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PARITY ASSIGNMENTS AT L IN THE LEAD SALT SEMICONDUCTORS

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ABSTRACT

It is concluded that the proposals of Glosser et al. (Phys. Rev. Lett. 33, 1027 (1974)) on parity assignments in PbTe are supported by consideration of the momentum matrix elements for the transitions in question. However, it is clear that further experimental studies, particularly of PbSe and PbS, are necessary before the present parity assignments at L in the lead salt semiconductors can be called into question.

In a recent letter,[1] Glosser et al. have indicated that the accepted parity assignments[2] for the bands at L are incorrect for PbTe. The purpose of this comment is to present additional evidence on this point, but also to suggest that further experimental work is necessary before the present parity assignments can be concluded to be incorrect.

The currently accepted parity assignments at L (given by Martinez et al.[2]) are shown in Table I, as is the scheme proposed by Glosser et al. The parity assignments for PbTe labeled (C) in Table I are those implicitly proposed by Glosser and are a set of assignments in which the parities of the band edges (L(5), L(7), L(8)) and of (L(3), L(4), L(6)) are the same. The scheme labeled (G) in Table I is the <u>only</u> one consistent with the parity assignments suggested by Glosser, and <u>also</u> with the accepted parities[3] (i.e., $L(6) = L_6^-$, $L(5) = L_6^+$) for the conduction

and valence band edges at L in PbS, PbSe and PbTe.

The evidence put forth by Glosser[1] is basically the non-observation of a critical point transition at L under circumstances (i.e., the Fermi level out of the band) under which one would expect to observe only critical point transitions. This null result is interpreted as meaning that the transition is forbidden because the initial and final state at L have the same parity.

It appears to the author that this conclusion is based on equating the Laporte selection rule[4] with its converse. This rule states that, under certain circumstances, matrix elements of the electric dipole moment operator vanish unless the initial and final states have opposite parities. It seems unjustified to use the converse of this selection rule to conclude that the non-observation on a transition means, first, that it is forbidden, and that, second, it is forbidden because of the parity selection rule above. It is one of the limitations of Glosser et al.'s letter that they do not consider any other possible reasons that the transition in question might not be observed. One of the purposes of this comment is to consider the possibility that the electric dipole matrix elements for the transitions in question are small, so that the transitions in question are not observed because they are simply weak, and not because they are forbidden at L.

Momentum matrix elements between a number of pairs of states at L and at Σ have been calculated[5] by M. Schlüter using the Martinez et al.[2] band structure. Some of these matrix elements are shown in Table II for several transitions which are parity-allowed at L in the scheme of assignments (A) in Table I, and are parity-forbidden at L in the scheme (G).

The energy separations $\Delta E \equiv (E_k - E_n)$ are those calculated[5] in the Martinez et al.[2] band structure. Table II shows that the values of $|M|^2$ for these transitions are all within a factor of two of $|M|^2 \cong 1 \times 10^{-39}$ g - erg, the value estimated[6] to correspond to the $\Gamma_8 \rightarrow \Gamma_7$ transition in InSb[7] at 3.4 eV. The observed value of $(\Delta R/R)$ in electro-reflectance for this $\Gamma_8 \rightarrow \Gamma_7$ transition is about 10^{-5}. The conclusion is that, given these calculated matrix elements at L and at Σ in PbTe, these transitions (if allowed) are strong enough to be detected with Glosser's quoted sensitivity of $(\Delta R/R) \approx 5 \times 10^{-7}$.

On the other hand, if these transitions <u>are</u> forbidden, then one may estimate[4] the relative intensities of allowed and forbidden electric dipole transitions at L for PbTe for the photon energy range in question. The forbidden transition would have a probability per unit time that is decreased[4] by a factor $(ka)^2$ relative to that of the allowed transition. Here k is the magnitude of the wave vector of the incident radiation, and a is the spatial extent of the relevant wave function, in this case that of a valence band electron. Taking $\hbar\omega = 1.5$ eV as a typical value, $k = 0.76 \times 10^5$ cm^{-1}, and taking a approximately equal to a lattice constant (6.5×10^{-8} cm) gives $(ka)^2 = 2.4 \times 10^{-5}$. One would thus expect the intensity of a forbidden electric dipole transition to be about 10^{-5} of the intensity of an allowed transition. Taking $(\Delta R/R) \approx 10^{-4}$ as typical[7] of an allowed transition, one would expect $(\Delta R/R)$ to be less than about 10^{-8} for a forbidden transition.

The conclusion of these matrix element considerations is that, if the transitions at L shown in Table I are allowed and have the quoted values of momentum matrix elements, then Glosser's quoted sensitivity is

sufficient to have observed them. If the transitions are forbidden, their intensities would be too small to be observed with that sensitivity. These results are thus consistent with Glosser's proposal that certain critical point transitions at L are forbidden.

However, it should also be pointed out that Glosser's proposed parity assignments in Table I have implications for PbSe and PbS. Since the only difference between bands L(3) through L(8) in PbTe and PbSe appears[2] to be the relative ordering of L(7) and L(8), then, if Glosser's proposed parity assignments are correct for PbTe, they are correct for PbSe and, by inference, very probably for PbS. It, therefore, is important to suggest that equivalent electro-reflectance band population experiments be performed on PbSe and PbS. This appears particularly important in view of the well known[8] peculiarities of the properties of the lead salt semiconductors. Glosser's proposal that the question of the parity assignments at L be reopened would be much more appropriate if the absence of expected transitions at L is observed for <u>all three</u> lead salt semiconductors.

In this vein, the author suggests also that optical experiments, by methods <u>other</u> than electro-reflectance, be done in the photon energy range between about 1.0 and 2.0 eV. It seems particularly important to obtain additional experimental data in this region containing energies at which several critical point transitions at L (see Table II) are calculated to take place. Even though the identification and assignment of such transitions is never completely unequivocal, the existence of additional experimental data can only help resolve these questions.

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REFERENCES

1. R. Glosser, J. Kinoshita and B. Rennex, Phys. Rev. Letters 33, 1027 (1974).
2. G. Martinez, M. Schlüter and M. L. Cohen, Phys. Rev. B 11, 651 (1975), Fig. 3.
3. I am assuming that Glosser et al. are not suggesting that the accepted parity assignments $L(6) = L_6^-$ and $L(5) = L_6^+$ be inverted for PbTe, PbSe and PbS. While there is no single experiment which unequivocally establishes these parity assignments, there is a great deal of experimental and theoretical evidence, which, while model-dependent, does support the accepted parity assignments for L(5) and L(6) in the lead salt semiconductors.
4. See, for example, L. I. Schiff, Quantum Mechanics (McGraw-Hill, 1968), 3rd ed., pp. 405-406.
5. M. Schlüter (private communication). These values are slightly (perhaps 0.01 of the Brillouin Zone diameter) away from the L point.
6. The author would like to thank the second referee for providing this estimate.

7. R. Glosser et al., Phys. Rev. B1, 1609 (1969), Fig. 3.

8. See, for example, R. Dalven, Solid State Physics, F. Seitz, D. Turnbull and H. Ehrenreich, eds. (Academic Press, 1973), Vol. 28, p. 179 ff.

Table I. Parity assignments at L for PbTe.

Band	PbTe (A)[a]	PbTe (G)[b]
L(8)	L_{45}^{-}	L_{45}^{+}
L(7)	L_{6}^{-}	L_{6}^{+}
L(6) = CB	L_{6}^{-}	L_{6}^{-}
L(5) = VB	L_{6}^{+}	L_{6}^{+}
L(4)	L_{45}^{+}	L_{45}^{-}
L(3)	L_{6}^{+}	L_{6}^{-}

[a]Ref. 2 (A = "accepted").
[b]Ref. 1 (G = Glosser et al.).
VB = highest valence band
CB = lowest conduction band

Table II. Momentum matrix elements and band separations ΔE in PbTe.[a]

Transition	$\lvert M\rvert^2 \equiv \lvert\langle n\lvert \underline{p}\rvert k\rangle\rvert^2$ (g-erg)	$\Delta E \equiv (E_k - E_n)$ (eV)
L(3 → 6)	0.53×10^{-39}	1.83
L(4 → 6)	1.84×10^{-39}	1.38
L(5 → 7)	0.49×10^{-39}	1.81
L(5 → 8)	2.16×10^{-39}	1.89
Σ(5 → 6)	0.91×10^{-39}	1.22

[a]Ref. 5.

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