# Pressure induced structural transitions in CoSi$_2$

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**Abstract**
Results of diamond anvil cell based electrical resistance and x-ray diffraction measurements
under pressure at room temperature on CoSi$_2$ are reported. The evolution of electrical resistance
and x-ray powder diffraction patterns confirms two structural transitions near 0.4 and 13 GPa.
There is small isostructural (0.71%) volume collapse near 20 GPa. The diffraction lines
gradually broaden with increasing pressure. A disorder that involves breaking of Co–Si and
Si–Si bonds and occupancy of vacant sites, which results in an intermediate bonding topology
between that of CaF$_2$ and adamantine structures, is suggested to be responsible for this
behaviour. This could be a general feature for CaF$_2$ structured materials (with directional
bonding nature) because of the presence of ordered vacancies and a competing adamantine
structure.

## 1. Introduction

Transition metal disilicides have been extensively studied both theoretically and experimentally [1–4] because of the possibility of employing these metallic materials for contacts in silicon based devices. These silicides have also attracted much attention due to the possibility of tuning the silicon bonds and the electronic doping, stimulating interest in their fundamental properties. Among all the transition metal disilicides, only CoSi$_2$ and NiSi$_2$ crystallize in the CaF$_2$ type structure (space group $Fm3m$; $Z = 4$) that has a slightly covalent Si–Co (Ni) bonding and retains the bonding topology of pure Si. Both CoSi$_2$ and NiSi$_2$ present many interesting features for microelectronics and optoelectronics. Because of the low resistivity (∼50 and 20 $\mu\Omega$ cm for NiSi$_2$ and CoSi$_2$ respectively) [5] and good lattice matching with the silicon (0.46% and 1.2% for NiSi$_2$ and CoSi$_2$ respectively) [6], these materials have become the most used disilicides in metal silicon metal transistor technology. Due to nearly perfect matching of lattice constants, integration in the silicon matrices could be possible with negligible strain and defect formation. It has also found applications for gate electrodes and Schottky barriers. Although these desirable properties are strongly dependent on crystal structure, studies of phase stability under different thermodynamic conditions that can identify structural transitions and metastable phases are sparse. Most of the studies on the disilicides have been focused on the interfaces between the silicon surfaces and silicides with much emphasis on the electronic properties as well as on the growth of different polymorphs under different thermodynamic conditions. For bulk material, pressure can be a powerful tool to control or manipulate the electronic structure and to obtain various polymorphs.

The low temperature electrical resistivity measurements for both CoSi$_2$ and NiSi$_2$ show the behaviour expected for a normal metal [5]. Though there are few reports of high pressure studies on $\beta$ FeSi$_2$ (orthorhombic) [7] and NiSi$_2$ [8], no literature exists for similar studies on CoSi$_2$.

Earlier we have studied the high pressure behaviour of CaF$_2$ type structured intermetallics of Au/Pt with In, Ga, Al, and NiSi$_2$ [9–12]. The intermetallics fall into two categories; those that undergo an electronic topological transition and those that do not. AuGa$_2$ and AuIn$_2$ undergo a structural transition preceded by an electronic topological transition (ETT) [9, 10]. AuAl$_2$, PtAl$_2$, and PtIn$_2$ do not show the ETT, but a structural transition to a low symmetry orthorhombic phase [11, 12] occurs. In NiSi$_2$ no structural transition is observed. However, considerable disorder is induced by pressure [8]. As an extension of these studies we have studied the high pressure behaviour of CoSi$_2$ at ambient temperature through electrical resistance and x-ray diffraction measurements.

## 2. Experimental details

### 2.1. Sample preparation

A polycrystalline sample of CoSi$_2$ was prepared by arc melting an appropriate amount of high purity Co and Si under
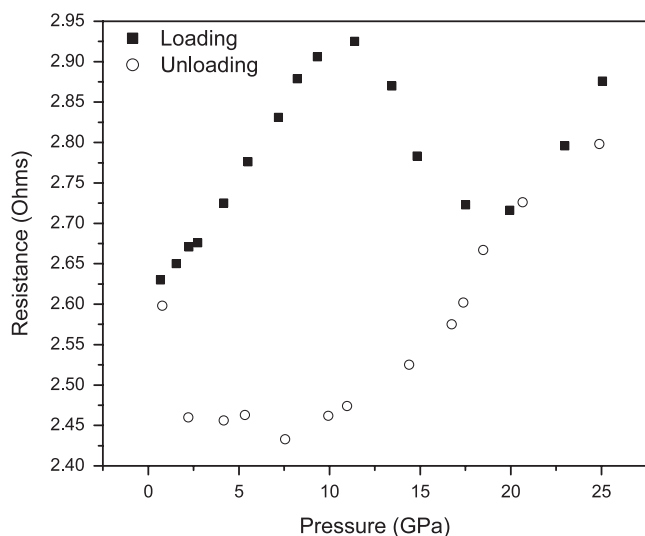
**Figure 1.** Evolution of electrical resistance as a function of pressure.



**Figure 2.** Evolution of x-ray diffraction patterns as a function of pressure up to 12.6 GPa.

argon atmosphere. Subsequently, these were annealed at 900 °C for one week for homogenization. The ambient x-ray diffraction pattern of the sample showed single phase with a lattice constant of 5.3644 Å, in agreement with the literature value [13].

### 2.2. Electrical resistance

Electrical resistance measurements were carried out using a diamond anvil cell (DAC) based technique [14]. A clamp type Merrill Bassett DAC with a diamond culet size of 400 $\mu$m and stainless steel gasket was employed. Mylar embedded alumina was used as the pressure transmitting medium. 20 $\mu$m diameter stainless steel wires, at a separation of ∼30 $\mu$m or less were used as leads for the quasi-four-probe measurements. Pressure was measured by the ruby fluorescence technique. A small rectangular piece of the sample (thickness ∼5 $\mu$m) was kept at the centre of the anvil face touching both wires. As the cell was slowly tightened, the pressure and resistance of the sample were measured. Full details of the measurement technique are given elsewhere [14].

### 2.3. ADXRD measurements

Angle dispersive x-ray diffraction (ADXRD) measurements were carried out at the powder x-ray diffraction beam line of the ELETTRA synchrotron source, Trieste, Italy (proposal no. 2004642). For high pressure experiments fine powdered samples of CoSi$_2$ were loaded in a Mao–Bell type DAC. A pair of diamond anvils with culet diameter of about 400 $\mu$m was used in the DAC. A hardened stainless steel gasket with a central hole of 100 $\mu$m diameter and thickness 50 $\mu$m contained the sample. The x-ray beam was collimated by a 80 $\mu$m diameter pinhole. A mixture of methanol–ethanol (4:1) was used as the pressure transmitting medium. The pressure was determined *in situ* by using silver powder mixed with the sample as pressure calibrant within an estimated error of 0.2 GPa. The wavelength of the x-ray employed and the sample
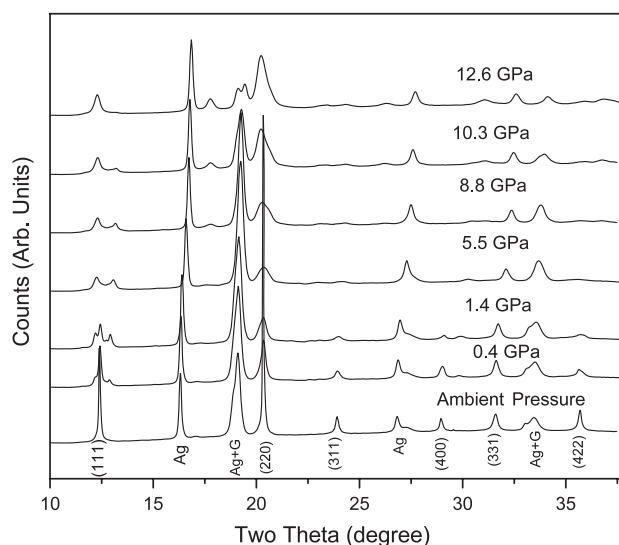
to image the plate distance were calibrated employing LaB$_6$ diffraction patterns. X-ray powder patterns at various pressures were collected employing x-rays of wavelength 0.6704 Å. Images of the powder diffraction rings were collected on a Mar345 image plate detector and read with a resolution of 100 × 100 pixel size. Typical exposure times of 20–30 min were employed for data collection at each pressure point. The powder rings thus obtained were integrated using the FIT2D [15] software and converted to the one dimensional 2$\theta$ versus intensity patterns. Patterns were collected up to 31.2 GPa. Data were also collected for the various pressures during the unloading cycle.

## 3. Results and discussions

The pressure variation of resistance for CoSi$_2$ up to 25 GPa is shown in figure 1. The resistance of the sample first increases up to 11.4 GPa and then starts decreasing up to 20 GPa. On further increasing the pressure, the resistance again increases up to 25 GPa, the highest pressure of the present measurements. This resistance behaviour indicates the presence of structural phase transitions driven by two concurrent mechanisms. As discussed below, these are the bond breaking—making and the structural distortion via occupation of the vacant sites.

On pressure release, the resistance is recovered along a path different than that of the loading, indicating the metastability of the high pressure phase. However, for recovering the high pressure phase it needs to be pressurized to well beyond 10 GPa as our attempt to prepare bulk metastable material employing Toroid anvil and Bridgman anvil apparatus in which the material was subjected to 5 GPa and 10 GPa respectively did not succeed.

Corresponding to the changes in electrical resistance, there are structural changes in the angle dispersive x-ray diffraction (ADXRD) patterns. In figures 2 and 3 the evolution of x-
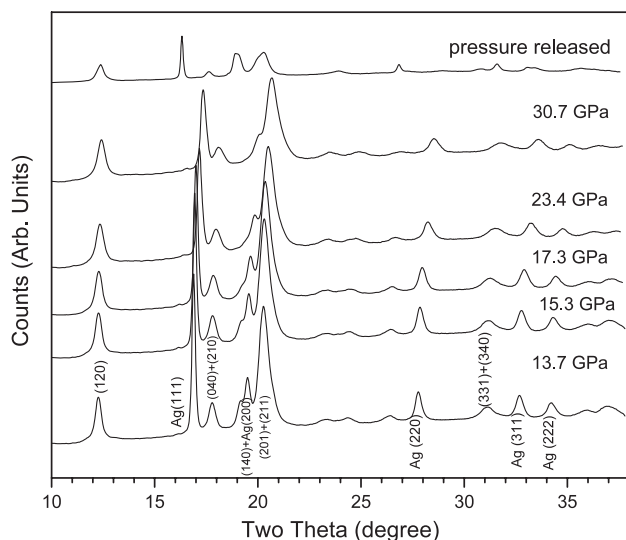
**Figure 3.** Evolution of x-ray diffraction patterns as a function of pressure up to 30.7 GPa.



**Figure 4.** Pressure variation of the separation between the two components of the [111] line of the original cubic phase.



**Figure 5.** Pressure volume data for $CoSi_2$. Filled and open symbols respectively show the loading and unloading path. Along the loading path, between 0.5 and 13 GPa, the structure is unknown. The $P–V$ relation shows a small discontinuity in the 20–22 GPa region where the electrical resistance again starts increasing.

ray diffraction patterns at various pressures is shown. From figure 2 it is clear that the diffraction pattern changes at 0.4 GPa, showing the occurrence of structural phase transition. The nature of the splitting and evolution of the lines implies a close relation of the high pressure phase to the $CaF_2$ phase. The fact that the line (111) splits into three components indicates that the symmetry is lowered at this transition. As the pressure is further increased, the (111) line, which was split into three components undergoes intensity re-distribution and further increase in splitting (figure 4). Finally it becomes two components. In figure 4 the separation of only these two lines is plotted versus the pressure region. It is clear that the increase in resistance correlates with the extent of distortion from the $CaF_2$ structure in this pressure region. It is interesting to note that the $\beta$ $FeSi_2$ phase is a distortion of the $CaF_2$ phase and is also semiconducting [16]. However, we could not index this phase to a $\beta$ $FeSi_2$ type cell, probably due to the large size of the cell and the few lines that are available from the high pressure powder pattern. Also our efforts to identify a cell with symmetry not lower than orthorhombic and satisfying constraint on volume were not successful. Thus this phase appears to have a large cell with low symmetry or this is a multiphase region. Hence no further attempt was made to index or solve the structure.

Above 13 GPa, where the electrical resistance has the maximum, the split (111) line of the cubic phase reverts back to a single line, clearly indicating a phase transition. The $d$ values beyond 13 GPa could be fitted to an orthorhombic cell ($A = 4.4615$ Å, $B = 8.8007$ Å, $C = 3.6098$ Å at 16.4 GPa). Because of the low symmetry and the absence of any prototype structure from which trial atom positions may be obtained, no attempt was made for a Rietveld structural analysis of the high pressure phase. However, a full pattern Lebail fitting with the space group $Pna2_1/Pnam$ was carried out using a general structure analysis system (GSAS) [17] for all the high pressure patterns beyond 13 GPa to obtain the lattice parameters. The $P–V$ data thus obtained from the Lebail fitting are shown in
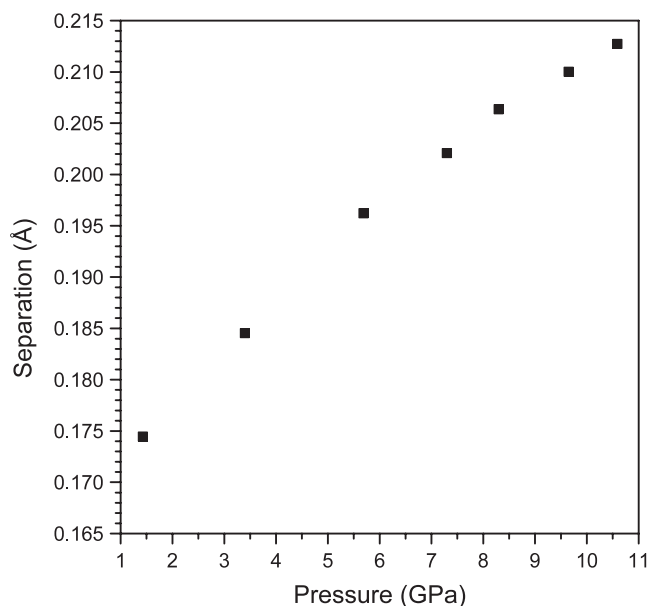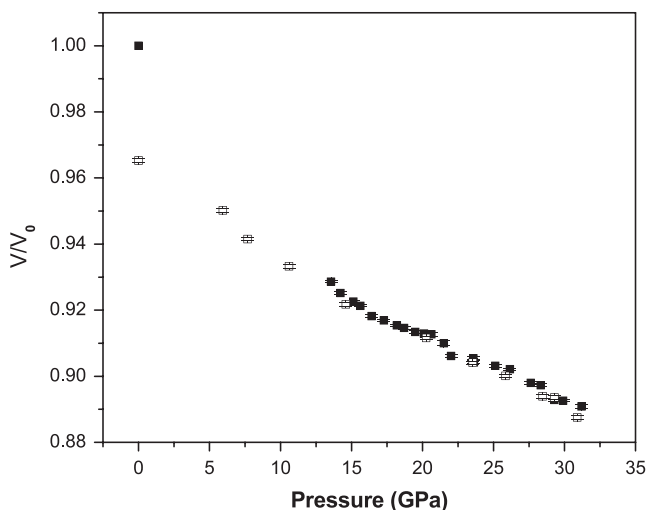
figure 5. Near 20 GPa, there is a 0.71% discontinuous change in volume (though the structure remains the same) and above this pressure the equation of state (EOS) data show a change in slope. It may be noted that in the same pressure region, the electrical resistance has a minimum. As mentioned earlier, any metastable phase cannot be recovered for materials subjected to pressure up to 10 GPa, implying that only the phase above 10 GPa is metastable.

It may be noted that the half-width of the lines of the high pressure phases (for example the strong [220] line of $CaF_2$ structure) keep on increasing with pressure along with a loss of intensity indicating disorder.

The x-ray diffraction pattern from the sample released from 30.7 GPa indicates that there is no back transformation and also the diffraction lines remain broad. These features should indicate a continuous structural disorder.

Calculated phonon spectra of $CoSi_2$ [3] show that optical phonon modes close to the zone edge $X$ (along the $L$–$X$ direction) and $W$ (along the $X$–$W$ direction) are flat; a condition favourable for disordering [18]. A possible model of such a disorder is one in which a structure intermediate between $CaF_2$ and adamantine structure, but deformed from cubic symmetry, is formed [19]. If in a cubic lattice one considers four interpenetrating fcc lattices with their origin at four sites A(0, 0, 0), B(0.25, 0.25, 0.25), C(0.75, 0.75, 0.75) and D (0.5, 0.5, 0.5), then in the $CaF_2$ phase, Co occupies A site, Si occupies B and C sites and site D remains vacant. This leads to Co–Si bonding that has strong covalent character and a bonding topology similar to pure Si. In the adamantine structure, Co will occupy site D and Si sites A and B, and C will remain vacant. It may be noted that in band structure calculations, the energy difference between the adamantine and $CaF_2$ phase is very small with the latter having lower energy [18]. The movement of Co to site D and Si from site C (and possibly B) to A with the accompanying bond breaking and making that is required in a transition between these two phases can lead to a disordered intermediate phase. In $CoSi_2$ under pressure, further, the symmetry is lowered below cubic. Consistent with this bond breaking and making scenario that can be kinetically hindered, material exhibits metastability.

The behaviour of $CoSi_2$ is similar to that of $NiSi_2$, which also shows pressure induced disorder [8]. However, in $NiSi_2$ the disordering is much more pronounced and there are no phase transitions. Also the disordered phase can be pressure ($\sim$10 GPa) and pressure–temperature (5 GPa, 800 °C in a toroid apparatus) quenched. The reverse Monte Carlo simulations of the x-ray diffraction patterns from pressure and pressure–temperature quenched $NiSi_2$ do support the above disordering mechanism in it [20]. In $CoSi_2$, the stronger Co–Si (Co–Si bond length is 2.323 Å in $CoSi_2$ as compared to 2.340 Å in $NiSi_2$) bond may be responsible for the less pronounced effects. Nevertheless, the same mechanism should be applicable here also.

The resistivity of $NiSi_2$ is large as compared to that of $CoSi_2$ and it increases linearly in both materials with defect concentration, introduced by irradiation with ions of energy in the nuclear energy regime [21]. The large change in resistivity induced by ion irradiation indicates [21] a high degree of susceptibility of $CoSi_2$ and $NiSi_2$ to disorder, virtually absent in ordinary metals. The only exception is A-15 compounds where it has been associated with the breaking of tetrahedral bonds. It may be noted that there is a tendency for disorder in $CoSi_2$ and $NiSi_2$ thin films also, even though the lattice mismatch is small [22]. Also, an adamantine layer exists at the interface of the $CaF_2$ structured outer layer and the substrate [23]. The mechanism for pressure induced disorder suggested here is consistent with the above facts. It will be interesting to see the behaviour of films deposited on substrates with large lattice mismatch. Also, since results presented here indicate that the high pressure phase will be metastable, the effect of irradiation on bulk materials by swift heavy ions that will generate dynamic high pressure and temperature conditions will also be worth investigating

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