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

V. N. Narozhnyi*

Institute for High Pressure Physics, Russian Academy of Sciences, 142190 Troitsk, Russia

(Received 24 October 2012; published 17 April 2013)

In this Comment, it is argued that Stishov *et al.* [Phys. Rev. B **86**, 064433 (2012)] incorrectly estimated concentrations of (supposed) paramagnetic centers with $\mu_{\rm eff} \approx 4.8\mu_{\rm B}$ in the investigated CoSi crystals. Correct estimation gives concentrations of such centers from 25 to 50 times smaller than reported (∼0.04%–0.16% instead of ∼2%–4%). Also, the reported data on temperature dependences of resistivity $\rho(T)$ of four CoSi crystals, prepared in different laboratories, are so close to each other at $T \approx 250$–300 K that it is extremely unlikely to be reproducible for any reasonable accuracy of resistivity measurements. These and some other problems in the paper are related to the key points of the authors argumentation. As a result, their main conclusions become unjustified.

DOI: 10.1103/PhysRevB.87.136401 PACS number(s): 75.50.−y, 71.27.+a, 75.40.Cx

In a recently published paper, Stishov *et al.*[1] have presented results on electrical, magnetic, elastic, and thermodynamic properties of CoSi single crystals. In this Comment, it is shown that there are significant problems with the reported data as well as with the proposed interpretations, at least, for electrical and magnetic properties.

Concerning *magnetic properties* of CoSi, Stishov *et al.*[1] have reported some data on temperature dependence of magnetic susceptibility $\chi(T)$ for four single crystals prepared in different laboratories. To analyze the $\chi(T)$ curves having clear minima for all samples, the authors used the expression $\chi(T) = \chi_0 + D \times T + C/(T - \Theta)$ where the first two terms are supposed to be connected with a diamagnetic contribution, whereas, the third term is a Curie-Weiss contribution.[2] Although this expression gives the possibility to fit the experimental data rather well, it should be underlined that the second term in it was introduced without any physical justification (*ad hoc*).

The same experimental data[3] have been analyzed using an approach without any *ad hoc* assumptions.[4,5] This analysis [based on a comparison of the data for, at least, two samples with considerably different Curie-Weiss contributions to $\chi(T)$, see Refs. 4 and 5 for details] gives the possibility to extract a magnetic susceptibility of a *hypothetical* "ideal" CoSi crystal (containing no paramagnetic centers, defects, etc.). Some of these results are shown in Fig. 1. Magnetic susceptibility of a hypothetical ideal CoSi (shown by full circles) is diamagnetic at $T = 5.5$–450 K. At high temperatures, $\chi(T)$ dependence of an ideal CoSi is close to linear, but at low T, it flattens. The character of $\chi(T)$ of an ideal CoSi is not very sensitive to the selection of samples for such an analysis, therefore, diamagnetic $\chi(T)$ dependence shown in Fig. 1 for a hypothetical ideal CoSi can be considered as *intrinsic* for CoSi,[4,5] contrary to the conclusion of Ref. 1 in which $\chi(T)$ with a transition from diamagnetic to paramagnetic on cooling is considered to be intrinsic.

This analysis also gives the possibility to more reliably determine Curie-Weiss contributions to $\chi(T)$ (and, hence, the Curie constants) of "real" investigated samples. As an example, the dashed line in Fig. 1 represents a paramagnetic term for sample No. 17. The sum of $\chi(T)$ dependence of an ideal CoSi and a paramagnetic Curie-Weiss term excellently fits the experimental data.

It should also be mentioned here that the idea of a "generation" of magnetic moments in CoSi on cooling[1] is not consistent with the excellent approximation of a paramagnetic contribution to $\chi(T)$ given by the Curie-Weiss formula. Naturally, in the case of generation of magnetic moments, i.e., when magnetic moments strongly depend on temperature, a $\chi(T)$ should considerably deviate from the dependence given by the Curie-Weiss expression.

Although the values of the Curie constants determined using this approach[4,5] [$C = (3.7; 4.9; 2.8; 0.84) \times 10^{-3}$ (emu K^{-1} mol^{-1} Oe^{-1}) for the samples Ames, Ural, Br144, and Br17, respectively (in the notation of Ref. 1)] are, to some extent, different from those reported by Stishov *et al.*;[1] *the main problem* related with magnetic properties reported in Ref. 1 is not connected with this moderate difference but with an *incorrect method* of estimation of concentrations of (supposed) Co^{2+} paramagnetic centers (with an effective magnetic moment $\mu_{\rm eff}$ of about $4.8\mu_{\rm B}$).

Direct calculation of concentrations of such centers from the Stishov *et al.*[1] reported Curie constants [(2–8) $\times 10^{-3}$ (emu K^{-1} mol^{-1} Oe^{-1}), mol in Ref. 1 is missed] using an expression for C for a diluted magnetic system $C = xN_A\mu_{\rm eff}^2/3k_B$ (N_A is Avogadro's number, k_B is Boltzmann's constant, and x is a concentration of paramagnetic centers, see, e.g., Ref. 6) gives values ∼0.04%–0.16%. These are from 25 to 50 times smaller than obtained by Stishov *et al.*[1] (∼2%–4%) using their "two-steps" method. Even much smaller mistakes in the estimation of magnetic properties (as, e.g., a mistake in 1.4 times in the determination of $\mu_{\rm eff}$) can, in some cases, completely demolish arguments of an original interpretation.[7]

It is easy to see that a miscalculation in Ref. 1 is connected with *linear* (instead of *quadratic*) scaling when concentrations were estimated from the effective numbers of magneton per formula unit.

It is clear that a rather small concentration (namely, ∼0.04%–0.16%) of supposed paramagnetic centers with $\mu_{\rm eff} \approx 4.8\mu_{\rm B}$ is sufficient to explain the observed Curie-Weiss contributions to $\chi(T)$ of the CoSi samples investigated in Ref. 1. Naturally, before any discussions of "self-doping

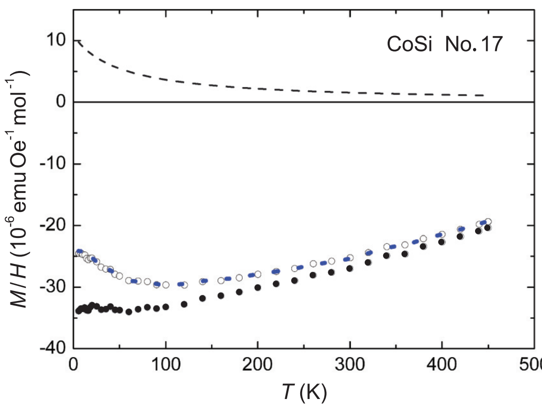

FIG. 1. (Color online) (1) M/H vs T for CoSi crystal No. 17 in magnetic field $H = 10$ kOe (open symbols). The data are the same as shown in Fig. 4 of Ref. 1 for the sample marked as Br17. (2) Paramagnetic contribution to M/H (dashed line in the upper part of the graph). (3) M/H of a *hypothetical* ideal CoSi sample (full symbols). (4) The sum of (2) and (3) shown as a dotted line going through open symbols. (After Ref. 5.)

effects,"[1] the simplest possible explanation (connected with the presence of a magnetic impurity of some kind, e.g., Fe^{3+} impurity[8] with $\mu_{\rm eff} \approx 5.9\mu_{\rm B}$) should be excluded. This was easy to ensure for the relatively large concentrations ∼2%–4% miscalculated in Ref. 1, but it becomes substantially more difficult for considerably smaller impurity content obtained in the analysis described above.

An estimation of an actual impurity concentration in the investigated samples performed by arc atomic emission spectroscopy have shown,[5] e.g., that the concentration of iron in CoSi sample No. 17 is $\sim(0.02 \pm 0.01)$ mass %. Therefore, it is not excluded that Fe impurity can be solely responsible for a paramagnetic contribution to $\chi(T)$ of this particular sample.[5] Iron impurity in the Br17 crystal can also give a natural explanation (connected with the Kondo effect) for a shallow minimum in $\rho(T)$ as well as for the small negative magnetoresistance reported for it in Ref. 1.

It should also be noted that the Curie-Weiss behavior in $\chi(T)$ of CoSi does not necessarily imply the existence of *local* magnetic moments. It is sufficient to mention MnSi (Ref. 9) and closely related $Co_{1-x}Fe_xSi$ alloys.[10–12] These are compounds with strong paramagnetic $\chi(T)$ dependencies, which are usually considered as connected with spin fluctuations of band electrons.

The next problem of Ref. 1 is connected with *temperature dependencies of resistivity* $\rho(T)$ of four different CoSi crystals. The reported data are so close to each other (within ∼1%) at $T \approx 250$–300 K that it is extremely unlikely to be reproducible for any reasonable accuracy of resistivity measurements.

To demonstrate this, it should be mentioned that, usually, an uncertainty in ρ measurement is mainly connected with the uncertainty of a geometrical factor. This is especially true for ρ measurements of relatively small single crystals as well as for experiments under pressure. For real samples with relatively small sizes, a typical accuracy in determination of ρ may be considered as ∼20%. To achieve a better result, very careful measurements of a sample' dimensions are necessary. Also, it is essential to take into account finite dimensions of electrical contacts as well as the possible nonhomogeneous character of current flow through the sample, etc. Taking all these points into consideration, it is very difficult to understand the very close values of reported resistivity for the four different CoSi crystals at $T \approx 250$–300 K. Moreover, careful examination of Fig. 1 from Ref. 1 has shown that $\rho(T)$ curves coincide within ∼0.25% for all crystals near $T = 273$ K. A rough estimation (given by elemental statistical analysis) of the probability of such a coincidence shows that it is extremely low, namely, $\sim 2 \times 10^{-7}$, *even in the case of ideally equal resistivity of all four samples*. (The probability remains very small $\sim 2 \times 10^{-5}$ in the case of much better accuracy of resistivity measurements ∼5%, which is really hard to achieve for real crystals.)

It is natural to ask whether it is possible to reproduce the reported results on $\rho(T)$? The answer is very simple: The probability to get similar results in two subsequent *independent* ρ measurements of four samples (that means making new contacts, etc.) is on the order of $(2 \times 10^{-7})^2 \approx 4 \times 10^{-14}$ ($\approx 4 \times 10^{-10}$ for ∼5% accuracy of resistivity measurements). Physically, this event can be considered as almost impossible, i.e., *the reproducing of a surprising coincidence in resistivity reported in Ref. 1 is practically impossible*. In the best case, it should be considered as an accidental event. [Actually, some other reasons, e.g., a normalization of the reported $\rho(T)$ curves at $T \approx 273$ K for some reason unmentioned in the paper, are far more probable than an accidental coincidence.]

A nice illustration for the above discussion can be obtained by comparison of Figs. 1 and 2 from Ref. 1. Figure 2 represents $\rho(T)$ curves for the Ames CoSi crystal determined at various pressures, including results at normal pressure. Data for *the same* CoSi crystal are also shown in Fig. 1. It is easy to see a difference in resistivity of *two samples of the same crystal* approaching ∼15% and ∼50% at $T = 300$ and 5 K, respectively.

It is unreasonable to discuss any questions connected with a comparison of ρ for *different* crystals as well as the problem of an applicability of the parallel resistor model (based on "practically the same" high-temperature asymptotic values of resistivity[1] of different samples of CoSi), etc., when the data for *two samples from the same crystal* vary from ∼15% up to ∼50%.

In conclusion, the problems of Ref. 1 discussed above concern key points of the authors argumentation. As a result, the main conclusions of this paper become unjustified.

Valuable discussions with V. N. Krasnorussky were greatly appreciated.

*narozhnyivn@gmail.com

[1] S. M. Stishov, A. E. Petrova, V. A. Sidorov, and D. Menzel, Phys. Rev. B **86**, 064433 (2012).

[2] Actually, in Ref. 1, this expression was mistakenly written as $\chi(T) = \chi_0 + D \times T + C/(T + \Theta)$.

[3] In Ref. 1, the reported results are connected with magnetization M linearly dependent on magnetic field H. Actually, raw experimental data contain some nonlinear terms in $M(H)$, which were subtracted after careful $M(H)$ measurements[4,5] at various T's.

[4] V. N. Narozhnyi and V. N. Krasnorussky (unpublished) (in Russian) [http://www.ioffe.ru/nt36/main_menu/nt36ba.pdf].
[5] V. N. Narozhnyi and V. N. Krasnorussky, Zh. Eksp. Teor. Fiz. **143**, 900 (2013).
[6] P. W. Selwood, *Magnetochemistry*, 2nd ed. (Interscience, New York, 1956).
[7] V. N. Narozhnyi and S.-L. Drechsler, Phys. Rev. Lett. **82**, 461 (1999).
[8] The problem of magnetic-moment formation on Fe impurity in $Co_{1-x}Fe_xSi$ is rather complicated, see, e.g., Refs. 10–12. It is not possible to discuss it in more detail here. Our estimation of the supposed iron concentration with $\mu_{\rm eff} \approx 5.9\mu_{\rm B}$ from the values of the Curie constants determined in Ref. 5 gives the values of $\sim$0.019% for sample No. 17 and $\sim$0.064%–0.11% for the other samples.
[9] T. Moriya, *Fluctuations in Itinerant Electron Magnetism* (Springer-Verlag, Berlin, 1985).
[10] S. Kawarazaki, H. Yasuoka, Y. Nakamura, and J. H. Wernick, J. Phys. Soc. Jpn. **41**, 1171 (1976).
[11] J. Beille, J. Voiron, and M. Roth, Solid State Commun. **47**, 399 (1983).
[12] J. Guevara, V. Vildosola, J. Milano, and A. M. Llois, Phys. Rev. B **69**, 184422 (2004).