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LETTER TO THE EDITOR

Band structure of new superconducting AlB_2-like ternary silicides $M(Al_{0.5}Si_{0.5})_2$ and $M(Ga_{0.5}Si_{0.5})_2$ (where M = Ca, Sr and Ba)

I R Shein, N I Medvedeva and A L Ivanovskii

Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences, 620219, Ekaterinburg, Russia

E-mail: shein@ihim.uran.ru

Abstract
The electronic band structures of the new superconducting ternary silicides $M(A_{0.5}Si_{0.5})_2$ (where M = Ca, Sr, Ba; A = Al, Ga)—with T_c up to 7.7 K—in the AlB_2-type structure have been investigated using the full-potential LMTO method. The calculations showed that the trend in transition temperatures does not follow the changes in the density d-states at the Fermi level and is probably associated with phonon-mode frequencies.

The discovery of superconductivity (SC) in layered AlB_2-like MgB_2 ($T_c \sim 39$ K) [1] and the creation of promising materials based on them [2–4] have attracted a great deal of interest in related compounds because of their potential as new superconductors. One of the remarkable results is the synthesis, by the floating zone and Ar arc-melting methods, of new ternary silicides $Sr(Ga_xSi_{1-x})_2$ [6], $Ca(Al_{0.5}Si_{0.5})_2$ [7] and $(Ca, Sr, Ba)(Ga_xSi_{1-x})_2$ [7, 8], except for $Ba(Al_xSi_{1-x})_2$, with transition temperatures T_c ranging from 3.3 to 7.7 K. They have the AlB_2-type structure, in which Si and (Al, Ga) atoms are arranged in honeycomb sheets, and alkaline-earth metals are intercalated between them. Furthermore, a series of $(Ca, Sr, Ba)(Al_xSi_{1-x})_2$ compounds was prepared by varying the proportion Al/Si ($0.6 < x < 1.2$) [9], and the maximum T_c for these phases appears at the 1:1:1 composition.

Electrical resistivity and dc magnetization results [5–8] revealed that these layered silicides are superconductors of type II. Seebeck coefficient measurements for $(Ca, Sr, Ba)(Al_xSi_{1-x})_2$ [9] indicate that their carriers are predominantly electrons, in contrast to holes in MgB_2 [1–4]. The observed difference in the values of T_c for these phases can be attributed qualitatively to the changes in the densities of states at E_F, $N(E_F)$ [8].

Recently, the first study of the band structures of $Sr(Ga_xSi_{1-x})_2$ and $Ca(Al_{0.5}Si_{0.5})_2$ silicides ($x = 0.375, 0.5$ and 0.625) has been undertaken [10]. It has been shown that the SC properties may be due to the high density of (Ca, Sr)d states at the Fermi level. In this letter we

Table 1. The lattice parameters (a, Å, c/a [8]), total and site-projected ℓ-decomposed DOS at the Fermi level ($N(E_F)$), states eV^{-1}), and transition temperatures (T_c, K) of silicides $M(A_{0.5}Si_{0.5})_2$ (where M = Ca, Sr, Ba; A = Al, Ga).

Parameters	$Ca(Al_{0.5}Si_{0.5})_2$	$Sr(Al_{0.5}Si_{0.5})_2$	$Ba(Al_{0.5}Si_{0.5})_2$	$Ca(Ga_{0.5}Si_{0.5})_2$	$Sr(Ga_{0.5}Si_{0.5})_2$	$Ba(Ga_{0.5}Si_{0.5})_2$
a	4.1905	4.2407	4.2974	4.1201	4.1875	4.2587
c/a	1.0498	1.1171	1.1967	1.0777	1.1331	1.1985
M-s	0.028	0.061	0.083	0.017	0.034	0.044
M-p	0.096	0.138	0.199	0.073	0.036	0.076
M-d	0.663	1.344	1.460	0.594	0.936	1.079
M-f	0.0	0.0	0.134	0.0	0.0	0.108
Al(Ga)-s	0.023	0.022	0.018	0.022	0.017	0.017
Al(Ga)-p	0.101	0.345	0.404	0.104	0.162	0.219
Al(Ga)-d	0.033	0.043	0.038	0.015	0.018	0.016
Si-s	0.023	0.013	0.009	0.019	0.014	0.013
Si-p	0.116	0.241	0.237	0.105	0.163	0.164
Si-d	0.044	0.067	0.066	0.042	0.051	0.051
Total	1.127	2.273	2.611	0.992	1.431	1.757
T_c (K)	7.7 [6] 7.8 [9]	4.2 [8]	<2 [8, 9]	4.3 [7]	5.1 [8, 9]	3.9 [8]

report the results of the first-principles calculations for all known 1:1:1 ternary isostructural and isoelectronic compounds $M(A_{0.5}Si_{0.5})_2$ (where M = Ca, Sr, Ba; A = Al, Ga) and analyse the band structure parameters in connection with the SC properties. The band structures of the above silicides were calculated using the scalar relativistic full-potential LMTO method [11] within the generalized gradient approximation [12]. The basis functions, electron density and potential were calculated without any shape approximation. They were expanded in a spherical harmonic series (with a 'cut-off' of $l_{max} = 6$) inside non-overlapping muffin-tin spheres and in a Fourier series in the interstitial region. The radial basis functions within the muffin-tin spheres were linear combinations of radial wavefunctions and their energy derivatives calculated at energies appropriate to a particular site and principal and orbital quantum numbers. Outside the muffin-tin spheres, the basis functions were combinations of Neuman or Hankel functions with a non-zero kinetic energy [11]. For bands and densities of states (DOS) in the irreducible wedge of the Brillouin zone, we used 640 special k-points. The lattice parameters that were used are listed in table 1.

The energy bands, total DOS and site projected ℓ-decomposed LDOS of $M(A_{0.5}Si_{0.5})_2$ are similar (see figures 1 and 2). For example, the valence band (VB) for $Ca(Al_{0.5}Si_{0.5})_2$ has a width of about 10 eV. The quasi-core s-like band located in the interval from 10.0 to 7.8 eV below the Fermi level is separated by a gap ($\sim$1.45 eV) from the hybrid (Al, Si)sp states, which form four $\sigma(2p_{x,y})$ and two $\pi(p_z)$ bands (see figure 1). The $E(k)$ dependences for the $p_{x,y}$ and p_z bands differ considerably. For the $p_{x,y}$-like bands, the most pronounced dispersion of $E(k)$ is observed along the $k_{x,y}$ direction (Γ–K of the Brillouin zone (BZ)). These bands are of the quasi two-dimensional (2D) type. They form a quasi-flat zone along k_z (Γ–A). The (Al, Si)$p_{x,y}$ orbitals participate in strong covalent σ states to form 2D honeycomb network bonds of sp^2 type with the s states. The (Al, Si)p_z-like bands are responsible for weaker $\pi(p_z)$ interactions. These 3D-type bands have maximum dispersion in the direction $k_z(\Gamma$–A). The s, p, d states of Ca are admixed to p-like bands. The $\sigma(p_{x,y})$ and $\pi(p_z)$ bands intersect at the Γ point of the BZ. It is important that the (Al, Si)p bands are located below E_F and do not contain any hole states like those in non-superconducting AlB$_2$ [2–4], which is isoelectronic to
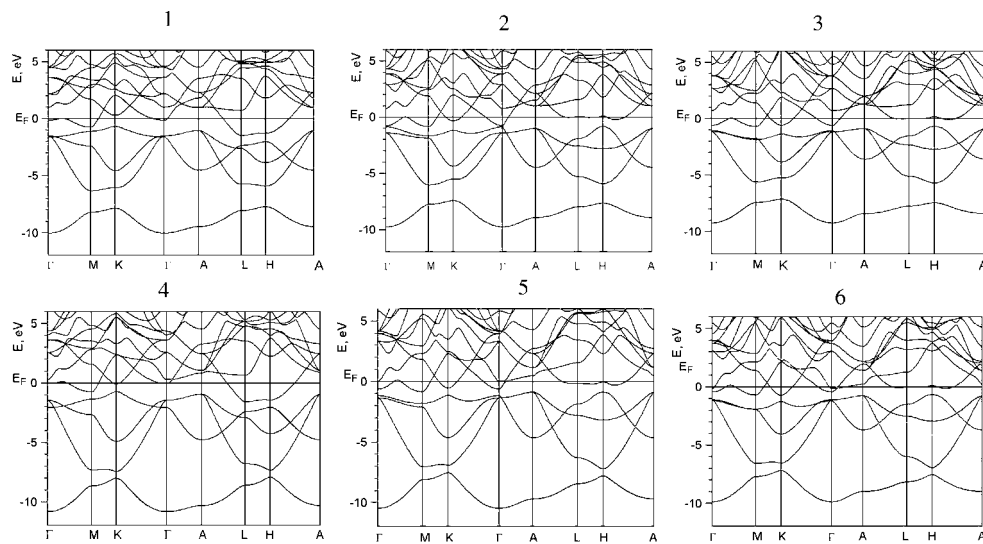
Figure 1. Energy bands: (1), $Ca(Al_{0.5}Si_{0.5})_2$; (2), $Sr(Al_{0.5}Si_{0.5})_2$; (3), $Ba(Al_{0.5}Si_{0.5})_2$; (4), $Ca(Ga_{0.5}Si_{0.5})_2$; (5), $Sr(Ga_{0.5}Si_{0.5})_2$; (6), $Ba(Ga_{0.5}Si_{0.5})_2$.
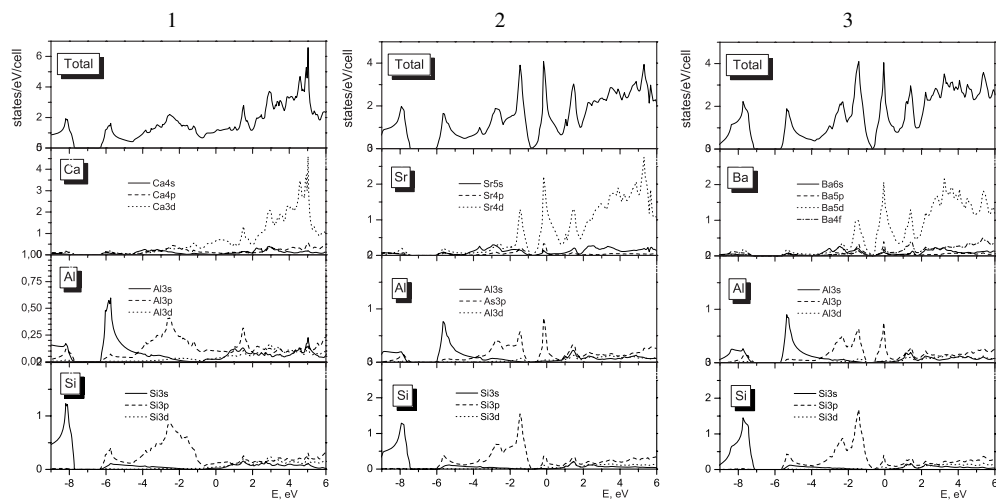
Figure 2. Total and site-projected ℓ-decomposed DOS of: (1), $Ca(Al_{0.5}Si_{0.5})_2$; (2), $Sr(Al_{0.5}Si_{0.5})_2$; (3), $Ba(Al_{0.5}Si_{0.5})_2$.

$Ca(Al_{0.5}Si_{0.5})_2$. The main contribution to the $Ca(Al_{0.5}Si_{0.5})_2$ DOS in the vicinity of the Fermi level is made by the Ca 3d states: their contribution to $N(E_F)$ is about 59% compared with 9 and 10% for Al-p and Si-p states, respectively.

The most obvious consequence of the alkaline-earth metal variation (Ca $\longrightarrow$ Sr $\longrightarrow$ Ba) is the decrease in the VB width from 10.0 ($Ca(Al_{0.5}Si_{0.5})_2$) to $\sim$9.1 eV ($Ba(Al_{0.5}Si_{0.5})_2$) caused by the increased cell volume. The (Sr, Ba)d states form nearly flat bands in the direction L–H close to E_F. As a result, sharp peaks in the LDOS appear for $Sr(Al_{0.5}Si_{0.5})_2$ and $Ba(Al_{0.5}Si_{0.5})_2$ (figure 2). $N(E_F)$ increases more than twofold when going from

$Ca(Al_{0.5}Si_{0.5})_2$ to $Ba(Al_{0.5}Si_{0.5})_2$. It is worth noting that the increase in $N(E_F)$ is due to the simultaneous growth of the LDOS of valence states for all atoms in the silicides (see table 1).

The differences in the band structures of $M(Al_{0.5}Si_{0.5})_2$ and $M(Ga_{0.5}Si_{0.5})_2$ are revealed by an increased dispersion of the σ, π-bands in the A–L–H directions and a decrease in the band gap (at $\sim$1.0–0.9 eV) between the s- and p-like bands for $M(Ga_{0.5}Si_{0.5})_2$ compared to $M(Al_{0.5}Si_{0.5})_2$. The VB width of $M(Ga_{0.5}Si_{0.5})_2$ increases by $\sim$1.3–1.0 eV. The change in the alkaline-earth metal in the sequence Ca $\longrightarrow$ Sr $\longrightarrow$ Ba causes an increase in the $N(E_F)$, the M-d states making the main contribution to the near-Fermi DOS (see table 1). Thus, the following findings have been obtained for $M(A_{0.5}Si_{0.5})_2$ compared to MgB_2:

(a) the filling of bonding $p_{x,y}$ bands and the absence of σ holes;
(b) an increase in covalent interactions (due to p–d hybridization) between graphene-like (Al, Si) or (Ga, Si) sheets and metal hexagonal layers; and
(c) the principal change in $N(E_F)$, where the alkaline-earth metal d states make the main contributions ($\sim$55–60%).

According to the experimental data [5–9]:

(a) in $M(Al_{0.5}Si_{0.5})_2$ silicides, T_c decreases monotonically when M changes from Ca to Ba;
(b) in $M(Ga_{0.5}Si_{0.5})_2$ silicides, T_c changes slightly (within 3.9–5.1 K) and is a maximum (5.1 K) for $Sr(Ga_{0.5}Si_{0.5})_2$.

In the framework of the BCS theory, T_c can be estimated by using the McMillan equation $T_c \sim \langle\omega\rangle \exp\{f(\lambda)\}$, where $\langle\omega\rangle$ is the averaged phonon frequency (inversely proportional to the atomic masses), λ is the electron–phonon coupling constant ($\lambda = N(E_F) \langle I^2\rangle/\langle M\omega^2\rangle$, where $\langle I^2\rangle$ is the electron–phonon matrix element and $\langle M\omega^2\rangle$ does not depend on the mass and is determined by force constants). The values of $N(E_F)$ (like the contributions to $N(E_F)$ from M-d and (Si, Al, Ga)p states) obtained here showed that:

(a) in silicides $M(Al_{0.5}Si_{0.5})_2$ and $M(Ga_{0.5}Si_{0.5})_2$, $N(E_F)$ increases monotonically when the alkaline-earth metal changes from Ca to Ba (opposite to the trend in T_c [5–9]);
(b) the value of $N(E_F)$ in $M(Al_{0.5}Si_{0.5})_2$ silicides is higher than that in $M(Ga_{0.5}Si_{0.5})_2$ silicides based on the same M.

This does not correlate with the observed critical temperatures either. Therefore the supposition [8] that there is a direct dependence between T_c and $N(E_F)$ for 'strong stoichiometric' silicides $M(A_{0.5}Si_{0.5})_2$ is erroneous.

It may be supposed that the main factor determining the variation in T_c in a number of isostructural and isoelectronic compounds $M(A_{0.5}Si_{0.5})_2$ is the change in phonon frequencies depending on the atomic masses. Additionally, the shape of the DOS (and the value of $N(E_F)$) may be changed due to disorder in the distribution of (Al, Ge)/Si atoms in honeycomb layers. As a result, alkaline-earth metals will be in different trigonal-prismatic positions. This may lead to a splitting of the near-Fermi bands and to a decrease in $N(E_F)$. This effect will be more pronounced for Sr- and Ba-containing silicides where, for the 'ideal ordering' state, the $N(E_F)$ is determined by narrow intensive DOS peaks. The possibility of chemical disordering and inhomogeneity in arc-melted silicides was noted in [7].

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