

# Exciting News from Indentations onto Silicon, Copper, and Tungsten

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## Abstract

Indentations onto crystalline silicon and copper with various indenter geometries, loading forces at room temperature belong to the widest interests in the field, because of the physical detection of structural phase transitions. By using the mathematically deduced  $F_N \propto h^{3/2}$  relation for conical and pyramidal indentations we have a toolbox for deciding between faked and experimental loading curves. Four printed silicon indentation loading curves (labelled with 292 K, 260 K, 240 K and 210 K) proved to be faked and not experimental. This is problematic for the AI (artificial intelligence) that will probably not be able to sort faked data out by itself but must be told to do so. High risks arise, when published faked indentation reports remain unidentified and unreported for the mechanics engineers by reading, or via AI. For example, when AI recommends a faked quality such as “no phase changes” of a technical material that is therefore used, it might break down due to an actually present low force, low transition energy phase-change. This paper thus installed a tool box for the distinction of experimental and faked loading curves of indentations. We found experimental and faked loading curves of the same research group with overall 14 authoring co-workers in three publications where valid and faked ones were next to each other and I can thus only report on the experimental ones. The comparison of Si and Cu with W at 20-fold higher physical hardness shows its enormous influence to the energies of phase transition and of their transition energies. Thus, the commonly preferred ISO14577-ASTM hardness values  $H_{ISO}$  (these violate the energy law and are simulated!) leads to almost blind characterization and use of mechanically stressed technical materials (e.g. airplanes, windmills, bridges, etc). The reasons are carefully detected and reported to disprove that the coincidence or very close coincidence of all of the published loading curves from 150 K to 298 K are constructed but not experimental. A tool-box for distinction of experimental from faked indentation loading curves (simulations must be indicated) is established in view of protecting the AI from faked data,

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which it might not be able by itself to sort them out, so that technical materials with wrongly attributed mechanical properties might lead to catastrophic accidents such as all of us know of. There is also the risk that false theories might lead to discourage the design of important research projects or for not getting them granted. This might for example hamper or ill-fame new low temperature indentation projects. The various hints for identifying faked claims are thus presented in great detail. The low-temperature instrumental indentations onto silicon have been faked in two consecutive publications and their reporting in the third one, so that these are not available for the calculation of activation energies. Conversely, the same research group published an indentation loading curve of copper as taken at 150 K that could be tested for its validity with the therefore created tools of validity tests. The physical algebraic calculations provided the epochal detection of two highly exothermic phase transitions of copper that created two polymorphs with negative standard energy content. This is world-wide the second case and the first one far above the 77 K of liquid nitrogen. Its existence poses completely new thoughts for physics chemistry and perhaps techniques but all of them are open and unprepared for our comprehension. The first chemical reactions might be in-situ photolysis and the phase transitions can be calculated from experimental curves. But several further reported low temperature indentation loading curves of silicon were tested for their experimental reality. And the results are compared to new analyses with genuine room temperature results. A lot is to be learned from the differences at room and low temperature.

### Keywords

Phase-Transition-Onset and -Energy, Indentation of Silicone, Copper, Copper Nanoparticles, Tungsten with Polymorphs, Low-Temperature Indentations, Detection of Faked Loading Curves, Protection of AI from False Advices, Risk of Catastrophic Crashes, Physical Hardness, Exothermic Copper-Transitions, Algebraic Calculations, Negative-Standard-Energy Polymorphs

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## 1. Introduction

The indentation onto silicon has been most frequently studied with pyramidal, conical, and spherical indenters onto different faces and the different polymorphs were identified by Raman spectroscopy [1]. The indentation data have been compared with anvil pressurising. A survey of the numerous publications is given in [2]. The anisotropies at different faces have been explained on the basis of crystal-packing images with respect of the channel angles (Table (8.3 in [2])). The 4 phase-transition onsets and endothermic energies thus differ under (001) data (up to 50 mN) from [3] and very likely the additional under (100) data (up to 100 mN load) from [4]. But in-situ Raman spectroscopy would be required for the determination of the crystal-structure for all of these. This would clarify and extend the rather complicated transformations of the Si-polymorphs upon

pressure relief, which clearly requires clarification. The results will be compared in Section 3.2.5 with the indentations onto much harder tungsten at 25°C and 243 K below.

Unfortunately, low temperature indentations did generally not find much interest even though much more could be expected for the behavior of phase-transitions. The common iterative and unphysical ISO-enforced analyses of indentations did not know that the mathematically deduced correct  $F_N \propto kh^{3/2}$  relation [5] allows for a simple algebraic determination of phase-transitions with their onsets, transformation energies and temperature dependent activation energies (Chapter 6 from [2]) just from the  $F_N$ - $h$  loading curves. Therefore, the numerous applications of these unexpected possibilities [2] (in its Chapters 7 and 8), [5] [6] [7], were not included in the ISO prescriptions that urgently require revision. This lack did not favour particular interest in the behavior of phase-transitions at low temperatures upon indentations. Conversely, the question of phase-transition energies would certainly have led researchers to consider that endothermic phase-transitions need energetic support and would be less likely at lower temperatures than exothermic ones that deliver energy. This has been clearly discussed and proved in [7] with very rare published experimental loading curves of the heavy-duty Al7075 alloy [7] at high 293 K - 123 K (two endothermic transitions) with comparison to the loading curve at 77 K (liquid nitrogen). Our clear-cut predictions with respect to the energy law revealed unprecedented results. There are two endothermic transitions at the high temperatures and only the low-force endothermic one can surprisingly still occur at 77 K with 0.71 N $\mu$ m/ $\Delta\mu$ m normalised transition energy. But at twice the force the transformation onset cannot be supplied anymore and one obtains an enormous exothermic transition with -54.4 N $\mu$ m/ $\Delta\mu$ m normalized transition energy and the loading curve continues until 3 times the force where it is truncated. Such enormous energy delivery is unprecedented. The transformed material has very high negative energy content. Such epochal news reveals an unprecedented new type of matter far away from our thermodynamics, opening particular interest for further studies. This was for the first time shown with the analysis of Al7075 alloy at liquid nitrogen temperature [7]. It opens interest in exciting yet unthinkable results and requires further examples of exothermic phase-transitions by keeping away the endothermic possibilities.

We therefore check the published loading curve of (100) silicon at 77 K [8]. Clearly, there is very considerable loss of information from this 77 K indentation onto silicon after withdrawing of the indenter, and the thawing up to room temperature gave sharp Raman peaks only upon indentation, whereas broad Raman bands were obtained when the indentations were made at low temperature with 0.98 N loads. But the observed formation of several sharp bands with the sharpest at 351.6 cm<sup>-1</sup> proved structural phase transition. Unfortunately, the analyses were only performed after retracting of the indenter and thawing up to room temperature. Additionally, only “shear-lines”, “radial/median cracks”, and

“no extruded material” were reported upon one-point Vickers impressions. The claim was that structural phase-transition into Si-II does not occur upon one-point Vickers indentation with 0.98 N at 77 K [8] (immersed in liquid nitrogen). The so obtained broad micro-Raman bands indicated only amorphous silicon in addition to a residual sharp Si-I peak at  $521.6\text{ cm}^{-1}$ . Upon reloading of the 77 K indentation only broadened the amorphous bands with Raman-shifting. It was reported that the room temperature indentation onto an amorphous silicon film without the  $521\text{ cm}^{-1}$  peak gave the very broad Raman bands and some sharp peaks, most prominent the one at  $354\text{ cm}^{-1}$  from Si-III [8]. Later, the same authors confirmed these views by studies with “electric resistivity”, and a theoretical pressure-temperature phase-diagram of silicon” was established [9].

We recently studied endothermic phase-transitions at ambient and high temperatures with physically correct closed algebraic formulas including the phase-transition energies. And we compared it with exothermic phase-transitions that only occurred at very low temperatures and explained it on the basis of the energy law [7]. With the hope to find further published indentation loading curves with, of course, exothermic phase-transitions we searched published indentation loading curves at low temperatures for their corresponding analyses. It thus appeared attractive to compare the low temperature ISO 14577 hardness values of silicon with the further materials [10] [11].

It looked enticing to analyze the report on indentations onto the Si (100) surface at 210 K, 240 K, 60 K, and 292 K, because the reported loading curves appear almost equal with the room temperature curve [12]. And similarly, the publication of [13] reports the indentations onto Si (110) at 150 K, 200 K, 250 K and 298 K with identical force-depth loading curves. All the differently coloured loading curves are almost indistinguishably overlaying. And there is phase-transition. The reason for the imaged pop-outs (only under Si (100) sloping) that cuts the free unloading curve is not addressed in [12] [13] (at room temperature, or only at 240 K) remains obscure. Such instrumental or environmental disturbances have to be avoided or repaired instead of being misinterpreted (Chapter 10 of [2]).

Structural phase transition occurred at room temperature onto Si (100) with Berkovich loads in the 100 mN region, as published by [3] and by [4] onto Si (001). These results have been summarized together with the phase-transformation energies in [2] (Table 8.3, page 113). A “cyclic loading curve” with Berkovich was reported by [1] at room temperature and the Raman spectrum proved the structural phase-transition. Another publication used amorphous silicon and reported on indentations onto Si (100) at 210 K, 240 K, 260 K and 292 K [12]. All these published loading curves are very similar in shape and incredibly close together. They follow the experimental  $F_N$  vs  $h^{3/2}$  relation, but this 292 K curve is very far away from the well-known already known results. The Raman spectra after retraction of the indenter and heating up to room temperature indicated amorphization showing very broad Raman bands and only at the 292 K run also sharp peaks as attributed to Si XII. The interpretation of these results is more

than awkward and requires clarification with the analysis of the indentation loading curves. The present author's analysis of their 292 K indentation reveals that the typically shaped Raman peaks are proving the structural phase-transition.

But, the 292 K and the 260 K are so close that an elucidation of the loading curve should be helpful. That would check the validity of the published curves.

Also amorphous silicon has been indented at room temperature. Some sharp Raman peaks ensued most prominently with the  $354\text{ cm}^{-1}$  peak from the transformed silicon that is attributed the Si-III structure on the remaining very broad amorphous silicon Raman bands [8].

And amorphous silicon was also found upon indentation of Si (100) at 210 K and 260 K [12]. And the very broad Raman bands and some amorphous Si were also found at their indentation in addition to the phase-transition with the sharp Raman peaks that were assigned to Si (III).

While the loading curves at lowered temperatures have been rare yet, the development of commercial instruments is proceeding now. For example, the quantitative in-situ nanomechanical testing down to 243 K and below is possible now with for example with the PI Cryo environmental stage for in-situ nanomechanical SEM testing of for example Bruker Company, and certainly numerous further technical devices will come to the market.

It appears now useful to repeat how we got to the physically correct formulas in the References [2] and [5] and why and how we located faked and forged indentation loading curves at low temperatures. We also repeat our continuous warnings of catastrophic crashes (e.g. of airliners) if the face-transition onset forces and phase-transition energies from easily and rapidly obtained indentations are not used to eliminate materials exhibiting too low values of these properties. The reason for such crashes is phase-transitions upon mechanical stress (e.g. turbulences) for the generation of polymorph interfaces as the sites for hardly seen pre-cracks that are nucleation sites for catastrophic crashes upon further mechanical stress. I also give reason that AI must be protected from faked and forged reports.

High risks arise, when faked or forged published indentation reports remain unidentified and unreported for the mechanics engineers by reading or via AI. When phase-transition onset forces remain undetected for technical materials at airplanes, windmills, bridges, etc) one cannot remove inferior materials with better ones (higher onset force and higher transition energy), where the pre-crack formations followed by catastrophic crashing are diminished. As instrumental indentations are most easy and rapidly performed for providing experimental loading curves, this technique should be used for identifying materials that more safely withstand the forces occurring upon their use (e. g. turbulences upon airliners etc). Only the experimental data must be used and their physically correct analyses are essential (without iterations to unsuitable standard materials and energy-law violations) provide the necessary data. AI has to be protected from faked data that look as if these might be experimental and properly analyzed. The widely used ISO14577-ASTM standards cannot detect phase-transition on-

set forces and energies, because they do not define a physical hardness  $k$  ( $\text{N}/\text{m}^{3/2}$ ) as the impression resistance against the impression force, in the case of conical or pyramidal indenters. That is the since 2013 and finally 2016 known resistance against depth and at the same time pressure-formation, both requiring force and thus energy. It is thus impossible to use all of the applied force  $F_N$  for the penetration and the still widely used  $H_{\text{ISO}}$  ( $\text{N}/\text{m}^2$ ) since the clear-cut physical deduction of 2016. With the pressure plus all from it produced changes besides the impression must be proportional to the volume of the impressing cone or pyramid (exponent 3) follows for the impression part  $F_N = k h^{3/2}$  (1) where  $k$  is the penetration resistance (physical hardness) as obtained by linear regression of such plot (sometimes called Kaupp-plot). All formulas (1) through (7) are deduced from it by basic mathematics and physics.

The most important reason for the non-authenticity of the overlaying curves as forged is their totally missing temperature influence in [12] [13]. This at first glance questions their being not authentic, because it would deny and disregard any temperature effect upon the energetic processes upon indentations below room temperature and 150 K. And that could be three times full-published in International Journals!? But that is not the only reason for now qualifying them as forged.

We list now the recipe a) through h) how forged curves might be found and sorted out, because AI must be told to not use them or to also learn to sort them out.

For the check of authenticity of published loading curves, we use several steps a) - h).

- a) Do they follow the  $F_N = kh^{3/2}$  law Equation (1)?
- b) Do they also contain the kink unsteadiness', indicating the phase-transition(s), as already known for the material in question or for related materials? If not, one must try at increased loading forces!
- c) Do the direct claims with such curves obey all common physical rules of energetics and kinetics? (Here was the missing temperature influence eye-catching)
- d) Did the authors draw a false sloping "pop-out" and two years later a horizontal "pop-out" both to one of the overlying unloading curves but both cutting the further three for trying to make happy the old-fashioned believers of such instrumental disturbance who falsely interpret them as "phase-changes"?
- e) Are the quoted results by far too precise and thus never be attainable for rather difficult not automated experimental measurements under the given conditions?
- f) Do the authors use measurements that were disturbed by instrumental disturbances rather than repeating them undisturbed or with cleaner surfaces or at different sites of the sample?
- g) Are there 7 co-authors in one publication and 7 new co-authors in a two years later publication? Can all of these be highly qualified and responsible for

proper data? Or could they not successfully protest when evidently falsely guided?

h) Are the reference curves far away from always known loading curves of the same material?

The three times published false claim (onto silicon and also referring to #1 and #2) that there must be no low temperature influence at all might have scared scientists to apply for low-temperature indentation projects or it might have encouraged reviewers to shut down hopeful projects by reasoning that these are less important or most likely unsuccessful.

## 2. Experimental

The analysis of the indentation loading curves use the linear  $F_N = kh^{3/2} + F_a$  plots with regression calculation from Excel\*. Regressions are always between 0.9995 and 0.9998.  $F_N$  means normal applied force; italic  $k$  is the penetration resistance or physical hardness (slope of the linear plot with kink unsteadiness in case of phase-transition at materials dependent load  $F_N$  and depth  $h$ ).  $F_a$  means axis cut force of such linear plots that is only needed for the calculation of the kink position and the transition energy. The calculated phase-transition energy  $W_{trans}$  is obtained after integration of the indentation loading curves. The distinction of indentation work  $W_{indent}$  and  $W_{applied}$  is required. They relate for cones and pyramids with the factor 1.25. The purely arithmetic calculation schemes are amply published with the formulas (1) through (7). The present data are taken from published loading plots. These are enlarged to near A4 size from the printed size. At least 20 equidistant data points are selected and their  $F_N$  vs  $h^{3/2}$  plot regression calculated with Excel\*. So called, though rare, pop-ins are repaired. We always analyze clear load-depth plots and detect phase transition kinks also if Raman spectroscopy showed that all was amorphous after pressure release and up-heating, because amorphous to amorphous transitions can also be detected. In-situ analyses are badly needed and developed using now available instrumentation. We repeat here the evaluation formulas as three times printed in [2] (on the pages 91, 106 and 227; but on page 227 in [2] formula (3) is unfortunately missing). This will facilitate in recognizing the mathematically secured strictness of the supposition-free correct calculations.

$$F_N = kh^{3/2} \quad (1)$$

$$F_N = kh^{3/2} + F_{1-a} \quad (2)$$

$$W_{1-applied} = 0.5h_{kink} (F_{N-kink} + F_{1-a}) \quad (3)$$

$$W_{1-indent} = 0.8W_{1-applied} \quad (4)$$

$$W_{2-indent} = 0.4k (h^{5/2} - h_{kink}^{5/2}) + F_{2-a} (h - h_{kink}) \quad (5)$$

$$\text{full } W_{applied} = 0.5F_{N-max} h_{max} \quad (6)$$

$$W_{transition} = \text{full } W_{applied} - \Sigma(W_{applied}) \quad (7)$$

### 3. Results and Discussion

Structural phase transition occurred at room temperature onto Si (100) with Berkovich loads in the 100 mN region, as published by [3] and by [4]. These results have been summarized together with the phase-transformation energies (Table 8.3, page 113 of [2]). A “cyclic loading curve” with Berkovich was reported by [1] at room temperature and the Raman spectrum proved the structural phase-transition. That represents an important basis. Another publication reported upon indentations onto Si (100) at 210 K, 240 K, 260 K and 292 K [12] and these must be importantly challenged. These curves are very similar in shape and close together. They cannot withstand a reality check, even when they follow the experimental  $F_N$  vs  $h^{3/2}$  relation, but the 292 K curve is very far away from the well-known already known results. And they lack the phase-transitions that would reveal in their  $F_N$  vs  $h^{3/2}$  plot. The Raman spectra after retraction of the indenter and heating up to room temperature indicated amorphization by showing very broad Raman bands and only at the 292 K run were also sharp peaks as attributed to Si XII. This requires discussion. The interpretation of these results are more than awkward and require clarification with the analysis of the indentation loading curves. The present author’s analysis of their 292 K indentation revealed the typical shape of Raman peaks, proving the structural phase-transition.

In particular, the 292 K and the 280 K are so close that an elucidation of the loading curve would become helpful. The validity of the published curves will have to be checked. This judgment will be grounded on basic arithmetic and physics.

While the loading curves at lowered temperatures have been rare yet, the development of commercial instruments is proceeding now. For example, the quantitative in-situ nanomechanical testing down to 243 K and below is possible now for example with the PI Cryo environmental stage for in-situ nanomechanical SEM testing of for example the Bruker Company, and certainly numerous further technical devices will come to the market. It will be shown where these must be urgently used.

#### 3.1. On the Behavior of Silicon

##### 3.1.1. The Room Temperature and 300°C Indentations onto Silicon

At very low indentation forces onto (100) Si at room temperature one observes a phase transition that is unimportant for the low temperature discussions as it is hidden within the initial effects of the high forces loading curves and thus corrected out as part of the axis cut in the  $F_N$  vs  $h^{3/2}$  plots. We only start with it for completion of the silicon story. The loading curve of paper [1] was calculated to give a phase-transition kink (calculated with the mN and  $\mu\text{m}$  units for better comparison with the ones of Table 1) at 0.0087 mN and  $0.3014 \mu\text{m}^{3/2}$  and the phase-transition energy is  $0.00687 \text{ mN}\mu\text{m}/\text{mN}$  [2]. However, a detailed comparison with the Table 1 values is not possible. We interpret the low value as the result from twinning and keep in mind that we probably always start with twinned silicon.



**Table 1.** The Berkovich indentations onto silicon at room temperature, 30°C, and 300°C.

Material	Temperature	$k$ , Physical Hardness $\text{mN}\mu\text{m}^{-3/2}$	$h_{\text{kink}}$ $\mu\text{m}$	$F_{\text{Nkink}}$ mN	$W_{\text{transition}}$ ( $\text{mN}\mu\text{m} / \text{mN}$ )	Data Origin
Silicon (100)	19°C	$k_1$ 123.2	0.4077	29.1622	0.1545	[3]
		$k_2$ 145.44				
		$k_3$ 151.53				
Silicon (001) (B-doped, p-Type)	25°C	$k_1$ 121.75	0.2522 0.3309	15.2899 25.2002	0.02687	[4]
		$k_2$ 155.62				
		$k_3$ 160.62				
Silicon (111)	30°C	$k_1$ 135.64	0.2030	13.0533	1.3728	[11]
		$k_2$ 162.07				
		$k_3$ 199.81				
Silicon (111)	300°C	$k_1$ 130.11	0.2057	12.4583	1.2939	[11]
		$k_2$ 152.07				
		$k_3$ 170.26				

We first refer now to the known room temperature results for comparison. Up to 40, 80, 100 mN load there are 3 phase-transition kinks determined (**Table 1**). The room temperature pyramidal indentations onto brittle crystalline silicon (space group Fd3m) are now well studied and analyzed. The Berkovich indentation onto the (100) face of silicon from [3] proceeds with the penetration resistances (physical hardnesses) at  $k_1 = 123.2$ ,  $k_2 = 145.44$ ,  $k_3 = 151.53 \text{ mN}\mu\text{m}^{-3/2}$ . The phase-transition onsets are calculated from [2] (its Table 8.3 on page 113) as 0.4077  $\mu\text{m}$  and 0.7245  $\mu\text{m}$ , the  $F_{\text{Nkink}}$  values at 29.16 and 81.0 mN and the normalized transition work are 0.1545 and 0.47  $\text{mN}\mu\text{m}/\text{mN}$ .

The values for the p-type B-doped (001) face from [4] (its Figure 7a) calculate to  $k_1 = 121.75$ ,  $k_2 = 155.62$ , and  $k_3 = 160.62 \text{ mN}\mu\text{m}^{-3/2}$  with the kinks at 0.2522 and 0.3309  $\mu\text{m}$  at 15.2899 and 25.2002 mN. The again endothermic normalized transition energies calculate to 0.02687 and 0.1942  $\text{mN}\mu\text{m}/\text{mN}$ , which is considerably smaller than from the (100) face. The reasons for this 5.7 and 2.4-fold decrease of the phase-transition energies derives from different angles between the crystal channels and the penetrating indenter face that facilitate more on (100) or less on (001) the required material-transport upon the phase-change. Importantly, these phase-transitions under load at room temperature proceed endothermic, but we expect completely unknown exothermic phase-transitions at low temperatures [7]. Also, the work of [11] yields endothermic transitions now onto Si (111). These authors studied the temperature dependence from 25 up to 800°C for the measurements of the Raman spectra and the determinations of the (unphysical) ISO-ASTM hardness of the transformed phases with Berkovich loads up to 50 mN in 11 steps. Two loading curves are published for 30°C and 300°C up to 50 mN load. Our careful analyses of these curves reveal three polymorphs (two phase transitions) within that range for comparison with further literature data. These are collected in **Table 1** for the comparison via the  $F_{\text{N}} \propto H^{3/2}$  law. We find in all of these experimental cases ( $F_{\text{Nmax}}$  never above 100 mN)

that we identify two phase transitions independent of the probed crystal face, and temperature at least up to 300°C.

Any initial axis cut  $F_{a1}$  reflecting initial effect and twinning peak is always corrected away. But we keep in mind that we might start in all reported cases with initially twinned silicon.

The regression analyses of Berkovich indentations onto Si (001), Si (100), and Si (111) at room temperature reveal the physical hardness values ( $k$ -values with dimension  $\text{mN}\mu\text{m}^{-3/2}$ ) for 2 phase transitions (that is 3 polymorphs each) in all of the 3 cases. These values are listed in **Table 1** together with the values onto the Si (111) at 300°C. **Table 1** also contains the calculated transition onsets (kink points), normalized phase-transition energies and References of the experimental data origin. The transition energy works are calculated and normalized to 0.154, 0.02687, 1.3728 for the first transition and 0.4684, 0.1942, and 8.7863  $\text{N}\mu\text{m}/\Delta\mu\text{m}$  for the second phase-transition. The respective values for (111) at 300°C of 1.2939 and 7.543 become slightly smaller at 300°C and that shows that the higher temperature energetically supports the endothermic transitions. The Berkovich indentation onto silicon (100) ((001) is also (100) for fcc crystals) of [1] was a so-called “cyclic indentation” with three-times intermediate unloading-reloading interruptions at the lower forces that did not destroy the good shape of the total loading curve (the hump at 0.39  $\mu\text{m}$  and of 30.4 mN load was repaired) (Chapter 10 in [2]). This proves the stability of the transformed material, whatever the claimed transformations of Si-II and further reversibility is. Two further reports [12] [13] (same research group) of a room temperature Berkovich indentation published force-depth curves that give straight  $F_N$  vs  $h^{3/2}$  lines without phase-transition kinks, that are impossible and must be rejected as not experimental, together with their low-temperature indentations in Section 3.1.2.

The data of **Table 1** show that the basic physical indenter-hardness (the  $k_1$ -value) is remarkably different upon indentation onto the different surfaces. Clearly, they strongly depend on the different orientations of the channel in the diamond-type structure with respect to the indenter angle, so that transformed material can be better or worse transported (Chapters 5, 7, 8, 15, and 16 in [2]). The smaller the first onset depth and onset force is. If we compare the room temperature results, we see that the larger  $k_1$ , the lower the onset force. The maximal difference is by 9%. And large onset force similarly reverses that series with respect to the onset force at (111). The (001)  $F_{N\text{kink}}$  value could be expected somewhat larger, but the exceptionally low transition energy, and the comparably low endothermic transition energy decrease that force. The maximal  $F_{N\text{kink}}$  difference is by respectable 55%. It is also seen, that the predictions become less clear for the second phase-transition onset. The anisotropy depends here on the interaction of too many geometric and energetic factors and the important phase-transition energies play their role. There is a maximal variation of 54% in the  $k_2$  values that should also be responsible by the comparably low phase-transition energy, the importance of which should not be underestimated. The comparably high

$k$ -values and low  $h_{\text{kink}}$  values of Si (111) are understandable, because the diamond-type crystal structure (Fd3m) packs very densely on that surface and the phase transition is also rendered more difficult at the 65° angle meeting the penetrating Berkovich with few channels that are rather small.

The temperature influence from 30°C to 300°C is not very large, so that we do not expect much change for the force-depth curve at 100°C in [11]. It would be nice to have reliable loading curves onto Si (110), because the diamond type structure exhibits its largest channel under that face.

A detailed comparison of the 19°C indentations onto Si (011) from the figure 3 of [12] or figure 13 of [13] with the values of our Table 1 is not possible, because they do not contain the necessary phase-transitions at all within their 80 or 100 mN loads upon the mathematical analyses (see also Section 3.1.2.). The slopes without kinks from silicon down to 80 mN load are not reported here, because they do not describe reality. Importantly, any pop-ins or pop-outs that sometimes occur in unloading curves at varied retracted loads are never indications of phase-transitions or for their onsets. It is only the kink unsteadiness of  $F_N$  versus  $h^{3/2}$  plots, which proves the phase-transitions by indentations, as is also shown here again.

### 3.1.2. The Low Temperature Indentations onto Silicon

Indentations at low temperatures are rare. The first trials of silicon indentations at 77 K provided unclear conclusions and what followed from 150 K upwards reported also amorphous materials at 292 K and 298 K. The reported data claim complete absence of temperature dependence. We therefore have to solve this obvious scientific dilemma very carefully and exhaustively by using the distinction of endothermic and exothermic phase-transitions, where the latter should be favoured at the low temperatures. Far-reaching temperature differences were used when Si (100) (from MTI Corporation in Hefei, China) was reported to have been indented at 292 K, 260 K, 240 K, and 210 K [12]. But from the blue, green, and red almost overlaying curves in [12] after a short unclear initial effect we obtain only one straight  $F_N$  vs  $h^{3/2}$  line, each up to 80 mN load. Their slopes at the respective temperatures have been calculated as 180.71 (210 K), 181.71 (240 K), 181.53 (260 K) and 181.49 (292 K) mN/ $\mu\text{m}^{3/2}$ . That is an average of  $181.36 \pm 0.5$ , a precision that is not experimentally attainable for 4 such very difficult measurements at these different low temperatures. And it is impossible in [13] where the overlaying curves are almost not distinguishable. This opposes sharply with the above reported values of Table 1, where the room temperature  $k_1$ -values are not larger than 136 mN/ $\mu\text{m}^{-3/2}$ . The 2 years later report [14] now with one co-worker of the same research group reported indentations upon Si (110) for 298 K, 250 K, 200 K 150 K ( $\Delta T = 148$  K) Now all printed curves with different colours are closely overlapping. Only the blue one could be more or less reliably extracted with some interpolation. Its analysis gave again only one straight line up to the 80 mN force with the therefrom regressed slope-value of 175.41 mN/ $\mu\text{m}^{-3/2}$ ). And for the hardly seen over-covered curves must be the

identical slope values up to 80 mN including the one with a 298 K label. Our crystallographic analysis under the Si (110) surface reveals a huge vertical channel and a favourable indentation angle is at  $65^\circ$ . But again in [14], the expected phase-transition kink is completely missing and so are the temperature effects. These curves cannot be experimental and must be rejected as faked and forged. The AI must be protected from this part of the publication inasmuch as a now horizontal “pop-out” is drawn to the 240 K labelled unloading curve that again proceeds steeper and cuts the other three unloading curves. None of these 4 identical curves can be experimental. All four are faked and forged with again not experimentally reachable precision. Beware of comparing the 292 K labelled curve with any one in **Table 1** of Section 3.1.1. But it is remarkable that the same two authors in the same publication also published an important valid low temperature indentation onto copper, as described and analyzed in Section 3.2.

These are hard words, but these were necessary, because falsified data must not enter the AI data bases and incorrect data might lead to catastrophic disasters (not only the airliner disasters, or the problems with large windmill wings, or the long-term stability of bridges, etc) so that we will have to clarify the issue in more detail.

According to **Table 1**, the distinctly analyzed room-temperature phase-transition onsets have continued in both cases with normalized phase-transition energy of 0.1545 and 0.4684  $\text{mN}\mu\text{m}/\Delta\mu\text{m}$  on Si (100) in [2] (its Table 8.3). That cannot be dismissed. All of these are endothermic phase-transitions at room temperature and  $300^\circ\text{C}$ . We expect at low temperatures exothermic phase-transitions as with Al7075 [7]. The large anisotropic differences are discussed in Section 3.1.1. The crystal packing analyses for the faces (100) and (110) of silicon have already been used in [15] for illustrating what the indenter tip encounters while penetrating and how that explains the anisotropies. But the crystal structures under the load of the created polymorphs should be elucidated. This task will require a micro-Raman scattering study, as used by [16], or perhaps better with the new PI Cryo environmental stage for the quantitative in-situ nanomechanical testing of for example the Bruker Company “down to  $-30^\circ\text{C}$  and below”, for SEM and certainly numerous further technical devices.

The almost indistinguishably overlaying force-depth curves of [12] were imaged as coloured loading curves for two different crystal surfaces. These images will be further analyzed for finding out. All of these printed curves analyze with giving only one straight  $F_N$  vs  $h^{3/2}$  line each up to 100 mN load. That is clearly disproved with the related room temperature indentation. Preceding authors ([3] and [4] published reliable loading curves of silicon, the analyses of which give (up to 60 mN or 120 mN load) two sharp phase-transition kinks. They are in support to the Raman spectra in [11]. Furthermore, there has been imaged exceptional (though impossible) “pop-outs” in [12] with cutting the regular direction of the unloading curve at 18 mN unloading force but only in the unloading curve that was labelled with 240 K as indentation curve. The same length now horizontal feature also with the same cutting of the regular unloading direc-

tion is printed in their later publication [13], but now placed at 40 mN instead of two years before at 18 mN to the corresponding unloading curve. This must also be questioned. Even a statistic of minuscule “pop-ins”, “pop-outs” and “elbows” were published in [12] and must be challenged when used for the detection of phase-transitions. When phase transitions require pop-outs in the unloading curve why are they then not imperative? Phase-transitions produce sharp kink unsteadiness in the  $F_N-h^{3/2}$  plot at their characteristic onset force without distortion of the extremely sensitive instrumental circuits. Both room temperature loading curve analyses onto two claimed different surfaces of silicon are not containing the repeatedly proven two phase-transition kink unsteadiness events. Only these would tell of the already proved phase-transitions as repeatedly listed in **Table 1**. There are after two years six new co-workers for the second paper. And all of the then 13 co-workers must urgently publish papers within a pop-in and pop-out hype period. We must judge that behavior as the result of pop-out hype for using a manual placement of an as large as possible “pop-out” feature as only choosing very rare curves with pop-out due to instrument distortions instead of repeating such measurement under not disturbing conditions. Clearly, the cited amorphization events might have longed for an indication in an indentation curve. Fortunately, there are badly needed valid low temperature results for copper, providing  $F_N-h^{3/2}$  plots with sharp phase-transition kinks (and no “pop-outs”) from the same research group. Their work will be presented and discussed in Section 3.2.

As to the occurrence of pop-outs, we can refer to [2] (its chapter 10), where the various reasons for such short instrumental repairable errors are listed. Genuine pop-ins and pop-outs follow after their force reinstallation the direction of the therefrom free unloading curve of silicon in, of course, all known further cases, and they appear due to incomplete shielding from external events (mechanical, shaking, roughness, audible sound, and ultra or infra sound, switching of heat sources, micro terraces or micro holes on the surface. Urgent remedy is repetition of the experiment! They are never needed for the occurrence and detection of phase-transitions, but they indicate insufficient casing or shielding of the indentation equipment from distortions or from the outside. Furthermore, the occurrence of pile-up or sinking-in is sometimes used. But that is never convincing and can thus also not be “generally accepted evidence of phase-transition”. A reason for the drawn but obviously not experimental “pop-out” in [12] is not existent. It is only claimed for 240 K, but not at the other temperatures, which strengthens our physical reasoning, because amorphization had been reported in all cases. Such instrumental or environmental disturbances have to be avoided rather than being used for physically false theories. The disturbed measurement should need repetition at different sample sites or at another time. And also, the present author encountered “difficult surfaces”. They must be repaired for the analysis of published not repeatable force-depth curves instead of being misinterpreted (cf. Chapter 10 of [2]). We can therefore neither trust this room temperature nor these overlying cryogenic loading curves in [12] [13] and [14]. All are without

unsteadiness kinks and the Excel calculation and regression of  $F_N$  versus  $H^{3/2}$  proved them as not experimental. We must complain their non-existence and have only the not-in-situ information of [8] that silicon indentation at 77 K yielded amorphization after release of pressure and heating to ambient temperature. The obscure claim that there was “no structural transition” is an invalid rush jump. Such claims might have impeded the planning and support of low temperature projects of others or, if applied, their acceptance. The Raman spectra of the residual indents show the peaks of Si-XII and Si-III for 292 K and other low temperatures also the ones with amorphization. Further in-situ structural clarification techniques are required.

Unfortunately, we now don't have experimental loading curves for cryoscopy-indentations of silicon, but we cannot dismiss the Raman spectroscopic evidence that tells us that phase transitions do occur at room temperature and also at 77 K, so that their occurrence was inevitable. And these must have exothermically occurred [7]. Energy law and the exothermic transitions of silica and in particular also the indentation results of copper below provide reason for this very safe precognition in Section 3.2.

The reported low temperature indentations onto silicon at 77 K used a sapphire indenter with Berkovich geometry so that their obvious construction did not provide something else than the physical  $F_N$  vs  $H^{3/2}$  [5]. This facilitated our above challenge of [12] [13]. The Raman spectra after retraction of the indenter and heating up to room temperature indicated amorphization with very broad Raman bands. But this does not allow for a conclusion that the complete amorphization at the lower temperatures and at 77 K exclude phase-transition in favour of (or because of) amorphization. The formed low-temperature polymorphs must be evaluated in-situ. That requires measurement without pressure release from the indenter and before heat-up. But such stability tests are necessary. One needs in-situ Raman spectroscopy or other techniques without unloading and heat-up. Only the not in-situ moderate low-temperature indentations of others provided broad and sharp ambient Raman peaks. The prominent  $396.3\text{ cm}^{-1}$  peak is attributed to the Si-XII structure and only a very low  $353\text{ cm}^{-1}$  Si-III peak at  $353\text{ cm}^{-1}$ . The  $k$ -values and phase-transition energies of experimental room temperature indentations onto silicon are listed in Table 1 and discussed for both phase-transitions each. The reasons for these interesting results are both geometric and energetic.

In the two years later republication of the same research group [13], all the loading curves at 298 K, 250 K, 200 K, and 150 K, show 4 completely overlying coloured curves. Only the blue one labelled 150 K could be analyzed with a minimal amount of interpolation. But the traces of visible black spots labelled 298 K could not be interpolated for a reasonable analysis. Therefore, the blue curve values in [13] must also be taken for the further three overlying curves. Clearly, the low temperature indentations were claimed to have the same ISO 14577-ASTM hardness (the physical hardness would be the  $k$ -value) at all of these temperatures.

The low-temperature Vickers indentation (up to 9.8 N) of silicon (100) with the Vickers pyramidal indenter that have been reported at 77 K by [8] and [9] are also not helpful, because there are no loading curves for Vickers one-point experiments and neither so in the second publication with electric resistance measurements. Thus, one cannot look at phase transitions with such data. The thermodynamic speculations concerning a Si-I to Si-II relation are useless without knowing any phase-transition energy that would be easily available from an experimental loading curve according to our arithmetic technique (see above). A “theoretical P-T diagram” is not helpful in that respect. Anyhow, the Raman spectrum gave the broad bands of amorphous silicon in addition to a residual peak of neat silicon that slightly broadened upon reload. Any in-situ tests will certainly provide different results from not decomposed unstable polymorphs. For example, the new developed PI Cryo system might be helpful in a repetition of the 77 K indentation.

It appears very clear, that the amorphization of silicon’s low temperature indentations occur upon pressure release and up-heating. Thus, experimental loading curves could have found the phase transition kinks with  $F_N$  vs  $h^{3/2}$ . But our analyses gave no phase-transition kink each. This shows that these printed loading curves are guessed or simulated with the strange premises that amorphization would not count as phase transition, and that there would be no temperature influence once these occur. Therefore, our analyses gave only single straight lines for each of them. The very important Raman spectra from the experimental indentations onto Si (100) from room temperature in several steps down to 210 K (Figure 4 of [12]) improved our understanding of its amorphization at 77 K [8] and the ones above 210 K in [12]. It showed that the ambient Raman spectra lost the peaks of the phase-transformed polymorphs Si-XII and Si-III. These decreased in favour of more and more very broad bands of amorphous silicon. At 210 K there were no sharp Raman peaks left and at 292 K there are already some broad bands. This tells us that in all room temperature indentations of others might also have been some amorphous but not searched for polymers. Conversely, the kinetic result, which is the loading curve, is not influenced by the fate of the primary products. That changes only when solid initial polymorphs can be directly further transformed. In fact, only the published Raman spectra of Si (100) in [12] after its low temperature indentations and the sharp Raman peaks from Si-XIII and Si-III from the room temperature indentation are available now. But all of the differently coloured low temperatures loading curve drawings in [12] superimpose with the room temperature curve and that part of the publication reports only faked data.

Only in the 240 K labelled unloading curve (Figure 3 of [12]) is the above challenged sloping and cutting “pop-out” of the unloading curve. It shall start now at a residual 40 mN load. From that point is drawn a 33.8 nm long horizontal line towards the lower depth readings. We dare to judge this so-called “pop-out” imaging as a product of an old-fashioned hype for a widespread though undue belief that phase-transitions and pop-outs would be connected to phase-transitions, or

that so-called “pop-outs” are interpreted as phase-transition events. That is however totally unreasonable and unphysical. We deal here with instrumental errors that shortly disable the force circuit. In particular, the pop-out (and elbow) discussion of [12], including statistics for the occurrence of usually hardly seen irregularities termed “pop-ins” is totally useless, but it points to an unprotected instrument environment. The genuine room temperature indentations onto silicon provided sharp Raman peaks upon indentation, which have also been imaged in [8]. The reason for the “pop-out” only in the room temperature indentation’s unloading image of [13] remains obscure (it is not told how often it appeared at this unloading force with cutting the 3 other undisturbed unloading curves), inasmuch as such instrumental errors are to be avoided by proper indentation conditions [17]. It is not reported that “thrive penetrations” were also valid for the pop-out (but there were actually none, at the claimed absence of the temperature influence). Clearly, the completely lacking temperature influence at a  $\Delta T$  of 82 K or 148 K “qualifies” all of these printed loading curves in [12] and [13] (their Figures 3 and 13) as **not experimental**. But what are the reasons for all the other unusual reports at the low temperatures? They must have (correctly) guessed that the values from Si (110) must be smaller than the ones from Si (001). But these drawn force-depth curves in [12] [13] and [14] are not in accord with the publication of [8]. We urgently hope for a retraction of these not real “loading curves” by the chief author. But the earlier room temperature indentations of silicon indentations of [3] and [4] analyze excellently (Table 1). Clearly in-situ nanomechanical testing will be required and should be used for all experimental low-temperature indentations down to 77 K.

All cited authors dealing with the present topic intended to see whether Si-I undergoes the endothermic phase transition to Si-II with its further transitions upon the pressure from the indenter. But as they only found amorphization they were happy with the ascertainment that Si-II is not formed at these low temperatures. Such amply expressed thinking is not well-founded. Did they really expect that the strong cooling stops all phase-transitions at lower temperature? After the energy law endothermic ones cannot be supported at very low temperatures! But exothermic transitions can now occur. These quantities can now be easily calculated. It is multiply demonstrated in Table 1 and in [2]. It was shown in 2023 [7] that the endothermic transition of Al7075 with the low  $W_{\text{transition}}$  of 0.71 mN $\mu\text{m}/\Delta\mu\text{m}$  switched at 77 K and 7.3 mN load to its first exothermic phase-transition. From that kink point in the  $F_N$  vs  $H^{3/2}$  plot was the force high enough for exceeding the thermal influence and the first of two exothermic phase-transitions could occur upon further force increase. The endothermic behavior of silicon is repeated in Table 1. The next question should be: Are there still unknown polymorphs of silicon and what is their structure? The only real detection for 77 K and the other low temperatures should be using in-situ techniques. These would be able to find out the real sequence of the various transitions and decays of silicon polymorphs and what their structures are. That will certainly be an interesting crystallographic topic and one might also find out



which applications for technical use will evolve. The energy of the exothermic phase transition at 77 K and perhaps also at the other low temperatures (where the room temperature ones remain questionable) required activation energy for the exothermic phase-transitions of silicon. It is supplied here by the pressure increase within the closed solid. Further exothermic phase transition onsets and energies are detected from the phase-transition kinks. In-situ spectroscopy will reveal the structural changes. And their also expectable direct amorphization (if any) might also follow structural transitions as already known from the penetrations onto amorphous silicon. Right now, we only know the result after pressure relief and heat-up to room temperature. The equipment is already available. The recent paper [7] worked this out for the alloy Al7075, and we will obtain a further example with copper in Section 3. 2.

Presently we only have the published Raman spectra showing the very broad ranges of amorphous silicon upon low temperature indentations after decomposition of such possible polymorphs of silicon. In particular, the “pop-out” (or elbow) discussion of [12] including statistics for the occurrence of hardly seen irregularities termed “pop-ins” is totally useless and misleading, but it would only point to a noisy environment of the instrument. Again, the curves in [12] and [13] can never be experimental ones. Only the Raman spectra are the result of experimental indentations. It is the genuine room temperature indentations onto silicon that provide sharp Raman peaks. These had already been imaged in [8].

Sorry to say, but I had to strongly challenge the published low temperature loading curve results, which explains why these published curves at the presumed temperatures cannot be used for the calculation of activation energies [6]. Such valuable scientific calculations would also be possible for the case of direct to amorphous transitions. In the present case such behaviour is certainly thinkable for 77 K indentations with amorphization, but more likely it would proceed via the most stable polymorph at 77 K. Again, such important questions of new low temperature indentation projects must use in-situ studies.

A further interesting experiment would be in-situ photochemistry upon holding both temperature and pressure so that eventually first knowledge about the chemistry of such polymorphs could be obtained for the minus-standard-energy polymorphs. There are several possibilities even with single atoms for producing exotic structures that can be stabilized by the very deep temperature.

Independently from so expected results, one will have to measure activation energies both for the formations of all of these, because several of them can be envisioned at the huge temperature and pressure ranges. The already studied and in Section 3.1.1 analyzed room temperature silicon indentations also require such kinetic experiments. The different and reliable results of the papers [3] [4], and [15] suggest that these will also be possible at low temperatures, but none of these were acknowledged or cited by [12] and [13]. As their authors believed in “pop-outs” they must also have believed that phase-transition was possible for the transformation into amorphous silicon. But they also claimed that such structural transition at the much lower temperatures and 80 mN load did not

occur. Their claims for the 250 K or 298 K indentations are just false. And one may ask who of the 7 co-workers of the leading author as named for [12] is responsible? It appears that an incredible “no-temperature-influence concept” should have been somehow substantiated. We must complain obvious manipulations of indentation data. Their aim was to strengthen an obscure false believe in the absence of temperature influence upon indentations. However, such false claims might have severely hampered the development of low temperature indentation projects. And there is a high dangerous risk that the AI databases cannot sufficiently sort out such falsification.

Furthermore, there are several misconceptions implicit in the thoughts over the indentations of Si (100) at 150 K and 210 K. It cannot be claimed that their also not experimental room temperature-loading curves should withstand against already existing ones from other research groups (see **Table 1**). And why do they claim that silicon-amorphization would be proving that there was no structural phase transition in [12], [13] and also for the experiments at 77 K from [8] and [9]. They even showed a Raman image of some residual Si XII and Si III peaks together with the broad bands. It is an awkward situation that a phase transition is nevertheless disdained because others had reported amorphization upon low-temperature silicon indentations. Furthermore, their belief in pop-outs as being necessary for phase-transitions is just false. And also, the occurrence of pile-up cannot be “generally accepted evidence of phase-transition”. Also, amorphization is a phase-transition. Furthermore, pop-in and or pop-out and shear lines are not connected to phase-transitions! Rather, the reason for the imaged but obviously not experimental “pop-out” is also not valid in [9]. Only when the scanning tip collides with terraces or falls into microscopic holes on the surface will pop-ins and pop-outs repeatedly occur. But such events are independent of the force changes upon scan [17], [18] and Chapter 10 of [2]. One must change the scan direction to avoid them or look for a flatter surface site. And the “statistics” of pop-out events with a particular silicon crystal in [12] are totally useless and misleading. Such surface roughness, instrumental, or environmental disturbances have to be avoided, circumvented, or repaired instead of being misinterpreted. We dare to judge that also these “pop-out” additions in [12] are also a product of an old-fashioned hype for a widespread though undue belief that phase-transitions and pop-outs would be connected to phase-transitions.

And there are further severe misconceptions that must be named and avoided. Why do scientists try to detect endothermic generated polymorphs that they used to detect at room temperature and at higher temperatures? Our phase-transition energy calculation possibility finally proves that such events require activation energy and phase-transition energy. It is absolutely unreasonable to consider the possibility for much thermal support at low temperatures. The present author’s calculation of activation energies for endothermic loading curves in [6] strongly indicates that also exothermic phase-transitions, where the pressure influence prevails, must no longer occur upon decreasing temperatures. Thus, negative activation energies are to be expected for exothermic transitions.

Thus, there should be expected and detected the unknown exothermic phase-transitions that obtain their activation by the applied pressure and they deliver their phase-transition energy [7]. Basic requirement is however the calculation of phase-transition energies that is only available on the mathematically sound arithmetic background that distinguishes positive (endothermic) and also negative (exothermic) transformation energies. Numerous results are collected in [2] and such calculations started in 2013 [18]. Again, Raman investigations require micro- and in-situ techniques, as used by [16] or perhaps with new PI Cryo environmental stage for the quantitative in-situ nanomechanical testing equipment. Fortunately, we found out the solution for several of these unresolved scientific problems with our formulas (1) through (7) that derive from the mathematically deduced physical  $F_N = k h^{3/2}$  law [5] that is, of course, always found in experimental conical or pyramidal loading curves. It is also found for the published experimental loading curves from the leading defenders of the still not updated false ISO14577-ASTM standard often also called “Oliver-Pharr method”. But these defenders (including the ones of the here challenged papers) are still using the  $h^2$  related unphysical ISO-H values instead of the physical k-values for untreated experimental conical and pyramidal indentations. That is for example seen in Table II of [13]. But they need and use iterations, simulations, data-treatments, and energy-law violation by still widely believing in the not yet reformulated ISO-ASTM standardizations. Thus, they continue using and citing the extremely complicated unphysical “Oliver-Pharr analysis method” with usually unrepeatably necessary assumptions. They can never get to such important facts as phase-transition-onset -energy or -work. That might be the reason why such impossible papers on silicon could be published. But several strange observations required now the further (with ISO AFM 14577 not possible or even thinkable) calculation of phase-transition energies for finding out, which of the published ones rely on non-experimental ones and must be discarded. They have here the correct exponent on  $h$  in [12] [13] and [14] for the silicon parts but there are severe unrelated inconsistencies that required the full arithmetic power of the physically correct analyses. These are revealed on the admittedly long way with the 6 strictly from basic sacrosanct mathematic calculation rules deduced formulas (2) - (7). These algebraic calculations used also the linear Excel® regressions. The basic physics is not requiring particular assumptions. Required is only experimental state-of-the-art-indentation loading curves. Several contradicting statements are so revealed here.

For the 77 K indentations onto silicon without loading curves, we may try to speculate that the known brittleness of silicon may not be impeding even though the paper [14] had now to be partly challenged. We hope that our results can be confirmed and completed in the future by indentations with in-situ imaging at 77 K. A comparison with the indentation of copper at 150 K in Section 3.2 is already helpful in that respect. The publication [16] presents an electron microscopic image for copper at a dwell time of 30 min at room temperature for copper. It is full of 1 nm wide remarkably regular rows of copper nanoparticles,

creating about 40 nm wide grains by “twinning” within grains of about 40 nm width. These were obtained from copper upon Vickers indentation at 77 K (see Section 3.2.), that was obtained by [9] upon Vickers indentations of copper at 150 K. This might look promising and certainly allows our predictions for silicon at its 77 K indentations, but in-situ studies must be performed. We only read yet from amorphous material after removal of the indenter and up-heating to room temperature. But we must strongly reject the undue claim that “Si-I was not transformed to Si-II” under these conditions. Si-II is known to be unstable upon thawing-up. This statement is conceptually incorrect and was unfortunately not acknowledged by the authors of [12] and [13]. That is a severe misconception. But even if that could be proved or disproved by in-situ studies, it is also known that amorphous solids can undergo phase transitions (for example amorphous a-Si to amorphous b-Si, or amorphous to crystalline [8] [10]). One may thus ask for the 77 K case whether any phase-transition could occur or not occur. But an endothermic phase-transition is per se excluded at 77 K, lacking energetic support and limits of extremely high-force application. A viable possibility would be (as yet not imaginable) phase-transition of silicon for a useful new polymorph, say by in-situ photolysis. This sight should also be substantiated by indentation onto homogeneous amorphous silicon at 77 K with in-situ analysis. One should be able to check, whether phase transitions, similar to fused quartz with a sharp kink at room temperature [19], are occurring. These should be analyzed with an instrumental indentation loading curve. The melting point of silicon is at 1412°C and there might be different states of amorphous Si. Their synthesis could be useful. And it is now well possible to perform in-situ analyses of instrumental indentations with very high forces (up to 50 N and 100 N and above) for obtaining analysable force-depth curves for the endothermic and exothermic generation of further unknown polymorphs of silicon at ambient or higher temperatures (the present Author used already instrumental indentation up to 100 N at room temperature for the discovery of new endothermic new NaCl polymorphs [20] (Chapter 6 in [2])). Unfortunately, the false exponent 2 on  $h$  is a fixed parameter in almost all indentation simulations, mostly for calculations of unphysical ISO-ASTM hardness and modulus. In that case, the compared so-called “experimental” curve is with high probability more or less “adapted”. If so, one cannot use it. But the Challenger must better not blame any possible anonymous Reviewers for his own papers, and he should unfortunately better forget about it. But there are also numerous cases where such adaptation does not occur and the physical  $h^{3/2}$  is retained even though their ISO ASTM-hardness uses the false  $h^2$ . It appears useful to continue checking the validity of the basis for the physical calculations, as in the present cases of silicon (not experimental) and copper (experimental). Non-experimental detection of technical materials properties of materials suffering high mechanical stress e. g. lightweight aluminium alloys or polymers or concrete is dangerous. These can produce catastrophically crashes. One should use the published optimization possibilities of easily and fast obtained indentations with their physical analysis. Poor

compatibility due to incorrect mechanical data against dangerous crashing by the use of innocent use of materials with low phase-transition onset force and energy ask for using materials with higher values. Such optimizations with better materials are most easily and fast controlled by physical analysis of indentations, providing physically correct mechanical parameters, but these are not obtained on the basis of ISO-ASTM standards. We refer here to the publication [20] that stresses the risks with not controlled phase-transition onsets and phase-transfer energies of light metal alloys for airliners. It shows how initial stable and undiscovered microscopic pre-cracks grow to catastrophic crashes upon further stressing them with further force applications. Shortly after the appearance of this open access publication with microscopic images showing 1.6  $\mu\text{m}$  broad and 3  $\mu\text{m}$  long for months stable pre-cracks. These pre-cracks grow catastrophically upon the application of further force to macroscopic breakage and the development is also imaged. Accidentally, the world suffered repeating catastrophic airliner crashes (China, Indian Sea, and Ethiopia) with many deplorable deaths and largely unclear reasons. But hardly detectable one micrometer wide stable pre-cracks found for the first-time interest and observance at the regular airplane service intervals. Fortunately, the AAA (American Air Administration) immediately grounded “over-night” 250 airliners for 18 months for repair and recertification for the sake of mankind’s safety. That was after they could have read my strongly warning open access publication half a year after its appearance. The 18 months grounding cost the big airplane producer the admitted and complained overall loss of 100 billion dollar. All of these 250 grounded airliners had before not objected micro cracks at their pickle-forks. These connect the wings with the fuselage where the most forces apply upon turbulences. These microscopic (1  $\mu\text{m}$  range) pre-cracks were before disregarded or overlooked. Another recent point of disaster is the now frequent dangerous losses of the huge wings of windmills for the energy production, or the necessary blasting and repair of concrete-bridges. It appears mandatory that the used plastic materials or concretes are optimized by using physically correct analyzed mechanical parameters in addition to the chemical stresses. That is **not** the unphysical ISO 14577-ASTM hardness and moduli. Some polymer data are in [2] (with its Table 8.2 in the Chapter 8). But these technical polymers are top secret. It is therefore the technical Employees of the producers who must correctly indent the different charges rather than using possibly unsafe literature or AI data.

This comparison with the general importance of real experimental and their algebraic analyses underlines the general importance of sorting out all false reports from AI as here in the case of silicon. One has to maximize the phase-transition onset forces and the phase-transition energies of the alloys, polymers and concrete preparations with their grain sizes.

There are additional supports for our unfortunate conclusion with respect to the faked silicon data in [12] [13] [14]. It is okay that no fitting formula was applied for transforming physical  $h^{3/2}$  into ISO-ASTM  $h^2$  (such formulas exist detectably in the literature). Thus,  $h^{3/2}$  must always be checked for the loading

curve. But next to the incredible non-temperature-dependency of their curves are rather poor claims of two pop-outs, one sloping, the later one not sloping. A totally useless “pop-out-occurrence statistics” from one particular silicon crystal does never present expertise with that subject. It shall only address to the pop-in/pop-out hype community. It is again useless and false but might create a short okay of their followers upon their fast reading. Apparently, one single Si (100) crystal plate was used for a “statistical regularity of pop-out events” image of relative number against temperature. That shall indicate several thousands of indentations if per relative value point were 10 of them required, because the search for pop-ins and pop-outs should also systematically check the various different sites on the (100) surface. Did they cover the a- or the b-axis directions and in-between, in the diagonal directions, etc.? No such information is provided. Are there co-workers for such a job for Figure 2 in [12]? Or were these automatically collected, indented and calculated in 2017 under the difficult instrumental conditions? And that without details of the impression distances. The roughness was 0.5 nm polished (but what type of roughness, perhaps terraces or micro-holes etc for knocks with them or for sudden falls into them of the scanning indenter?). Also missing are pre-treatment information's. And numerous different crystals should have been analyzed. And the different faces must be compared. That is not a “statistic” and who else shall use it? Furthermore, one cannot claim both a phase-transition and no influence to the loading curve contents. Thus, one must determine and know the transition onset at force and indentation depth and the phase-transition energy (work), because different polymorphs have different qualities and crashing risks increase at the interfaces of different polymorphs. Polymorph interfaces facilitate the nucleation of catastrophic crashes upon further mechanical stresses. It is therefore necessary to choose materials with as high as possible phase-transition forces and energies. But these properties can only be obtained with physically correct onset force and energy values, but not on the dictated ISO 14577-ASTM hardness and moduli by violating the energy law.

Fortunately, the paper [14] from the same research group presents a positively checked experimental valid indentation result of copper at low temperatures that can be compared with the ambient room temperature indentations of others from the literature (Table 2).

All what is required for the calculation of phase-transition energies of materials are reliable experimental loading curves of pyramidal or conical indenters. This paper therefore reports how we can find out whether such published loading curves are experimental ones or in fact guessed or simulated or manufactured ones. The latter have to be eliminated from any use by AI, so that this does not become disastrous in the technical application of tabulated false mechanical data. The comparison of experimental and non-experimental reports on indentation is therefore of utmost importance. Both types that occurred in the same research group with silicon and copper at low temperature at almost the same time are analysed here to stress the difference.

One needs a tool box for distinction of forged or simulated and experimental indentations for revealing of probable fraud. False data are more frequently occurring from research groups that are claiming that their indentation simulations should be better than the experimental ones. A false exponent is easily detected by checking the exponential relation. If it is not precisely the  $h^{3/2}$  relation of (1) their claims should not enter the AI databases. An exponent 2 on  $h$  should no longer be used. It is unphysical despite the enforced standards of ISO14577-ASTM, because only a part of the applied indentation force is responsible for the penetration depth.

As compared with the previous Si (110) exhibiting huge vertical channels under that face, there are numerous small vertical smaller channels under Si (100). These measurements are again published in the third paper [14], now from only two Authors. But these did still not recognize that these curves at 210 K, 240 K, 260 K, and 292 K indented curves were faked in [12]. While crystal structure considerations are thus again irrelevant and the missing temperature effect are retained, we have to again discuss also that paper part of [14] even though there are no phase-transition kinks in the  $F_N$  vs  $h^{3/2}$  plot regression. These 4 coloured loading curves are close together again as in [12] with one now not sloping horizontal “pop-out” now to the red unloading curve labelled with 292 K that from its end continues more steeply for cutting the further three unloading curves. And the  $F_N$  vs  $h^{3/2}$  plot gives again only one straight line without phase-transition kink. These curves are therefore still faked and not experimental, according to our strict criteria. But we measured again the slopes of the different  $F_N$  vs  $h^{3/2}$  plots to give again the steepness of  $185 \pm 0.5 F_N/h^{3/2}$  with a fantastic precision that cannot be reached for experiments at very complicated condition (the 2% difference to the above value are the result of image distortions upon print). The authors should retract these claims. It is the same forged curves with the same reproduced Raman spectra of 2017.

Not even the 292 K curve reproduced the long-known phase transitions. In reality the distinctly analyzed transformation onsets of silicon (two of them each at (100) and (111) with their transition energies) are listed in **Table 1**. All of these are endothermic transitions. The large differences between these two surfaces are the different orientations of the channel in the diamond-type structure. Crystal packing images for these different faces of silicon are imaged in [15] for illustrating what the indenter tip encounters while penetrating. The crystal structures under the load of the transformed polymorphs are still not elucidated. This task will require a micro-Raman scattering study, as used by [16], or perhaps better with the new PI Cryo environmental stage for the quantitative in-situ nanomechanical testing down to  $-30^\circ\text{C}$  and below, for SEM and certainly numerous further technical devices.

Also, amorphous silicon has been indented at room temperature. Some sharp Raman peaks ensued most prominently with the  $354\text{ cm}^{-1}$  peak from the transformed silicon that is attributed the Si-III structure on the remaining very broad

amorphous silicon Raman bands [8]. Amorphous silicon was also reported upon indentation of Si (100) at 210 K and 260 K [12] and only the very broad Raman bands of some amorphous Si was also found at their indentation in addition of the phase-transition with the sharp Raman peaks that were assigned to Si (III).

The formation of amorphous silicon was reported upon indentations with a sapphire Berkovich indenter onto Si (100) at 210 K, 240 K, 260 K and 292 K [12]. All these published loading curves are very similar in shape and close together. They follow the experimental  $F_N$  vs  $h^{3/2}$  relation, and the 292 K curve is pretty close to the already well-known results. The Raman spectra after retraction of the indenter and heating up to room temperature indicates amorphization showing very broad Raman bands. Only the 292 K run provided also sharp Raman peaks and the prominent very large  $396.3 \text{ cm}^{-1}$  peak is attributed to the Si-XII structure and only a very low  $353 \text{ cm}^{-1}$  Si-III peak of the Si-III peak at  $353 \text{ cm}^{-1}$ . This and the following publication of the same research group where all the loading curves at 298 K, 250 K, 200 K, and 150 K gave four coloured overlying curves from where only the blue one at 150 K could be analyzed, but not the black one taken at 298 K, from where only traces of a few spots could not be interpolated for a reasonable analysis. But the slopes, as obtained from not experimental but obviously faked curves, are not worth for being told here.

The low-temperature Vickers indentation (9.8 N) of silicon (100) with 9 the Vickers pyramidal indenter have also been reported at 77 K by [8] and [9]. There are no loading curves in Vickers one-point experiments and neither so in the second publication with electric resistance measurements. So, we cannot look at phase transition with these data. The thermodynamic speculations concerning a Si-I to Si-II relation are useless without knowing any phase-transition energy that would be available from a loading curve according to our arithmetic technique (see above), not by a “theoretical P-T diagram”. The Raman spectrum gave the broad bands of amorphous silicon in addition to a residual peak of silicon that slightly broadened upon reload. Any in-situ tests will certainly provide different results. For example, the new developed PI Cryo system might be helpful in a repetition of the 77 K indentation. The corresponding room temperature indentation gave “several sharp Raman peaks, indicating structural phase transition” that are imaged.

It appears clear, that the amorphization occurred upon pressure release and up-heating. In-situ analysis is urgently required for finding out what had happened. Even if there should the amorphization have directly occurred at the low temperatures one should have obtained phase-transition kinks. But these are missing in the trial plots so that the drawn low-temperature curves with a temperature label are useless. The ones labelled with 292 K or 298 K are even contradicting the well-established experimental loading curves in **Table 1**. These findings underline the importance of our arithmetic beyond the correct  $h^{3/2}$  tests. The published Raman spectra show the very broad ranges of amorphous silicon upon indentation at 150 K, 200 K, 250 K, and some of it 292 K onto (110) of silicon [12]. But all of their differently coloured low temperature loading curves



superimpose in [13] with the room temperature curve. Only in the unloading drawing deviates the black one (labelled 298 K) below the 40 mN residual load marks. From that point starts a long horizontal line towards the lower depth readings with an outstanding cutting of a regular shaped unloading drawing upon its downward continuation. We dare to judge this so-called “pop-out” imaging as a fake. It does not even serve the old-fashioned hype with a widespread though undue belief that phase-transitions and pop-outs would be connected to phase-transitions, which is however totally unreasonable. In particular, the pop-out (or elbow) discussion of [12], including very poor “statistics” for the occurrence of hardly seen irregularities termed “pop-outs” is totally useless, but it points to a noisy instrument environment. The perfect linear  $F_N \cdot h^{3/2}$  relation does here not prove that all of these curves are experimental ones, because the phase-transition kinks are missing, even though the authors claim amorphization. Their Raman spectra of their figure 4 in [12] showed also Raman peaks of Si-III and Si-XII. These are their experimental room temperature indentations onto silicon that provided sharp Raman peaks upon indentation, which also have been imaged in [8]. The reason for this so called “pop-out” in the room temperature or 240 K labelled drawings [13] must no longer be evaluated. One should be reminded that instrumental errors due to various reasons are to be avoided by proper indentation conditions including sub microscopic surface imaging [17]. Reasons for different results at low temperature indentations upon different crystal surfaces are differences of the widths and angles of its anisotropy (numerous crystallographic studies in [2]). There is certainly good reason that indentations onto Si (110) with its wide vertical channels must behave different from Si (100) or with their less favourable geometries (see **Table 1**). We must admit that the earlier room temperature indentations of [3] and [4] were perhaps not totally free from some not searched for amorphization. But an experimental indentation at  $-13^\circ\text{C}$  would be so close to room temperature that the structural phase-transitions of silicon should prevail. Clearly in-situ nanomechanical testing will be required and should be used for all indentations on the way down to 77 K.

With these in the absence of experimental force-depth curves not very successful low-temperature results onto silicon we continue with a further low temperature indentation study of copper that will show an exothermic phase-transition due to low temperature as in the case of Al7075 of [7].

### 3.2. The Room and Low Temperature Indentations onto Copper

The necessary comparison with room temperature indentations is compiled in **Table 2**. The low force indentation up to 1.2 mN of [21] ends without a phase-transition (its  $k$ -value is  $0.3804 \mu\text{Nm}^{-3/2}$ ). We conclude that we will not have initial twinning up to 100 mN at room temperature upon Berkovich indentations onto copper. All of the amply available experimental high force indentations on various crystal surfaces and pre-treatments from the literature reveal

2 phase transitions (three  $\text{mN}\mu\text{m}^{-3/2}$   $k$ -values) by our purely algebraic analyses entry 1 in **Table 2**. The size of the phase-transition  $W_{\text{trans}}$  (transition-work = transition-energy) values are most likely indicating fcc into hcp transitions of copper with the least atomic rearrangements possible, as twinning can be excluded.

We at first remind the above challenged obvious rush jump for the “twinning at 77 K” conclusion in [16]. They reproduced an image from a high force indentation onto copper at 77 K of others from the literature, even though there are no loading curves for copper to support it at low force. That is discussed in Section 3.1.2. But the first entry in **Table 2** below for indentation onto face-centred-cubic (fcc) up to 1 mN loading force at 298 K onto (100) copper does not exhibit a twinning transition kink (similar to the one of silicon). It would be expected to occur within that load-range. We thus feel confirmed that this 77 K result upon high loading force rather proves a more profound phase-transition of copper at 77 K, whatever its fate upon the release of pressure and the heating to room temperature. Again, an in-situ investigation of copper indentations at 77 K will be highly fruitful.

**Table 2.** Berkovich Indentations onto Copper and Tungsten at, 298 K, 413 K and 150 K.

Entry	Copper (fcc)	Temperature	$F_{\text{max}}$ mN	$F_{\text{Nkink}}$ mN	$h_{\text{max}}$ $\mu\text{m}$	$h_{\text{kink}}$ $\mu\text{m}$	$k_{\text{value}}$ $\text{mN}/\mu\text{m}^{3/2}$	$W_{\text{applied}}$ $\text{mN}\mu\text{m}$	$W_{\text{trans}}$ (mN $\mu\text{m}/\Delta\mu\text{m}$ )	Data Origin
1	(100)	298 K	1	1 (the end)	0.19		$0.3804 \mu\text{N}/\text{nm}^{3/2}$			[21]
2	(111) ( $\varepsilon = 0$ )	298 K	90	29.7906	2.5	1.3648	$k_1$ 18.641 $k_2$ 24.149	20.3765 68.2484	6.5020	[22]
3	(111) ( $\varepsilon = 0.61$ ) <sup>a)</sup>	298 K	90	32.4851	1.6	1.6076	$k_1$ 34.151 $k_2$ 51.093	15.2143 37.9863	16.488	[22]
4	(100)	298 K	100	36.9647 81.0015	2.1	1.2325 1.7293	$k_1$ 28.980 $k_2$ 33.748 $k_3$ 40.878	21.1227 32.1838 40.3584	10.244 31.454	[3]
5	(100) <sup>b)</sup>	150 K	80	25.3944 42.9631	2.3	0.9068 1.4037	$k_1$ 29.261 $k_2$ 21.971 $k_3$ 19.028	11.4559 25.6467 45.1673	-4.9276 -26.2426	[13]
6	Sintered Nanoparticles <sup>c)</sup>	413 K 140°C	60	18.8763 46.5218	2	0.6608 1.2588	$k_1$ 35.572 $k_2$ 31.587 $k_3$ 24.181	6.23675 23.901	-2.769 (-3.276) <sup>d)</sup> -34.682 (-24.343) <sup>d)</sup>	[23]
7	Tungsten	298 K	2000	669.8709 1630.9617	8.55	4.50532 6.49505	$k_1$ 75.342 $k_2$ 81.553 $k_3$ 98.840	1334.97 2334.84 2640.43	1369.649 2799.739	[24]
8	Tungsten	243 K	2000	857.97756	10	9.88065	$k_1$ 57.473 $k_2$ 75.402	1072.47	315.938	[24]

<sup>a)</sup> after previous pressing to reach a “plastic strain of  $\varepsilon = 0.61$ ”; <sup>b)</sup> this Berkovich indenter was out of hexagonal sapphire with the c-axis parallel to the indentation direction for better thermal drift rates, and the tip under load for over 40 min before starting with the indentation at 150 K; <sup>c)</sup> 250 and 50 nm nanoparticles 1:8 after pressurizing to 30 MPa before sintering at 300°C in a vacuum for 40 min and polishing; <sup>d)</sup> crystallization energy after weighed rule-of-three correction as described in the text.

The nanoindentation with Berkovich onto copper (100) at room temperature up to 1000  $\mu\text{N}$  load [21] gave after an initial effect of 1 mN the single straight-line  $F_N = 0.3804h^{3/2} + 10.775$ . It follows, that we can exclude any preceding twinning of copper, which could have been hidden under the initial effects of its 80 mN indentations (apparently no initial twinning of copper).

The ‘‘Sapphire Berkovich’’ indentation onto copper (001) at 298 K gave after a short initial effect (up to about 4 mN) a straight  $F_N$  vs  $h^{3/2}$  line up to 80 mN load ( $R^2 = 0.9998$ ) The result is  $F_N = 23.816h^{3/2} + 1.5774$  with  $R^2 = 0.9998$ , and the applied work calculates to 88.688 mN $\mu\text{m}$ . We analyze here the curve in the more recent publication of [7]. Surprisingly, we do not have any phase-transition here as in the above examples, but this does not interfere with the low temperature result. This new curve at 150 K with the endothermic phase-transitions does now prove experimental. It gave a totally different result. From it calculated  $F_N$  vs  $h^{3/2}$  plot provides two exothermic kinks with (after a short initial effect ( $<0.4$  mN load, these data points are not part of the regression) by equalization of  $F_{N1} = 29.261h^{3/2} + 0.1275$  and  $F_{N2} = 21.971h^{3/2} + 6.422$  and this  $F_{N2}$  with  $F_{N3} = 19.028h^{3/2} + 11.317$ . Clearly, already the decrease of the physical hardness ( $k$ -value mN/ $\mu\text{m}^{3/2}$ ) with increasing loading force and the increase of the axis cut indicate exothermic phase-transitions. The only choice for phase-transitions at very low temperatures is: these must be exothermic, as expected because endothermic ones cannot be thermally supported at sufficiently low temperatures (energy law and [7]). Fortunately, we can physically calculate the transition energies from the loading curves and normalize them per  $\mu\text{m}$  of their existence range within the impression region. The so calculated [Equations (3) through (7)] values are collected and discussed in **Table 2**. These are  $W_{\text{trans1}} = -4.9276$  mN $\mu\text{m}/\Delta\mu\text{m}$  and  $W_{\text{trans2}} = -26.2426$  mN $\mu\text{m}/\Delta\mu\text{m}$ . For the rather low negative value of  $W_{\text{trans1}}$  we have to consider that there was considerable initial positive transformation energy summing up to the kink position and the highly negative one would also become more negative by the preceding less negative transition. If numerically required, the data can be further corrected by also using the non-physical initial axis-cut data (the  $F_a$  values are included in the text, so that everything can be recalculated) as the formulas (3 - 7) correct these out. But their evident weighted rule of three was never executed for simplicity (except for the calculation of the crystallization energies in **Table 2**, where their naming them so required). But we do not include weighted rule of three to them into the **Table 2**, for a better survey, inasmuch the plus or minus outcome appears sufficient.

The Berkovich indentation onto copper at 150 K from their figure 12 in [14] is of particular importance, because the experimental loading curve’s  $F_N$  vs  $h^{3/2}$  plot exhibits the required phase-transition kinks. It was required at 150 K by these authors for the demonstration of a ‘‘contact drift’’ at low temperature indentations. However, their old drawing for room temperature indentation without detectable phase-transition onset kinks does not correspond with the other room temperature results, as compiled in **Table 2**. There is certainly thermal deforma-

tion of the indenter and of the sample during the nanoindentation process at a  $\Delta T$  of 148 K. However very fortunately, our analyses of the now experimental loading curve at 150 K from [14] revealed a fantastic energetic activation of two different as yet unimaginable exothermic phase transition onsets, verifying our expected negative conversion energies. Our expectation from [7] is totally fulfilled: we found another very important case for exothermic phase transitions with them per  $\mu\text{m}$  normalized conversion energies of  $-4.9276$  and  $-26.2426$   $\text{mN}\mu\text{m}/\Delta\mu\text{m}$  (cf also the <sup>d)</sup> in **Table 2**, which is not applied). Clearly, two as yet unimaginable copper polymorphs are achieved, because thermal support for endothermic phase-transitions is shut down in very cold environments. These are urgently subject to in-situ structural evaluation. These phase-transition onsets at 150 K occur with Berkovich at 25.394 mN and 42.963 mN load at the depths of 0.907 and 1.404  $\mu\text{m}$ . Their phase-transition onsets were again obtained by two sharp unsteadiness kinks from the Excel regression. The for the kink calculations necessary physical hardness values  $k$  are at 29.26, 21.97 and 19.03  $\text{mN}\mu\text{m}^{-3/2}$ . This decreasing series tells already that we have exothermic events and the calculated transition energies are indeed negative. We report here the standardized values per  $\mu\text{m}$  depth (division by  $\Delta h$  from kink to kink and last kink to final depth), so that these can be compared with the standardized endothermic transition energies in **Table 2** and those of other materials. Both new exothermically obtained polymorphs have delivered part of their thermal energy content to the environment. The cold environment could not provide that work, and this is the unusual chance to obtain them. One will have to check whether these unusual polymorphs will hopefully survive upon pressure release. If so, they should be isolable as materials with minus standard energy content for further ambient use, with certainly unforeseeable applications. This is the first case for the proof of negative standard energy content polymorphs above the liquid nitrogen temperature. The first negative standard energy polymorphs of Al7075 at 77 K were published in [7]. And the ones from copper are now again presenting epochal news. We first suggest an easily available in-situ photolysis that could produce interesting new chemical reactions of the copper atoms, and there appear several possibilities. The low temperature will stabilize what will be produced and spectroscopically characterized.

### 3.2.1. The Number of Phase-Transitions within $F_{N\text{max}}$ (Entries 2-3 and 4-6)

The Berkovich loadings up to 90 mN are not high enough for reaching more than one phase-transition at room temperature onto the (111) surface of copper, but upon (100) we find two phase-transitions up to 100 mN maximal load. That can be easily understood by the crystallographic analysis of the fcc crystal faces. The (111) surfaces and their parallel layers inside the crystal are most densely packed leaving practically no large channels and the indenter must shovel away much more also not transformed material for opening its way down. More of its material than on (100) [= (001) in the fcc-case], where there are penetration

depth facilitating vertical and horizontal channels. Only two kinks were resolved upon (100) at 298 K and at 150 K. In these cases, the Berkovich uses from the indenter supplied kinetic energy more efficiently for the creation of polymorphs. It consumes less work for the penetration part by descending through a vertical crystallographic  $a/2$  channel ( $a$  is the crystal constant). At 150 K the phase transitions start earlier at lower force, again more efficient and now exothermic.

### 3.2.2. The Anisotropy (Entries 2 and 4)

A published loading curve on (100) of copper was checked to enable the comparison with (111) (entries 2 and 4). The one of [3] with Berkovich at 25°C ends at 100 mN load and it provides two endothermic phase-transition unsteadiness by indentation onto the (100) face.

The comparison of the different (phases at the same temperature (entries 2 and 4) has to explain the totally different crystal conditions.

The indentation process with phase-transitions combines the penetration that provides residual pressure, but it must constantly shovel away both the not transformed and later the transformed material. The penetration is slightly facilitated by the vertical  $a/2$  channel under (100) and the lattice constant ( $a$ ) for copper is 3.59 Å. That looks like an advantage for the penetration under (100). But we must also consider the energetic aspects. The indenter loses under (100) less of its total kinetic energy, as delivered from the indenter drive, and it has the necessary energy part for its lower phase-transition work earlier under (100) (entry 2) than under (111). The latter goes deeper with lower kink-force and lower transition work (Entry 4) Thus it requires deeper penetration for being possible to start with phase-transition when its total energy has sufficiently increased also for the phase-transition. The increased hardness-value  $k_1$  at (001) can be similarly explained with counteractive effects.

Thus, the  $k_1$  ratio of unstrained (111) over (100) is 18.6/28.98 and the depth ratio is 1.37/1.23, the applied work  $W_{\text{applied}}$  20.38/21.12 and the endothermic transition energy 6.50/10.24. Clearly, for the first transition at 298 K of the unstrained copper, the (111) surface penetration requires a deeper penetration for a lower kink force, a smaller  $k$ -value ( $\text{mN}/\mu\text{m}^{3/2}$ ) and a smaller phase-transition energy than the (100) face. This is exactly the expectation from the crystal structure analysis results in accordance with the energy law (Table 2), which cannot be disregarded. Thus, more material has been transformed at the same depths on the (100) work for obtaining the phase-transition. It is not very different as expected. We thus also understand that a second kink for the published copper indentations upon the (111) surface was not found at the maximal force of 90 mN. Unfortunately, the energy-law violation by ISO 14577-ASTM standards (as revealed by e. g. [2] [5] [7] [18]) are still enforcing the industries. And unfortunately, it is still widely accepted by academics who can so not obtain physically correct material's properties. They, of course, still obtain experimental indentation loading curves with  $h^{3/2}$ . The exponential analyses would yield the physically correct exponent 3/2 on  $h$  in relation to the force of conical or pyramidal inden-

tations. But mostly these colleagues ignore it with respect to the standards, well knowing that there exist multi-parameter fitting formulas [25] that had been used for hardly detectable misuse for transfer of  $h^{3/2}$  into  $h^2$ . Anyhow, such disastrous data treatments lose all of the straightforward algebraic analyses' wealth. The equations (1) through (7) derive from the physically correct [5]  $h^{3/2}$ . Their unprecedented application makes the complicated experimental facts of **Table 2** understandable.

### 3.2.3. The Pre-Straining Effect (Entries 2 and 3)

Straining of metals is an often used means for the strengthening of materials.

The Berkovich indentation up to 80 mN load at room temperature onto polished uncompressed (“ $\varepsilon = 0$ ”) copper (111) gave two linear branches with  $F_{N1} = 18.641h^{3/2} + 0.0706$  and  $F_{N2} = 24.149h^{3/2} - 8.711$ . A sharp  $F_{N\text{kink}} = 29.791$  mN and  $h_{\text{kink}} = 1.3648$   $\mu\text{m}$  were obtained and an endothermic normalized transition energy  $W_{\text{trans}} = 6.502$  mN $\mu\text{m}/\Delta\mu\text{m}$  was calculated. When the Cu (111) sample was strained before up to  $\varepsilon = 0.61$  between two flat plates with the tungsten carbide anvil the indentation analysis linear branches changed enormously. The now obtained  $F_{N1} = 34.151h^{3/2} - 2.0527$  and  $F_{N2} = 51.093h^{3/2} - 19.193$  give a kink at 32.4851mN at 1.0076  $\mu\text{m}$  and a normalized endothermic transition energy of 9.497 mN $\mu\text{m}/\Delta\mu\text{m}$ . We do not know what happened to the compression of the Cu (111) sample. But it is important that the increased transition energy stays endothermic.

One remarks in **Table 2** that the physical hardness ( $k$ -values, penetration resistances) values roughly double when the very densely closed surface of Cu-(111) (crystal analysis reveals only minuscule vertical channels on fcc (111) is pressed between plates before the indentation, until the so-called plastic strain is elevated up to “ $\varepsilon = 0.61$ ” according to SGP (strain gradient plasticity) theory. On that basis, and with the help of the disproved still not corrected ISO 14577-ASTM standards, we achieve a complete understanding. It was claimed that a “heavily deformed Cu (111)” ensues and produces the observed differences (**Table 2**). However, the very complicated and lengthy argumentation on the incorrect ISO ASTM basis is not convincing. Our comparison with the indentation of the not pressed crystal, in particular the transition energy comparison on the correct physical basis that gave a 2.5 times higher conversion energy (Entries 2 and 3) would lead to a different conclusion. It appears more likely that the pressed fcc copper produced a more stable copper polymorph (most likely to hdp-copper), rather than only disorder of the fcc structure. A Raman study will certainly help for the final clarification. But they also reported pile-up with strained “( $\varepsilon = 0.61$ )” and the sink-in with unstrained “( $\varepsilon = 0$ )” copper that cannot convincingly decide. At lower strain both polymorphs might coexist.

### 3.2.4. The Low-Temperature Effect (Table 2, Entries 4 and 5)

As the same principles must be valid and applied for 150 K indentation we understand that only 1 phase transition kink occurs within the 80 mN range for the

indentation onto fcc (001) = (100) copper surface. The only by about 1% larger  $k_1$ -value upon (100) (28.980 and 29.261) result from smaller depth and smaller kink force. Also, the lower penetration depths at 150 K with respect to 298 K (25.39 against 36.97  $\mu\text{m}$ ) are easily understood for a  $\Delta T$  of 148 K. We have the same arguments as in 3.2.2. It's a similar process and the depth is only 9% lower, so that the compensation due to less transitioned material remains low. The first kink forces are at 150 K by 31.3% and the  $W_{\text{applied1}}$  values are by 45.8% smaller at the lower penetration, because much less materials must be transformed at 26.43 times lower penetration. The  $k_2$  and  $k_3$  values cannot be similarly compared any more, due to the now exothermic phase-transitions. The reason for it has been discussed before and with the foot-note<sup>d)</sup> in **Table 2**. Thus, the physical analysis of these thermal influences is well understood with well-established crystallographic and geometric effects alone. We do not need extremely complicated hardly repeatable simulations and fittings against the physical reality. Not predictable are the sizes of material's properties. It is thus remarkable that the second might occur shortly after the first one. Particularly the second one follows with about the same depth distance as at room temperature but within the endothermic and even shorter in the exothermic case at low temperature.

### 3.2.5. The Indentations of Tungsten at Room Temperature and 443 K (Entries 7 and 8)

Tungsten is a very hard metal. It undergoes two phase-transitions at room temperature with considerable applied work and huge phase-transition energies. At the  $-30$  C indentation one obtains up to 2000 mN load only the first phase-transition with a phase-transition energy that is 4.34 times smaller, but still highly respectable (**Table 2**) [24]. We are here in a new league of force, depth, and energy, but the rules are unchanged. The behavior of tungsten is of particular interest, due to the influence of now much higher hardness. The physical hardness ( $k$ -value) is responsible for the penetration depth. Thus, the  $k_1$ -values are always smaller before the phase-transition kink as after it in the cases of endothermic phase-transitions. And vice versa in all cases of exothermic phase-transitions. Unfortunately, the latter could not be developed by tungsten at the 243 K indentation, because the loading forces up to 2000 mN were not sufficiently high. The calculated data are nevertheless important for the verification of the results with Al7075 in [7]. One recognizes that tungsten is 2.6 times harder than copper (100) (entries 4 and 7) or 3.55-fold harder than Al7075. This influence of  $k_1$  is consistently seen in **Table 2**. The entries 4 and 7 show, that we need about 20 times more load for a 4 times deeper impression onto tungsten.

For tungsten at 298 K and 243 K at the same force we have an increase at 243 K. We thus understand that the kink depth increases 2.93-fold, and the kink force increases 1.281-fold (entries 7 and 8). However, the applied work decreases (factor 0.803). The normalized phase-transition energy decreased considerably (factor 0.231). Importantly, these drops in the energies reflect the less efficient help of the environmental temperature to provide environmental energy. For the

phase-transition number one of tungsten that is much easier at room temperature. Clearly, we have the same polymorph at 243 K, but would need energy for heating it to 25°C. Unlike Al7075 with  $k_1 = 21.238 \text{ mN}\mu\text{m}^{-3/2}$  [7], the applied loading force was not large enough to achieve an exothermic conversion of tungsten

### 3.3. Indentation onto Compressed Nanoparticles of Copper

Compressed nanoparticles are interesting new materials. The indentation of which are an important research field. We also compare the Berkovich indentation of a compressed and sintered 1 to 8 mixture of 250 and 50 nm copper nanoparticles [23], even though it is performed at a high temperature. The results are also added to **Table 2** above. A microscopic image shows that these nanoparticles are still separated in the surface, and we measure very large physical hardness values. The transition energies are negative at 140°C. We must conclude that there is an exothermic stabilization by the energy release owing to crystallization. These exothermic analysis results appear similar or related to exothermic crystallizations from melts (cf e.g. the exothermic ice-formation). So achieved crystal structures are of course not perfect, but distorted with defects that make them harder. A Raman study would nevertheless be useful. The complicated analytic techniques with XRD and the theoretical described investigations are very complicated [26]. They require numerous force variations that are not available here. Our loading curve  $F_N$  vs  $h^{3/2}$  regression provides three  $F_N$  vs  $h^{3/2}$  branches:  $F_{N1} = 35.572h^{3/2} - 0.2317$ ,  $F_{N2} = 31.587h^{3/2} + 1.909$  and  $F_{N3} = 24.181h^{3/2} + 12$  with the  $k$ -values decreasing at higher load and axis-cuts increasing, which indicates two exothermic transitions. Their onsets (kink positions) are 18.876 mN at 0.661  $\mu\text{m}$  and 46.522 mN at 1.259  $\mu\text{m}$  with the normalized crystallization energies of  $-2.7694$  and  $-34.6824 \text{ mN}\mu\text{m}/\Delta\mu\text{m}$ . When we consider that these values contain the energy before the kink positions, we may correct them for obtaining the final “crystallization energies”. For achieving this task, we have to multiply the normalized transition work with the fraction of the weighted (same  $\Delta F$  and measured  $\Delta h$ ) rule of three calculation in percent (before and after the kink). The so corrected and normalized per  $\mu\text{m}$  crystallization energies are  $-3.369 \text{ mN}\mu\text{m}/\Delta\mu\text{m}$  and  $-24.343 \text{ mN}\mu\text{m}/\Delta\mu\text{m}$  for making them comparable with crystallizations from melts. The first of these around the kink becomes smaller as the endothermic part was corrected for. In the second case the smaller exothermic part before the kink decreases the exothermic value, as expected. All the other  $W_{\text{transition}}$  data in this publication are without such correction, because the main goal (endothermic or exothermic transitions) is always reached without such further complicating correction. Only here was it necessary for naming them crystallization energies. The two-step crystallization tells that the 50 nm particles crystallize at the lower force and the 250 nm particles follow at the higher force. We have here a totally different effect than in the structural phase-transitions of crystals. But we cannot compare with the results



of amorphous solids, where there is not a comparable endothermic phase-transition, as not all of them are observed for the same penetration length.

Exothermic conversions are rarely occurring upon indentations of crystals. These can be found in [2] and [27]. Particularly interesting in view of the exothermic crystallization energies of compressed nanoparticles are the exothermic cube corner phase-transitions onto five of the  $\alpha$ -quartz ( $P3_22_1$ ) surfaces [(100), (010) (011), (101), and (110)]. The reported  $k_1/k_2$  ratios are all larger than 1, so that all of these proceeded exothermic, presumably either by twinning or by amorphization [15] [17] and the phase-transition of the amorphous fused quartz test samples are now endothermic. Unfortunately, we had not published the axis cuts that are necessary for the calculation of the phase-transition onsets and there from their phase-transition energies. The at that time calculated  $W_{\text{tot}}$ -values are not the now calculated phase-transition-energies  $W_{\text{transition}}$  of Equation (7), but they compare the energies of the total indentation.

#### 4. Conclusions

All what is required for the calculation of phase-transition energies of materials are reliable experimental loading curves of pyramidal or conical indenters. This paper therefore reports how we can find out whether published indentation loading curves are experimental ones, because AI must be protected from forged, manipulated, or simulated scientific publications. Falsified mechanical data must be eliminated for severe safety reasons. A whole series of misconception has been revealed, listed and critically explained. A tool box for the distinction of reliable from faked reports is herewith provided for the elimination of eight published low temperature indentation loading curves in three full publications of international scientific journals. And the wealth of a clearly experimental indentation curve from the same research group is outlined and stressed. The important low-temperature indentation onto copper has been tested as being experimental, with the epochal result of two negative standard-energy containing polymorphs. The large general tool box for the distinctions of faked and experimental indentations is build up and provided, because AI must be enabled to sort out the faked ones for avoiding the risk of catastrophic crashes. Such sorting out must collect numerous hints in addition to strictly using basic physics and the now already long known purely arithmetic calculations with simple closed formulas. The still present ISO 14577-ASTM standards cannot help in that respect. The details are precisely outlined and numerous as yet unavailable mechanical parameters become available. The comparison of materials by physical hardness and phase transition energy, crystal structures for anisotropies (channel sizes and orientations) phase-transition onset (force and depth) can be precisely and detailed understand. These consistently explain important indentation-effects also on the basis of the crystal packing. This helps in designing better technical materials with increased phase-transition onset forces and phase-transition energies for minimizing crashing risks. It is particularly impor-

tant to safely protect AI (artificial intelligence) from faked mechanical data, because it might not be able to detect such forbidden behaviours by itself. The detection of phase-transition onset forces and phase transition energies for endothermic phase transitions creating polymorph interfaces must be stressed by the most easy and versatile instrumental indentations. These must be experimental and their loading curves must be physically and mathematically correct analysed, but not with ISO14577-ASTM standards that do not have the possibility to detect and consider the phase-transitions of technical materials under load. Such phase-transitions are dangerous and must be avoided with better materials. They form polymorph interfaces with microscopic pre-cracks that survive and can accumulate until they grow to catastrophic crashes upon further forces (e. g. turbulences to airliners, or windmill blades, etc). Such risks must be controlled minimized by increasing the onset forces and phase-transition energies with better alloys or polymers. These must avoid such more efficient nucleation sites than point defects. Our necessary concern can be exemplified with airliner crashes and the groundings of 250 airliners with microscopic pre-cracks for 18 months repair, after this crashing mechanism via microscopic pre-cracks had been imaged and published in [20].

Most exciting is the low temperature indentation of copper at 150 K. Low temperature indentations produce as yet rare exothermic phase transitions yielding polymorphs with minus standard energies and this could be confirmed with copper for the first time already at 150 K now far above 77 K. But in-situ Raman spectroscopy should further characterize them. The algebraic analysis of loading curve revealed two exothermic phase transitions with enormous  $-5$  and  $-26$   $\text{mN}\mu\text{m}/\Delta\mu\text{m}$ . The so obtainable polymorphs of copper are the first ones with negative standard energy content that were obtained at a temperature above 77 K of liquid nitrogen. These are again [7] epochal news. So, we can expect more of such highly exciting negative standard energy containing polymorphs. Their behaviour in-situ or perhaps after their hopefully pressure-less isolation at room temperature will open up a totally new area of thinking and of the present thermodynamics for unforeseeable applications in chemistry, physics, and techniques. And we suggest in-situ irradiation for starting a new field of photochemistry that should be the first chemical reactions of these exotic materials, and further other materials await similar treatments. Room temperature exothermic phase transitions are upon indentations upon quartz (rock salt) and upon compressed nanoparticles. From the latter we calculated crystallization energies as these compare with ice-formation and crystallizations of metals from their melts that are also exothermic. Numerous technical applications are discussed and applied.

The very recently [24] obtained indentations onto very hard tungsten ( $k_1 = 75.342 \text{ mN}\mu\text{m}^{-3/2}$ ) was correspondingly calculated for demonstrating the value and reliability of the physically correct algebraic formulas (1-7) and to demonstrate the enormous influence of the indentation hardness to depths, energies

and phase-transition-energies both at room temperature and low temperatures. All these algebraic calculated results are collected in **Table 2** and compared. They demonstrate that not only faked indentations, but also the common use of energy-law violating unphysical ISO 14577-ASTM iterated “H-values” would strongly falsify most important materials’ properties, which would create enormous disasters by their hardly avoidable use of AI. This demonstrates that one must use  $k_1$  from indentations as the physical hardness.

## Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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