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Self-doping effects in cobalt silicide CoSi: Electrical, magnetic, elastic, and thermodynamic properties

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We report electrical, magnetic, elastic, and thermodynamic properties of CoSi. A low resistivity residual ratio and tendency of the resistivity to saturate near room temperature identify CoSi as a disordered metal, which nevertheless reveals the clear presence of T^2 contribution of nonmagnetic nature below ∼30 K. The Sommerfeld constant of CoSi, following from heat capacity measurements, does not show any enhancement over values typical of simple metals. The magnetic susceptibility of CoSi changes from diamagnetic at high temperature to paramagnetic at temperatures below ∼25 K, indicating the existence of local magnetic moments. The elastic moduli of CoSi show an anomalous decrease on cooling. An explanation of these phenomena is based on the concept of electron localization with formation of local magnetic moments. These phenomena probably arise as a result of a self-doping effect due to the polyvalent character of Co and the nonstoichiometric nature of CoSi.

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I. INTRODUCTION

Cobalt monosilicide (CoSi) has been studied widely primarily as a candidate for thermoelectric applications.[1,2] These studies include measurements of the resistivity, magnetic susceptibility, thermoelectric power, Hall coefficient, and heat capacity of CoSi, and calculations of the band structure and electron density of states.[1–10] Based on these results, one may think of CoSi as a diamagnetic semimetal with a very high residual resistivity, probably indicating a large density of defects. It should be stressed that CoSi, as well other transition metal silicides, belong to a class of nonstoichiometric compounds (berthollides) having a silicon deficiency.

New experimental data[11] made it clear that the physics of CoSi is rather complicated. In particular, it appears that the magnetic susceptibility is diamagnetic at high temperatures and changes sign near 25 K, and the elastic moduli continuously decrease on cooling from ∼50–60 K down to the lowest temperature achieved in the experiments (∼2 K). Note that normally the temperature dependence of all thermodynamic properties of a substance decreases at $T \ll \theta$ (θ-Debye temperature) (see, for instance, behavior of the heat capacity and thermal expansion coefficient of CoSi[11]). The intriguing and somewhat controversial results obtained in Ref. 11 have not been adequately explained and the fundamental question of whether the observed features are intrinsic or are caused by impurities and/or structural defects has not been resolved. It should be added here that, in contrast with conclusions,[4,11] a temperature independent diamagnetic susceptibility was claimed in CoSi over a broad range of temperature in Ref. 3. This situation served as a motivation for the present study.

A straightforward approach to the problem is to investigate samples of CoSi of significantly different origin, in addition to the sample previously studied.[11] Therefore, samples cut from a single crystal of CoSi grown by the Czochralski technique more than 20 years ago in Ekaterinburg (Ural, Russia) were used in the current study. The sample used in Ref. 11 was grown by the Bridgman technique in Ames Laboratory (USA) in 2010. That should ensure somewhat different impurity composition and defect structure in the samples. In the course of the study two more samples of CoSi (Br17 and Br144) grown in Braunschweig (Germany) by the Czochralski method became available for investigation. One of the Braunschweig samples was diamagnetic in the entire temperature range from 350 to 2 K.

Lattice parameters of the samples of CoSi determined by powder x-ray diffraction are given in Table I. Chemical analysis performed with an electron probe x-ray microanalyzer showed some deviation from the stoichiometric chemical composition (silicon deficiency ⩽1%) of all samples. The impurity content determined by atomic emission spectroscopy and mass spectroscopy included a noticeable amount of Ni (∼0.01%) in all samples, about 0.02% of Al in the Br17 sample, and 0.03% and 0.01% of W in the Br144 and Br17 samples, respectively. Fe content was below the sensitivity level [(5×10^{-4})%] of these measurements.

II. EXPERIMENT

In the present paper we report measurements of various physical properties of the different samples of CoSi, including the electrical resistivity and magnetic susceptibility of the Ural and Braunschweig samples, new measurements of the Ames sample, extended measurements of electrical resistivity of the Ames sample down to 0.2 K and to high pressure up to ∼5 GPa, sound velocities in the Ural sample, and heat capacities of the Ames and Braunschweig samples. The resistivity (ρ) was measured by standard four-terminal dc and ac techniques. Measurements of the magnetic susceptibility (χ) were performed with a LakeShore vibrating sample magnetometer and a Quantum Design SQUID magnetometer. Sound velocities were measured using a digital pulse echo technique.[11] The experiments at high pressures were carried out in a quasihydrostatic toroid cell.[12] Heat capacity (C_p)

TABLE I. Lattice parameters of the CoSi samples.

CoSi	Lattice parameter a (Å)
Ames	4.444(1)
Ural	4.443(1)
Br144	4.445(1)
Br17	4.441(1)

was measured by the relaxation technique, incorporated into a Quantum Design PPMS.

All CoSi samples demonstrate quite similar behavior of their resistivity and magnetic susceptibility. Three samples (Ames, Ural, and Br144) reveal the existence of T^2 term in resistivity below ∼30 K. The high but considerably different residual resistivities of the samples indicate different defect concentrations. The magnetic susceptibility of these samples passes from "high temperature" diamagnetism to "low temperature" paramagnetism at about 20 K. The elastic "anomalies" observed in the Ames sample are well reproduced in the Ural sample. All the data obtained would suggest the intrinsic nature of electrical, magnetic, and elastic properties of CoSi, related to self-doping effects, but the properties of the Br17 sample may question this interpretation. The resistivity of the sample Br17 displays a temperature minimum near 40 K and its Sommerfeld constant about half that of the Ames and Br144 samples. The magnetic susceptibility of the Br17 is entirely diamagnetic in the temperature range 5–450 K, though in contrast to the data of Ref. 3 it reveals a quite distinct temperature dependence and contains a paramagnetic tail somewhat masked by the overwhelming diamagnetic response (see below).

The experimental results are displayed in Figs. 1–6. The resistivities of the samples are shown in Fig. 1. The high residual resistivity along with the low residual resistivity ratio (RRR) and tendency to saturation at high temperatures place these samples in the category of so-called strongly disordered metals, whose resistivity can be described by a parallel resistor model.[13,14] This model, though not completely explained theoretically, reflects a situation where the mean free path, limited by defects, becomes comparable to the interatomic spacing.[15] Note that the high temperature asymptotic values of resistivity of different samples of CoSi are practically the same and do not depend on the residual resistivity, in agreement with the parallel resistor model. This kind of behavior represents an obvious example of Mattiessen's rule violation, which is another feature inherent to strongly disordered metals.[16] In the extreme case of high defect concentrations, the temperature coefficient of resistivity ($d\rho/dT$) may become negative.[13,16] One can see this kind of behavior in the sample Br17 (Fig. 1).

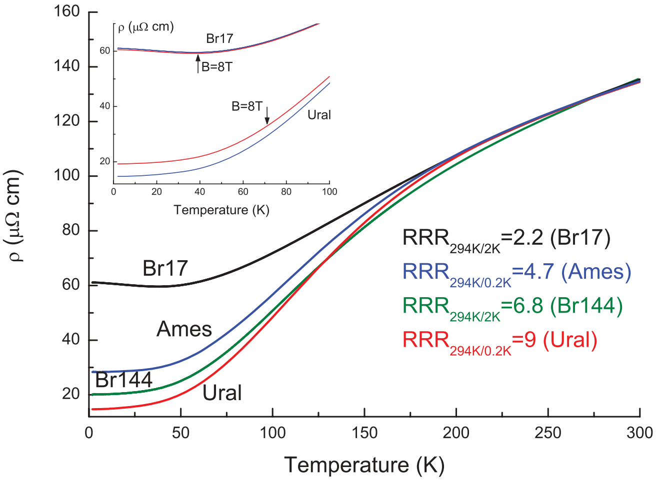

FIG. 1. (Color online) Temperature dependent resistivity of single crystals of CoSi. The inset illustrates the influence of magnetic field on resistivity. Note that the Br17 sample has negative magnetoresistance, which hardly is noticeable in the figure.

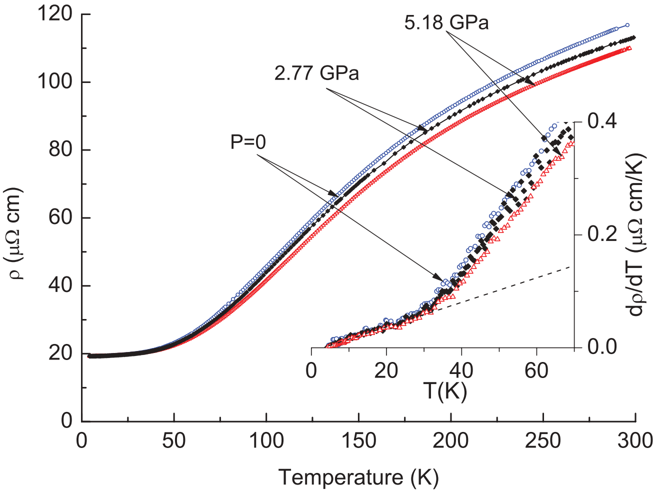

FIG. 2. (Color online) Temperature dependent resistivity ρ and its temperature derivative $d\rho/dT$ (in the inset) of the Ames CoSi single crystal at different pressures. The dashed line in the inset is an extrapolation of the linear part of the $d\rho/dT$.

The general resistivity behavior of CoSi does not change much with pressure (Fig. 2), though CoSi is a semimetal and a small change in band overlap could make a big difference. To the contrary of this expectation, high pressures up to ∼5 GPa do not change the situation, but pressure clearly discloses the T^2 term in the resistivity [see the inset in Figs. 2 and 3(c)].

The existence of a T^2 term in the low temperature resistivity is one more specific feature observed in some disordered metals which we also see in our samples (Fig. 3). The temperature-dependent part of resistivity of these samples is described in the best way by a combination of the T^2 and T^5 terms up to 40–50 K, but T^2 dominates at low temperatures. Some deviation from T^2 behavior at lowest temperatures [Fig. 3(c)] can probably be ascribed to a violation of Mattiessen's rule at high defect concentration. To verify a nonmagnetic nature of the observed characteristics of the CoSi, resistivity measurements of all samples were carried out at high magnetic field (8 T) (see some example in Figs. 1 and 3). As is seen in the inset of Fig. 1 a field of 8 T does not destroy the minimum in the resistivity of Br17. Also, the T^2 term still dominates the resistivity at low temperatures [Fig. 3(b)]. Note that the relative change in magnetoresistance ($\Delta\rho/\rho$, where $\Delta\rho$ is the change of resistivity in magnetic field) is normal (positive) for the Ural, Ames, and Br144 samples, whereas it is slightly negative for the Br17 sample.

Now we turn to Fig. 4, which shows the magnetic susceptibility of the four samples of CoSi. As one can see,

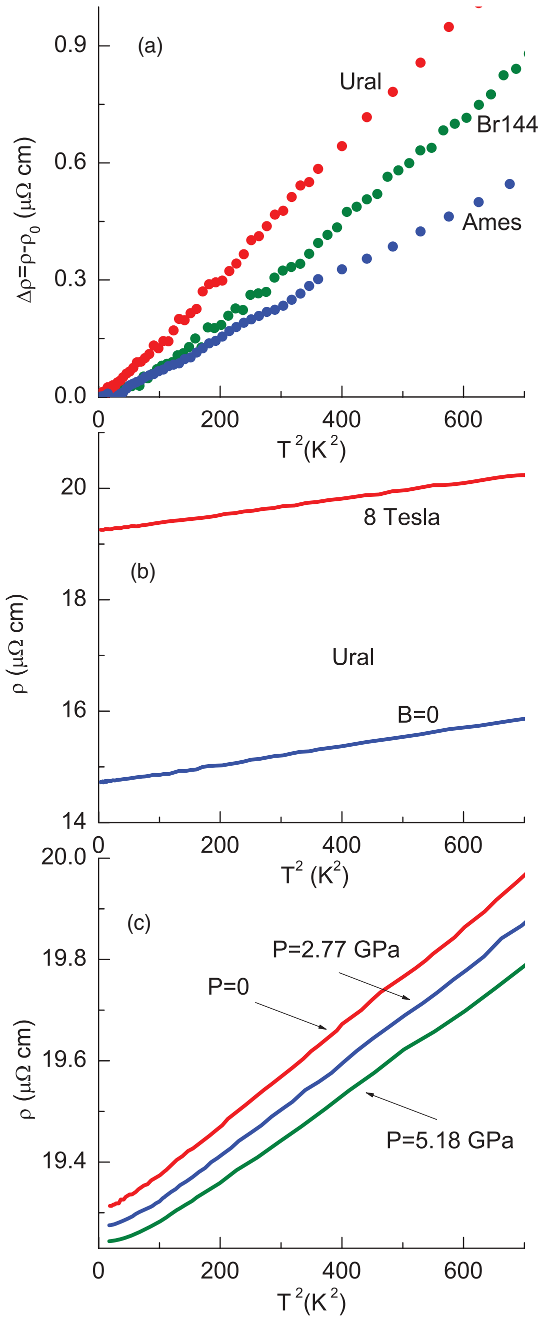

FIG. 3. (Color online) (a) Resistivity of Ural, Ames, and Br144 samples of CoSi as a function of T^2 at ambient pressure. (b) Resistivity of Ural sample as functions of T^2 in magnetic field. (c) Resistivity of the Ames sample of CoSi as a function of T^2 at different pressures.

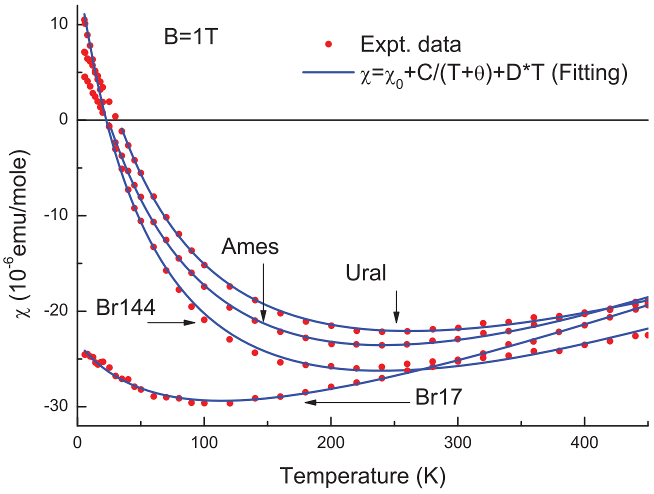

FIG. 4. (Color online) Magnetic susceptibility of single crystal samples of CoSi.

the magnetic susceptibility of the samples is diamagnetic at high temperatures and starts to bend toward zero values with decreasing temperature. The magnetic susceptibility of the Ames, Ural, and Br144 samples cross zero line and become paramagnetic at $T < 25$. The steep growth of the paramagnetic magnetic susceptibility at low temperatures reveals existence of paramagnetic moments. All the magnetic susceptibility curves in Fig. 4 can be fitted successfully by the expression $\chi = \chi_0 + D \times T + C/(T + \Theta)$, where two first terms supposedly describe the diamagnetic contribution to the susceptibility, whereas a third term is the standard Curie-Weiss expression describing the magnetic susceptibility of a system of interacting magnetic moments. Fitting of the experimental data to the above expression gives values of the Curie constant C and Weiss temperature Θ, which are in the range $(5–8) \times 10^{-3}$ emu K and $(-70$ to $-100)$ K for the Ames, Ural, and Br144 samples. The Br17 sample has the smallest Curie constant ($\sim 2 \times 10^{-3}$ emu K), but its Weiss temperature Θ (~ -100 K) is in agreement with the other samples. Note that a nonzero, negative value of the fitting parameter Θ indicates the existence of an antiferromagnetic exchange interaction in the system. Probably this interaction is responsible for deviations of the magnetic susceptibility of the Ames and Ural samples from a Curie-Weiss law below ~ 20 K. The effective number of magnetons, implied from values of the Curie constant, are 0.1 to 0.2 μ_B per formula unit. But assuming that the magnetic moments are situated at the Co sites and taking into account that the magnetic moment

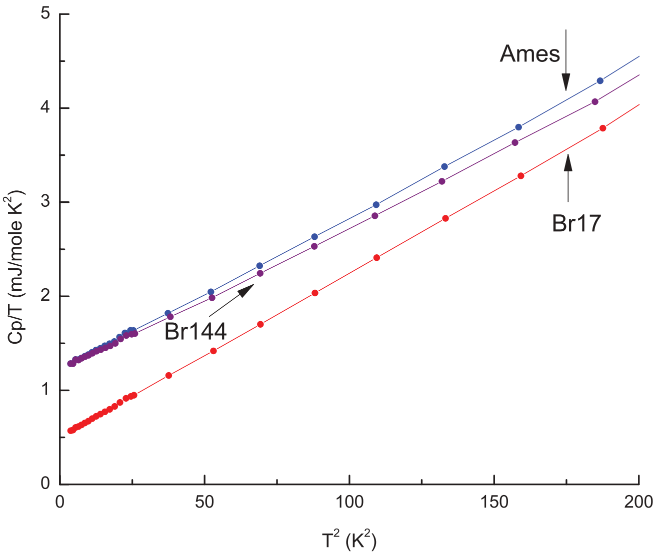

FIG. 5. (Color online) Heat capacity of CoSi single crystals, plotted as specific heat divided by temperature C_p/T versus T^2.

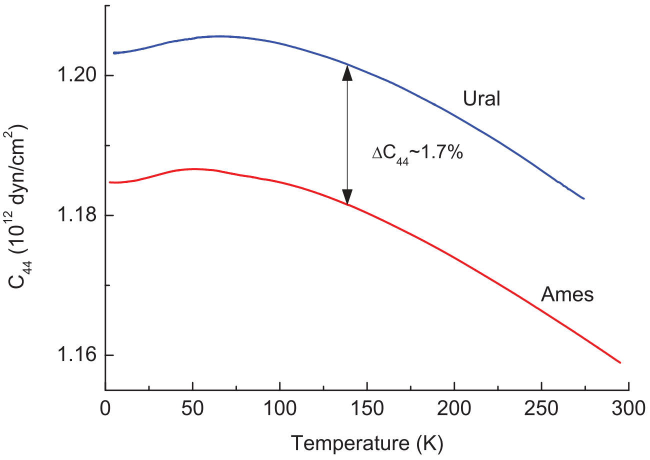

FIG. 6. (Color online) Temperature dependence of the elastic modulus c_{44} for two samples of CoSi.

for the ion Co^{+2} is about 4.8 μ_B,[17] one may estimate the concentration of paramagnetic centers in CoSi as ∼2–4%, therefore validating the dilute nature of the paramagnetic subsystem in CoSi. The corresponding calculations give the concentration of paramagnetic centers in the B17 sample as ∼1–2%.

Before describing results of the heat capacity measurements, we point out that a necessity for new measurements of the heat capacity arose in connection with the extraordinary properties of the Br17 sample. New measurements were performed on the samples Br17, Br144, and Ames. The Ames sample was measured before by the classical adiabatic pulse method[11] and the present measurements were to verify a validity of the relaxation technique. Conventionally, the results of measurements are displayed as C_p/T versus T^2 in Fig. 5. Extrapolation of C_p/T to zero temperature gives a value of the Sommerfeld constant, γ proportional to the electron density of states $D(E_f)$. As is seen in Fig. 5 the Ames and Br144 samples are characterized by practically the same $\gamma = \sim 1.2$ mJ/mole K^2, whereas the "anomalous"Br17 sample has $\gamma = \sim 0.5$ mJ/mole K^2. This difference can be connected with the decreased number of carriers or/and with the decreased effective mass, though the latter seems to be highly unlikely.

It is instructive to calculate the magnetic susceptibility of a free electron gas based on values of the Sommerfeld constants, following from Fig. 5. Taking $\gamma = 1.2$ mJ/mole K^2 one obtains a Pauli susceptibility $\chi = 1.6 \times 10^{-6}$ emu/mole. Adding the Landau diamagnetic contribution will give a total value 1×10^{-6} emu/mole, which demonstrates a great difference between the electron subsystem in CoSi and the ideal electron gas (see Fig. 4).

Earlier ultrasound experiments[11] observed that the elastic moduli of the Ames sample of CoSi unexpectedly started to decrease on cooling continuing to the lowest temperature (∼2 K). In the current study we performed sound velocity measurements using the Ural sample, which was properly cut and polished and oriented using x rays. With a transducer glued on the (100) surface, we were able to study the variation of the c_{11} and c_{44} elastic moduli with temperature. Comparison of the c_{44} moduli for the Ural and Ames samples in Fig. 5 shows an almost complete agreement between the two sets of the data. The same is true for the c_{11} moduli. The small, quantitative differences in Fig. 6 can be explained by not quite perfect orientations of the samples. Unfortunately, the small size of the "anomalous" Br17 sample prevented us from measuring its elastic moduli.

III. DISCUSSION

Thus we have measured the resistivity, magnetic susceptibility, heat capacity, and elastic properties of four CoSi samples of different origin. Judging by their low residual resistivity ratios and the tendency for resistivity saturation above room temperature all the samples can be identified as disordered metals (Fig. 1). Three of the samples reveal a T^2 term in resistivity at temperatures below ∼40 K, which survives at high pressure and at high magnetic field (Figs. 2 and 3). Normally associated with electron-electron scattering, the T^2 term in resistivity is also observed in some transition metals, A15 compounds, Chevrel-phase materials, and numerous magnetic substances at unusually high temperatures.[18–22] A T^2 term in resistivity arises in magnetic materials due to electron scattering on spin fluctuations, but it is not applicable to CoSi, as a magnetic field does not influence its T^2 resistivity (Fig. 3). Moreover, normally spin fluctuations are accompanied by an enhancement of the Sommerfeld constant γ, which implies a corresponding enhancement of the electron effective mass. But as seen below it does not happen in this case. The *s-d* scattering and/or scattering of electrons on local vibrations, caused by defects, were considered to be responsible for the existence of a T^2 term in resistivity of nonmagnetic materials.[23–25] But the situation is still unclear and the question of a possible link between disorder and the existence of T^2 term is open.

As emphasized above, some physical properties of the Br17 CoSi sample deviate from those of other CoSi samples investigated in the current work. Specifically, the Br17 sample displays a small but distinct minimum in resistivity around 50 K and a slightly negative magnetoresistance. Both of these features clearly illustrate effects of localization that occur in sample Br17, as well as in Ames, Ural, and Br144 samples, as implied from magnetic measurements.

Discussing the magnetic susceptibility, it has to be emphasized that samples of CoSi were cut from single crystals grown under very different conditions. However, as is seen in Fig. 4, the magnetic susceptibility of these samples behaves very similar, which certainly supports the intrinsic nature of magnetic susceptibility variations in CoSi. This idea also agrees with early measurements.[4] The magnetic susceptibility of the anomalous Br17 sample also contains a paramagnetic contribution. However, the decreased number of carriers and paramagnetic centers in Br17 still remains a puzzle, but strong disorder may be a clue. In any event the term "intrinsic" should be applied to the overall character of the magnetic susceptibilities. The Curie-Weiss paramagnetic contribution to the magnetic susceptibility reveals the existence of local magnetic moments in the system. The question is whether the local moments exist over an extended range of temperatures or are created on cooling. Indeed, the local magnetic moments may not be seen at high temperatures due to their small paramagnetic contribution to the total magnetic susceptibility according to the Curie-Weiss law. Though, taking into account the disorder nature of the samples and some evidence indicating localization effects, one may conclude that the magnetic moments are generated in CoSi on cooling, most probably as a result of electron localization on still unidentified centers. Noting the polyvalent character of Co and the nonstoichiometric nature of CoSi, one may consider Co sites as candidates for the localization centers.

An antiferromagnetic interaction, developing between localized spins may account for the elastic anomaly observed in ultrasound measurements (Fig. 6).

IV. SUMMARY

In summary, we found that CoSi is a disordered diamagnetic metal with defect-generated paramagnetic centers. A T^2 term of nonmagnetic nature dominates the resistivity of CoSi below 30 K. The magnetic susceptibility of most CoSi samples changes from diamagnetic to paramagnetic at temperatures below ~25 K, indicating formation of local magnetic moments. The elastic moduli of CoSi experience an anomalous decrease on cooling. A tentative explanation of the observed phenomena involves the concept of electron localization, with formation of local magnetic moments. Consequently, the spin-spin and spin-lattice coupling may cause softening of the elastic moduli. All these phenomena probably arise as a result of a self-doping effect due to the polyvalent character of Co and nonstoichiometric nature of CoSi.

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