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Possible Inverted Band Structure in PbPo

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Based on empirical evidence, it is suggested that the energy band structure in PbPo may be inverted from that in PbS, PbSe, and PbTe. This inversion would result in PbPo having an L_6^+ conduction-band edge and an L_6^- valence-band edge, implying a negative value of the energy gap $E_G = [E(L_6^-) - E(L_6^+)]$, and a *negative* value of dE_G/dT. We propose an experiment to test this hypothesis.

The band structure of PbS, PbSe, and PbTe is currently believed to be inverted[1] from that of SnTe. By this is meant that in these lead compounds, the conduction-band edge is an L_6^- state and the valence-band edge is an L_6^+ state; in SnTe the inverse is the case. The purpose of this Letter is to suggest, based on empirical evidence, that PbPo, the fourth member of the series, may have a band structure inverted from those of PbS, PbSe, and PbTe. This possibility is amenable to a direct experimental test by relatively simple means.

A knowledge of the energy gap E_G of PbPo would be useful in the study of the well-known anomaly[2] $[E_G(\mathrm{PbTe}) > E_G(\mathrm{PbSe})]$ in the series of the energy gap values of PbS, PbSe, and PbTe. However, the only experimental data[3] available for PbPo are that it has the face-centered cubic crystal structure with lattice constant $a_0 = 6.590$ Å at room temperature. The fact that PbPo has the same rock-salt crystal structure as do PbS, PbSe, and PbTe suggests that PbPo has the same general band structure (a semiconductor with a direct energy gap at the L point) as do the other three lead salts. To obtain an estimate of the energy gap of PbPo, the well-known empirical relation[4] between energy gap E_G and lattice constant a_0 was considered. This relation, which states that E_G is directly proportional to $1/a_0^2$ for a series of related semiconductors, was known[4] to hold reasonably well for the group IV elemental semiconductors, diamond, Ge, Si, and α-Sn.

The validity of this relation has been investigated for a number of semiconductors with the rock-salt structure. Values of energy gap were plotted as a function of $1/a_0^2$ for (1) BaS, BaSe, BaTe,[5,6] (2) CaS, CaSe, CaTe,[5,6] (3) SrS, SrSe, SrTe,[5,6] (4) solid solutions of SnSe in PbSe,[7,8] (5) solid solutions of SnTe in PbTe.[9,10] The results were that, within the uncertainty of the experimental data, E_G was a linear function of $1/a_0^2$ for each series of semiconductors. A representative result is given in Fig. 1, which shows a plot[11] of E_G as a function of $1/a_0^2$ for several solid solutions of SnSe in PbSe. It should be noted that the data cover both positive and negative values of $E_G = E(L_6^-) - E(L_6^+)$. Since the empirical relation $E_G \propto 1/a_0^2$ holds for a large number of semiconductors with the NaCl fcc structure, it appeared reasonable to use this relation to calculate a value of the energy gap of lead polonide.

Using values of the energy gap[12] at 77 and 300 K, and lattice constants a_0 at ~300 K,[13] E_G was plotted as a function of $1/a_0^2$ for PbS, PbSe, and PbTe, as shown in Fig. 2. It is seen that the PbS-PbSe line has been extrapolated; the point for PbTe has not been used. The justification for this procedure is as follows. In proposing[2] that PbTe is the irregular member of this series, it was pointed out that the outer s-electron energies of the S, Se, and Po atoms are a linear function of their atomic numbers Z, whereas the Te 5s electron energy does *not* lie on the S-Se-Po

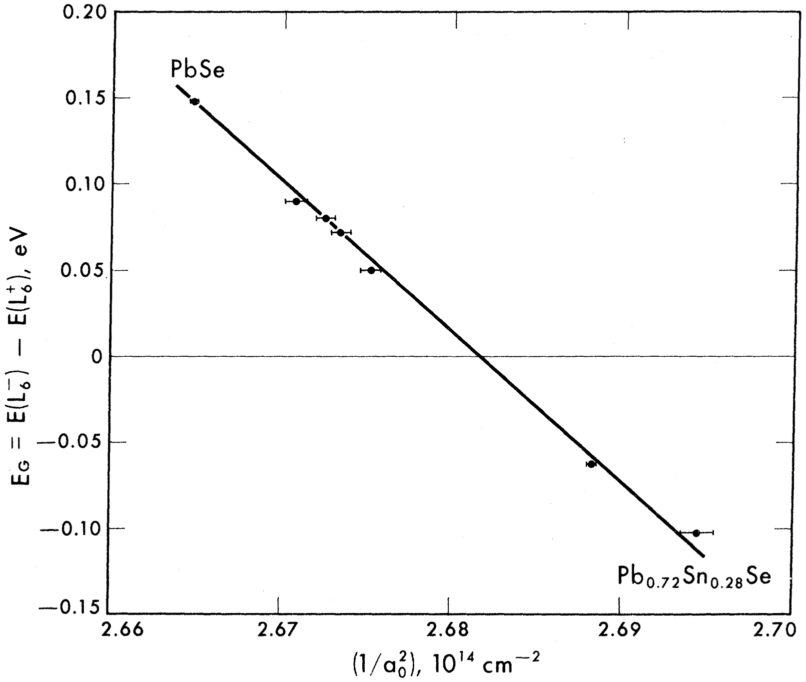

FIG. 1. Energy gap $E_G = E(L_6^-) - E(L_6^+)$ at 12 K as a function of (lattice constant)$^{-2}$ at 300 K for several semiconducting solid solutions of SnSe in PbSe.

line. Based on this regularity of the S-Se-Po series, it is reasonable it assume (given also the common crystal structure) that PbS, PbSe, and PbPo form a regular sequence of semiconductors with related properties. Specifically, it is assumed that (1) E_G for PbPo is smaller than E_G for PbSe; (2) E_G for PbPo may be determined by extrapolation of the PbS-PbSe line on the plot of E_G as a function of $1/a_0^2$. It is seen that the lines for both 77 and 300 K, when extrapolated, intersect the value of $1/a_0^2$ for PbPo at *negative* values of E_G. This result suggests the conclusion that the energy gap of lead polonide is negative in that the conduction and valence bands of PbPo are inverted from those of PbS, PbSe, and PbTe. In PbPo the conduction-band edge would then be an L_6^+ state and the valence-band edge would be an L_6^- state. Since dE_G/dT is positive for PbS, PbSe, and PbTe, it is of special interest that band inversion would imply a *negative* value of dE_G/dT for PbPo between 77 and 300 K. This effect has been observed in semiconductors which are solid solutions of SnSe in PbSe.[7,14]

The prediction of a negative value of dE_G/dT for PbPo provides a direct experimental test of the proposal of band inversion by a determination of the sign of dE_G/dT. While the radioactivity of the polonium presents possible technical difficulties, measurements of diffuse reflection[15] from powdered samples as a function of photon energy offers a method of measuring E_G and determining the sign of dE_G/dT. From Fig. 1, the calculated value of $E_G \cong 0.1$ eV at 77 K. The sharp increase in diffuse reflectivity, which correlates well with the fundamental absorption edge, should

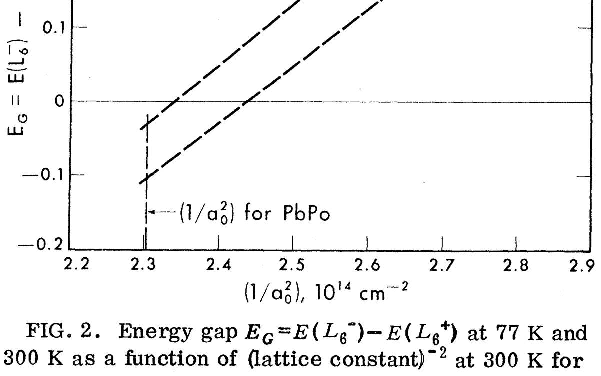

FIG. 2. Energy gap $E_G = E(L_6^-) - E(L_6^+)$ at 77 K and 300 K as a function of (lattice constant)$^{-2}$ at 300 K for PbS, PbSe, PbTe, and PbPo.

occur near 12 μm, a fairly convenient region of the spectrum. Measurement of the diffuse reflection spectrum of PbPo at 77 K should yield E_G. Heating the sample to 300 K, and observing whether the absorption edge shifts to longer or shorter wavelengths, would then determine the sign of dE_G/dT. It would probably be preferable, of course, to measure values of E_G at 77 and 300 K (say, by optical absorption measurements on thin films), but the experiment suggested appears to be the simplest that will conclusively test the possibility of band inversion. Since the extrapolation made in Fig. 2 explicitly assumes[2] that PbTe is the irregular member of the series, measurements of E_G and of the sign of dE_G/dT would also provide further information on the correctness of this assumption.

In summary, application of a well-founded empirical relation to the semiconductor sequence PbS-PbSe-PbPo has resulted in the calculation of a negative value of E_G for PbPo. The existence of band inversion (which, if verified, would be the first instance in a nonalloy series of semiconductors) may be tested experimentally by a measurement of the sign of dE_G/dT for PbPo. It is hoped that this proposal will stimulate interest in both experimental and theoretical studies of lead polonide.

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