PHYSICAL REVIEW B **69**, 180512(R) (2004)

Electronic structure and superconductivity of CaAlSi and SrAlSi

I. I. Mazin and D. A. Papaconstantopoulos
Naval Research Laboratory, code 6390, 4555 Overlook Avenue SW, Washington, DC 20375-5320, USA
(Received 30 December 2003; published 26 May 2004)

We report full-potential linear augmented plane-wave calculations for CaAlSi and SrAlSi in ordered structures and in the virtual-crystal approximation, at normal and elevated pressures. We also estimate the electron-phonon coupling using frozen-phonon calculations at the zone center, and the rigid muffin-tin approximation. We conclude that there is no simple way to explain the recently reported qualitative disparity in the superconducting properties of the two compounds. An assumption of an ultrasoft phonon mode, on the other hand, allows to reconcile the experimental findings with the theory in a reasonable way.

DOI: 10.1103/PhysRevB.69.180512 PACS number(s): 74.25.Jb, 74.25.Kc, 74.62.Fj, 74.70.Ad

Introduction. The discovery of superconductivity in MgB_2 called attention to materials with the AlB_2 (C32) crystal structure. Some of them, though electronically entirely different from MgB_2, demonstrated interesting superconducting and normal properties. Specifically, CaAlSi and SrAlSi (see Refs. 1–3, and references therein) show superconductivity at ≈ 8 and ≈ 5 K. Moreover, a closer look reveals a number of interesting and unusual characteristics,[1] for instance, a large and opposite in sign pressure coefficient in the two compounds, despite close similarity in the electronic structure. Moreover, thermodynamic measurements suggest the strong-coupling limit for CaSiAl, while SrAlSi is a weakly coupled BCS superconductor.

To understand the physics of these new and interesting systems, we performed accurate band-structure calculations, as well as calculations of zone-center phonon modes and their coupling with electrons, and rigid muffin-tin estimations of the total electron-phonon coupling constants. While the electron-phonon coupling is sufficiently strong to explain superconductivity at $T_c \lesssim 10$ K, the qualitative difference between the two materials does not find a direct explanation from the electronic or lattice properties.

Electronic structure. X-ray diffraction yields the same hexagonal crystal structure $P6/mmm$ (No. 191) for both CaAlSi and SrAlSi, with parameters (a,c) equal to (4.189, 4.400 Å) and (4.220, 4.754 Å), respectively,[1] which implies that Al and Si are randomly distributed over the $2d$ sites. One may think that upon annealing Al and Si will exhibit some ordering, the simplest models being alternating Al and Si layers with the same symmetry group and twice larger c, or in-plane ordering with symmetry lowering to $P\bar{6}m2$ (No. 187), but with the same unit cell. Note that the former ordering is easy to detect by x rays, while the latter, because Al and Si are neighbors in the periodic table, may be missed. The latter seems more plausible also from kinetic considerations, and is energetically more favorable in the calculations. One can assume that at least some degree of short-range ordering in plane is always present, therefore we performed most of the calculations in the ordered $P\bar{6}/m2$ structure. To estimate disorder effects, we also performed calculations in the average, $P6/mmm$ structure, using the virtual-crystal approximation (VCA) to average over Al and Si.

We used the full-potential, all-electron linear augmented plane-wave method.[4] A standard setup was used, with the radii of 2.3 bohr for Ca and Sr and 2 bohr for Al and Si. The cutoff parameter $RK_{\max}$ was chosen as 7, which is sufficient due to use of local orbitals and APW's.[5] Generalized gradient approximation (GGA) was used for the exchange-correlation potential.[6] The resulting bands are shown in Fig. 1, for both the ordered structure and the disordered VCA phase. The following observations can be made.

(1) Both compounds have very similar bands near the Fermi level; ordering does not change the band picture much either.

(2) The bands that play the key role in MgB_2 are fully occupied here and of no relevance for superconductivity.

(3) Only one band crosses the Fermi level. This band is mainly of Ca $d_{3z^2-r^2}$ character, and therefore is quite three dimensional. Note that in the VCA an additional small pocket appears near the K point, mainly of Si and Al p_z character. Ordering makes the bonding and the antibonding bands at K anticross and this pocket practically disappears in the ordered structure.

Density of states (DOS) is plotted in Fig. 2. Decomposition of the DOS (not shown) indicates that all states included in the picture are strongly hybridized and, for instance, the peaks at $\approx \pm 1.5$ eV cannot be ascribed to any of the three atoms, in accord with the fact that there is little difference between the DOS for ordered and disordered structures. Our results for CaAlSi agree rather well with the previous calculations,[7] however, we do not find the large peak at the Fermi level in SrAlSi, reported in Ref. 7, nor the flat band near L, responsible for this peak.[8] The DOS at the Fermi level, $N(E_F)$, is 1.10 st./eV f.u. in CaAlSi and 1.33 st./eV f.u. in SrAlSi, or, in the VCA, 1.00 and 1.15 st./eV f.u., respectively. The plasma frequencies are $\omega_{p\parallel}=5.2$ eV, $\omega_{p\perp}=5.7$ eV for CaAlSi and $\omega_{p\parallel}=5.7$, $\omega_{p\perp}=5.9$ for SrAlSi, where $\parallel$ and $\perp$ stand for the in-plane and out of hexagonal plane polarizations. This implies small resistivity anisotropies $\rho_\perp/\rho_\parallel=1.2$ and 1.03, respectively. The corresponding Fermi velocities are 0.46×10^8 and 0.55×10^8 cm/sec for CaAlSi and 0.48×10^8 and 0.50×10^8 cm/sec for SrAlSi. Experiments suggest, at least in CaAlSi, a much larger resistivity anisotropy of 3.1,[2] while the coherence length and the penetration length anisotropies, which in the first approximation should follow the Fermi velocity anisotropy, or the square root of the resistivity anisotropy, are of the order of 2,[2,3] rather than -10%. Either an unexpectedly anisotropic

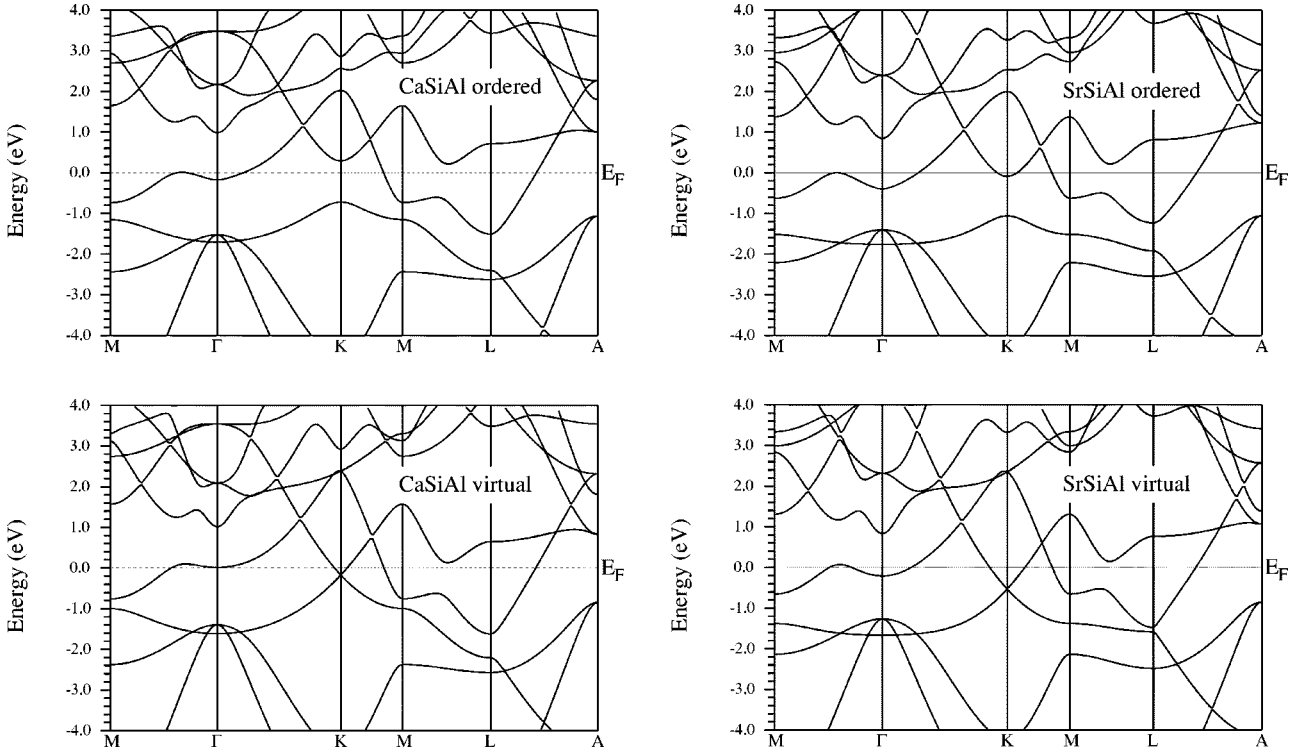

FIG. 1. Band structures of CaSiAl and SrSiAl in the (in-plane) ordered structure and in the virtual-crystal approximation.

scattering takes place at very low temperatures or the conventional band-structure calculations are in serious error for these two materials. In either case this would be highly unusual.

On the other hand, this discrepancy can be understood at least in CaAlSi, if another type of ordering is present, i.e., alternating layers of Al and Si. Indeed, this produces a large anisotropy with the right sign, in fact, a factor of 2 too large $(\omega_{p\|}/\omega_{p\perp}\approx 4)$, but, as mentioned, kinetic arguments speak against this possibility. However, if such ordering has a substantial energetic advantage, it may occur. To get more insight, we performed total-energy calculations for both types of ordering. We found, however, that the in-plane ordering is substantially lower in energy, by 38 mRy (CaAlSi) and 19 mRy (SrAlSi) per formula (we optimized the positions, but used the experimental lattice parameters). Therefore the mystery of the transport anisotropy remains.

Phonons. We used the standard frozen-phonon technique to calculate the frequency of the zone-center phonons and to estimate their coupling with electrons (see, e.g., Ref. 9). In the $P\bar{6}m2$ structure (in-plane ordering) there are six optical phonons (Table I): two nondegenerate A_2'' modes (Si and Al displacing along z), and two double degenerate E' modes (in-plane). As in MgB_2, only the phonons of the E symmetry can couple with electrons at the zone center. However, since the σ bands in these compounds never cross the Fermi level, we do not expect large coupling, as in MgB_2. Because we do not believe that these phonons play a particularly important role here, we did not investigate their coupling constants in detail. It sufficed to estimate the coupling constant for E_{2g} in the virtual-crystal approximation, which corresponds to the higher of the two E' modes in the ordered structure. Although we did not force the integration through to the full convergence, we can safely estimate the corresponding λ to be less than 0.05 per each of the two E_g modes, an order of magnitude less than in MgB_2.

Becoming convinced that all phonons in the entire Brillouin zone couple with the phonons at the same level, we also computed the integrated coupling constant in the rigid muffin-tin approximation (RMTA), using a muffin-tin APW code, as described in Ref. 10. In this approximation the total coupling constant is expressed as $\lambda\approx\Sigma_i\eta_i\Phi_{ii}^{-1}$, where the summation is over all atoms, η is defined only by the electronic characteristics at the Fermi level, and Φ is the corresponding component of the force matrix, a quantity of the order of the atomic mass times an averaged squared phonon frequency.[11] Our results are given in Table II.

Since we did not know the full dynamic matrix, we took the force matrices used to compute the frequencies in Table I; using the E' representation, we obtain for λ in CaSiAl 0.11, with 65% coming from Ca, 10% from Al, and 25% from Si, or, using the A_2'' representation, 0.37, this time, with 15% from Ca, 20% from Al, and 65% from Si. Averaging these results, keeping in mind the degeneracy of the E' representation, we got λ_{RMT} (CaSiAl)$\approx$0.20. For SrSiAl the corresponding numbers are $\lambda=0.16$ (70%:10%:20%) and $\lambda=0.37$ (20%:20%:60%). The average λ_{RMT}(SrSiAl)$\approx$0.23. The difference between the two compounds is much smaller than the inaccuracy of the rigid muffin-tin approximation. Interestingly, exactly the same numbers for λ result from substituting $\Phi_{ii}^{-1}\approx 1/M_i\langle\omega^2\rangle$ by $1/M_i\omega_D^2$, where M is the atomic mass and the Debye frequencies ω_D are from Ref. 1 (for monoatomic metals it is customary to use $\langle\omega^2\rangle=\omega_D^2/2$,

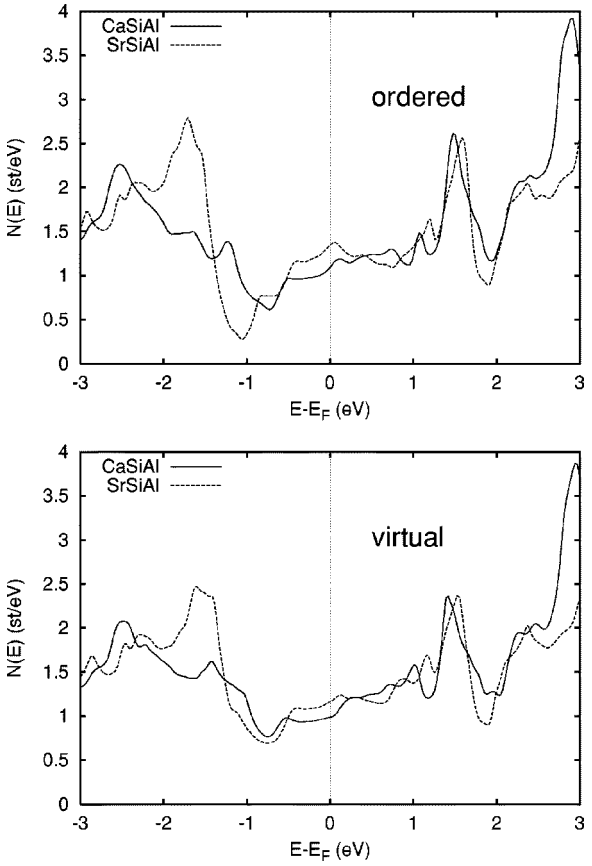

FIG. 2. Densities of states of CaSiAl and SrSiAl in the (in-plane) ordered structure and in the virtual-crystal approximation.

but taking into account optical branches should make the average frequency larger than $\omega_D/\sqrt{2}$).

It is well known that for the *s-p* metals the RMTA strongly underestimates the electron-phonon coupling, while for *d* metals it works well.[12] Since CaSiAl and SrSiAl have a prominent *d* component in their DOS, we expect that they represent an intermediate case. We can conclude that rigid muffin-tin calculations are consistent with the observed superconductivity.

Superconductivity. We shall now try to compose a picture of superconductivity in these compounds as it emerges from the experiment. Probably the most unusual fact about it is that the thermodynamic experiments[1] point to two opposite limits in terms of the coupling strength, and, in a sense, are internally contradictory. Indeed, the measured electronic specific-heat coefficients for the two materials are 5.04 and 5.42 mJ/mol K^2. Ascribing the difference between these and our calculated DOS to the electron-phonon coupling, we get the coupling constant of CaSiAl to be $\lambda=0.95$ and of SrSiAl to be $\lambda=0.73$. This agrees with our intuitive expectations that the coupling should be comparable in both materials, and also with the fact that the transition temperatures differ by 50–60 %. Indeed, for a Coulomb pseudopotential $\mu^*=0.1$, $\lambda=0.95$, and $\lambda=0.73$, the McMillan formula, $T_c=(\omega_{\ln}/1.2)\exp[-1.04(1+\lambda)/(\lambda-\mu^*-0.62\lambda\mu^*)]$, produces a critical temperature difference of 67%, if the average frequency is the same. This, however, places both compounds in a rather strong-coupling limit, even too strong (with the above λ's the McMillan formula requires the logarithmic frequency of the order of 90 cm^{-1}, which is unrealistically small).

TABLE I. Calculated frequencies of the zone-center phonons in the ordered structure, in cm^{-1}.

	A_2''	A_2''	E'	E'
CaAlSi	100	212	187	456
SrAlSi	111	178	151	438

TABLE II. Electronic (Hopfield) factor of the electron-phonon coupling constant in the rigid muffin-tin approximation, in eV/Å^2. "o" stands for the in-plane ordered structure, "v" for the virtual crystal approximation.

	Ca-o	Ca-v	Al-o	Al-v	Si-o	Si-v
CaSiAl	0.21	0.18	0.12	0.21	0.28	0.21
SrSiAl	0.33	0.27	0.14	0.22	0.29	0.22

Let us now try to estimate λ entirely from the experiment. We will use the specific-heat jump from Ref. 1, $\delta C_p/\gamma T_c=2.0$ for CaSiAl and 1.4 for SrSiAl. We shall then make use of semiempirical formulas of Carbotte,[13] $\delta C_p/\gamma T_c\approx 1.43[1-53\alpha^2\ln(3\alpha)]$, where $\alpha=T_c/\omega_{\ln}$. Assuming a 5% error bar in the experiment, we get the following limits on α: In CaSiAl $0.061<\alpha<0.078$; in SrSiAl $0<\alpha<0.013$. Now we can use the experimental gap ratios, and the formula[13] $2\Delta/kT_c\approx 3.53[1-12.5\alpha^2\ln(2\alpha)]$, to get another estimate for α (again, assuming 5% error bars): For CaSiAl, $0.061<\alpha<0.103$, for SrSiAl, $0<\alpha<0.035$. These ranges are compatible with the one obtained from the specific-heat jump, and in fact are larger, so we shall use the first set in the following.

Now we will see what range of λ's this range of α's is compatible with. Using the McMillan equation and assuming $\mu^*=0.12$, we see that $0.061<\alpha<0.078$ translates into $0.98<\lambda<1.15$, which is compatible with our earlier estimate of 0.95, but the condition $\alpha<0.013$ requires $\lambda<0.55$, quite below our earlier estimate of 0.73. Furthermore, given the difference in T_c of only 50%, even the lowest estimate for α in CaSiAl, 0.061, when combined with the highest estimate for α in SrSiAl, 0.013, requires the logarithmic phonon frequency in SrSiAl to be three times higher than in CaSiAl. This contradicts common wisdom, our calculations for the zone-center phonons, and the Debye frequencies measured in Ref. 1. We conclude that although the experimental data for the specific-heat jump and for the reduced gap are consistent with each other for each material separately (CaSiAl thus being in the strong, and SrSiAl in the weak-coupling regime), they are radically inconsistent with the relatively small difference in T_c in the two materials.

We do not see any natural possibility to reconciles these data. A not-so-natural possibility is to assume that the electron-phonon coupling in CaSiAl is enhanced by a soft mode, while in SrSiAl this mode is missing. Indeed, Carbotte's analysis does not apply to systems with "unusual" structure of the Eliashberg function, $\alpha^2F(\omega)$. In particular,

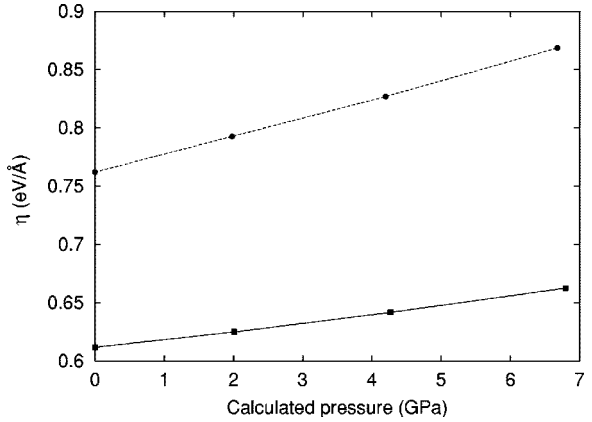

FIG. 3. Electronic (Hopfield) factor of the electron-phonon coupling constant in the rigid muffin-tin approximation in the (in-plane) ordered structure. The full line corresponds to CaSiAl and the dashed one to SrSiAl.

soft modes of the order of $2\pi T_c$ (~ 35 cm^{-1}, for CaSiAl) may increase both $\delta C_p/\gamma T_c$ and $2\Delta/kT_c$ without raising T_c (see, e.g., Ref. 14). But it is hard to understand why such a mode would exist in one compound, but not in the other. One possibility is that the soft mode is associated with presence (or absence) of a short-range ordering. Another is that there is an inherent instability against formation of a superstructure (all calculated zone-center phonons are quite stable), and in fact CaSiAl is much closer to instability than SrSiAl. The third possibility is that the mode exists in both materials, but is insufficiently soft (compared to T_c) in SrSiAl to play an important role in superconductivity. We would like to emphasize that our calculations do not specifically indicate an existence of a soft mode, but do suggest that there are unexpectedly important effects beyond the standard treatment, adopted in the current paper, and soft mode may be one of them.

Pressure effect. Finally, let us discuss the pressure effect on T_c, which appears to be substantial in both compounds,[1] but positive in CaSiAl and negative in SrSiAl. To estimate the pressure effect on the electronic structure, we performed the rigid muffin-tin calculation at three other volumes, with uniform linear compressions of 1, 2, and 3% (Fig. 3). We evaluated the corresponding pressure using the calculated LAPW-GGA equation of states, which gives the equilibrium lattice parameter with excellent accuracy (0.5% in SrSiAl and $<0.1\%$ in CaSiAli; the calculated bulk moduli are 0.60 and 0.63 Mbar, respectively). Note that even when RMTA substantially underestimates the coupling constant, it is usually still reliable in investigating structural trends. We found, however, that the calculated factor η *increases* in both compounds, although the DOS, as usual, decreases with compression (the increase of η is due to increasing strength of the electron-ion scattering, predominantly on Ca/Sr). Therefore the observed disparity of the pressure dependence between the two compounds[1] must be due to lattice effects. However, the calculated bulk moduli show similar pressure dependence in both compounds ($dB/d\ln V = -2.9$ Mbar in CaSiAl and -2.7 Mbar in SrSiAl), indicating that the average phonon frequency probably behaves similarly. An ultrasoft mode discussed above remains a valid possibility. A soft phonon mode is most efficient in raising T_c if its frequency is close to $2\pi T_c$,[13] that is, around 35 cm^{-1} for CaSiAl. Therefore, if a mode of such frequency is present in CaSiAl and in SrSiAl, its hardening with pressure will depress T_c in the latter, but not in the former compound.

Conclusions. We report full-potential well converged calculations of the electronic structure and zone-center phonons in CaSiAl and SrSiAl, in order to gain better understanding of disparate superconducting properties of these otherwise very similar compounds. We also estimated the trends in electron-phonon coupling, using an approximate rigid muffin-tin method. We also assessed the stability of the disordered materials with respect to in-plane ordering and layered-type ordering, and found considerable tendency to the former. Our results indicate that it is hardly possible to reconcile the superconducting properties of CaSiAl and SrSiAl using their electronic properties and conventional wisdom about the phonon-induced superconductivity. It may be possible to explain main experimental facts, assuming an ultrasoft mode of the order of 30–40 cm^{-1}, coupled with electrons. Whether this mode reflects a vicinity of a structural instability at some finite wave vector in an ordered crystal or is somehow associated with short-range ordering is unclear. Experimental studies of ordering in CaSiAl and SrSiAl, and particularly connection (if any) between ordering and superconductivity is highly desirable, as well as low-energy lattice dynamics studies.

We are grateful to B. Lorenz, M. Iliev, and A. Litvinchuk for calling our attention to these materials and sharing their unpublished results with us.

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