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Comments on the Probable Electronic Structure of the Group II Polonides

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ABSTRACT

Based on empirical evidence, it is concluded that the polonides of calcium, strontium, and barium are ionic semiconductors with band gaps of 4.1 eV, 3.5 eV, and 3.3 eV, respectively. The properties of zinc polonide and calcium polonide are probably similar to those of the corresponding chalcogenides with the same zinc-blende structure. However, the crystal structure of HgPo is that of NaCl, suggesting that its band structure differs from that of semi-metallic HgTe with the zinc-blende crystal structure.

Of the intermetallic compounds with the formula $A^{II}B^{VI}$, the Group IIB (zinc, cadmium, and mercury) chalcogenides (sulfides, selenides, and tellurides) have been extensively studied, while the corresponding Group IIA (calcium, strontium, and barium) compounds have been less thoroughly investigated. However, because of the experimental difficulties involved, the Group II polonides have been the subject of only one experimental study, and, to the author's knowledge, no theoretical work at all. The object of this note is a discussion of the data presently available, and its use to obtain some qualitative conclusions concerning the electronic structure of the Group II polonides. It is also hoped that this work will stimulate further study of these potentially interesting intermetallic compounds.

The crystal structures and lattice parameters of several Group II polonides were measured at room temperature by Vier et al[1]; this is the only experimental study published to date on these materials. The compounds CaPo, SrPo, and BaPo were all found to have the NaCl crystal structure, and their lattice constants a_o at room temperature are 6.514 Å, 6.796 Å, and 7.119 Å, respectively. It is known that the Group IIA sulfides, selenides, and

tellurides all have the NaCl crystal structure[2] and that all are semiconductors with large (> 3 eV) energy gaps[3] at 80°K. It is also known[4] that the values of the energy gap E_o and lattice constant a_o for the calcium, strontium, and barium chalcogenides satisfy the empirical relation

$$E_o \ \alpha \ (1/a_o^2) \ . \qquad (1)$$

Given these facts, equation (1) may be used to calculate values of the energy gap for CaPo, SrPo, and BaPo, assuming that, since the Group IIA polonides have the same crystal structure as do the corresponding chalcogenides, it is likely that all have similar band strucures and are semiconductors. The calculated values[5] of E_o at 80°K are as follows: for CaPo, E_o = 4.1 eV; for SrPo, E_o = 3.5 eV; for BaPo, E_o = 3.3 eV. These are the first energy gap values reported for the Group IIA polonide semiconductors. Band structure calculations on these semiconductors would be most interesting, particularly with regard to spin-orbit effects. Further, we may conclude, from their NaCl crystal structure, in the context of Phillips' treatment[6] of ionicity, that these crystals are all highly ionic in nature, with ionicities f_i larger than the critical value f_c=0.785.

The crystal structures of the Group IIB polonides (ZnPo, CdPo, HgPo) were also studied by Vier et al[1]. It was found that ZnPo and CdPo have the zinc-blende (ZB) structure, with lattice constants of 6.309 Å and 6.665 Å, respectively. The same ZB structure is exhibited by the zinc and cadmium chalcogenides[7], so the band structures of the polonides would be expected to be similar, but with larger spin-orbit effects present.

However, it is more interesting that HgPo has the face-centered cubic NaCl structure with a lattice constant of 6.250 Å at room temperature. The fact that HgPo has this structure implies, from the point of view of Phillips' theory, it is more ionic in its bonding than is HgTe, which has the zinc-blende structure. Further, the change in crystal structure on progressing from HgTe (a semimetal) to HgPo suggests that the band structure of HgPo is probably different from that

of HgTe. In particular, it would be interesting to determine (experimentally or theoretically) whether HgPo is a semimetal (as one might expect if HgTe and HgPo had the same crystal structure) or is a semiconductor.

In summary, it is suggested, based on empirical evidence, that the polonides of calcium, strontium, and barium are semiconductors and that their bonding is strongly ionic in nature. The polonides of calcium and zinc are very likely similar in their electronic structure to the corresponding chalcogenides with the zinc-blende structure. However, HgPo is probably qualitatively different in its band structure from HgTe because the former has the NaCl crystal structure.

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2. R.W.G. Wyckoff, "Crystal Structures" (Wiley, New York, 1963), Second Edition, Volume 1.
3. R.H. Bube, "Photoconductivity of Solids" (Wiley, New York, 1960), p. 233.
4. R. Dalven, Phys. Rev. B, 4 (to be published 15 December 1973).
5. Since the values of the energy gaps reported (Reference 3) for the Group IIA sulfides, selenides, and tellurides are somewhat uncertain due to exciton effects, the calculated values of E_o for the polonides are equally uncertain. See R. Dalven, Phys. Rev. Letters 28, 91 (1972), Footnote 5, for details.
6. J.C. Phillips, Rev. Mod. Phys. 42, 317 (1970).
7. The hexagonal crystal structure is sometimes the more common and easily prepared form, rather than the zinc blende structure.

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