Comment on "Structural, electronic, and optical properties of the C-C complex in bulk silicon from first principles" [J. Appl. Phys. 123, 161421 (2018)]

E. V. Lavrov[a)]

Technische Universität Dresden, 01062 Dresden, Germany and Tomsk State University, 634050 Tomsk, Russia

Recently, Timerkaeva *et al.* [J. Appl. Phys. **123**, 161421 (2018)] reported the results of a first principles study of the di-carbon (C_sC_i) complex in silicon. The authors have found that C_sC_i may occur in four configurations labeled *A*, *B*, *C*, and *D*. The *C* form is claimed to have the lowest energy of all four forms. Based on this, the authors suggest that the *C* form was misinterpreted as the *B* form in some experimental studies. This comment provides arguments that the conclusions of Timerkaeva *et al.* [J. Appl. Phys. **123**, 161421 (2018)] do not match the well-known experimental results. *Published by AIP Publishing.* https://doi.org/10.1063/1.5040456

It is well-known that irradiation of carbon-doped silicon with high energy particles, e.g., electrons, results in the formation of a di-carbon complex C_sC_i. The properties of C_sC_i were extensively investigated for decades by means of electron paramagnetic resonance,[1] optically detected magnetic resonance,[2] deep-level transient spectroscopy,[3] photoluminescence,[4] and IR absorption.[5] It was established that the complex is metastable and occurs in two configurations labeled *A* and *B*. The *A* form represents the global minimum for the singly positive and singly negative charge states, whereas the *B* form is energetically favored in the neutral charge state. First principles calculations came up with atomic structures of both forms.[6,7]

Recently, Timerkaeva *et al.* have reported the results of a first principles study of C_sC_i.[8] The authors have found that this complex may occur in two more configurations labeled *C* and *D*. Interestingly, the *C* form was found to be the most stable one with the binding energy at least 0.4 eV higher compared to any other configuration. This led Timerkaeva *et al.* to the conclusion that the *C* form was misinterpreted as the *B* form in some experiments.

In order to corroborate their conclusions, Timerkaeva *et al.* calculated local vibrational mode (LVM) frequencies for all four configurations of C_sC_i. Each of the "new" forms turned out to have a LVM between 1100 and 1200 cm^{-1}. On the other hand, all IR absorption lines due to this complex reported in the literature have frequencies below 960 cm^{-1}. To bypass this difficulty, Timerkaeva *et al.* claim that "*this peak was not observed since, like in the study of Lavrov* et al., *the spectral range is often only scanned up to 1000 cm^{-1}.*"

In fact, the spectra Timerkaeva *et al.* referred to were measured in the range from 450 to 7800 cm^{-1} since in the accordance with the Fellgett's advantage of the Fourier transform spectroscopy information about all wave numbers is sampled simultaneously at no additional cost.[9] Only the parts relevant for the C_sC_i complex were presented.

Figure 1 shows sections of the same spectra as those given in Ref. 5 but expanded up to 1200 cm^{-1}. The spectra were recorded for a Si:^{12}C sample irradiated with electrons at $T \leq 200$ K after annealing it at room temperature for 10, 45, 80, 110, 130, 160, and 820 min. All spectra were subtracted by the spectrum measured directly after irradiation, which explains the negative sign of the peaks due to C_s (607 cm^{-1}) and C_i (922 and 932 cm^{-1}). The formation of C_sC_i via appearance of the modes at 540, 543, 580, 641, 730, and 842 cm^{-1} can be clearly followed. No line with comparable intensity and similar annealing behavior appears in the
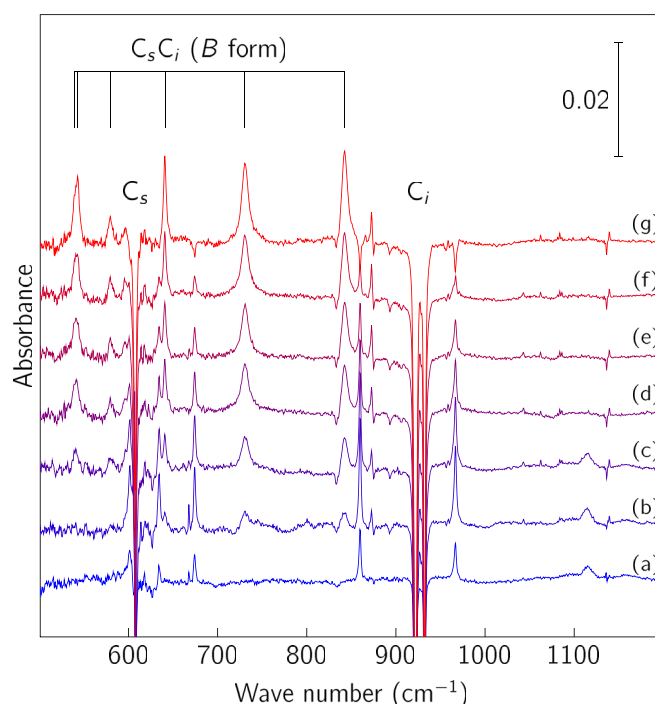

FIG. 1. Sections of IR absorption spectra obtained at 10 K from a Si:^{12}C sample irradiated with electrons at $T \leq 200$ K. The spectra were recorded after annealing the sample at RT for: (a) 10, (b) 45, (c) 80, (d) 110, (e) 130, (f) 160, and (g) 820 min. All spectra were subtracted by the spectrum measured directly after irradiation.

a)eduard.lavrov@tu-dresden.de

spectral range 1000 and 1200 cm^{-1}. In fact, this is not surprising, since the complex may have only $2 \times 3 = 6$ modes.

The assignment of the six lines seen in the figure to the B form of C_sC_i was made on the basis of the correlation with the photoluminescence G line.[5] Importantly, the G line reveals LVM replicas with frequencies of 543, 580, and 730 cm^{-1},[4,10] which is a perfect match to those observed in the IR absorption spectra.

Moreover, LVMs of the A form would not be possible to unveil without the knowledge of activation energies of the conversion reactions between the A and B forms previously established from the DLTS and EPR studies.[11] LVM frequencies of both forms are in excellent agreement with those obtained from *ab initio* theory.[6,7] Putting all these findings together leads to an obvious conclusion: the G line and the 540-, 543-, 580-, 641-, 730-, and 842-cm^{-1} modes originate from the B form of C_sC_i. IR absorption studies do not justify the existence of another modification of this complex in an appreciable amount.

Finally, we note that Table II in Ref. 8 quotes two LVMs at 527 and 749 cm^{-1} assigning them to a not identified carbon-related complex. The reference given is our paper entitled "*Local vibrational modes of two neighboring substitutional carbon atoms in silicon*" where this defect was addressed by means of IR absorption and first principles theory.[12] Strong evidence was presented that the 527- and 749-cm^{-1} modes are due to the neutral and the negative charge state of the C_sC_s complex, respectively. Timerkaeva *et al.* present no arguments in order to explain why they disagree with our assignment and qualify the defect as "*not identified.*"

[1]K. L. Brower, Phys. Rev. B **9**, 2607 (1974).

[2]K. O'Donnell, K. Lee, and G. Watkins, Physica B & C **116**, 258 (1983).

[3]L. W. Song, B. W. Benson, and G. D. Watkins, Appl. Phys. Lett. **51**, 1155 (1987).

[4]G. Davies, Phys. Rep. **176**, 83 (1989).

[5]E. V. Lavrov, L. Hoffmann, and B. Bech Nielsen, Phys. Rev. B **60**, 8081 (1999).

[6]P. Leary, R. Jones, S. Öberg, and V. J. B. Torres, Phys. Rev. B **55**, 2188 (1997).

[7]R. B. Capaz, A. Dal Pino, and J. D. Joannopoulos, Phys. Rev. B **58**, 9845 (1998).

[8]D. Timerkaeva, C. Attaccalite, G. Brenet, D. Caliste, and P. Pochet, J. Appl. Phys. **123**, 161421 (2018).

[9]R. J. Bell, *Introductory Fourier Transform Spectroscopy* (Academic Press, New York/London, 1972).

[10]E. C. Lightowlers and A. N. Safonov, Mater. Sci. Forum. **258–263**, 617 (1997).

[11]L. W. Song, X. D. Zhan, B. W. Benson, and G. D. Watkins, Phys. Rev. B **42**, 5765 (1990).

[12]E. V. Lavrov, B. Bech Nielsen, J. R. Byberg, B. Hourahine, R. Jones, S. Öberg, and P. R. Briddon, Phys. Rev. B **62**, 158 (2000).