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Electronic structure and electron–phonon interaction in CaAl_2Si_2

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Abstract

We calculate the electronic structure, phonon spectrum and electron–phonon (EP) interaction for CaAl_2Si_2 using a full-potential, density-functional-based method. It is found that CaAl_2Si_2 is a semimetal with a small overlap between the conduction and valence bands. The transport properties of CaAl_2Si_2 are discussed in combination with its special electronic structure. It is shown that in CaAl_2Si_2 both the electronic density of states at the Fermi level and the EP coupling strength are very small, resulting in vanishing superconductivity.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The ternary Ca–Al–Si systems have two kind of compounds with characteristic layered structures. One is $\text{Ca}(\text{Al}_x\text{Si}_{1-x})_2$ ($0.225 \leq x \leq 0.675$), which is a superconductor and displays a T_c peak at $x = 0.5$ ($T_c = 7.8$ K) [1, 2]. This compound is isostructural with the recently discovered MgB_2 with a relatively high T_c of 39 K [3]. In this structure, the Ca ions occupy the Mg sites and the Al/Si are randomly distributed among the boron sites in honeycomb planes. The electronic structure, phonon spectrum and electron–phonon interaction for CaAlSi have been studied using first-principles calculations [4–7]. The other kind of ternary Ca–Al–Si compound is CaAl_2Si_2 . It has the trigonal La_2O_3 -type structure [8], where Si and Al atoms are arranged in chemically ordered double-corrugated hexagonal layers and Ca atoms are intercalated between them. This compound is not superconducting above 1.4 K [9]. Recent transport measurements [10] showed that the Hall coefficient R_H in CaAl_2Si_2 is positive below 150 K while it is negative above 150 K. This peculiar transport behaviour must be sensitive

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to its electronic structure. Only the band structure of ionized double-hexagonal corrugated $\text{Al}_2\text{Si}_2^{2-}$ layers was calculated [11]. However, the electronic structure of the ternary CaAl_2Si_2 compound has not been studied up to now. To understand why CaAlSi is superconducting while CaAl_2Si_2 is not above 1.4 K, calculations of their phonon structure and electron–phonon (EP) interactions are highly desirable.

In this work, we carry out first-principles calculations for CaAl_2Si_2 . The electronic structure is calculated by the self-consistent full-potential linear muffin-tin orbital (LMTO) method [12]. The transport properties of CaAl_2Si_2 are discussed in combination with its special electronic structure. We also calculate the phonon spectrum and the EP interaction using the full-potential linear response program of Savrasov [13]. The differences in electronic and phonon structure between CaAlSi and CaAl_2Si_2 are studied in an effort to understand the difference in superconducting behaviour between them.

2. Computational method

The method is the same as that used in our previous work for calculations for MAiSi ($M = \text{Ca}$, Sr and Ba) [5, 7]. The self-consistent full-potential LMTO calculations for the electronic structure are carried out with the generalized gradient approximation [14] for the exchange–correlation potential. The charge density and potential are represented by spherical harmonics up to $l = 6$ inside non-overlapping spheres and by plane waves with about 109 Ryd energy cut-off in the interstitial region, respectively. The full-potential linear response program of Savrasov [13] is used to calculate the dynamical matrices, the phonon dispersion and the EP interaction. This program has been proven to be able to provide reliable estimates for the phonon spectra and EP interactions in a large variety of systems [13, 15]. The dynamical matrix is generated for 24 phonon wavevectors in the irreducible Brillouin zone, corresponding to a mesh of (6, 6, 4) reciprocal lattice divisions. The integration over the Brillouin zone is performed with the improved tetrahedron method [16] using a (18, 18, 12) grid, and the integration over the Fermi surface has a more accurate sampling with a (24, 24, 16) grid. This multigrid technique is outlined in [13]. For the finite-temperature electronic structure calculation, the effect of temperature is modelled by introducing the Fermi–Dirac distribution for the one-electron states, and a finite-temperature tetrahedron method [17] is used for the Brillouin zone integration. The muffin-tin radii for Ca, Al and Si are taken to be 2.8, 1.8 and 1.8 au, respectively. We optimize the lattice constants a and c via total energy minimization. The values of a and c obtained turn out to be (4.142, 7.137 Å), in good agreement with the experimental values (4.141, 7.133 Å) [10].

3. Results and discussion

In CaAl_2Si_2 , the Si atoms form a slightly distorted hexagonal close-packed system with an ordered arrangement of Ca atoms in half of the octahedral holes and Al atoms in half of the tetrahedral holes. A main feature of this structure is a double layer of puckered AlSi hexagons. The internal coordinates for Ca, Al and Si are (0, 0, 0), (1/3, 2/3, z_1) and (2/3, 1/3, z_2), respectively. Our optimized internal parameters are $z_1 = 0.630$ and $z_2 = 0.262$.

The calculated band structures along some high symmetry lines are shown in figure 1. For convenience, the Fermi level $E_F = 0$ is taken. Before discussing the band structures, we first examine the bonding nature. In CaAl_2Si_2 , there are two AlSi layers per unit cell, each one having in-plane sp_{xy}^2 bonding and out-of-plane sp_z bonding. These orbitals interact between the layers to form a bound AlSi double layer. In the upper part of the valence bands there are

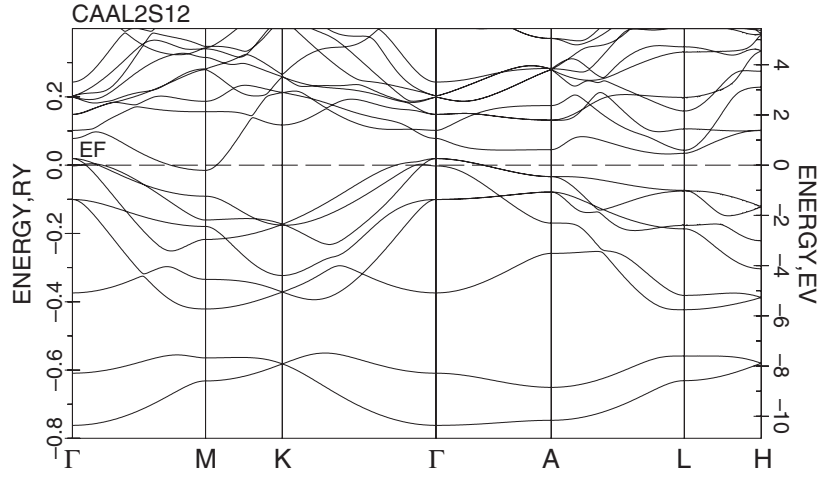


Figure 1. Band structure for CaAl₂Si₂, in which the dashed line stands for the Fermi level.

two sp_z hybrid bands (π bands) and four sp_{xy}^2 hybrid bands (σ bands). The π bands have a 3D character, while the doubly degenerate σ bands have only weak dispersions along the Γ –A direction, exhibiting a quasi-2D character. The two π bands and two of the four σ bands are filled, while the other two σ bands cross over E_F . On the other hand, the Ca d-like conduction band is found to cross over E_F , so there is a small overlap between the valence bands and conduction band. It then follows that CaAl₂Si₂ is a semimetal, its Fermi surface consisting of two small hole pockets centred at the Γ point and one small electron pocket centred at the M point. According to our calculation, the density of electrons is about 0.017 electrons per formula unit, compensated by an equal number of holes. This conclusion is consistent with electrical resistivity and Hall coefficient measurements of CaAl₂Si₂ [10], in which both electrons and holes make contributions to the transport properties.

The total density of states (DOS) and atom partial DOS of CaAl₂Si₂ are presented in figure 2. It can be seen that E_F is just located at the dip of the total DOS curve. There is a hybridization of Ca 3d and (Al, Si) 2p in the region of the valence band. The bottom of the conduction band is mainly of Ca 3d character, while the top of the valence band comes mainly from Si 2p because of its electronegative valency effect. There appears little Al DOS in the vicinity of E_F . The total DOS at the Fermi level is 0.42 eV⁻¹ for each cell, which is much smaller than that for the CaAlSi compound (1.09 eV⁻¹ in [5]). This conclusion is consistent with the transport measurements. The experimental results of Imai *et al* [10] showed that both the electrical resistivity and the Hall coefficient of CaAl₂Si₂ are greater than those of CaAlSi by one order of magnitude, suggesting that the number of carriers in CaAl₂Si₂ is less than the number in CaAlSi.

For the case where the charge carriers consist of holes and electrons, the Hall coefficient R_H and the resistivity ρ can be written as follows in the drift velocity approximation [10, 18]:

$$R_H = \frac{n_h \mu_h^2 - n_e \mu_e^2}{e(n_h \mu_h + n_e \mu_e)^2} = \frac{n_h - n_e b^2}{e(n_h + n_e b)^2} \quad (1)$$

$$\frac{1}{\rho} = en_e \mu_e + en_h \mu_h \quad (2)$$

where n_e and n_h are the carrier densities of electrons and holes, μ_e and μ_h are the mobilities of electrons and holes, and b is the ratio of the mobility of electrons to that of holes μ_e/μ_h .

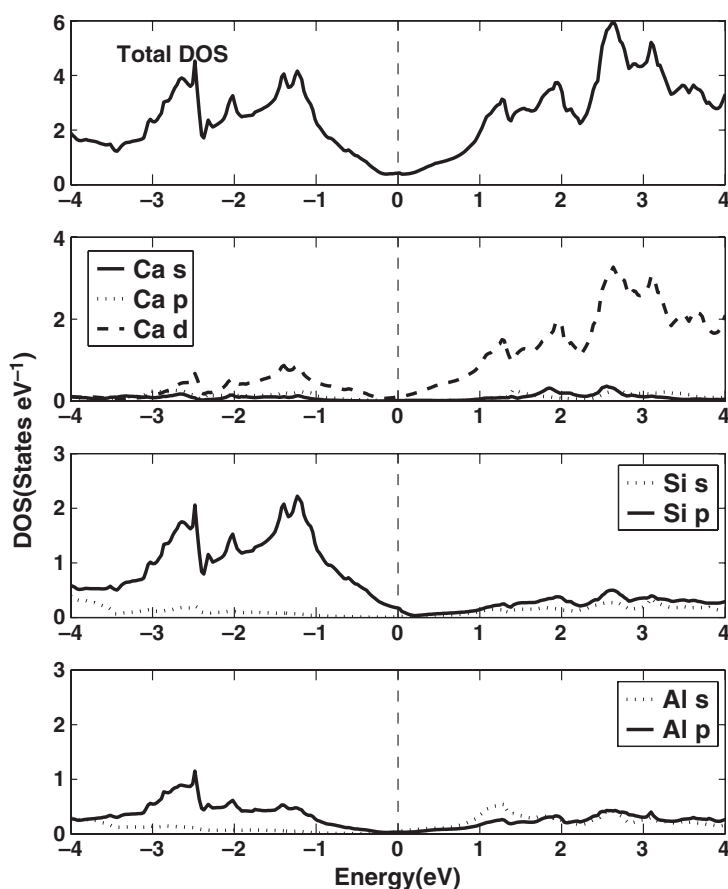


Figure 2. Total and atom partial DOS for CaAl_2Si_2 , in which the vertical dashed line stands for the Fermi level.

The Hall coefficient R_H of CaAl_2Si_2 measured by Imai *et al* [10] is positive below 150 K while it is negative above 150 K, so they suggested the possibility that n_e and/or b^2 becomes larger with increasing temperature. However, our electronic structure calculations clearly show that CaAl_2Si_2 is a compensated metal having an equal number of electrons and holes. After performing a finite-temperature electronic structure calculation ($T = 300$ K) for CaAl_2Si_2 , we find that the position of E_F shows little change but the density of electrons is slightly increased to 0.019 electrons per formula unit. The density of electrons is still equal to that of holes at finite temperature. Our results clearly show that the change of sign of R_H is not caused by the different carrier densities but by the different temperature dependences of the mobilities of the two types of carriers. The sign reversal in R_H with increasing temperature was also reported for other semimetals such as CaSi_2 [19] and TiSi_2 [20]. So it can be considered as typical behaviour of a semimetal.

The measured resistivity ρ of CaAl_2Si_2 is found to first increase with temperature, and then almost saturate around 200 K [10]; its temperature dependence does not obey Bloch–Grüneisen theory. This behaviour of ρ may be qualitatively understood on the basis of the semimetallic band structure of CaAl_2Si_2 . The resistivity ρ defined by equation (2) is a function of mobilities and carrier densities. Both μ_h and μ_e decrease with increasing temperature, so ρ has a metallic

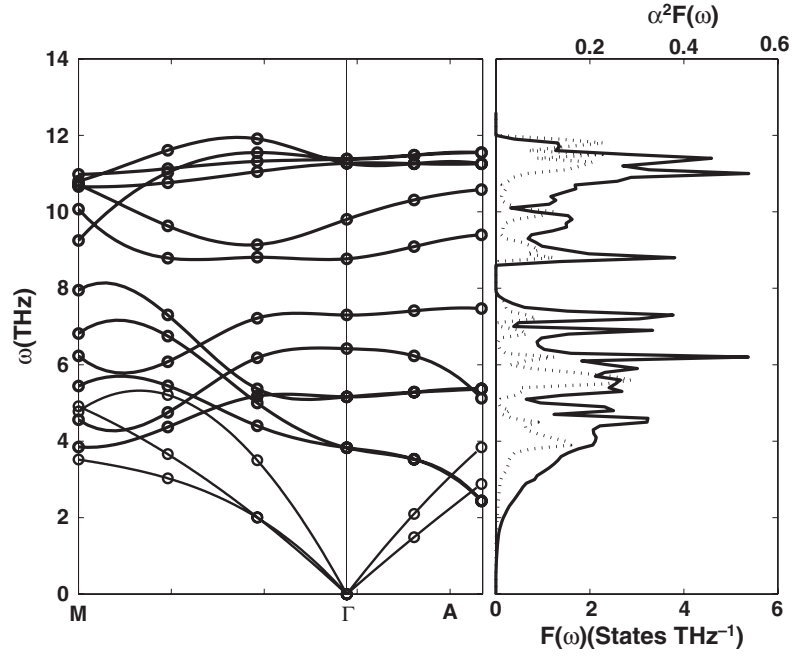


Figure 3. Left: the calculated phonon dispersion curves for CaAl_2Si_2 . Right: the phonon density of states $F(\omega)$ (solid lines) and Eliashberg spectral function $\alpha^2 F(\omega)$ (dotted lines).

Table 1. The calculated frequencies (THz) of the optical modes at Γ in CaAl_2Si_2 .

E_g	E_g	E_u	E_u	A_{1g}	A_{1g}	A_{2u}	A_{2u}
3.83	11.38	5.16	11.27	7.30	8.77	6.42	9.80

temperature dependence at low temperatures. As temperature is further increased, the increase of the number of charge carriers due to thermal excitations will compensate the decrease of mobilities, so ρ exhibits a weak dependence on temperature.

The calculated phonon dispersions and corresponding phonon DOS $F(\omega)$ for CaAl_2Si_2 are shown in figure 3. It is found that the phonon modes can be divided into two groups in frequency. The gap in the phonon DOS is found to be about 0.8 THz. Following Stokes and Hatch [21], the Γ point modes in CaAl_2Si_2 may be decomposed as $2A_{1g} + 3A_{2u}$ polarized along the c axis and $2E_g + 3E_u$ polarized in the basal plane. The $2E_g$ and $2A_{1g}$ modes are Raman active, while the $2E_u$ and $2A_{2u}$ modes are infrared active. In addition to acoustic modes, there are eight distinct optical modes, whose frequencies are listed in table 1. The in-plane Al–Si puckering mode E_u and in-plane Al–Si bond-stretching modes E_g are at high frequencies (about 11.3 THz).

In the phonon structure calculations for CaAlSi [5, 7], the B_{1g} mode (Al against Si along the z direction) is very soft, and there appear imaginary frequencies at some \mathbf{q} points. The strong instability for the B_{1g} mode is the origin of the formation of a superstructure in CaAlSi , as observed by Ghosh *et al* [22]. For CaAl_2Si_2 , however, no singularity appears in the phonon spectrum of figure 3, indicating that the CaAl_2Si_2 structure is stable.

In what follows we calculate the EP interaction in an effort to understand the vanishing of superconductivity in CaAl_2Si_2 compounds. The Eliashberg spectral function $\alpha^2 F(\omega)$ is

given by [23]

$$\alpha^2 F(\omega) = \frac{1}{N(E_F)} \sum_v \sum_{\mathbf{k} \mathbf{q} \mathbf{j} \mathbf{j}'} |g_{\mathbf{k}+\mathbf{q} \mathbf{j} \mathbf{k} \mathbf{j}}^{\mathbf{q} \mathbf{v}}|^2 \delta(\epsilon_{\mathbf{k} \mathbf{j}} - \epsilon_F) \delta(\epsilon_{\mathbf{k}+\mathbf{q} \mathbf{j}'} - \epsilon_F) \delta(\omega - \omega_{\mathbf{q} \mathbf{v}}), \quad (3)$$

where $g_{\mathbf{k}+\mathbf{q} \mathbf{j} \mathbf{k} \mathbf{j}}^{\mathbf{q} \mathbf{v}}$ is the EP matrix element, which can be determined self-consistently using linear response theory [13]. The EP coupling constant λ and the logarithmically averaged frequency ω_{ln} are obtained by evaluating

$$\lambda = 2 \int_0^\infty \omega^{-1} \alpha^2 F(\omega) d\omega = \sum_{\mathbf{q} \mathbf{v}} \lambda_{\mathbf{q} \mathbf{v}}, \quad (4)$$

$$\omega_{\text{ln}} = \exp\left(\frac{1}{\lambda} \sum_{\mathbf{q} \mathbf{v}} \frac{\gamma_{\mathbf{q} \mathbf{v}} \ln \omega_{\mathbf{q} \mathbf{v}}}{\pi N(E_F) \omega_{\mathbf{q} \mathbf{v}}^2}\right). \quad (5)$$

The calculated Eliashberg spectral function $\alpha^2 F(\omega)$ is shown in the right panel in figure 3. We can see from figure 3 that the phonon DOS $F(\omega)$ (solid line) and $\alpha^2 F(\omega)$ (dotted line) differ slightly. The calculated electron–phonon coupling constant λ is equal to 0.17, indicating that the EP interaction is very weak in CaAl_2Si_2 . The calculated logarithmically averaged frequency ω_{ln} is 274 K. Using the McMillan expression for T_c and taking a typical value of $\mu^* = 0.15$, we obtain $T_c \simeq 1.5$ mK. In fact, such a small λ makes McMillan's equation come near to the pole. The present calculated result indicates that CaAl_2Si_2 is unlikely to be superconducting, in agreement with the experimental observation [9].

Finally, let us make a comparison as regards superconductivity between CaAl_2Si_2 and CaAlSi by analysing their different electronic and phonon structures. It is well known that there are three main factors determining T_c for the BCS-type superconductors: the electronic DOS at the Fermi energy $N(E_F)$, the logarithmic average frequency ω_{ln} and the strength of the electron–phonon coupling. As has been discussed above, $N(E_F)$ for CaAl_2Si_2 is much smaller than that of CaAlSi . As regards the phonon structure, while there is a soft mode in CaAlSi , there is not in CaAl_2Si_2 . Both the soft phonon mode and the high electronic DOS at the Fermi level are favourable to superconductivity. Although the soft mode leads to a smaller ω_{ln} , it makes a large contribution to λ . As pointed out in our previous work [5, 7], the soft mode plays a dominant role in the superconductivity of CaAlSi .

In summary, the electronic structure, phonon spectrum and EP interaction of CaAl_2Si_2 have been calculated using a full-potential, density-functional-based method. It is found that CaAl_2Si_2 is a semimetal, in which there is a small overlap of two valence bands and one conduction band, and its carriers are both electrons and holes. Its Fermi surface includes two small hole pockets centred at the Γ point and one small electron pocket centred at the M point. The Fermi level is just located at the dip of the DOS curve, at which the DOS is small. The peculiar transport behaviour of CaAl_2Si_2 is attributed to its semimetallic band structure. There is no singularity found in the phonon curves, and so the CaAl_2Si_2 structure is stable. The calculated EP coupling strength is very small, indicating that CaAl_2Si_2 is unlikely to be superconducting.

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