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Low temperature properties of calcium mono- and disilicides

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Abstract

Low temperature electronic and lattice properties of polycrystalline CaSi and $CaSi_2$ have been studied by means of specific heat, resistivity, Hall effect and magnetoresistance measurements. Although these metals have comparable density of electronic states at the Fermi level (0.42 states/eV atom and 0.19 states/eV atom for CaSi and $CaSi_2$ respectively) the resistivity of $CaSi_2$ ($\rho_{273\ K}$=33.2 μΩ cm) is almost one order of magnitude lower than that of CaSi ($\rho_{273\ K}$=282 μΩ cm). The analysis of magnetotransport properties suggests that both these materials are compensated metals and the estimated density of carriers is one order of magnitude higher for $CaSi_2$ than for CaSi. In agreement with electronic band structure calculations we concluded that electrons of the Ca d-band play a dominant role for the charge transport. The Debye temperature estimated from different experiments is higher for $CaSi_2$ than for CaSi and this confirms that the Ca–Si interaction increases as the Si concentration increases. © 1998 Elsevier Science S.A.

Keywords: Silicides; Specific heat; Transport properties

1. Introduction

Despite the fact that it is not easy to handle alkaline earth metals, it is possible to prepare, with special care, high purity silicides of these metals suitable to study bulk properties [1,2]. From a fundamental point of view the study of these compounds provides complementary information on the silicon–metal bond: the alkaline earth metals do not contain d electrons and one expects a rather different behaviour from that of transition metal silicides.

Studies on calcium silicides also are of a particular importance because $CaSi_2$ can be epitaxially grown on silicon yielding heterojunctions which have a technological interest [3]. A great deal of work has been devoted to calculate the electronic structures of several calcium compounds [4–8]. Results of calculations generally are in good agreement with spectroscopic investigations: Bremsstrahlung isochromat spectroscopy [5], synchrotron-radiation photoemission [6], inverse photoemission [7] and Auger valence electron spectroscopy [9]. A special attention has also been paid to the surface of the material [10] and to its interface with silicon [11]. No systematic studies have been, however, performed on the properties of the bulk material, although this type of investigation provided deep insights in the fundamental properties of transition metal silicides [12,13].

Ca and Si can form three compounds: $CaSi_2$, CaSi and Ca_2Si. The two former are metals and the later is expected to be a semiconductor [6]. In this work we report measurements of specific heat and transport properties of polycrystalline CaSi and $CaSi_2$ at low temperature. We shall compare our results to those obtained on other metallic disilicides and to band structure calculations.

2. Sample preparation

The two silicides were prepared by melting Ca and Si in the stoichiometric proportion in tantalum crucibles closed by arc welding under inert gas atmosphere. Samples were annealed for 7 days at 800°C (CaSi) or 900°C ($CaSi_2$) in order to obtain homogeneous single phase intermetallic compound. X-ray diffraction and micrographic analysis were used to check the structure of these compounds and spurious phases were estimated to be less than 3%. The crystal structures are quite complex with two molecules

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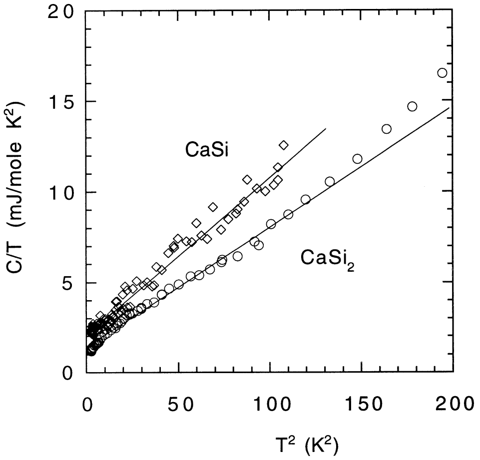

Fig. 1. Specific heat of CaSi and $CaSi_2$ measured in the temperature range $1.6<T<15$ K and plotted as C/T vs T^2.

per unit cell [14]. CaSi has a base centred B33 (CrB) orthorhombic Bravais lattice with a=4.59 Å, b=10.795 Å and c=3.91 Å. The space group is *Cmcm*. The lattice of $CaSi_2$ is trigonal C12 with a=10.4 Å and α=21°30′. The space group is $R\bar{3}m$.

3. Results

Heat capacity measurements were performed between 1.6 K and 15 K by a quasi-adiabatic method with typical temperature pulses equal to 2% of the bath temperature [15]. Polycrystalline samples were cut in disk form and they have a typical mass of 200 mg. The specific heat (C) of both CaSi and $CaSi_2$ is shown in Fig. 1 in a conventional C/T vs T^2 plot. It is clear from this graph that the electronic γ value (i.e the intercept of the C/T vs T^2 straight line) as well as the lattice term β (corresponding to the slope) of CaSi are larger than those of $CaSi_2$. A linear fit of the data allows to determine the γ and β coefficients which are reported in Table 1. For the fitting procedure we used only data below 10 K, that is well below the Debye temperature. For $CaSi_2$ we may indeed observe a departure from a linear C/T vs T^2 behaviour above 10 K suggesting that the simple βT^3 Debye approximation does not work well for $T>10$ K. From the γ values we estimated the electronic density of states at the Fermi level $N_0(1+\lambda)$ calculated by the conventional Sommerfeld formula:

$$N_0(1+\lambda)=\frac{3\nu\gamma}{\pi^2 N_A k_B^2}$$

where γ is in eV/K^2 mol, ν is the number of molecules per unit cell ($\nu=2$ for both compounds), N_A the Avogadro number and k_B the Boltzmann constant. The renormalization factor $(1+\lambda)$ accounts for the electron–phonon coupling and we expect this parameter to be close to one (there is no indication of strong electron–phonon coupling in these compounds). It should be noted that if we normalized the density of electronic states per atom, it turns out that N_0 is smaller for $CaSi_2$ than for CaSi (see Table 1).

The Debye temperature is deduced from the β coefficient by the expression:

$$\theta_D=\left[\frac{12}{5}\frac{rR\pi^4}{\beta}\right]^{1/3}$$

where R is the gas constant and r the number of ions per molecule. In low temperature experiments $r=1$ is usually taken assuming that only 3 average phonon branches are active while in real materials there are 3r of them. The latter choice turns out to be more convenient if one wants to compare θ_D with experiments at room temperature as we discussed in length in [13]. Results are reported in Table 1 in which we also report θ_D deduced in the same manner for the parent metallic disilicides $TiSi_2$ [13] and VSi_2 [15] and the Ca and Si constituting elements [16].

The resistance was measured by a four-probe ac method. Samples were cut in a flat parallelepiped shape with typical dimensions $4\times2\times1$ mm^3 and electrical leads were attached with silver paint in the Van der Pauw or a linear array configuration. Due to the small dimension of the samples, the form factor was determined only with a poor accuracy (especially for CaSi) and this gives an uncertainty as large as 20% in absolute value of the resistivity. The magnetic field ($B_{max}=7.8$ T), for magnetoresistance and Hall measurements, was applied perpendicularly to the plane of the current. For Hall measurements we systematically reverse the magnetic field and average data

Table 1
Main characteristics obtained by the analysis of the specific heat

	γ (mJ/K^2 mol)	β (mJ/K^4 mol)	$N_0(1+\lambda)$ states/eV atom	N_0 calc. states/eV atom	θ_D (K) $r=1$	θ_D (K) $r=2$ or 3
Ca					229	
CaSi	2.02±0.1	0.090±0.01	0.42	0.399	278	351
$CaSi_2$	1.32±0.1	0.068±0.01	0.19	0.304	306	440
$TiSi_2$	3.35	0.0201	0.47			662
VSi_2	6.08	0.020	0.86			665
Si					645	

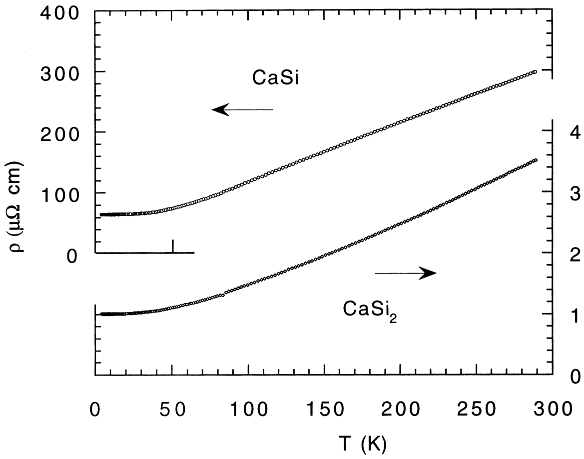

Fig. 2. Temperature dependence of the resistivity ρ of CaSi and $CaSi_2$.

were taken with the two orientations of B as described in [13].

In Fig. 2 the resistivity of CaSi and CaSi is plotted as a function of temperature and the salient values are reported in Table 2. Both compounds exhibit metallic behaviour with resistivity residual ratio $\rho_{(273\ K)}/\rho_{(4.2\ K)}$~4. The resistivity ρ of CaSi is higher than that of $CaSi_2$ by a factor ~8 in the whole range of temperature (4.2 K to 300 K). Our data for $CaSi_2$ are similar to those reported for single crystal material [2]. We note, however, that the resistivity ρ of our $CaSi_2$ sample is smaller by a factor ~2 than that of the single crystal studied in [2]. This fact, as well as the poor $\rho_{(273\ K)}/\rho_{(4.2\ K)}$ ratio, seems to be related to the high value of the residual resistivity ρ_0 which, in turn, may be due to a high density of defects present in the available bulk materials.

The thermal variations of ρ are quite different for the two compounds. The upwards curvature of ρ vs T is restricted within the low-temperature range ($T<100$ K) for CaSi, while it extends up to room temperature for $CaSi_2$ (see Fig. 2). This different behaviour is also apparent if we fit the ideal resistivity $(\rho-\rho_0)$ with the Bloch–Grüneisen law:

$$\rho = \rho_0 + A(T/\theta_D)^n \int_0^{\theta_D/T} \frac{z^n dz}{(e^z-1)(1-e^{-z})} \tag{1}$$

The best fit is obtained with $n=5$ for CaSi while $n=3$ is used for $CaSi_2$, as it can be seen in Fig. 3 where $(\rho-\rho_0)$ is plotted as a function of temperature. It is also evident in Fig. 3 that the initial thermal variation of $(\rho-\rho_0)$ goes as T^5 for CaSi while it varies as T^3 for $CaSi_2$. The corresponding values of θ_D estimated by this procedure are reported in Table 2. For a $CaSi_2$ single crystal, Hirano [2] obtained the best fit with the Bloch–Grüneisen expression (1) with $n=3$ and the θ_D value is in good agreement with our analysis, too.

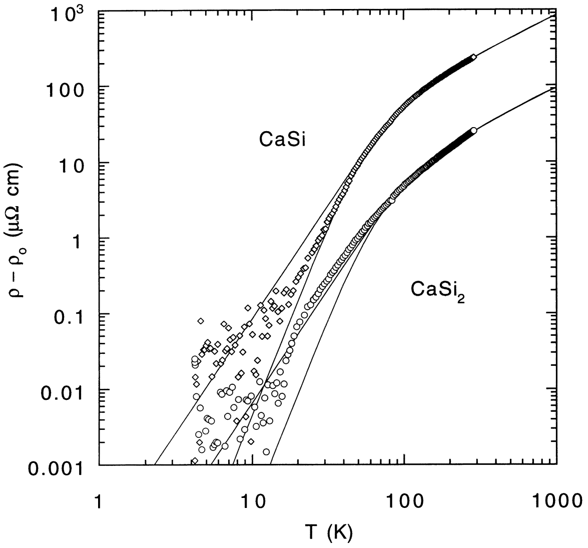

Fig. 3. Comparison of the temperature dependence of the ideal resistivity $(\rho-\rho_0)$ with the Bloch–Grüneisen curves.

The temperature dependence of the Hall coefficient R_H is shown in Fig. 4 for the two calcium silicides. R_H is

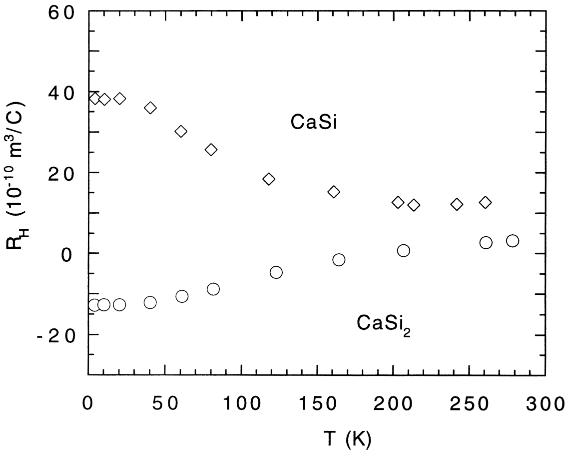

Fig. 4. Temperature dependence of the Hall coefficient R_H of CaSi and $CaSi_2$.

Table 2
Main characteristics obtained by the analysis of the transport properties

	$\rho_{4.2\ K}$ (μΩ cm)	$\rho_{273\ K}$ (μΩ cm)	$\rho_{293\ K}/\rho_{4.2\ K}$	θ_D (K) $n=3$	θ_D (K) $n=5$	α^2 (T^{-2})	R_{Hh} 10^{-10} m^3 C^{-1}	$n_h=n_e$ 10^{20} cm^{-3}
CaSi	65	282	4.6	383	311	15×10^{-4}	500	1.2
$CaSi_2$	10.1	33.2	3.5	456	363	3×10^{-4}	35	18

positive for CaSi in the whole range of temperature although it decreases as T increases. For $CaSi_2$, R_H is negative at low temperature and (small and) positive at room temperature. This behaviour is similar to that observed for most metallic silicides [13,17,18] and it is characteristic of compensated metal for which electrons and holes contribute in an equivalent way to the conductivity. Electronic band structure calculations performed by Fahy and Hamann [8] have shown that the Fermi surface of $CaSi_2$ actually consists of a hole pocket and smaller pockets of heavier electrons and this support our interpretation of the Hall coefficient. Hirano [2] found a (small) negative $R_H = -10\times10^{-10}$ m^3 C^{-1} at room temperature for a $CaSi_2$ single crystal. This different result can be, however, ascribed to different compensation (a slightly different mobility, for instance) in materials of different quality. The shape of the Fermi surface of CaSi has not be reported yet, to our knowledge. However, the temperature dependence of the Hall coefficient that we have found suggests that a sort of compensation between two different type of carriers is also present in this compound.

The magnetoresistance $\Delta\rho/\rho$ measured at 4.2 K is shown in Fig. 5. $\Delta\rho/\rho$ varies as B^2 up to 7.8 Tesla for $CaSi_2$ and up to ~5 T for CaSi which exhibits a larger magnetoresistance. Based on the previous considerations, we interpret the magnetoresistance data within the framework of the simplest model for compensated metal [19], assuming that holes and electrons have the same concentration $n_h = n_e$ and identical effective mass and relaxation time (or mobility) at the same temperature. The magnetoresistance $\Delta\rho/\rho$ can be expressed as follows:

$$\frac{\Delta\rho}{\rho} = \alpha^2 B^2$$

with

$$R_{Hh} = -R_{He} = \frac{1}{n_h e} = 2\alpha\rho$$

where R_{Hh} and R_{He} are the Hall contribution for holes (with sign +) and for electrons (with sign −) respectively. R_{Hh} an n_h calculated with equation (2) are shown in Table 2. In this very simple model the Hall coefficient should be zero. If we take into account possible difference in the effective mass or in the mobility of the two types of carriers, R_H is given by:

$$R_H = \frac{(\sigma_h^2 R_{Hh} + \sigma_e^2 R_{He})}{\sigma^2}$$

where σ_h and σ_e are the contribution to the conductivity σ of holes and electrons respectively. As expected $R_{Hh}(-R_{He})$ deduced from magnetoresistance is much larger than the experimental R_H (see Table 2) while the thermal variation of the Hall coefficient can be ascribed to the temperature dependence of the mobility of the two types of carriers. Similarly to what occurs for the conductivities, the carrier concentration reported in Table 2 is larger for $CaSi_2$ (1.8×10^{21} cm^{-3}) than for CaSi (1.2×10^{20} cm^{-3}).

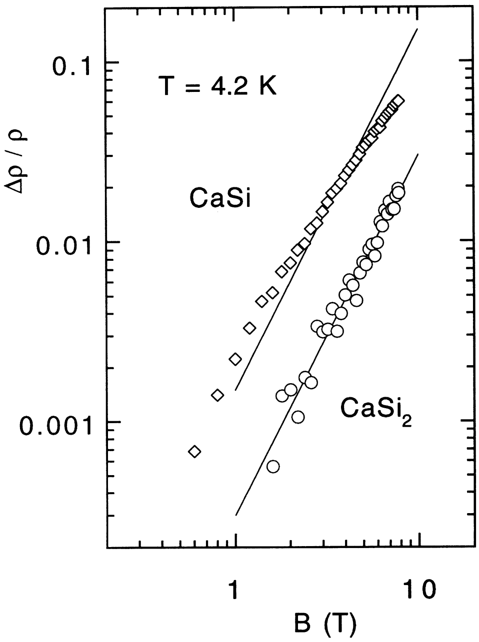

Fig. 5. Magnetic field dependence of the magnetoresistance measured at 4.2 K. Straight lines represent the B^2 variation.

4. Discussion

Calculations of the density of electronic states for metal silicides from Ca–Si to Cu–Si have been performed for isostructural mono-, di- and trisilicides by Weaver et al. [4]. They showed that the d-bands dominate the density of states and move from above the Fermi level E_F (for Ca silicides) to below E_F as the atomic number of the metals increases. Electronic bands with s- or p-character are located at the same energy for all the metals of the 3d series. The p–d combinations, which result from hybridisation of metal-derived 3d states with Si-derived 3p states, determine the stability of the compound and they have a bonding character from Ti up to the end of the series.

The character of the Ca–Si bond and its role in the determination of the electronic structures of calcium silicides (Ca_2Si, CaSi and $CaSi_2$) was deeply studied by Bisi et al. [6]. They found that a covalent character, together with some ionic contribution, is present in the Ca–Si bond and that the strength of this interaction increases with Si concentration. Differently from what occurs in other 3d metal silicides in which only the d-states of metals interact with Si, all the s–p–d-states of Ca interact with Si states. Moreover it turns out that the occupation of the d-states of Ca increases as the Si concentration increases (i.e. from Ca_2Si to $CaSi_2$). Fahy and Hamann [8] calculated the electronic properties of several polymorphs of calcium disilicide which differ by the stacking sequences of the crystallographic plans. They found little dependence of the band structure on these different arrangements. They have also shown, as noted above, that the Fermi surface of $CaSi_2$ consists of Ca d-like electron conduction band and Si_p–Ca_d hybridized valence bands of holes. Spectroscopic experiments are in agreement with these theoretical results and in particular they confirmed covalent character of the Ca–Si bond and, at the same time, they evidenced some ionic character of this bond [4–7]. The low temperature investigation reported in this work provides complementary information on these compounds.

In Table 1, we report the density of electronic states $N_0(1+\lambda)$ evaluated from the γ coefficient of the specific heat and we may compare this value with that calculated by Bisi et al. [6]. Experimental and calculated N_0 values are in very good agreement for CaSi while the experimental N_0 value is smaller than that calculated by Bisi and coworkers for $CaSi_2$. Van de Walle [11] calculated a N_0 quite close to what we estimate from our experiments (0.19 states/eV atom) for $CaSi_2$. It should be noted that results of calculations show that the density of states rapidly varies near the Fermi level thus the agreement between experiments and calculations can be considered in any case within the accuracy of the respective techniques. We already noted that the density of states N_0 (normalized per atom) is larger for CaSi than for $CaSi_2$ and this experimental result confirms the expectations of Bisi et al. [6]. The different N_0 values found for CaSi and $CaSi_2$ result from a different filling of the electronic bands and the larger N_0 found for CaSi than for $CaSi_2$ does not give a more metallic character to this compound as it turns out from the analysis of the transport properties. We observe that the γ coefficient, and consequently N_0, is smaller for $CaSi_2$ than for $TiSi_2$ and VSi_2. This result is in good agreement with the calculations by Weaver et al. [4] who predicted that, filling the d-band by moving from Ca to heavier 3d metals, the density of the d-states is expected to attain its maximum value for V-silicide.

From the analysis of the transport properties it turns out that the resistivity of $CaSi_2$ is lower than that of CaSi by almost one order of magnitude. The analysis of the Hall effect and magnetoresistance gives a density of charge carriers one order of magnitude larger for $CaSi_2$ than for CaSi and this is probably the origin of the lower resistivity of the former. For compounds with more than one atom per unit cell, like silicides, it is difficult to achieve an accuracy in the calculations of the electronic bands better than 1 eV, while reliable quantitative predictions for transport coefficients generally require a larger precision. Thus, here we concentrate on a qualitative comparison. We already noted that the temperature dependence of the Hall coefficient observed in both CaSi and $CaSi_2$ is evidence that both these compounds are compensated metals. Band structure calculations showed that electron like bands essentially arise from the Ca d-states while valence hole-like bands arise from the Si_p–Ca_d hybridization. Moreover the filling of the d-states is expected to increase as the Si concentration increases. Holes dominate in CaSi according to the fact that the Hall coefficient is positive in the whole range of temperature. As the electron d-band is further filled, moving from CaSi to $CaSi_2$, the Hall coefficient can be dominated by the negative type of carriers and this is what we actually found. In summary, although these two compounds have similar density of states at E_F, the charge carriers that seem to dominate the transport properties come from the electron Ca d-band. This result may give some insight for the understanding of the mechanism of the Ca/Si barrier.

In Tables 1 and 2 we report the Debye temperature estimated for the two Ca silicides from different experiments. Although the value of θ_D (for the same compound) depends on the analysis of data, if we compare θ_D values obtained from the same experiment, significant and systematic changes of the Debye temperature are in evidence among different materials. Taking data obtained from the specific heat ($r=1$), for instance, it turns out that θ_D is smaller for CaSi ($\theta_D=278$ K) than for $CaSi_2$ ($\theta_D=306$ K) and these are in between the values of the pure constituent elements: Ca ($\theta_D=229$ K) and Si ($\theta_D=645$ K). If we consider the series of the metal disilicides, θ_D (calculated from specific heat data, with $r=2$ or 3) increases when moving from $CaSi_2$ to VSi_2.

Phonon frequencies, and consequently θ_D, are proportional to $\sqrt{\alpha/M}$, where M is the mass of atoms and α is the elastic constant [18]. We have recently demonstrated the $1/\sqrt{M}$ dependence of θ_D in the isoelectronic and isostructural silicides VSi_2, $NbSi_2$ and $TaSi_2$ [15]. Here we restrict our analysis to 3d-metal silicides for which the mass changes only slightly and we may therefore neglect the variation of θ_D with M. If we also neglect some structural differences, we may simply relate the different θ_D values to the stiffness of materials and have a comparison of the strength of the bond.

The higher θ_D value observed for Ti- and V-disilicide as compared to that of $CaSi_2$ (see Table 1) is probably related to the increasing strength of the silicon p-metal d bond for the former silicides. According to the calculation of Bisi et al. the Ca–Si bond has a covalent character and its strength increases as the Si concentration increases. This is the origin of the higher θ_D that we estimated for $CaSi_2$ than for CaSi. An immediate proof of the different stiffness of materials is found in the experiments: While $CaSi_2$ is a quite robust material, it is difficult to handle CaSi and Ca_2Si (not studied in this work).

Finally it is worth reminding the reader that superconductivity was reported for two alkaline earth metal disilicides: $CaSi_2$ in the body-centred tetragonal form is superconducting at 1.58 K [20] and trigonal $BaSi_2$ is a superconductor with an onset temperature of 6.8 K [21]. These structures are metastable and have to be synthesised under pressure. The trigonal structure of $BaSi_2$ is almost the same as $CaSi_2$. However, no superconducting transition was observed down to 0.32 K in $CaSi_2$ [20]. We have pursued this search on our samples of $CaSi_2$ and CaSi by a resistive method. No sign of superconductivity was found down to 30 mK.

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