dielectric constant and of the longitudinal-optical-phonon frequency were used, as were literature values of the static dielectric constant calculated from the Lyddane-Sachs-Teller relation. The values of α obtained are for PbS, $\alpha = 0.33$; for PbSe, $\alpha = 0.23$; for PbTe, $\alpha = 0.15$. These values of α show the same decrease with increasing anion mass as do the values reported for several III-V semiconductors. In addition, their magnitudes are in accord with the strongly ionic character suggested by the rocksalt crystal structures of the PbS group. Since $\alpha \ll 1$, measured values of the electron effective mass are within a few percent of the bare-electron effective mass.

In the course of an investigation[1] of the application of the f-sum rule to the band edges of PbS, PbSe, and PbTe, an examination of the literature values of the carrier effective masses in these semiconductors was made. The aim of this work was to investigate the magnitude of the effect of the crystal ionicity on the measured carrier effective masses. For this reason, and since no values of polaron coupling constants for PbSe and PbTe were available in the literature, a calculation of the electron–optical-polaron coupling constants α and effective masses m^*_{pol} was made for PbS, PbSe, and PbTe. Recent data on the electrical and optical properties of these semiconductors were used in the calculation.

The interaction of conduction electrons with longitudinal optical phonons was considered. Assuming weak coupling and the applicability of perturbation theory, the polaron coupling constant α is given by[2]

$$\alpha = (2e^2/4\hbar\omega_{\text{LO}})(2m^*\hbar\omega_{\text{LO}}/\hbar^2)^{1/2}(\epsilon_\infty^{-1} - \epsilon_0^{-1}) \; . \quad (1)$$

In Eq. (1), e is the electronic charge, $\hbar\omega_{\text{LO}}$ is the energy of the longitudinal optical phonon, m^* is the electron effective mass, ϵ_∞ is the dielectric constant at optical frequencies, and ϵ_0 is the static dielectric constant.

Recently reported values of these quantities for PbS, PbSe, and PbTe were used to calculate values of the coupling constant α. The data used are shown in Table I. For simplicity, an average electron effective mass $m^* = 3m_l m_t/(2m_l + m_t)$ was calculated from values[3] of the longitudinal and transverse masses m_l and m_t at 4.2 °K. The values of $\hbar\omega_{\text{LO}}$ ($k = 0$) at 4.2 °K were determined from tunneling data.[4] Experimental values[5] of ϵ_∞ at 77 °K and calculated values[6] of ϵ_0 appropriate for 77 °K were used. Since the dielectric constant is expected to vary more strongly with temperature than do the values of m^* and of $\hbar\omega_{\text{LO}}$, the calculated values of α are reported for 77 °K.

Equation (1) was used to calculate values of the coupling constant α from the data in Table I. The results, for 77 °K, are

$$\text{PbS: } \alpha = 0.33 \; ; \quad \text{PbSe: } \alpha = 0.23 \; ;$$

$$\text{PbTe: } \alpha = 0.15 \; .$$

An earlier report[7] gave a value of 0.16 for the quantity $\alpha(m/m^*)^{1/2}$ for PbS. The present calculation gives a value $\alpha(m/m^*)^{1/2} = 1.12$ for PbS. (It is believed that the earlier value of 0.16 is incorrect due to the use of an inaccurate value of $\epsilon_0 = 17.9$.) The fact that the calculated values of α are considerably less than unity indicates that the customary perturbation theoretic approach is applicable to the PbS group of semiconductors.

Phillips's recent theoretical study[8] of the ionicity of the bonding in crystals does not list explicit values of the ionicity f_i of the bonds in PbS, PbSe, and PbTe. However, his results imply that $f_i \geqslant 0.785$ for all the members of the PbS group since they all crystallize in the rocksalt structure. The values of α calculated in this paper for the PbS group are in accord with a strongly ionic (large f_i) character for these crystals. To show this a comparison may be made with the reported[8,9] values of α and of f_i for InSb, InAs, InP, GaSb, GaAs, and GaP. For these III-V semiconductors, the largest value of α is 0.1 (for GaP), and the largest calculated value of f_i is 0.421 (for InP). The values of α for the PbS group are all greater than 0.1 and thus correlate with their higher values of f_i. Their greater ionic char-

TABLE I. Experimental data used to calculate values of α for PbS, PbSe, and PbTe.

Datum	T(°K)	PbS	PbSe	PbTe	Ref.
m^*/m	4.2	8.7×10^{-2}	4.7×10^{-2}	3.4×10^{-2}	3
$\hbar\omega_{\text{LO}}$ (erg)	4.2	4.21×10^{-14}	2.64×10^{-11}	2.18×10^{-14}	4
ϵ_∞	77	18.4	25.2	36.9	5
ϵ_0	77	190	280	450	6

acter presumably is reflected in a greater ionic polarizability and hence a larger value of $(\epsilon_0 - \epsilon_\infty)$, to which, from Eq. (1), α is directly proportional. Burstein *et al.*[6] have suggested that the large values of ϵ_0 for the PbS group are due to low values of the transverse-optical-phonon frequency ω_{TO}, which, in turn, are due to a phonon frequency shift caused by the atomic dipole Lorentz field. We may also compare the values of α and of f_i for the PbS group with the values for ZnO[7] ($\alpha = 0.85$, $f_i = 0.616$) and for ZnS[7,10] ($\alpha = 0.81$, $f_i = 0.623$). The fact that the coupling constants for the PbS group are smaller than those for ZnO and ZnS, in spite of the larger calculated ionicities of the former, may be explained by the larger effective masses of electrons in the zinc-compound semiconductors. Thus it appears that the magnitudes of the coupling constants for the PbS group are in accord with the strongly ionic character suggested by high values of f_i.

In view of the well-known anomalies in the band structures of these semiconductors, it is also of interest to note that there appears to be no unusual trend in the progression of the values of α from PbS to PbSe to PbTe. The value of the coupling constant decreases with increasing anion mass in a manner similar to that reported for several III-V semiconductors.[9]

The following relation for the polaron effective mass

$$m^*_{\text{pol}} \cong m^*[1 + \tfrac{1}{6}\alpha] , \qquad (2)$$

is valid for weak coupling.[11] In Eq. (2), m^*_{pol} is the electron-polaron effective mass, m* is the bare-electron effective mass, and α is the coupling constant. Using the calculated values of α, it was found that, for PbS, $m^*_{\text{pol}} \cong 1.05m^*$; for PbSe, $m^*_{\text{pol}} \cong 1.04m^*$; for PbTe, $m^*_{\text{pol}} \cong 1.03m^*$. Electron-polaron effective masses in the lead salts are thus within a few percent of the bare-electron effective masses, and measured values of electron effective masses are a good approximation to bare-electron effective masses.

In summary, values of the electron-polaron coupling constant $\alpha \ll 1$ have been calculated, in the weak-coupling limit, for the PbS group of semiconductors. The values of α show no anomalous trend with anion mass and are in accord with the strongly ionic character implied by their rocksalt crystal structures.

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[2] See, for example, C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1963), Chap. 7, Eq. (51).

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[9] F. C. Brown, in Ref. 7, p. 339, Table II.

[10] This value of α was calculated by the author from the value of $\alpha(m/m^*)^{1/2} = 1.3$ for ZnS given in Ref. 7, using the value of $m^*/m = 0.39$ calculated by M. Cardona, J. Phys. Chem. Solids 24, 1543 (1963).

[11] See, for example, Ref. 2, Eq. (58).