New Semiconductors with New Combinations of Properties

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Tetrahedral semiconductors have so occupied the R&D scene that most workers scarcely realise that non-tetrahedral semiconductors even exist, let alone that they are extremely numerous and can show interesting and unusual combinations of properties. This paper attempts to indicate some of the range of materials and properties that are on offer with the explicit aim of encouraging academic scientists to work on them; industry is not likely to investigate such unfamiliar territory - yet;

Present research on semiconductors, both experimental and theoretical, is largely blinkered by "tetrahedrality", since it is tetrahedral semiconductors: Si, Ge, SiC, and the III-V and II-VI compounds, that have played an entirely dominant role in science and technology. In fact many other structure types can give rise to semiconductivity, which is not a rare phenomenon found with just a few rather special materials but a relatively common property of solids. However, apart from a few layer lattices (e.g. MoS_2) and the PbS family, these have scarcely received any study at all. One guide to the great variety of semiconductors that exists can be obtained from extremely early research on materials showing good point contact rectification, almost all of them minerals[1][2]. Table I lists a number of these found by Wherry[2] to show good rectification, which property, as is now known, is associated with the materials in question being semiconductors. These compounds all obey normal chemical valence relationships (note that Pb is divalent and Bi and As tervalent), and many of them do

not have tetrahedral bonding.

Chemical bonding criteria can in fact provide some guide to the actual semiconducting properties[3]. Thus for PbS they indicate that a band derived from the very stable $6s^2$ state of Pb will lie at the top of the valence band (see Fig. 1), giving rise, as is typical for all
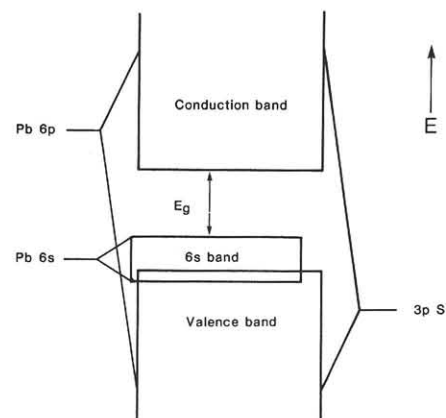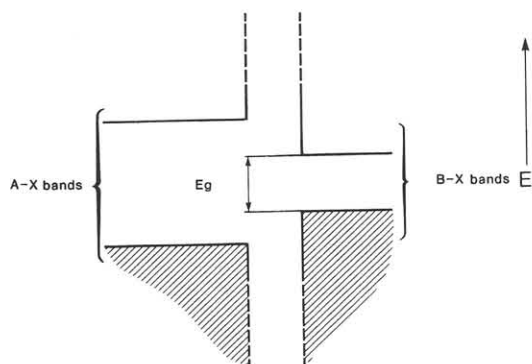

Fig. 1

compounds of divalent Pb, to a relatively low energy gap. Again, if two (or more) different types of bond are present, as for example in chalcopyrite (Fe-S and Cu-S

bonds), then these will correspond to "energy gaps in parallel", the effective gap of the material being determined by the smaller (smallest) of these[3] (see Fig. 2). This is a useful guide to

"Band structures in parallel" for two-bond-type system of compound ABX_2

Fig. 2

complex materials, for example to the 17 compounds formed between PbS and Sb_2S_3, four of which are shown in Table II. These have complicated crystal structures[4], but all four appear to show similar octahedral coordination for Pb and Sb. Accordingly, following Fig. 2, they will have almost identical energy gaps, but there will be small but possibly significant differences in transport properties, refractive index, thermal conductivity, etc., which could prove important for optimising performance in specific device applications. Equally complex groups of compounds are found in the phase diagrams formed between other end-member compounds, e.g. corresponding tellurides, which would have still lower energy gaps. It is, however, less straightforward to move towards higher energy gaps, because the lighter elements tend to make more use of their full valence, hybridising their orbitals to give tetrahedral bonding. Even so one can get significant contribution from non-tetrahedral bonding in materials such

as SiP or SiAs (which are indeed semiconductors with large gaps, see for example [5],[6]) and it is interesting to suggest a "mineralogical survey" for possible new semiconducting complex phases in systems such as SiP – Mg_3P_2. Alternatively one can approach the topic via "cross-substitution"[3] from the NaCl structured compound ScN – but here the problem of d-bands bridging or at least limiting the gap requires careful attention, particularly with early transition elements, e.g. scandium to chromium, inclusive.

Relatively ionic chemical bonds, of course, give rise to strong polar optical scattering and, hence, reduced carrier mobilities. For many applications, therefore, the need for high mobilities requires that care be taken to ensure that the choice of a new material takes into account the need for minimum difference in electro-negativities of the constituent elements[3].

So far only traditional valence compounds have been considered. Many other semiconducting compounds in fact exist which on first encounter do not seem to obey valence rules. Some of these are shown in Table III, which is specifically concerned with boron compounds. In the most complex group (incorporating B_{12} icosahedra as building blocks) $B_{12}P_2$, for example, has an energy gap of about 3 eV and reasonably high hole mobility[7]. This kind of material also shows unusually low thermal conductivity[8]. Semiconducting properties of the other materials in Table III will also be discussed. The difficulties of preparing such refractory and chemically reactive compounds, see for example [9], has effectively prevented very much work being done. However, new

techniques such as MOCVD and MBE could make vapour growth of pure, homogeneous material with control of stoichiometry much more straightforward. Other little studied materials, e.g. polyaluminides such as $MnAl_3$ (see for example[10]), will also be mentioned.

It is the purpose of this paper to draw attention to the challenge offered by less conventional semiconductors, and in particular to the possibilities they offer for obtaining combinations of properties not only unusual by present standards but highly desirable too, e.g. high mobilities at high temperatures or improved thermoelectric figures of merit. The latter could prove particularly important if only because even a doubling of existing values (essentially unchanged since the mid-1950s) could greatly widen the field of application of, say, thermo-electric cooling, or power generation.

In the present economic climate industry would not welcome even one completely new material, with all its associated new problems in preparation, processing, contacting, etc.. It therefore will not be investigating novel semiconductors until they have been demonstrated to possess valuable properties unattainable with better-known materials. It follows then that this is a field with special attraction for academic research: it offers new opportunities for scientific exploration without the danger of competition from industry, as well as the assurance that if unusual results were indeed obtained industrial support would rapidly be forthcoming.

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TABLE I

SOME MINERALS SHOWING GOOD POINT CONTACT RECTIFICATION

Beegerite	$Pb_6Bi_2S_9$
Berzelianite	Cu_2Se
Chalcopyrite	$CuFeS_2$
Enargite	Cu_3AsS_4
Galena	PbS
Guanajuatite	Bi_2SSe_2
Guitermanite	$Pb_3As_2S_6$
Pyrites	FeS_2
Tennantite	$Cu_{10}Fe_2As_4S_{13}$

TABLE II

SOME INTERMEDIATE PbS – Sb_2S_3 PHASES

Fuloppite	$Pb_3Sb_8S_{15}$
Plagionite	$Pb_5Sb_8S_{17}$
Heteromorphite	$Pb_7Sb_8S_{19}$
Semseyite	$Pb_9Sb_8S_{21}$

TABLE III

BORON BASED SEMICONDUCTORS WITH UNCONVENTIONAL VALENCE RELATIONSHIPS

MATERIAL	BORON ARRANGEMENT
$B_{12}P_2$, $B_{12}As_2$, $B_{12}C_3$, etc.	B_{12} icosahedra
CaB_6, SrB_6	B_6 octahedra
TiB_2, ZrB_2	Hexagonal B layers