

LETTERS TO THE EDITORS

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Once more about the experimental investigation of the thermal properties of carbon

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In September 2001 the authors of the present letter, after making a report at the theoretical seminar held at the P N Lebedev Physics Institute of the Russian Academy of Sciences and following a suggestion made by V L Ginzburg, prepared and submitted an article to *Uspekhi Fizicheskikh Nauk* [*Physics – Uspekhi*] [1]. The article aroused interest, since it presented a new view on the phase diagram of carbon near the solid – liquid – vapor triple point. The result was a change in the parameters of the triple point and, as the authors believe, a consistent version of the phase diagram of carbon explaining the entire set of experimental data that existed at that time.

However, in no way did we think then (nor do we think now) that our version of the phase diagram of carbon was final. On the contrary, we expected a lively discussion, the more so since, as noted in our article [1], several views exist on the specific problems and the data on triple point parameters. Moreover, several of our reports at scientific seminars provoked quite an exchange of opinion. One example is the 'Carbon' seminar we organized at the Joint Institute for High Temperatures, where each scientist involved in specific research could explain his point of view on the problem in a dignified atmosphere of scientific discussions. Several researchers invited from other scientific institutions were also given the chance to explain their views on the subject.

We note, reiterating the conclusions made by many researchers on the topic of graphite properties, that the problem of building a final version of the phase diagram of carbon is far from complete, and new research and papers that would interpret the data correctly are only to be welcomed.

However, in his letter [2], A I Savvatimskiĭ criticised many aspects of Ref. [1]. But what is the essence of these critical remarks made in connection with our model of the phase diagram proposed in Ref. [1]?

'The main difference of the data published in Ref. [1] from other...', the author of Ref. [2] assumes, 'is the low value of the graphite melting point' (p. 1372 [p. 1295]). We will return to this statement, but at this point we would like to say that it is false. Actually, the main difference in our line of reasoning in Ref. [1] is that our value of the pressure at the triple point differs by a factor of 100 from the values given in other works. On the other hand, our values of the temperature at the triple point are close to 4000 K, which is customary in carbon research. The corresponding comparison is given, say, in Ref. [3]. It must be noted that Savvatimskiĭ in Ref. [2] questions not only our results in Ref. [1] but the results of several other scientists. For instance, he believes that the measurements done by Whittaker [4] are not reliable (p. 1372 [p. 1295]) and that the validity of the experiments of M Pirani (p. 1376 [p. 1295]) is doubtful. But it was precisely Whittaker who was the first to irrevocably prove that carbon melts at relatively low parameters (having discovered drops of liquid, including carbyne) and was also the first to place the respective curves in the phase diagram of carbon, while the thermal physicist M Pirani is known as the designer of fine thermophysical devices, e.g., a thermoelectric manometer combined with a resistance thermometer and a constant-volume gas thermometer, used in measuring low pressures [5].

This is how passion (possibly provoked by somebody else), together with the absence of knowledge on the topic being discussed, has let Savvatimskiĭ down.

The main part of Savvatimskiĭ's letter [2] is simply an attempt to cast discredit on all the measurements described in Ref. [1] and on the thoroughness of the present authors in selecting literature for the sake of comparing the data. The style of his letter is roughly the following: the authors of Ref. [1] measured a certain parameter in this or that way, but the point of view of researcher X is the following, etc., etc.

Into the present brief response we cannot hope to place all the commentaries to Ref. [2], and we really believe that *Uspekhi Fizicheskikh Nauk* [*Physics – Uspekhi*] is not the place to do this. Rightfully, this should be done at specialized seminars. However, some of the questions require our answers.

Let us return to the main topic that bothers Savvatimskiĭ so much: is the melting point of carbon 4000 K or is it 5000 K? Repetitions are inevitable here, since otherwise it is difficult to understand the crux of the problem, which already has some history behind it.

In our work [1], we took the 10 papers most often cited and discussed in the related area of research (see Table 1 in Ref. [1]). The results of these papers demonstrated that steady-state experiments yield $T_{\rm m} \approx 4000$ K, while pulsed techniques of measurements yield different temperatures, which proved to be high, about 5000 K. We must immediately note that we in no way are criticising the methods of pulsed measurements in general. Usually, a well-organized

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pulsed experiment yields reliable results, it is simpler than a steady-state experiment, and its results agree with those of steady-state experiments. This is all true, provided that 'along the way', i.e., in the process of heating, the substance is not transformed, say, in a phase transformation accompanied by a thermal effect of some sort and thus requiring certain time. In such cases, pulsed techniques are not really useless, but their output is doubtful since, having very short proper times, they react to the properties of the initial material (e.g., graphite, since the graphite – carbyne transition, which requires several seconds for its completion, will not even be 'felt' by the experiment). Naturally, one cannot expect that the melting of the more fusible fraction (compared to the main material) will be recorded or, in other words, that the first drop of the liquid (in our case, presumably, carbyne) will be noticed.

So what does the author of Ref. [2] propose in such a situation? He suggests 'analyzing a wider spectrum of experimental data', i.e., 13 papers instead of 10. According to Ref. [2], the number of works cited in Ref. [1] in this connection is five. This statement is actually untrue, as well as many other statements of Ref. [2].

So what has Savvatimskiĭ included in this 'extended' list of papers?

Two works, Refs [6, 7], were done under the guidance of one of the authors of Ref. [1]. The group of researchers used the thermogram method to study the liquid – vapor coexistence curve (the boiling curve). The work was successfully completed and its results are given in full in Ref. [1]. Melting was not specially studied in those two works, and the figures in row 1 of Table 1 in Ref. [2] appeared as a result of the following chain of events. At the beginning of the 1980s, no one doubted (at least no doubts were expressed at the time) that carbon melts at $p \geqslant 100$ bar. The theoretical work of Leider et al. [8] clearly pointed to such a situation. Thus, we took the point on the boiling curve at 100 bar and assumed it to be close to the temperature of the triple point. Of course, this line of reasoning seems simplistic, but it is the only one possible in this brief reply. All details have been published in papers and theses. Thus, we can say that $T_{\mathrm{m}} \simeq 5000$ K is our invention, i.e., the invention of the authors of Refs [6, 7]. Only much later, at the end of the 1990s, when pondering the phase diagram of carbon, did we come to the conclusion expressed in Ref. [1].

Savvatimskiĭ in Ref. [2] suggests taking the second figure in row 2 of Table 1 as the basic figure, since it is the later one and, in his opinion, more reliable because of this. Although row 3 of the same table does not contradict the line of reasoning that led us to Table 1 of Ref. [1], we would prefer not to consider it, since the high-pressure region does not belong to our area of interest. Row 4 in Table 1 of Ref. [2] is present in Table 1 of Ref. [1], and so is row 8.

There are still some works, dealing mainly with high pressures, that were done by consistent followers of the idea that $T_{\mathrm{m}} \cong 5000$ K, including the author of Ref. [2], whose results, however, have not been published. To discuss each of these would be a waste of time, since all of them deal with very short (in the microsecond range) heating times and $T_{\mathrm{m}} = 5000$ K.

If the author of Ref [2] had at least made an attempt to list in his Table 1 some of the results of steady-state research, the meaning of the tables in Refs [1, 2] would be similar. But even without such an addition we can agree with one of the conclusions arrived at in Ref. [2] (p. 1372 [p. 1295]). There are two groups of works: rapid heating yields $T_{\mathrm{m}} \cong 5000$ K, while slow (quasistationary) heating yields $T_{\mathrm{m}} \cong 4000$ K. The specific dependence of T_{m} on the heating time is of no interest to us.

The only explanation for Savvatimskiĭ's complete rejection of the idea that $T_{\mathrm{m}} = 4000$ K lies, apparently, in the following. Unfortunately for us, several years ago A I Savvatimskiĭ conducted pulsed (explosion) experiments with carbon and found (Fig. 6 in Ref. [2]) the curve of the rise in temperature in a specimen with $T_{\mathrm{m}} \cong 5000$ K. This curve was criticised many times at seminars held at the Institute of High Energy Densities not because of the value of the melting point but because of the poor (or simply no) $p - T$ diagnostics. Today the temperature behavior seems to be known, but the pressure inside the sample is not. We believe that to represent this curve in thermodynamic coordinates is simply incorrect. However, the author of Ref. [2] continues to ponder the 'principal' question (in his opinion) of whether the melting point of carbon is 4000 or 5000 K. And now this question is being discussed in *Uspekhi Fizicheskikh Nauk* [*Physics – Uspekhi*]!

We believe it is inexpedient to discuss all the possible errors of measurements that appear in Refs [1, 2], all the more so since many aspects touched on in Ref. [2] often lie far from those discussed in Ref. [1].

Undoubtedly, the first to announce that there is a graphite – carbyne solid-state transition was Whittaker [4]. We believe that we have corroborated this statement in full. We also agree that studies of thermal explosions should be continued. However, we cannot agree with the insulting accusation of being selective in our choice of references in Ref. [1]. We also reject all accusations of careless research.

In conclusion we would like to assure the editorial board of *Uspekhi Fizicheskikh Nauk* [*Physics – Uspekhi*] that it is impossible to extract any useful conclusions from Ref. [2]. Almost everything that was written in Ref. [2] is well-known and has been discussed many times.

We, of course, are aware of the fact that Ref. [1] has its weaknesses and drawbacks (the same can be said of almost any work). We have ideas on how to improve it and continue our research, trying to establish the correct phase diagram for carbon.

We hope that in the case of success in this complicated experimental research the editorial board of *Uspekhi Fizicheskikh Nauk* [*Physics – Uspekhi*] will agree to publish a continuation of our paper [1].

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