Atomic volume and semiconducting properties in pnictides and chalcogenides of non-transition elements

Deviations of the atomic volume from additivity in compounds of transition elements among themselves and with non-transition are discussed [1–3]. The present note considers these deviations in binary compounds (Tables I to IV) of non-transition elements with P, As, Sb (pnictides) and S, Se, Te (chalcogenides), many of which are semiconducting.

The percentage deviation of the atomic volume (V) from the sum of its components ($\Sigma\Omega$) is given by:

$$K = \frac{\Sigma\Omega - V}{V} 100 = \frac{\Delta V}{V} 100 \qquad (1)$$

the atomic values being based on the data in [4–6].

Tables I and II shows that metallic properties in

TABLE I Pnictides of germanium and silicon

Compound	Structure	$\frac{\Delta V}{V}100$	E_g(ev)
As_2Si	$GeAs_2$	−8	sem.
As Si	As Si	−7	2.2
As_2Ge	orth.	−6	1.1
PSi	orth.	−4	sem.
P_2Si	$GeAs_2$	−3	1.9
AsGe	AsSi	−3	0.6
SbGe	tetr.	−1	–
PGe	AsSi	0	sem.
As_2Si	cub.	+15	met.
P_2Si	cub.	+27	met.
SiSi film	fcc	+49	met.
GeGe film	fcc	+52	met.

TABLE III Chalcogenides of non-metallic elements

Compound	Structure	$\frac{\Delta V}{V}100$	E_g(eV)
Te_2Si	CdI_2	−17	–
Se_5P_4	orth.	−15	–
S_3P_4	orth.	−14	–
S_9P_4	cub.	−13	–
Se_2Si	S_2Si	−12	–
S_3As_4	orth.	−11	–
SAs	monoc.	−6	2.0
S_5As_4	monoc.	−6	–
S_2Si	orth.	−5	–
S_3As_2	monoc.	−4	1.6
S_2Ge	orth.	−2	3.6
Te_7Sb_2	cub.	0	–
S_3As_2	monoc.	+2	2.5
Te_2Sb_2	hex.	+3	–
Te_3As_2	monoc.	+3	1.0
Se_2Ge	GeS_2	+3	2.3
TeGe	NaCl	+4	0.2
Te_3Sb_2	hex.	+4	0.3
Se_3Sb_2	S_3Sb_2	+6	1.2
SeGe	GeS	+9	1.1
Se_4As_4	monoc.	+9	1.7
S_3Sb_2	orth.	+12	1.5
SGe	orth.	+18	2.0

TABLE II Pnictides of non-transition metallic elements

Compound	Structure	$\frac{\Delta V}{V}100$	E_g(eV)	Compound	Structure	$\frac{\Delta V}{V}100$	E_g(eV)
α-SnSn	diam.	−26	0	AsGa	β-ZnS	−9	1.4
SbAl	β-ZnS	−19	1.5	SbCd	orth.	−9	0.5
As_2Cd_3	Zn_3P_2	−18	0.1	P_5Tl	orth.	−9	–
SbIn	α-ZnS	−17	0.2	PSn	hex.	−8	–
As_2Zn	monoc.	−17	0.9	SbZn	orth.	−7	0.5
Sb_2Cd_3	monoc.	−16	–	P_2Cd_3	Zn_3P_2	−5	0.6
AsAl	β-ZnS	−16	2.2	P_4Cd	monoc.	−5	1.0
As_2Cd_3	tetr.	−15	–	PGa	β-ZnS	−5	2.2
P_2Cd	tetr.	−14	2.0	PIn	β-ZnS	−5	1.2
AsIn	β-ZnS	−14	0.3	As_3Sn_4	hex.	−1	met.
As_2Zn_3	tetr.	−13	0.9	SbSn	NaCl	0	met.
As_2Cd	tetr.	−13	1.0	P_3Sn	GeP_3	+2	–
P_2Zn	monoc.	−12	1.3	AsSn	NaCl	+3	met.
SbGa	β-ZnS	−12	0.7	P_3Sn_4	As_3Sn_4	+3	met.
PAl	β-ZnS	−12	3.1	PSn	GeP	+5	–
P_2Zn	tetr.	−11	1.7	PSn	NaCl	+8	–
P_2Zn_3	tetr.	−11	1.2	SbIn	tetr.	+8	met.

TABLE IV Chalcogenides of non-transition metallic elements

Compound	Structure	$\frac{\Delta V}{V}100$	E_g(eV)	Compound	Structure	$\frac{\Delta V}{V}100$	E_g(eV)
$TeIn_2$	orth.	−20	0.5	TeTl	tetr.	−3	0.2
TeCd	β-ZnS	−16	1.4	Se_3In_4	orth.	−3	–
Se_6In_5	monoc.	−14	–	Se_3In_2	hex.	−3	–
TeHg	β-ZnS	−14	0	Te_3Tl_5	Cr_5B_3	−3	0
TeZn	β-ZnS	−13	2.2	SeTl	STl	−1	0.7
SeCd	α-ZnS	−13	–	Te_4In_3	hex.	0	1.6
$SeIn_2$	orth.	−13	0.8	SePb	NaCl	0	0.2
SeCd	β-ZnS	−12	1.7	α-Se_3In_2	hex.	+1	–
Te_3In_2	cub.	−12	1.0	S_5Tl_2	orth.	+1	sem.
Te_3In_2	β-ZnS	−12	1.0	Se_3Sn_2	tetr.	+1	–
SeIn	hex.	−11	1.8	SeSn	NaCl	+1	0.9
TeGa	hex.	−11	–	SeSn	GeS	+1	0.9
TeGa	monoc.	−10	1.7	TeIn	NaCl	+2	–
SeHg	β-ZnS	−10	0.3	SZn	β-ZnS	+2	3.5
$SeTl_2$	tetr.	−9	0.1	S_5Tl_2	orth.	+2	sem.
Te_3Ga_2	orth.	−8	1.1	SZn	α-ZnS	+3	3.7
Te_5In_2	monoc.	−8	1.3	SGa	hex.	+5	2.5
SCd	α-ZnS	−7	2.5	STl	tetr.	+5	1.6
SeZn	α-ZnS	−7	–	SHg	tetr.	+5	1.0
Te_3In_4	In_4Se_3	−7	–	Se_7In_6	monoc.	+5	0.3
Se_3Al_2	monoc.	−7	–	Se_2Sn	CdI_2	+6	2.0
SeZn	β-ZnS	−6	2.6	S_3Tl_4	monoc.	+6	–
SCd	β-ZnS	−5	–	SPb	NaCl	+7	0.4
TeIn	tetr.	−5	0.2	SSn	NaCl	+7	1.2
TePb	NaCl	−5	0.3	SSn	GeS	+8	1.3
STl_2	hex.	−5	sem.	S_3Ga_2	monoc.	+8	2.0
β-Se_3In_2	hex.	−4	1.4	S_3In_2	tetr.	+10	1.2
TeSn	NaCl	−4	0.2	SIn	orth.	+11	1.9
Te_3Tl_2	monoc.	−4	0.7	S_3Sn_2	orth.	+12	0.9
δ-SeGa	hex.	−4	2.0	S_7In_6	monoc.	+13	–
SeGa	hex.	−3	–	S_2Sn	CdI_2	+16	0.2
SeGa	GaS	−3	2.0				

pnictides of non-metals are associated with intensive contraction, while in those of metals, contraction, may be slight. These data may be considered as a generalization of the familiar fact that for the elements Sn, Si, Ge [7]; P, As, Sb, Bi; S, Se, Te polymorphic transition from the semiconducting (or semi-metallic) to the metallic modification is associated with intensive contraction. In interpreting the data in the above tables, however, the following should be borne in mind.

In [8, 9] it was shown that the electrical and galvanomagnetic properties of As_2Si, P_2Si (pyrite structure), and As_3Sn_4, P_3Sn_4 are those of metals; on the other hand, minima of the reflection coefficient were observed at the infra-red end of the optical spectrum. (The ultraviolet was not studied for these compounds.) In the authors' view, this may be interpreted as indication of a semi-metallic character, but it should also be borne in mind that minima in the infra-red and visible ranges may also indicate inter band transitions as is the case with Mg [10] Zn [11] and Cd [12].

Tables III and IV show that, unlike the pnictides of non-transition elements, their chalcogenides may be semiconducting not only under negative deviations from additivity, but also under positive ones. This is apparently related to the fact that in a series of compounds the chalcogenic elements have higher valencies than usual, which makes for intensive additional contraction.

Comparison of the atomic volume of $P(V = 19\,\text{Å}^3)$, As, Sb with those of their neighbours [6] (allowing for the excess atomic volume in non-metals compared with metals), shows that their valency is 5, i.e. the highest possible for them;

on the other hand, the corresponding data for S, Se, Te and their neighbours indicates that their valency is 4. It may thus be assumed that the valency of the latter group, in their semiconducting compounds characterized by intensive contraction, is 6. This supposition may probably be verified with the aid of the Mössbauer effect.

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Non-axial dislocations in reaction-sintered silicon nitride

The exploitation of silicon nitride as an engineering material necessitates an understanding of the deformation, creep and fracture characteristics of both the hot-pressed and reaction-sintered forms of the material. These characterizations obviously require knowledge of the defect microstructures that are likely to occur. This information is most readily obtained by the use of transmission electron microscopy and in the literature there have been several reports [1–4] of examinations of the microstructure using this technique. One common feature of all these reports was the lack of complete unambiguous characterization of the dislocations that are frequently observed. Ambiguity arises because although these workers found it possible to identify dislocations with a Burgers vectors along the c axis they could not unambiguously identify those dislocations which also possessed basal plane components in their Burgers vector. The difficulty which was encountered with these non-axial dislocations was the inapplicability of the standard $\mathbf{g} \cdot \boldsymbol{b} = 0$ invisibility due to the failure to obtain total invisibility of the dislocation image for some reflections. This factor coupled with the frequent observation of multiple images has led to the suggestion by Evans and Sharp [4] that this behaviour may be due to a dislocation dissociation. Since the Burgers vector for the $\frac{1}{3}\langle 1\,1\,\bar{2}\,3\rangle$ dislocation is large in magnitude, a dissociation would appear to be a probable occurrence but it is also possible that the observed contrast behaviour is related to the complex crystal structure of the material. It is clearly important to establish whether dislocations with a $\frac{1}{3}\langle 1\,1\,\bar{2}\,3\rangle$ Burgers vector are present and if so whether they are dissociated since there have been no reports of the presence of the smaller Burgers vector $\frac{1}{3}\langle 1\,1\,\bar{2}\,0\rangle$. A study has therefore been made of the two possible explanations of the observed contrast behaviour and in this letter we report the results.

The observations in this note were obtained from thin foils of reaction-sintered silicon nitride. Specimens suitable for electron microscopy were obtained by a combination of mechanical grinding and ion-beam thinning. After thinning, the specimens were lightly coated with carbon to minimize charging effects and then examined in a Philips EM300 electron microscope.

In order to be able to unambiguously identify the presence of dislocations with a non-axial Burgers vector, it is first necessary to eliminate from considerations those dislocations which possess Burgers vectors in the c direction. This is most easily achieved by imaging the dislocations using the six basal $\langle 2\,0\,\bar{2}\,0\rangle$ and $\langle 1\,1\,\bar{2}\,0\rangle$ type reflections. The visibilities and invisibilities given