

Electronic structure of semiconducting alkali-metal silicides and germanides

M. Tegze* and J. Hafner

Institut für Theoretische Physik, Technische Universität Wien, Wiedner Hauptstrasse 8-10, A-1040 Wien, Austria

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We present self-consistent linearized-muffin-tin-orbital calculations of the electronic structure of three alkali-metal germanides and silicides (KGe, NaGe, and NaSi). Like the alkali-metal-lead compounds investigated in our earlier work [M. Tegze and J. Hafner, *Phys. Rev. B* **39**, 8263 (1989)] the Ge and Si compounds of the alkali metals form complex structures based on the packing of tetrahedral Ge_4 and Si_4 clusters. Our calculations show that all three compounds are narrow-gap semiconductors. The width of the energy gap depends on two main factors: the ratio of the intracluster to the intercluster interactions between the group-IV elements (which increases from Pb to Si) and the strength of the interactions between the alkali-metal atoms (which varies with the size ratio).

Very recently we have presented a detailed theoretical analysis of the electronic structure of metallic and semiconducting alkali-metal-lead compounds.¹ We could show that these compounds can be classified according to their chemical bonding properties: in the *octet compounds* with the "stoichiometric" composition A_4X (A stands for an alkali metal and X for Pb or another group-IV element) the Fermi level falls into a very narrow ionic gap separating the fully occupied anions bands from the lowest cation band. However, most real compounds tend to be slightly off-stoichiometric so that the alloys are bad metals rather than semiconductors. The equiatomic compounds of the alkali metals Na, K, Rb, Cs (but not Li) with Pb form *polyanionic cluster compounds* containing isolated Pb_4 tetrahedra. These compounds are narrow-gap semiconductors. The Fermi level falls into a covalent gap which originates from the splitting of states which are bonding or antibonding within the tetrahedra. The lowest cation band lies above the highest anion band. Finally if the overlap between the Pb states becomes large enough (such as in the CsCl-type phase LiPb, in the AuCu₃-type phase NaPb₃, or in the hexagonal Laves phase KPb₂) *metallic compounds* are formed whose electronic structure approaches that of pure lead, but here again the alkali levels lie above the Fermi level.

In all three types of compounds the electronic structure is entirely dominated by the strong attractive Pb potential. However, the delocalized nature of the Pb orbitals leads to rather unusual bonding properties: formal ionicities defined in terms of net ionic charges are small, despite the existence of an "ionic" gap in the octet compounds; the bonding within the Pb_4 clusters is rather far from a classical covalent bond describable in terms of localized two-electron-two-center bonds.

In this paper we extend our study of the electronic structure of polyanionic alkali-metal-group-IV compounds to the silicides and germanides of sodium and potassium. In all these compounds the group-IV atoms form isolated tetrahedra in slightly different arrangements. The crystallographic description is summarized

in Tables I–III; for the NaPb structure see Table II in Ref. 1. In all three structures the group-IV atoms form isolated tetrahedra. The alkali-metal atoms are surrounded by the tetrahedra so that the number of direct alkali-metal neighbors is small. The essential difference between the four structures lies in the ratio of the distance between the group-IV atoms within a tetrahedron to the distance between two atoms belonging to different tetrahedra. In the NaPb structure assumed by the equiatomic compounds of Na, K, Rb, and Cs with Sn and Pb the shortest intercluster distance is only 15% larger than the shortest intracluster distance. In the germanides and silicides the intercluster distance is 1.5–1.9 times larger than intracluster distance [Table IV(a)]. The second important difference concerns the distances between the alkali atoms in the Na and K compounds. Due to the large volume contraction in KPb and KGe [Table IV(b)], the shortest K-K distance in the compound is considerably smaller than in pure K. In KGe even the second-nearest-neighbor distance is shorter than the nearest-neighbor distance in K. In NaPb and NaGe the Na-Na distances are of the same order as in pure Na, but very short Na-Na distances appear also in NaSi.

The self-consistent linear muffin-tin-orbital (LMTO) calculations of the electronic structure of NaPb and KPb described in Ref. 1 and the augmented-spherical-wave (ASW) calculations of Springelkamp *et al.*⁴ for the isostructural compound NaSn have shown that the energy bands of the polytetrahedral compounds are obtained by broadening the molecular energy levels of an isolated Pb_4^{4-} or Sn_4^{4-} tetrahedron into band states, confirming an earlier conjecture of Geertsma *et al.*^{5,6}

The s states of Pb or Sn form two separate narrow bands at low energies. The p levels are split into two complexes, one with states which can be described as bonding combinations of p orbitals within each tetrahedron, and one with combinations of orbitals which are antibonding within the tetrahedra. The Fermi energy falls into the narrow gap separating these two complexes. The bandwidth of both the valence and the conduction band

TABLE I. Crystallographic description of the NaSi structure.^a

Pearson symbol: $mC32$ -base-centered monoclinic							
Space group: C_{2h}^6							
$a=12.19 \text{ \AA}$							
$b=6.55 \text{ \AA} \quad b/a=0.5373$							
$c=11.18 \text{ \AA} \quad c/a=0.9171$							
$\beta=119^\circ$							
Atomic positions							
	Na ₁	(8f)	0.351	0.662	0.358		
	Na ₂	(8f)	0.632	0.900	0.455		
	Si ₁	(8b)	0.440	0.210	0.314		
	Si ₂	(8f)	0.597	0.463	0.357		
Coordination							
	Na ₁	Na ₂	Si ₁	Si ₂	Na	Si	Total
Na ₁	0 (+3)	2 (+4)	3 (+1)	3 (+1)	2 (+7)	6 (+2)	8 (+9)
Na ₂	2 (+4)	1 (+2)	3	2 (+1)	3 (+6)	5 (+1)	8 (+7)
Si ₁	3 (+1)	3	1	2	6 (+1)	3	9 (+1)
Si ₂	3 (+1)	2 (+1)	2	1	5 (+2)	3	8 (+2)
Interatomic distances (in \AA)							
$d_{\text{Na-Na}}$		(3.22–3.50) ^b		(3.75–4.19) ^c			(5.01) ^d
$d_{\text{Na-Si}}$		(2.92–3.40)		(3.66–3.85)			(4.32)
$d_{\text{Si-Si}}$		(2.40–2.49)					(4.47)
Wigner-Seitz radii							
	$R_{\text{Na}}=2.05 \text{ \AA}$		$R_{\text{Si}}=1.45 \text{ \AA}$		$R_{\text{Na}}/R_{\text{Si}}=1.41$		

^aAfter Ref. 2.^bNearest-neighbor distances.^cDistances only slightly larger than nearest-neighbor distances (coordination numbers given in parentheses).^dShortest distances in the second coordination shell.TABLE II. Crystallographic description of the NaGe structure.^a

Pearson symbol: $mP32$ -monoclinic										
Space group: C_{2h}^5										
$a=12.33 \text{ \AA}$										
$b=6.70 \text{ \AA} \quad b/a=0.5434$										
$c=11.42 \text{ \AA} \quad c/a=0.9262$										
$\beta=119.9^\circ$										
Atomic positions										
	Na ₁	(4e)	0.097	0.435	0.365					
	Na ₂	(4e)	0.393	0.354	0.123					
	Na ₃	(4e)	0.397	0.679	0.493					
	Na ₄	(4e)	0.142	0.635	0.093					
	Ge ₁	(4e)	0.193	0.976	0.345					
	Ge ₂	(4e)	0.323	0.961	0.225					
	Ge ₃	(4e)	0.325	0.279	0.350					
	Ge ₄	(4e)	0.127	0.185	0.134					
Coordination										
	Na ₁	Na ₂	Na ₃	Na ₄	Ge ₁	Ge ₂	Ge ₃	Ge ₄	Na	Ge
Na ₁	0	0 (+1)	1	3	2 (+1)	0 (+1)	1	3	4 (+1)	6 (+2)
Na ₂	0 (+1)	0	3 (+1)	1	1	2	2	1	4 (+1)	6
Na ₃	1	3 (+1)	1	0 (+2)	1	2	2	0	5 (+3)	5
Na ₄	3	1	0 (+2)	1	2	1	1	2 (+1)	5 (+2)	6 (+1)
Ge ₁	2 (+1)	1	1	2	0	1	1	1	6 (+1)	3
Ge ₂	0 (+1)	2	2	1	1	0	1	1	5 (+1)	3
Ge ₃	1	2	2	1	1	1	0	1	6	3
Ge ₄	3	1	0	2 (+1)	1	1	1	0	6 (+1)	3

TABLE II. (Continued).

Interatomic distances (in Å)			
$d_{\text{Na-Na}}$	(3.44–3.79) ^b	(3.91–4.06) ^c	(4.28) ^d
$d_{\text{Na-Ge}}$	(2.94–3.58)	(3.70–3.85)	(4.13)
$d_{\text{Ge-Ge}}$	(2.53–2.58)		(3.97)
Wigner-Seitz radii			
$R_{\text{Na}} = 2.08 \text{ Å}$		$R_{\text{Ge}} = 1.48 \text{ Å}$	
$R_{\text{Na}}/R_{\text{Ge}} = 1.41$			

^aAfter Ref. 2.^bNearest-neighbor distances.^cDistances only slightly larger than those of the direct neighbors (coordination numbers given in parentheses).^dShortest distances to the second-neighbor shell.

is determined by the interactions between the tetrahedra. At the bottom of the valence band the states are bonding within as well as between the tetrahedra. As the energy increases the states remain bonding within the tetrahedra, but become antibonding between the tetrahedra at the top of the valence band. Hence we expect that both the width of the energy gap and the width of the valence band will change when the ratio of the intracluster to the intercluster coupling varies.

Our self-consistent electronic-structure calculations have been performed using the LMTO method of Andersen *et al.*^{7,8} in the atomic-sphere approximation. Scalar relativistic effects are included, but spin-orbit coupling was neglected. Exchange and correlation effects are described in a local-density approximation.⁹ The electronic

density of states was calculated using the linear tetrahedron method.^{10,11} 80 *k* points in the irreducible part of the Brillouin zone were used for NaSi, and 18 *k* points for NaGe. For the very complex structure of KGe (64 atoms per unit cell) only 10 *k* points have been calculated. For such a small number of *k* points the tetrahedron method cannot be used, and a continuous DOS was derived from the discrete eigenvalue spectrum by applying a Gaussian broadening (halfwidth of the Gaussians 0.15 eV). Therefore, the DOS of KGe must be considered as slightly less accurate in its details.

The results for the total, site-, and angular-momentum decomposed DOS are shown in Figs. 1–3. Qualitatively the DOS is very similar to that of NaSn, NaPb, and KPb, but quantitatively some important differences are found.

TABLE III. Crystallographic description of the KGe structure.^a

Pearson symbol: <i>cP</i> 64–simple cubic							
Space group: T_d^4							
$a = 12.78 \text{ Å}$							
Atomic positions							
	K_1	(8 <i>e</i>)	0.332	0.332	0.332		
	K_2	(24 <i>i</i>)	0.336	0.142	0.064		
	Ge_1	(8 <i>e</i>)	0.071	0.071	0.071		
	Ge_2	(24 <i>i</i>)	0.064	0.320	0.422		
Coordination							
	K_1	K_2	Ge_1	Ge_2	K	Ge	Total
K_1	0	3	3	3	3	6	9
K_2	1	0 (+1)	1	5	1 (+1)	6	7 (+1)
Ge_1	3	3	3	0	6	3	9
Ge_2	1	5	0	3	6	3	9
Interatomic distances (in Å)							
d_{K-K}		3.68 ^b			3.98 ^c		(4.20) ^d
d_{K-Ge}		(3.37–3.61)					(4.62)
d_{Ge-Ge}		(2.56–2.58)					(4.88)
Wigner-Seitz radii							
$R_K = 2.32 \text{ Å}$			$R_{Ge} = 1.45 \text{ Å}$			$R_K/R_{Ge} = 1.60$	

^aAfter Ref. 3.^bNearest-neighbor distances.^cDistances only slightly larger than those of the direct neighbors (coordination numbers given in parentheses).^dShortest distance to the second coordination shell.

TABLE IV. (a) Intracuster distances d_1 and intercluster distances d_2 in the polytetrahedral alkali-group-IV compounds. (b) Volume contraction ΔV (%) and shortest distances between the alkali-metal atoms d_1^{A-A} in the intermetallic compound and ratio of these distances to the nearest-neighbor distance in the pure alkali metal A .

	(a)		
	d_1 (Å)	d_2 (Å)	d_1/d_2
KPb	3.38	3.92	1.16
NaPb	3.15	3.64	1.16
NaGe	2.53	3.97	1.57
NaSi	2.40	4.47	1.86
KGe	2.56	4.88	1.91

	(b)		
	ΔV (%)	d_1^{A-A} (Å)	d_1^{A-A}/d_1 (pure A)
KPb	-23.5	3.98	0.88
KGe	-30.5	3.68	0.81
NaPb	-8.5	3.69	1.01
NaGe	-15.0	3.44	0.94
NaSi	-15.5	3.22	0.88

(a) The width of the gap increases from about $E_g = 0.3$ eV in the three NaPb-type compounds to $E_g = 0.5$ eV in KGe, and to $E_g = 1.0$ eV in NaGe and NaSi. (b) The width of the valence band is also increased from $W_p = 2.5$

eV (KPb) and $W_p = 3.1$ eV (NaPb) to $W_p = 3.2$ eV (NaGe), $W_p = 3.4$ eV (KGe), and $W_p = 3.7$ eV (NaSi). (c) The s states of Si and Ge are slightly shifted to lower energies, their bands are even narrower in the germanium and silicon compounds than in the lead compounds.

Again the changes in the electronic structure may be interpreted on the basis of the eigenstates of the tetrahedron. With a basis of (s, p_x, p_y, p_z) states on each atom the sixteen-dimensional representation of the tetrahedron point group reduces in the following way:^{5,6,12} the s states reduce to the A_1 and T_2 irreducible representations, the p states to A_1 , E , $2T_2$, and T_1 . With any reasonable assumption for the transfer integrals the s levels (A_1, T_2) fall always far below the p levels which are grouped into the three bonding levels A_1, T_2 (triply degenerate), and E (doubly degenerate), and the three antibonding levels T_1 and T_2 (both triply degenerate).

With twenty electrons per tetrahedron, the Fermi level falls into the gap between the E and T_1 levels, the width of the gap being given by the sum of the $(pp\sigma)$ and $(pp\pi)$ transfer integrals, $E_g = V(pp\sigma) + V(pp\pi)$. According to Harrison¹³ the transfer integrals are given by $V(l'l'm) = \eta_{ll'm} h^2 / md^2$, where d is the interatomic distance and the $\eta_{ll'm}$'s are universal constants. Hence the increase of the width of the gap in the series NaPb-

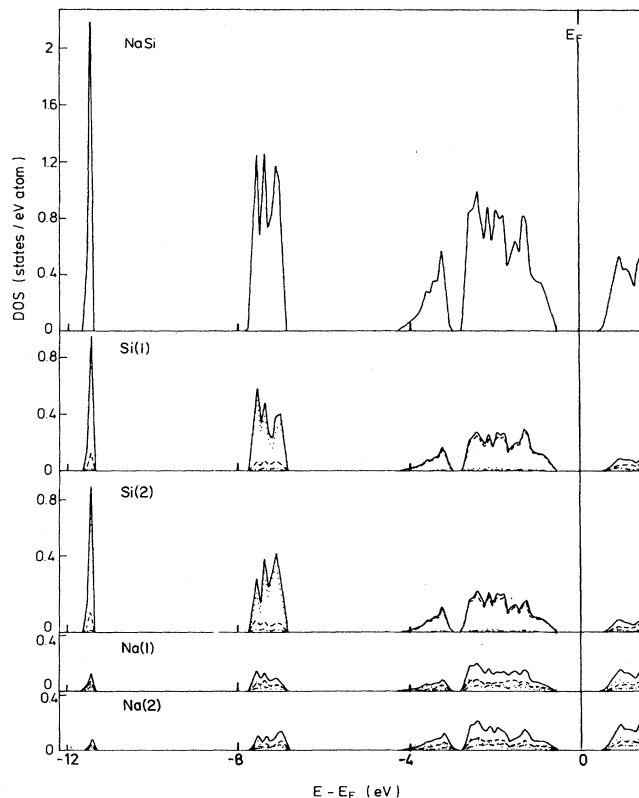


FIG. 1. Total, site-, and angular-momentum-decomposed electronic density of states for NaSi. Solid lines, total and site-decomposed DOS; dotted lines, partial s -electron DOS; dashed lines, partial p -DOS; dot-dashed lines, partial d -DOS.

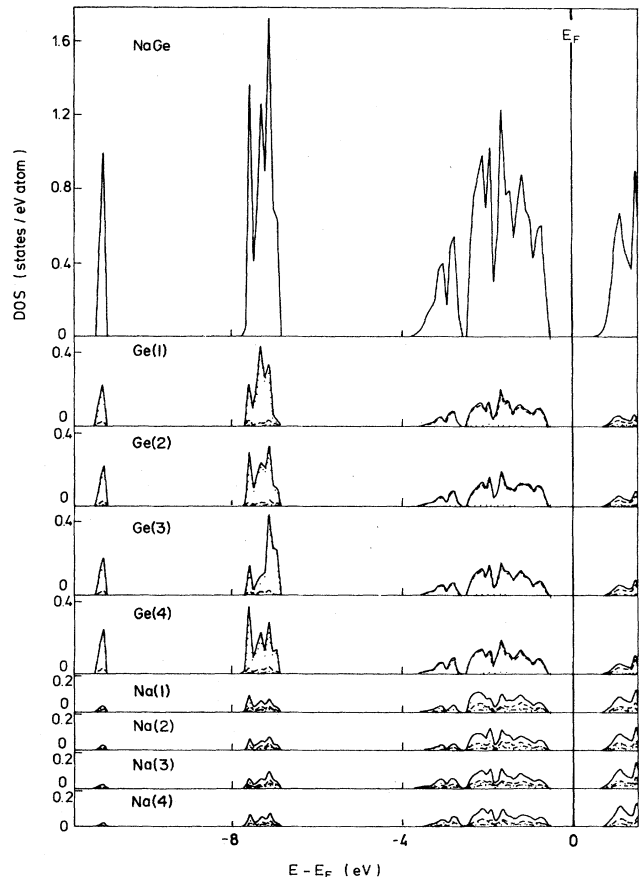


FIG. 2. Total, site-, and angular-momentum-decomposed electronic density of states for NaGe. Same symbols as Fig. 1.

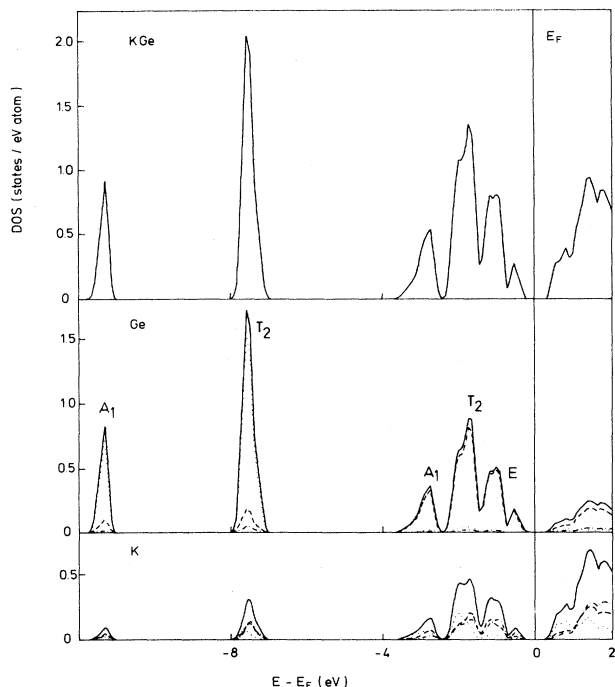


FIG. 3. Total, site-, and angular-momentum-decomposed electronic density of states for KGe. Same symbols as Fig. 1. The irreducible representations of the point group of the Ge_4 tetrahedron from which the individual bands are derived are indicated (see text).

NaSn-NaGe-NaSi arises from the stronger p - p interactions in the lighter group-IV elements. However, for an energy gap to be formed, it is also necessary that the energies of the alkali-metal s levels are pushed above the Fermi energy. For NaSn , Springelkamp *et al.*⁴ have shown that this happens only if the Na atoms are isolated from each other by the Sn tetrahedra. A distortion of the structure which leads to the formation of closer Na-Na contacts causes the formation of an alkali-metal band across the gap between the bonding and antibonding p -

band complexes. This is important for understanding the difference between the Na and K compounds. In the K compounds the strong volume contraction ($\Delta V = -23.5\%$ in KPb and $\Delta V = -30.5\%$ in KGe against only $\Delta V = -8.5\%$ in NaPb , $\Delta V = -15\%$ in NaGe , and $\Delta V = -15.5\%$ in NaSi) leads to K-K distances which are considerably shorter than the nearest-neighbor distances in pure K [Table IV(b)]. Hence there is a non-negligible K-K interaction, even though the number of direct K-K neighbors is small. This leads to a lowering of the K s states and to a reduction of the gap—in KGe there is a considerable K contribution to the lowest conduction band (Fig. 3). The same effect also counterbalances at least part of the increasing bonding-antibonding splitting in the series $\text{NaPb-NaSn-NaGe-NaSi}$.

The changes in the valence bands are a direct consequence of the stronger intracluster and weaker intercluster interactions: the former leads to a larger splitting of the eigenstates of the tetrahedron, the latter to a reduced broadening. In all the three germanides and silicides the bonding p -band complex is split into three parts. The area below the three peaks is distributed roughly according to the degeneracy of the molecular eigenstates, $A_1:T_2:E = 1:3:2$ (see Fig. 3).

To summarize, we have extended our investigations of the electronic structure of equiatomic I-IV compounds to include the germanides and silicides of Na and K. We find that the width of the energy gap is determined by two competing effects: an increasing bonding-antibonding splitting within the p -band complex stabilizing the polyanionic clusters going from the Pb to the Si compounds, and a stronger interaction between the alkali-metal atoms with a decreasing size ratio of the group-IV element relative to the alkali metal leading to a lowering of the lowest conduction-band state derived from the alkali-metal s states.

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*On leave of absence from Central Research Institute for Physics, Hungarian Academy of Sciences, P.O. Box 49, H-1525 Budapest, Hungary.

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