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# Heat capacity and thermodynamic properties of some Ca silicides

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## Abstract

The heat capacities of three Ca compounds, namely  $\text{CaSi}_2$ ,  $\text{Ca}_3\text{Si}_4$  and  $\text{Ca}_{14}\text{Si}_{19}$ , were measured in the 3–300 K temperature range by adiabatic calorimetry. No thermal anomalies were found in the whole temperature range. In the three Ca silicides, from an analysis of the low temperature data ( $T < 40$  K), a power law lower than three in the lattice heat capacity behaviour was observed and tentatively ascribed to the layered structure of the compounds, in agreement with structural informations. From heat capacity data the thermodynamic functions entropy, enthalpy and Gibbs energy were calculated at 298 K. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Calcium silicides; Adiabatic calorimetry; Heat capacity; Thermodynamic functions

## 1. Introduction

Ca-silicides were widely investigated in the past with respect to their electronic properties. These were analysed through experimental techniques (Auger Electron Spectroscopy, Bremsstrahlung Isochromat Spectroscopy, Inverse Photoemission), as well as from theoretical studies performed by self-consistent calculations of the electron states carried out with the Andersen linear muffin-tin orbital method [1–3]. More recently, the discovery of superconductivity at 14 K under pressure in a new polymorph of the  $\text{CaSi}_2$  stoichiometry [4] and the determination of the crystal structure of the semiconductor  $\text{Ca}_{14}\text{Si}_{19}$  [5], induced us to re-analyse the Ca–Si phase diagram in the whole composition range [6].

However, up to now, no thermodynamic measurements have been performed on the Ca-silicides. For this reason we present here the results concerning measurements of the heat capacity of the  $\text{CaSi}_2$ ,  $\text{Ca}_3\text{Si}_4$  and  $\text{Ca}_{14}\text{Si}_{19}$  phases in a wide temperature range (3–300 K) as well as some calculations to obtain thermodynamic informations at standard temperature (298 K) on enthalpy ( $H_{298\text{ K}}^0 - H_{0\text{ K}}^0$ ), entropy ( $S_{298\text{ K}}^0$ ) and Gibbs energy ( $G_{298\text{ K}}^0 - G_{0\text{ K}}^0$ ).

## 2. Experimental

Elemental Ca (99.5 wt.%) and Si (99.999 wt.%) were used for direct synthesis of the compounds. Weighed amounts of the elements (total mass of about 2 g) were closed, due to the high vapor pressure of Ca, in a tantalum crucible, then heated in a high frequency induction furnace and shaken to ensure homogenization. The  $\text{CaSi}_2$  compound was then cooled down to room temperature, while for the  $\text{Ca}_3\text{Si}_4$  and the  $\text{Ca}_{14}\text{Si}_{19}$  phases a quenching procedure from the liquid state was applied. The samples were then sealed in quartz tubes under reduced Ar pressure and annealed:  $\text{CaSi}_2$  at 1273 K for 3 days,  $\text{Ca}_3\text{Si}_4$  at 1173 K for 20 days and  $\text{Ca}_{14}\text{Si}_{19}$  at 1333 K for 25 days.

Metallographic examination performed on the three samples with standard techniques, showed that they were all single phase.

X-ray analysis was carried out by means of a Guinier-Stoe camera (Cu  $K\alpha$  radiation) with silicon as internal standard. Lattice parameters agree well with those of Ref. [6].

A commercial Oxford Maglab System<sup>2000</sup> measurement platform was used to measure the heat capacity (adiabatic method) of the compounds (cylinders of about 0.6 grams each) in the 3–300 K temperature range under a dynamic vacuum better than  $10^{-6}$  mbar. A calibrated Cernox-type thermometer from Lake Shore was used as temperature sensor. The estimated error in the heat capacity experimen-

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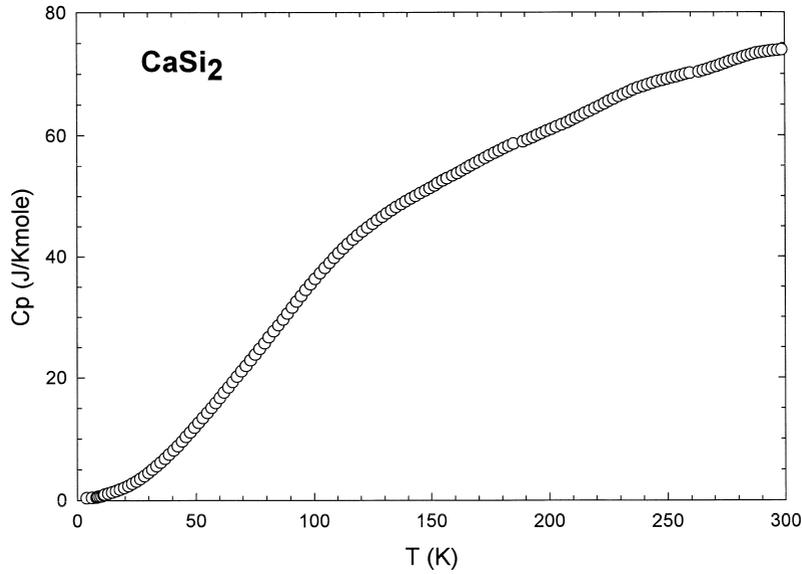


Fig. 1. Heat capacity of  $\text{CaSi}_2$  in the 3–300 K temperature range.

tal data is about three per cent in the whole temperature range.

### 3. Results and discussion

In Figs. 1–3 the heat capacities of the three compounds  $\text{CaSi}_2$ ,  $\text{Ca}_3\text{Si}_4$  and  $\text{Ca}_{14}\text{Si}_{19}$  respectively, are reported. For all compounds the heat capacity increases monotonically up to 300 K. No evidence of structural transitions or thermal anomalies was observed. At 298 K, the heat capacity values of the three compounds are 73.9 J/K mol ( $\text{CaSi}_2$ ), 179 J/K mol ( $\text{Ca}_3\text{Si}_4$ ) and 985 J/K mol ( $\text{Ca}_{14}\text{Si}_{19}$ ).

Below 40 K the hypothesis of comparable values of  $C_p$  and  $C_v$  seems reasonable, so the experimental data were firstly tentatively analysed in the framework of the Debye theory which claims a  $T^3$  dependence of the lattice heat capacity on temperature, but the fitting procedure was unsatisfactory. The best fit was obtained for the three phases using the following equations:

$$C_p(T)_{\text{CaSi}_2} = A \cdot T^{1.87 \pm 0.02} \quad A = (8.0 \pm 0.6) \cdot 10^{-3}$$

$$C_p(T)_{\text{Ca}_{14}\text{Si}_{19}} = A \cdot T^{2.09 \pm 0.01} \quad A = (4.7 \pm 0.3) \cdot 10^{-2}$$

$$C_p(T)_{\text{Ca}_3\text{Si}_4} = A \cdot T^{2.67 \pm 0.02} \quad A = (8.7 \pm 0.5) \cdot 10^{-4}$$

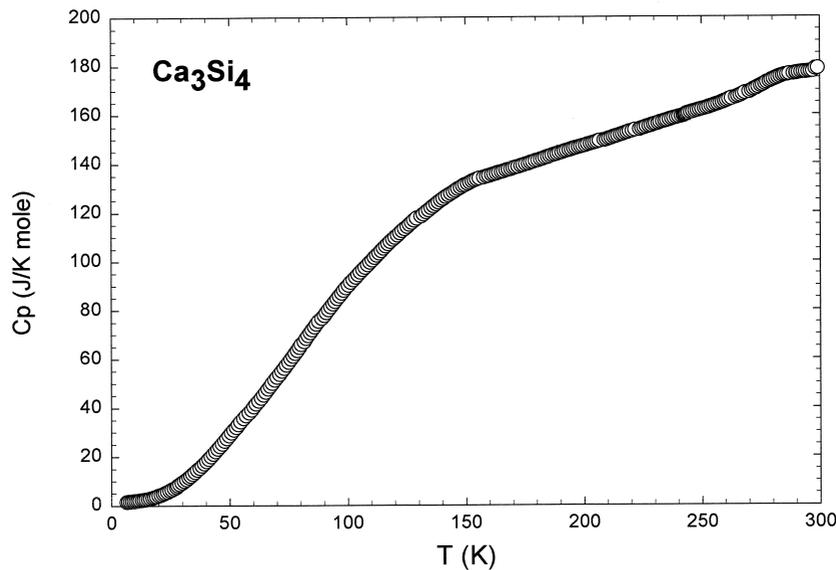


Fig. 2. Heat capacity of  $\text{Ca}_3\text{Si}_4$  in the 3–300 K temperature range.

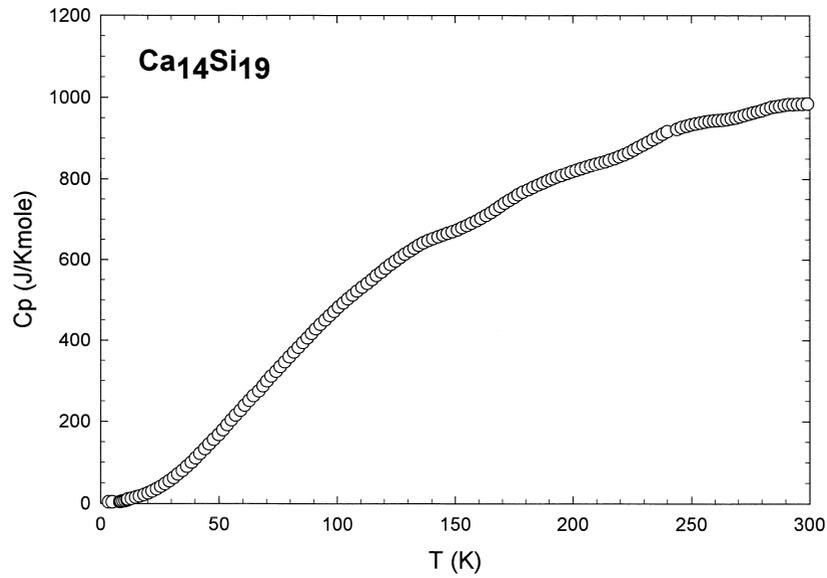


Fig. 3. Heat capacity of  $\text{Ca}_{14}\text{Si}_{19}$  in the 3–300 K temperature range.

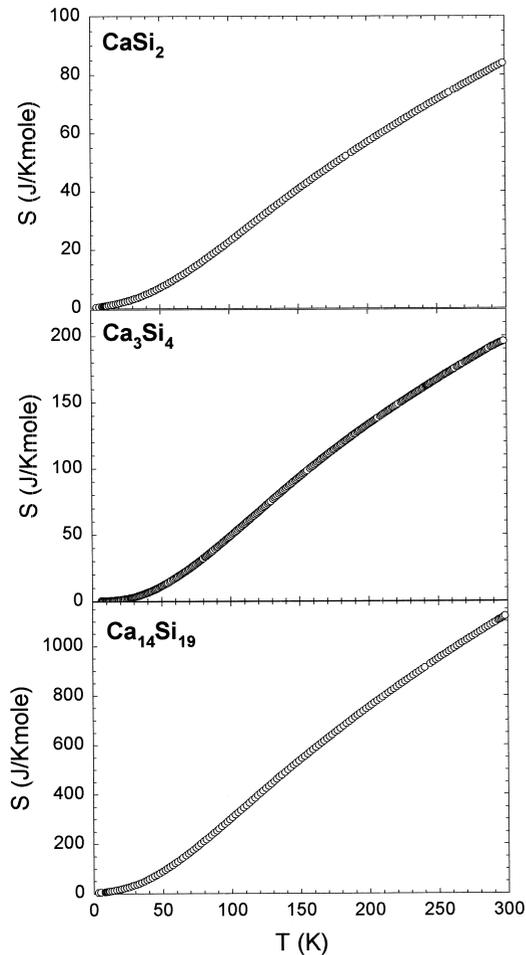


Fig. 4. Calculated entropy behaviour ( $S^0(T) - S^0(0 \text{ K})$ ) of the three compounds in the 3–300 K temperature range.

Table 1

Thermodynamic data at 298 K obtained from heat capacity measurements

Compound	$H_{298 \text{ K}}^0 - H_{0 \text{ K}}^0$ (KJ/mol)	$S_{298 \text{ K}}^0 - S_{0 \text{ K}}^0$ (J/K mol)	$G_{298 \text{ K}}^0 - G_{0 \text{ K}}^0$ (KJ/mol)
$\text{CaSi}_2$	13.3	84	-11.7
$\text{Ca}_3\text{Si}_4$	32.4	197	-26.3
$\text{Ca}_{14}\text{Si}_{19}$	181	1140	-158.7

The crystal structure of the three examined compounds is characterized by a pronounced silicon sublattice:  $\text{CaSi}_2$  is trigonal [7,8] with two layered modifications, i.e., the three- (3R) and six-layer (6R) types, while in  $\text{Ca}_{14}\text{Si}_{19}$  and  $\text{Ca}_3\text{Si}_4$  the silicon framework shows a two-dimensional feature. These crystal structure characteristics could be related to the anomalous power in the temperature dependence of the specific heat. In fact a power law in temperature lower than three has been observed in layered structures as graphite or boron nitride [9].

The numerical integration of the smoothed values of heat capacity allow information to be obtained on the total entropy ( $S^0(T) - S^0(0 \text{ K})$ ): the thermal dependence of the entropy for the three compounds is reported in Fig. 4 while Table 1 shows the values at room temperature (298 K) of the thermodynamic functions derived from heat capacity.

Heat capacity measurements on the other three phases of the Ca–Si phase diagram, namely  $\text{Ca}_2\text{Si}$ ,  $\text{Ca}_5\text{Si}_3$  and  $\text{CaSi}$ , are now in progress in order to better clarify the influence of the lattice structure on the phononic vibrations and to complete the room temperature thermodynamic information.

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