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# Phase-Transitions at High, Very High, and Very Low Temperatures upon Nano-Indentations: Onset Forces and Transition Energies

**Gerd Kaupp**

Chemistry Department, University of Oldenburg, Oldenburg, Germany
Email: gerd.kaupp@uni-oldenburg.de

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## Abstract

This paper describes the phase-transition energies from published loading curves on the basis of the physically deduced $F_N = k \cdot h^{3/2}$ law that does not violate the energy law by assuming $h^2$ instead, as still do ISO-ASTM 14,577 standards. This law is valid for all materials and all "one-point indentation" temperatures. It detects initial surface effects and phase-transition kink-unsteadiness. Why is that important? The mechanically induced phase-transitions form polymorph interfaces with increased risk of crash nucleation for example at the pickle forks of airliners. After our published crashing risk, as nucleated within microscopic polymorph-interfaces via pre-cracks, had finally appeared (we presented microscopic images (5000×) from a model system), 550 airliners were all at once grounded for 18 months due to such microscopic pre-cracks at their pickle forks (connection device for wing to body). These pre-cracks at phase-transition interfaces were previously not complained at the (semi)yearly checkups of all airliners. But materials with higher compliance against phase-transitions must be developed for everybody's safety, most easily by checking with nanoindentations, using their physically correct analyses. Unfortunately, non-physical analyses, as based on the after all incredible exponent 2 on $h$ for the $F_N$ versus $h$ loading curve are still enforced by ISO-ASTM standards that cannot detect phase-transitions. These standards propagate that all of the force, as applied to the penetrating cone or pyramid shall be used for the depth formation, but not also in part for the pressure to the indenter environment. However, the remaining part of pressure (that was not consumed for migrations, etc.) is always used for the elastic modulus detection routine. That severely violates the energy-law! Furthermore, the now physically analyzed published loading curves contain the phase-transition onsets and energies information, because these old-fashioned authors innocently (?) published (of course correct) experimental loading curves. These follow as ever

the physically deduced $F_N = k \cdot h^{3/2}$ relation that does not violate the energy law. Nevertheless, the old-fashioned authors stubbornly assume $h^2$ instead of $h^{3/2}$ as still do ISO-ASTM 14,577 standards according to an Oliver-Pharr publication of 1992 and textbooks. The present work contributes to understanding the temperature dependence of phase-transitions under mechanical load, not only for aviation and space flights, which is important. The physical calculations use exclusively regressions and pure algebra (no iterations, no fittings, and no simulations) in a series of straightforward steps by correcting for unavoidable initial effects from the axis cuts of the linear branches from the above equation exhibiting sharp kink unsteadiness at the onset of phase transitions. The test loading curves are from Molybdenum and Al 7075 alloy. The valid published loading curves strictly follow the $F_N = k \cdot h^{3/2}$ relation. Full applied work, conversion work, and conversion work per depth unit show reliable overall comparable order of magnitude values at temperature increase by 150˚C (Al 7075) and 980˚C (Mo) when also considering different physical hardnesses and penetration depths. It turns out how much the normalized endothermic phase-transition energy decreases upon temperature increase. For the only known 1000˚C indentation we provide reason that the presented loading curves changes are only to a minor degree caused by the thermal expansion. The results with Al 7075 up to 170˚C are successfully compared. Al 7075 alloy is also checked by indentation with liquid nitrogen cooling (77 K). It gives two endothermic and one very prominent exothermic phase transition with particularly high normalized phase-transition energy. This indentation loading curve at liquid nitrogen temperature reveals epochal novelties. The energy requiring endothermic phase transitions (already seen at 20˚C and above) at 77 K is shortly after the start of the second polymorph (sharply at 19.53 N loading force) followed by a strongly exothermic phase-transition by producing (that is losing) energy-content. Both processes at 77 K are totally unexpected. The produced energy per depth unit is much higher energy than the one required for the previous endothermic conversions. This exothermic phase-transition profits from the inability to provide further energy for the formation of the third polymorph as endothermic obtained at 70˚C and above. That is only possible because the very cold crystal can no longer support endothermic events but supports exothermic ones. Both endothermic and exothermic phase-transitions at 77 K under load are unprecedented and were not expected before. While the energetic support at 77 K for endothermic processes under mechanical load is unusual but still understandable (there are also further means to produce lower temperatures). But strongly exothermic phase-transition under mechanical load for the production of new modification with negative energy content (less than the energy content of the ambient polymorph) at very low temperature is an epochal event here on earth. It leads to new global thinking and promises important new applications. The energy content of strongly exothermic transformed material is less than the thermodynamic standard zero energy-content on earth. And it can only be reached when there is no possibility left to produce an endothermic phase-transition. Such less than zero-energy-content materials should be iso-

lated, using appropriate equipment. Their properties must be investigated by chemists, crystallographers, and physicists for cosmological reasons. It could be that such materials will require cooling despite their low energy content (higher stability!) and not survive at ambient temperatures and pressures on earth, but only because we do not know of such negative-energy-content materials with our arbitrary thermodynamic standard zeros on earth. At first one will have to study how far we can go up with temperature for keeping them stable. Thus, the apparently never before considered unprecedented result opens up new thinking for the search of new polymorphs that can, of course, not be reached by heating. Various further applications including cosmology and space flight explorations are profiting from it.

## Keywords

Aluminum Alloy, Aviation, Cosmology, Epochal News, High and Liquid Nitrogen Temperature Indentations, Negative-Energy-Content Polymorph, Molybdenum, Phase-Transition-Energy

## 1. Introduction

Phase-transitions under mechanical load are most easily and rapidly detected by indentation, just by correct analysis of the load-depth curves. After all that should be the most important reason for undertaking instrumented nano, micro and macro indentation. But phase-transitions upon indentations are mostly disregarded, (if not detected by synchrotron X-ray or Raman spectroscopy) because they are not part of the ISO-ASTM standards 14,577. Unfortunately, most indentation users still believe in these enforcing standards that use indentation hardness (force over iterated projected contact area) and modulus as the most important goals of indentations by using the false ISO 14,577 standard definitions. It still suffers from violation of the energy law on the basis of elasticity theory with very old complicated formulas requiring multi (e.g. 3 + 8) freely iterated parameters for fitting to poor standards not considering their known phase-transitions. But phase-transitions under mechanical load are most easily and rapidly detected by indentation, just by correct analysis of the load-depth curves. After all that is actually the most important reason for undertaking instrumented nano, micro and macro indentations. But our unprecedented applications are mostly disregarded, because they are not part of the ISO-ASTM standards 14,577. Unfortunately, most indentation users still accept and believe in these enforcing standards that claim indentation hardness and modulus as being the most important goals of indentations by using the ISO 14,577 standard. It still suffers from violation of the energy law on the basis of elasticity theory with very old formulas from 1882 of Hertz [1] who did only deal with surface contact at all but not with penetration [2]. Nevertheless, such contact consideration was used over the years with very complicated mathematics for approximations, iterations, and

simulations for the Boussinesq equation by Love [3] and Sneddon [4]. Also, the false so-called Johnson Formula [5] has been frequently used. Hainsworth *et al.* [6] tried with $F_N$ versus $h^2$ curves but only in very late parts with restriction to very short ones, where these curves more and more start to approach lines with only minor deviations at short distances. Even a very complicated falsification fitting-formula for producing "$h^2$" for the loading curve force-depth data has been published in Ref. [7]. The ISO-ASTM standards rest on the Oliver-Pharr publication of 1992 [8], who tried with iterations of three plus eight free parameters for approaching to rather poor standards (primarily fused quartz and aluminium, but not considering their phase-transitions upon indentation already at low loads). It is well known that the so obtained ISO-H and ISO-$E_r$ values are not only unphysical but also very imprecise, not to speak of their dependence on striking energy-law violations. None of the involved authors and ISO-ASTM 14,577 standard users with their black-box software equipments thinks or thought of checking themselves the real exponent 3/2 on $h$ of their own experimental loading curves. And none of these are using the angle and volume of their indenters for the easiest deduction [9] of the physically correct exponent on the penetration depth $h$. Rather a quacking trick claimed to prove "$h^2$" from the totally false projected area of the unphysical ISO-hardness definition ($P_{max}/A_c$) by some mathematical manipulations, ending with widely applauded "$h^2$ for the loading curve from cones and pyramids" [10]. It was a fight against the clear-cut physical law deduction from the indenter volume and angle [9]. They unduly tried to discredit the physically proved $F_N$ versus $h^{3/2}$ plots as "Kaupp fittings" instead of "analytical Kaupp plots" ([9]). These are the easiest check by using Excel® calculation for deciding, whether their (or a published) loading curve is experimental or simulated or otherwise fitted. It must be linear with $h^{3/2}$. One obtains the initial effects (these are not part of the regression!), physical hardness as penetration resistance ($k$, the linear slope) and sharp kink-unsteadiness at every phase transition onset.

The ISO-ASTM believers do not consider that the force does not only create displacement, but also the pressure to the environment of the indenter, which is claimed to require zero work. A striking energy-law violation! But both events require force and thus energy. This neglecting of the fact that energy is required both for the displacement and also for the pressure (that may in part be lost by sidewise movements of materials and phase changes) is the violation of the energy law. This mistake led to the false formulation of the loading curve as normal force "$F_N$ = const $h^2$" for "one-point indentations". That is unfortunately still worldwide used, and phase-transitions cannot be detected with such faking "formula". And ISO-ASTM-H is calculated as "$F_N$ = const $h_c^2$" by the iterating software of their black-box instruments. Extremely complicated simulation of additional effects and data-fitting or data-treating equations are needed to construct the experimental data for concurring with the experimental ones. It finally appeared from 2014 in 2016 [9] that the energy-law obeying correct formula $F_N$

= $k{\cdot}h^{3/2}$ was undeniably mathematically deduced and in 2013 [11]) that the depth/non-depth ratio is 80/20 in all cases of conical or pyramidal indentations. By obeying basic physics and simple algebra everything is very simple now. And we detect kink unsteadiness = phase-transition onset in the $F_N$ versus $h^{3/2}$ plots that can be generated with Excel® calculation as available in every private computer now, providing the physical hardness $k$ (mN/μm$^{3/2}$) by regression instead of faking "ISO-ASTM-H" denying or even fighting against phase-transitions under mechanical load. This proved recently disastrous. Shortly after our frequently read paper [12] finally appeared where microscopic (5000-fold and 3D) stable cracks upon indentation were presented. These remained untouched stable for months. But upon cautious application of increased load these developed again from the submicroscopic trail of polymorphs interface and it led to macroscopic crash. Importantly, at considerably higher force one could also depict a microscopic crack and finally also catastrophic crack from a local microscopic fault in the same material. This second crack was almost certainly triggered by the first catastrophic one. The only conclusion is that micro-cracks develop with increased probability at phase-transitions with their polymorph interface formations rather than at local defects. Thus, phase-transition onsets are to be avoided with more compliant material and their onset forces and energies must be determined by indentations. Thus, after three airliner crashes (with uncleared reasons) and shortly after our warnings that TiAl alloys suffer from relatively low phase-transition onsets [13] or very closely with the development of macroscopic cracks in comparison with local defects there was a drastic response: All the combined instantaneous groundings of 550 airliners with enormous financial costs for the producer (>100 billion $) was dictated in USA. The timely correspondence is more than suggestive. The grounding of 550 airliners for 18 months by the FAA (Federal Aviation Administration) was due to the microscopic cracks at the pickle forks (the device for the connection of wing to body) at all of these 550 airliners. These microscopic pre-cracks were previously not seen, or disregarded, or judged as being harmless upon the inescapable half yearly checking procedures of every airliner. Furthermore, the Aviation Herald for Pilots (https://www.avherald.com/) told comment-less that large wing parts of the crashed airplane of flight MU-5735 on March 21, 2022 in China were found "about 12 km west of the crash site", and there are the respective photos. It was just not clear before that μm range cracks at phase-transition within polymorph interfaces are dangerous, due to increased crack nucleation probability. Thus, the easy detection and characterization of the materials' phase-transition with their polymorph interfaces and increased crash probability (at higher forces) is the most important task of nanoindentation. The apparently on flight turbulences created very frequent microscopic pre-cracks at the pickle forks out of less-than-optimal alloys cannot be tolerated for safety reasons. It is therefore important to evaluate and discuss the temperature dependence of phase-transitions under mechanical load, not only for aviation and space flights. But temperature-dependent loading curves are rare due to particular difficulties with the instrumental design

and they deserve critical selection and mathematical control. These must be experimental loading curves or original $F_N$-$h$ data without iterations, without data-fitting, and without simulations. We therefore check and discuss very high and elevated temperature as well as an indentation at liquid nitrogen temperature after carefully checking the experimental data.

## 2. Materials and Methods

The physical calculations use exclusively regressions and pure algebra (no iterations, no fittings, and no simulations) in a series of straightforward steps by correcting for unavoidable initial effects from the axis cuts of the linear branches from the above equation, exhibiting sharp kink unsteadiness at the onset of phase transitions. The analyzed loading curves are taken from the literature. Pop-ins that occurred in the Al 7075 loading curves at high and very low temperatures were "repaired" by the successful procedure [14]. The algebraic formulas are repeated here to show their strictness. All calculation steps were performed with a pocket calculator Rebell® SC2050 always with 10 figures and the tabulated and text values reasonably rounded. The loading curves were scanned and enlarged to A4 size for the data point sections for Excel® regression calculations. The regression lines of the linear branches provide the axis cuts and the slopes as $k$-values (the physical hardness) for the precise calculation of the kink positions (phase-transition onset). These are the basis for the calculation of the indentation parameters according to the given formulas. The transition work is normalized per depth unit by division with their depth ranges to make them comparable. These results are, of course, indenter angle dependent. But the claimed similarity of cone with Berkovich pyramid is no longer correct [15]. We repeat here all the used closed arithmetic equations for stressing the simplicity.

$$F_N = kh^{3/2}$$

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

$$W_{1\text{-applied}} = 0.5h_{kink}\left(F_{N\text{-kink}} + F_{1\text{-a}}\right)$$

$$W_{1\text{-indent}} = 0.8W_{1\text{-applied}}$$

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

$$\text{full } W_{applied} = 0.5F_{N\text{-max}}h_{max}$$

$$W_{transition} = \text{full } W_{applied} - \Sigma\left(W_{applied}\right)$$

## 3. Results and Discussion

Room temperature, elevated temperatures and extremely high temperature indentations from literature loading curves are physically analyzed (no iterations, no data-fittings, no simulations) The influence of temperature to the phase-transition energies shows that these decrease with increasing temperature as the latter helps endothermic processes. Exothermic phase-transitions are less likely at elevated temperatures. The claims of indentation at 1000˚C are controlled and

found to be experimental indeed for the exclusion of iterations and simulations from these authors. The gross comparison with a 150˚C temperature increase difference of a different material gave over all related phase-transition energy effects.

The physical analysis of the indentation at 77 K is particularly interesting, because it leads to as yet not imaginable new intellectual and practical applications with respect to exothermic phase-transitions giving more stable (less energetic) polymorphs that are not available at high temperatures or that at best provide metastable or unstable polymorphs. This exothermic (negative) phase-transition energy at 77 K is very high when compared with the endothermic (positive) ones. These unexpected epochal results will have numerous suggested applications.

### 3.1. The Indentation at 1000˚C of Molybdenum

Molybdenum is a useful material for fusion reactors, but nanoindentation onto this promising metal is not frequent or well-established.

The data for **Figure 1** [16] (the thinner lines in **Figure 1** are the regression lines) at room temperature at least are experimental, as the physical $F_N$ vs $h^{3/2}$ plot analysis gives required linear regression lines with two endothermic phase-transitions, as their slopes still increase and create the kink unsteadiness at the phase-transition depths and loads. These cannot be iterated or simulated but at least the room temperature curve must be experimental. However, the authors still deny phase transitions and report ISO-H and ISO-$E_r$ values by getting stuck with the mathematically disproved exponent 2 (instead of 3/2) on *h*. That violates the energy law and thus misses the important phase-transition under load with increased risk of catastrophic failures not only of airliners. The regressions are excellent ($R^2$ approaching 0.9999 in all of these branches). It appears strange that also these authors still believe in the quacking deduction starting with the

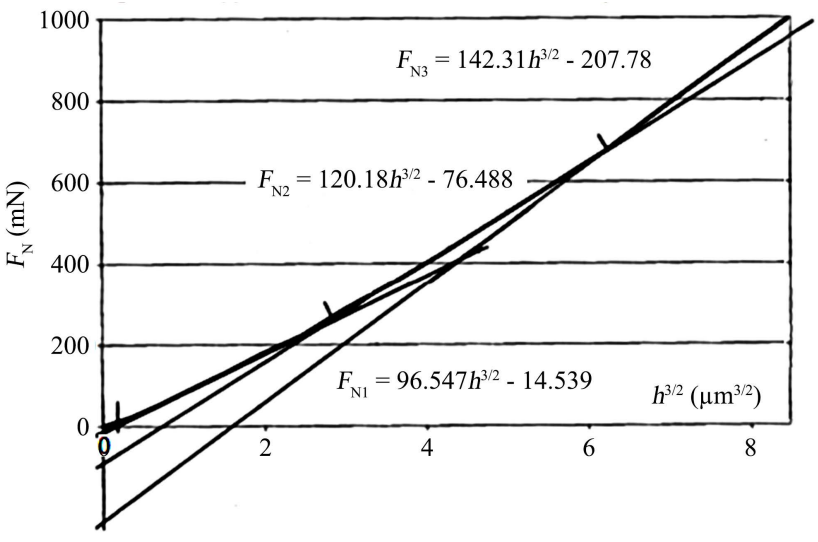


**Figure 1.** Sapphire-Berkovich indentation onto molybdenum at 20˚C.

unphysical ISO-hardness of force proportional to false exponent 2. Clearly, the authors (of [10]) were putting their "answer ($h^2$)" already into their "question" for faking an exponent 2 at the depth $h$ [10]. On the other hand, these authors are engaged in data-fitting and simulation projects, so that we had to check the validity of their high-temperature loading results that, of course, also analyze linearly despite their fighting against the physically correct exponent 3/2 on $h$!

The behavior of molybdenum at high and extremely high temperature appears unusual, as the $F_N$ versus $h^{3/2}$ plots at 20˚C (**Figure 1**) and 1000˚C (data comparison in **Table 1**) look quite similar. There, the conversion energy is decreased after a temperature increase of almost 980˚C by 30.6% for the first and 40.5% for the second phase-transition. We may ask whether these values are reasonable, since the present authors had recently hardly fought against the use of $h^{3/2}$ and the physical calculations on that basis, because there is the risk of simulations from the room temperature loading curve that might have been treated by these authors, while assuming a non-physical "$F_N$ vs $h^2$" relation. They published ISO-hardness and ISO-indentation modulus again in this paper over all polymorphs and there is no retraction of their quacking trick ("$h^2$" for the loading curve as deduced from "ISO-H = $F_{max}/h_c^2$)" also here [10]. Molybdenum parameters are found in [17]. Molybdenum (with melting point 2622˚C; melting heat 37.48 kJ/mol; thermal expansion coefficient at 900˚C: $5.5 \times 10^{-3}$) exhibits two endothermic phase transitions in the loading range of 1 N load. The required force is only 1.81 times lower at 1000˚C. Conversely, the first kink at the 1000˚C experiment occurs by a factor of 1.72 deeper than at 20˚C. That means the material becomes only slightly more resistant by the penetration. This makes refrain from also studying the intermediate temperatures in that case. The main factors for the thermal behavior of these published loading data [16] are the expected expansion at the extremely high temperature and it should be the higher environmental energy that can favor the endothermic conversion. The now available calculation of the normalized conversion energy per µm depth [13], [18] gives a factor of 1.4405 higher at 1000˚C for the first conversion. For the second phase transformation the corresponding ratio is 1.68.

**Table 1.** Indentation onto molybdenum with Berkovich at RT and 1000˚C.

| Temperature ($F_{Nmax}$) | $k$-value (N·µm$^{-3/2}$) | $F_a$ (N) [a)] | $h_{kink}$ (µm) ($h_{end}$) | $F_{N\text{-}kink}$ (N) ($F_{Nend}$) | $\Sigma W_{applied}$ (N·µm) | Full $W_{applied}$ (N·µm) | $W_{conversion}$ (N·µm) | $W_{convesion}$/µm depth[b),c)] |
|---|---|---|---|---|---|---|---|---|
| 20˚C | 0.09655 | −0.014519 | 1.9022[c)] | 0.2388 | 0.9489 | 1.0414 | 0.0926 | 0.0675 |
| | 0.12016 | −0.076468 | 3.2756 | 0.6359 | 1.8498 | 2.0804 | 0.2306 | 0.2605 |
| | 0.14231 | −0.20778 | (4.156) | (0.996) | | | | |
| 1000˚C | 0.037 | −0.0081 | 2.7992 | 0.1652 | 1.2604 | 1.3783 | 0.118 | 0.0468 |
| | 0.0421 | −0.0594 | 5.1855 | 0.5183 | 3.4764 | 3.8383 | 0.3619 | 0.1551 |
| | 0.0535 | −0.1379 | (7.5556) | (0.9736) | | | | |

[a)]The axis cuts are necessary for the calculations (this also corrects the initial effects); [b)]the division by $\Delta h$ attributes the conversion energies to the separate conversion ranges; [c)]all values were calculated with 10 figures and reasonably rounded.

The experimental loading curves in this paper [16] are valuable, but the still used ISO-H and ISO-$E_r$ as "Young's modulus" are in error. We can and must therefore analyze the printed loading curves with the physically and mathematical correct exponent 3/2 on $h$ [9] (**Figure 1**), and we determined the phase-transitions with very good regression ($R^2$ with near four nines). The two consecutive phase transitions of molybdenum are found both at 20˚C and 1000˚C. Furthermore, we proved that both are experimental; because simulations with some of the known and frequently used simulation routines cannot find phase-transition unsteadiness. Only $F_N$ versus $h^{3/2}$ plots from experimental loading curves reveals the kink-unsteadiness of phase-transitions. Such useless simulations are for example published for a spherical indentation onto Molybdenum with forces up to 0.2 or 0.4 N loads and unsuitably rough loading curves without any value [19].

But we have to secure our so obtained conclusion. It is thus highly rewarding that such checking is now possible by comparison with the high temperature studies of a technical heavy-duty light metal alloy Al 7075, with the result, that even moderately high temperatures provide comparable results [20].

### 3.2. The Indentation onto the Heavy-Duty Al-Mg Alloy Al 7075 in the 20˚C - 170˚C Ranges

The alloy Al 7075 contains in weight %: Al 89.66, Si 0.09, Fe 0.19, Cu 1.6, Mn 0.04, Mg 2.6, Cr 0.20, Zn 5.6, Ti 0.02, and it is a heavy-duty light metal alloy. Therefore, both its high and very low temperature mechanical properties are of high interest. **Figure 2** shows the $F_N$-$h^{3/2}$ plot [9] at room temperature, as calculated from the "repaired" (from pop-in events) [14] published loading curve. As the room-temperature indentation and the ones at 70˚C, 170˚C, and −196˚C are nanoindentations in Figure 5 of [20], we replace the unfortunate "k" of impossible "kN" units by N at 77 K and mN at room temperature and above. The depth

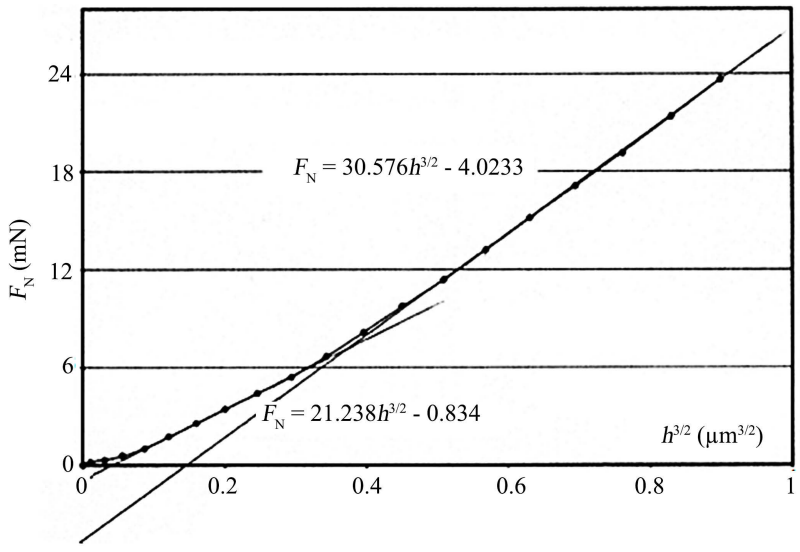


**Figure 2.** Conical indentation onto AI 7075 Alloy at 20˚C.

notations ("mm") are in either case by μm. Only the latter compare with the dimensions in related nanoindentations and must be correct for exponential quantities. Fortunately, the calculations with the formulas that are repeated in Section 2, are independent from the dimension of the force notations at the axes. Their numbers do not depend of what is written at the axes for the drawn $F_N$ versus $h$ loading curve in Figure 5 of [20]. The dimensions of the numbers at the loading curve axes are corrected and "repaired" [14]. Only the $F_N$-$h$ curve from indentation at 77 K becomes flatter from what was called a "pop-in". But our linear $F_N$ versus $h^{3/2}$ plot at 2.35 N and 0.907 μm (0.863 $\mu m^{3/2}$) shows that it is an exothermic phase-transition unsteadiness (see Section 3.3 below). The authors for correspondence of [20] have been informed about these corrections. **Their loading curves are of outstanding value for the nano-indentation and beyond**. The numbers are not influenced by the dimension that is written on the axis and the kN can be changed into N. On the other hand, the dimension of the exponential scale cannot be changed. As the values of $h^{3/2}$ from room temperature and 77 K are nearly identical it means: they must have the same dimension both for the values at room temperature and at 77 K. Therefore, all of these must be at the μm scale by necessity. All of the present superalloys that are indented at room temperature with N forces require the μm scale for the depth. We reported on it in [13]. We are thus enforced to use it also here for room temperature or above and also for 77 K. If we did not do so, these could not be displayed within one Figure 5 in [20]. Our corrections are therefore safe and very well founded. There seem to have been language problems with k and μ only with these abbreviations. In particular, the earlier publications of the authors perform nanoindentations. And the related Al 7050 indentation from [21] penetrates with an indentation force of ca. 50 mN loads at room temperature down to roughly 1 μm depth, as in [13]. The low temperature part of Al 7075 is separately addressed in Section 3 with the mN and μm units.

Figure 2 shows only one phase-transition in the loading range of up to 24 mN. The original curves of Al 7075 have so-called "pop-ins" at 0.444 and 0.689 μm depths that had to be "repaired" [14] for the physical analysis with basic algebra (no iterations, no data-fittings, and no simulations). The pretty high forces that are needed for reaching this phase transition (more than 6 mN) is remarkable. For airliners production one should compare with pure Al (12 mN) or the much inferior $\gamma$-TiAl (1.8 mN) and other better superalloys (see [13]). Such information is hidden in the initial part of Figure 2. Nevertheless, the development of moderate temperature increase at the present loading range is fruitful both for the present phase-transition and its conversion energy per μm depth. Table 2 depicts these relevant data.

Table 2 compares indentations at the same penetration displacements of 1 μm. The physical hardness ($k$-value by steepness regression) does not significantly change and the physical hardness of the transformed material (second branch steepness) changes comparably. A second phase-transition is not occurring up to 1 μm depth. It occurs at considerably higher depth and force at the

**Table 2.** High load indentation onto Al 7075 alloy with conical WC-Co indenter radius 8.63 μm, angle 141.02˚ simulating the Berkovich geometry (but that is incorrect [15]).

| Temperature $F_{Nmax}$ (mN) | $k$-value mN·μm$^{-3/2}$ | $F_a$ [a)] (mN) | $h_{kink}$ (μm) ($h_{end}$) | $F_{N\text{-}kink}$ (mN) (end) | $\Sigma W_{applied}$ (mN·μm) (up to truncated end) | Full $W_{applied}$ (mN·μm) | $W_{conversion}$ (mN·μm) | $W_{conversion}$/μm depth |
|---|---|---|---|---|---|---|---|---|
| 20˚C 24 | $k_1$ = 21.238 | −0.835 | 0.4875 | 6.3936 | 9.7442 | 11.3198 | 1.5756 | 3.4566 |
| | $k_2$ = 30.576 | −4.0133 | (0.9423) | (24) | | | | |
| 70˚C 30 | $k_1$ = 21.125 | −0.4387 | 0.4351 | 5.6276 | 6.8876 | 8.0508 | 1.1632 | 3.1442 |
| | $k_2$ = 33.014 | −3.8483 | 0.8051 | 20.004 | 11.8225 | 12.0776 | 0.2551 | 1.9686 |
| | $k_3$ = 40.665 | −9.3761 | (0.9788) | (30.293) | | | | |
| 170˚C 32 | $k_1$ = 23.486 | −0.2536 | 0.375 | 5.1369 | 6.4129 | 7.3662 | 0.9533 | 2.7110 |
| | $k_2$ = 36.918 | −3.3403 | 0.7902 | 22.598 | 7.2785 | 7.3662 | 0.0877 | 0.1565 |
| | $k_3$ = 46.525 | −10.097 | (0.9346) | (32.091) | | | | |

[a)]These axis cut values are required for the calculations (this also corrects the initial effects).

increased temperatures and diminishes pretty fast by the temperature increase of 150˚C. These values are too small for avoiding phase transitions that occur above 6.4 mN mechanical interactions to form polymorphs interfaces. It is best seen in the conversion energy column of **Table 2**. The first endothermic values decrease rather drastically by 21.6% upon relatively moderate temperature increase. And these values are rather low. The second transitions are also strongly diminished upon temperature increase. This material shall certainly only be used at low temperatures and low expected mechanical interactions. The comparison with the Molybdenum result at 1000˚C (**Table 1**) has to consider that the depth ranges differ 4-fold. The physical hardness 5.7-fold, and ΔT ranges 6.5-fold. We come to the conclusion that the above values for the Molybdenum had fortunately been obtained without iterations and/or simulations and that these loading curves are experimental: It follows our physical $F_N = k{\cdot}h^{3/2}$ law [9] that detects phase transitions by kink unsteadiness. With their assumption of $h^2$ that the authors of [16] and [10] continue to heavily fight for, despite their innocently also here $F_N = k{\cdot}h^{3/2}$ loading curves at room temperature and up to 1000˚C (with correlation coefficients $R^2$ of 0.9999!). We firmly and carefully secured it also for these of their curves in order to check that also these loading curves in question are experimental ones. These authors apparently never checked their exponent on h for decades! They must be advised to do so by loading their force and depth data into Excel® of their computer and calculate the $F_N$ versus $h^{3/2}$ straight lines or intersecting branches with regression in seconds with all of the thousands of data pairs per measurement. If they would try with $h^2$ instead they would not obtain straight lines for experimental nanoindentation curves with cones and pyramids as indenters. Phase-transitions unsteadiness was denied by these authors because they could, of course, not be found with $h^2$. The published experi-

mental loading curves of the authors from [10] and [16] firmly agree with our phase-transition kink-unsteadiness events, but the publishing authors should now be consequent and also use the penetration resistance $k$ [mN/μm$^{3/2}$] (penetration resistance) as physical indentation hardness, rather than their still publishing unphysical ISO-ASTM hardness H values. This clarification is another important result of phase-transition energy calculations and it underlines their importance.

Upon restriction to depths of 1 μm one obtains only two intersecting linear branches (one phase transition) at 20˚C. The indentation at 70˚C gives three intersecting branches, the second of them truncated (two phase transitions), and at 170˚C four intersecting linear intersecting branches, the fourth considerably truncated so that no slope regression was useful with the still steeper standing data points (3 phase-transitions). The conversion parameters in **Table 2** show that the phase-transition energies become smaller by 21.5% by a temperature increase of only 150˚C and that this occurred in a 1 μm range with a heavy-duty alloy.

All endothermic conversion energies become lower at the higher temperatures both for the first phase-transition, but slightly increasing with the second one. That is also seen with the kink force decrease at the higher temperatures, which is reasonably expected. The phase-transition is facilitated in both cases, but the type of the phase transition must be separately detected in any case. Crystallographic studies have been executed, but the reasons for serration and "effective strain-rate" considerations remained vague within the rather complicated interpretations and the mostly not repeatable thoughts (e.g. diffusion rate simulations without their directions, etc.) from unphysical interpretations of the indentation loading curves that cannot obtain physically sound results and thinking. For example, some migration impediment might be created by closing or opening of cleavage planes or channels in relation to the angle of the indenter face that determines the ease or impediment of molecular migrations [13], [18]. Simulation approaches do not help in that respect. Only constituent particles in Al 7075 have been characterized using X-ray synchrotron tomography [22]. Further information provides the temperature-dependent conversion energies. These normalized values decrease from 20˚C to 70˚C as might be expected. But we see from 70˚C to 170˚C a considerable increase of the first and the second phase-transition interface. This might mean a mismatch of migration possibilities by shifting away former cleavage plane or channel orientations as reason for the increase. Also, local melting effects or inhomogeneities might intervene. X-ray studies secured grains but not under what crystal structure conditions these grew or disappeared. They could not specifically be indented due to their smallness, so that one has a kind of homogeneity at least at the mN and μm level. The conversion energy is a new previously not even thinkable way for proceeding on a physical basis. We can safely predict that exothermic phase-transitions would not be supported by higher temperatures.

### 3.3. The Indentation onto the Heavy-Duty Al 7075 Alloy at Liquid Nitrogen Temperature

Low temperature phase-transition properties must be of concern for aviation materials often at much lower temperatures and also for very high mountains and (ant-) arctic regions' equipment. But one has to also care for the increased brittleness. The (ICAO) (International Civil Aviation Organization) defines the standard temperature in aviation around −55˚C, but the space-flight encounters also much lower temperatures. Very low temperature indentations are rather difficult but necessary for aviation and space flights, for which proper materials have to be found and mechanically characterized at these temperatures. One must expect that phase-transitions under mechanical load behave different from room temperature, not to speak of low-temperature modifications. That is particularly important for very low temperatures of boiling liquid nitrogen or even boiling helium and even indentation onto solid nitrogen (<63 K) at liquid helium temperature (4.2 K, pretty close to absolute zero). Liquid nitrogen (77 K) is more frequently chosen. A review but mostly without experimental loading curves collects numerous results and points out numerous aspects [23]. But unfortunately, all of these are deduced by using the ISO-ASTM approach with its iterative false physical background, which enforces extremely complicated mathematical formulas and reasoning. The experimental loading curves can never be reproduced with "$h^2$", except by (strictly forbidden) data-treating, using unfortunately existing fitting formulas. While ceramics appear to have problems with increased brittleness and therefore cracking (that requires more repetitions of the indentation), metals appear easier in avoiding these, and any "pop-ins" in the loading curve can be "repaired" [14].

Fortunately, we found an unspoiled experimental printed $F_N$ versus $h$ loading curve at liquid nitrogen temperature (77 K) of a heavy-duty "AlMg alloy" (Al 7075) that could be "repaired" for the strict algebraic analysis. The regression results are listed in **Table 3**. The impossible kN (kilo-Newton) notions in the Figure 5 axis of [20] have already been safely corrected in Section 3.2. We use N (Newton) for the force and μm for the depth at the 77 K indentation, assuming language problems with the abbreviation k for kilo, which means thousand.

**Table 3.** Indentation onto Al 7075 alloy with conical WC-Co indenter radius 8.63 μm and angle 14.02˚ at liquid nitrogen temperature (77 K).

| Temperature $F_{Nmax}$ | $k$-value (N/μm$^{3/2}$) | $F_a$ (N)[a)] | $h_{kink}$ (μm) ($h_{end}$) | $F_{N\text{-}kink}$ (N) (truncated end) | $\Sigma W_{applied}$ (Nμm) (to truncated end) | Full $W_{applied}$ (Nμm) | $W_{conversion}$ (Nμm) | $W_{conversion}$/μm depth |
|---|---|---|---|---|---|---|---|---|
| 77 K 22.3 N | $k_1$ = 21.299 | −0.0761 | 0.4933 | 7.3038 | 8.5582 | 8.8526 | 0.2945 | 0.7123 |
| | $k_2$ = 23.645 | −0.889 | 0.9067 | 13.5266 | 13.3615 | 10.8078 | −2.5537 | −14.672[b)] |
| | $k_3$ = 19.893 | +2.3515 | (0.9623) | (22.3) | | | | −54.363[c)] |

[a)]These axes cut values are required for the calculations (they also correct for the initial effects); [b)]up to 22.3 N load contains both the endo- and the exothermic conversions; [c)]separate calculation only for the exothermic phase transition.

At first glance we see that the physical hardness (the regression slope) increases upon transformation into the second polymorph and decreases to the lowest value for the third one. These values are considerably larger than at room temperature above in Table 2. The physical hardness $k$ differs strongly and we therefore separated Table 2 from Table 3. We have at the beginning two endothermic branches, as with the room temperature case. That is followed by an exothermic one, giving two consecutive phase-transitions and three polymorphs. And the algebraic analysis of the $F_N$ versus $h$ loading curves remains, of course, unaltered. Nevertheless, we never know, whether we have to deal from the beginning with low-temperature polymorphs, basic or transformed ones. It is well known that pure aluminium becomes more ductile and malleable at 77 K, but we cannot use that here and for the alloy. We might ask whether endothermic phase-transition should be frozen out at liquid nitrogen temperature, as the thermal support vanishes. But the first kink comes at almost the same penetration depth and only the second phase transition freezes out from the second polymorph for a second endothermic kink. The happening of the endothermic transition at 77 K (by further cooling of the environment) is for the first time observed and analyzed. It is surprising for the very cold environment. But the second and the third polymorph endothermic transition range cannot be tolerated any more at 77 K of the system. It is ready now from the 7.3 N kink point at 13. 5 N load for a more suitable exothermic phase-transition that does no longer need energy but produces energy. This exothermic phase-transition is not observed at room-temperature and above. It continues up to 22.3 N load at the end of the 1 μm depth range. It appears already remarkable that we initially (at the lower forces) have the endothermic conversions at all and not already the exothermic one from the beginning of this indentation. That indicates a rather high energetic barrier for this exothermic transition. Even this strongly exothermic transition starts only upon the high loading force from the second polymorph directly for a further polymorph that is not the same as obtained at 70˚C and 170˚C. We observe it for the first time from the measurement of Ref. [20] and the material is Al 7075. It is really an epochal new result that we can present now. Our development is explained as an easily understood phenomenon that is only observed at very low temperature: Make the endothermic transition impossible to generate an exothermic one. We can use it now for producing new polymorphs at very low temperatures that are more stable (negative-energy-content) than the initial or preceeding polymorph due to its exothermic generation. Such yet not thinkable polymorphs could therefore survive moderate thawing. This negative-energy-content polymorph is well below our thermodynamic Al 7075 zero standard and yet the presently most stable polymorph on earth, provided that not deeper ones would emerge at still higher forces and or deeper temperatures. We must now no longer falsely think that we have and see the most stable polymorphs of our materials at standard conditions. At least we know now that our technical Al 7075 is not the most stable polymorph of it. It is at best one for the average temperature on earth. Chemists will have to synthes-

ize and study these negative-energy-content polymorphs from various materials. They will have to find out up to what temperatures these will be storable and what properties will they have and what unforeseeable reactions will these undergo. But the negative-energy-content polymorphs will probably not survive at room temperature. We do not have such materials on earth though. They might take up environmental energy when they feel like in a "baking oven" at the normal temperatures on earth. We do not know yet how deep we have to cool the most stable polymorph of Al 7075 or hopefully soon further materials to keep them stable for storing and using. That will certainly become a topic for our thermodynamic standards, but these are only valid for our earth. It must be of highest interest for cosmologists and cosmonautics, as it opens up completely new fields in physics and chemistry. The possible prospects are highly rewarding.

The production of thermodynamically most stable polymorphs with negative-energy-content opposes the production of unstable or at best metastable polymorphs at high temperature loads that are energetically above the thermodynamic zero. Our perfectly new results required the calculation of phase-transition onsets and energies at high and very low temperatures with nanoindentations. The great value of these results and possibilities is evident and deserves widespread consideration. Only our physical and algebraic analyses of indentation loading curves can detect the phase-transitions. These are not only important for preventing crashes of airplanes, turbines, bridges, etc., but also for the creation of unexpected new developments: The use of the high exothermic transition energy of a crystalline material at 77 K is highly rewarding. The new facts are a physical revolution by creating polymorphs at liquid nitrogen temperature and still further below. It should be synthetically used with broad mechanical impact equipment with force onto strongly cooled materials within stable vessels for the synthesis and study of new polymorphs with negative-energy-content. That could not have been thought of before. We detected very high negative transformation energy in the present case. Under the very cold conditions the exothermal phase-transition of Al 7075 with increased forces occurs up to the end of the fixed depth range by taking 37 per cent of the $h^{3/2}$ scale. For the separation of the positive endothermic part from the negative exothermic part the positive conversion energy's part was removed from the composite value and the exothermic part was obtained and normalized

Indentations at 77 K should be urgently tried with NaCl single crystals, in order to see whether its metallic polymorph could be obtained. It was not seen at room temperature up to 50 or 80 N indentation force [12]. Comparison with numerous further materials at 77 K is very desirable. The use of 77 K indentation is presently the only possible choice for obtaining such exothermic phase-transitions, because endothermic conversions are not supported from the very cold environment at increased forces. Completely new practical applications are now thinkable. But also really new knowledge and intellectual reasoning power is opened by the present results.

While looking for new endothermic phase transitions at higher and higher temperatures yielding more and more unstable polymorphs is important for technical materials that run at high temperatures, one should do it also at deeper and deeper temperatures to produce more stable polymorphs with less and less negative-energy-content after suppressing the endothermic transitions. Exothermic phase-transitions are energy providing to the environment and the negative conversion-energy can be removed by it. So, what we need is a mechanical impact and a solid surface with stable cooling capacity. More stable polymorphs are certainly possible.

Our proof of exothermic transformations at low-enough temperatures under mechanical stress open up new imagination for experiments with regard to mechanical impact at very low temperatures. And exothermic phase-transition products are always the more stable ones. One should therefore try to make use of the new knowledge for the interpretation of impacts onto very cold moons, asteroids, and ice-free planets. And the by ISO-ASTM as yet unthinkable phase-transition conversion energies are straightforwardly, easily, and rapidly available. What will cosmonauts find on very cold liquid-, gas- and ice-free surfaces? Are these perhaps minus-energy-content polymorphs of materials due to million years of impacts with comets, friction events, etc. and also staying very cold, so that these cannot take up energy for reforming our "normal" polymorphs on earth?

There is no relation between onset force (at the kink unsteadiness) and physical indentation hardness $k$ with dimension $N/m^{3/2}$, because we detect characteristic material's data. Numerous of them (all at room temperature) are collected in the open access e-Book [24]. The first phase-transition kink in $F_N$ versus $h^{3/2}$ plots shows the first phase-transition-onset. The force for it must not be exceeded in the materials' technical use for avoiding polymorph interfaces (that are shifted away from the mechanical impact site). Such polymorph interfaces bear the increased risk of nucleating crack- and crash-formation probabilities. Again: it's increased probabilities and requires additional forces for the final crash. The corresponding conversion energy should be as large as possible for minimizing the risk of catastrophic crashes.

Another point of interest is the optimized material of space flight vessels to very distant space objects in very cold environments far away from sun-heating. Impacts by (micro) meteorites might suffer from exothermic phase transitions that are more severe than endothermic ones. Space flight materials should be indented at 77 K and physically analyzed. Hard landings on cold moons or planets must be avoided.

## 4. Conclusions

The detection of phase-transition onsets and the straightforward calculation of their transition energies are of primary importance. Striking examples are from the aviation field, as described above, because polymorph interfaces must be

avoided. Nanoindentations are presently the only means for fast and easy success. Their comparison at different temperatures increases the value and leads to important new knowledge in physics by using the most simple and convincing principles from the energy conservation law (rather than violating it). All of it is based on the correctly deduced physical law $F_N = k \cdot h^{3/2}$ for "one point" conical and pyramidal indentations, which describes the normal force versus depth curves relation [9]. The tip-dependent *k*-value (the penetration resistance in e.g. $mN/\mu m^{3/2}$ units) is the physical indentation hardness. Technical materials have to be improved for increasing both their onset force and their endothermic transformation energy, but that is only possible with the correct physical law and not by stubbornly insisting on historical errors. We use here the important possibility to distinguish the experimental part from simulated and/or iterated indentation reports. Only untreated experimental loading-curves reveal the resulting phase-transition onsets and energies. The great value of not using assumptions, iterations, data-fittings or simulations but only algebraic calculations with closed formulas is evident. It is not only much easier than the incredible energy-law violations, but it is also highly rewarding and develops unprecedented applications:

**1)** The continued violation of the energy law by the ISO-ASTM 14,577 standards, by claiming that the pressure to the tip's environment (as always used for modulus detections!) would occur without any energy requirement (!) and the out there following definition of $F_{max}$ over projected contact area (e. g. $\pi r^2$ of the cone face area) for the "one-point indentations" as hardness, are disastrous. It has been quacking used (by putting the answer $h^2$ of an area already into the question for the loading exponent) for a so-called "theoretical confirmation" of an assumed but unphysical "$F_N$-$h^2$ relation" for indentation loading curves in Ref. [10]. As there also exist complicated means for the manipulation of experimental data to create $h^2$ (a published fitting-equation can be read in [7], etc.), the loading curves of the quacking authors' [10] data from [16] had to be checked, because they again used ISO-ASTM hardness ("$H = P_{max}/A_c$") and modulus ("$E_r = \pi^{1/2} S / 2\beta A_c^{1/2}$"), and that falsely over two kink unsteadiness events (three polymorphs with very different properties) (see **Figure 1**). That is strikingly inconsequent (no excuse for innocence!). But fortunately, their published loading curves from 20˚C up to 1000˚C are untreated and left experimental **as these correctly relate with $h^{3/2}$ but not with $h^2$**. These curves could thus be reasonably analyzed and the obtained phase-transition onsets and transition energies in **Table 1** (but only these) are reliable. These authors of [10] and [16] are urgently asked to themselves check their own loading curves for their correct exponent most easily with Excel® calculation (for example 30,000 computer data pairs in a few seconds), which they stubbornly renounced to do so for decades.

**2)** The reliability of the up to 1000˚C results in **Table 1** (not only volume expansion) has been secured by comparison with the 20˚C to 170˚C indentations onto heavy-duty alloy Al 7075 (**Table 2**), where the phase-transition onsets and transition energies are at least in a comparable order of magnitude to the ones of

Molybdenum at 1000˚C, if the different physical hardnesses $k$ and penetration depth influences are also roughly taken into account. This leads to an easily understood decrease of the conversion energy per depth unit upon temperature increase, as the mostly found endothermic phase-transitions are preferred upon heating.

**3)** The indentation onto Al 7075 alloy at liquid nitrogen temperature (Table 3) also follows the $F_N = k \cdot h^{3/2}$ law. Surprisingly, there is also the first endothermic phase transition that must provide the required energy at these very low temperatures. However, at an increasing force and depth after the start of the second polymorph this energy cannot be provided any more. The material simply decided for a strongly now exothermic phase-transition (to produce a low temperature very low energy-content-polymorph) with energy production at 77 K. The high activation energy for this exothermic process could only be surmounted at the increased force creating increased pressure. The adhering crystal and its environment had to take up the evolved energy and dissipate it. This unexpected epochal result is the first proof of a material on earth with lower energy-content than the thermodynamic zero of the ambient modification. That opens a series of new thinking and applications on a cosmologic level. And what about the materials in the cold cosmic space with its continuous large and minor collision impacts and frictional events? These are very new questions. A complete new physics and chemistry is on the wake that should be used from now on. Direct applications are in cosmology, space-craft, and cosmonautic areas. Phase-transitions are not only important for the safety of all of us, but also for epochal new future developments on earth.

**4)** The further prospects of the data in Table 3 (its last column) derive from the efficiency of the exothermic phase-transition at 77 K. What kind of applications will ensue from this new knowledge? In short: if we want to have polymorphs that are more stable than ambient crystalline material (negative-energy-content below the thermodynamic zero) we must go to (very) low temperatures that prevent or sufficiently block endothermic transitions that require energetic support. This result with Al 7075 is apparently the first case where this has been proved, by phase-transition energy calculations. There is no reason why it should not be possible to prepare and isolate such super-stable polymorphs for the elucidation of their physical, crystallographic, and chemical properties. Upon heating to room temperature, it is to be expected that these will take energy from the environmental energy as in a "baking oven" to finally reinstall the thermodynamic zero standards. But how deep must we go with cooling to make them survive for being stored? Or how far can we increase the temperatures above 77 K by avoiding the endothermic transitions for still obtaining the exothermic phase transition with the present and also with other materials? And indentations at liquid Helium temperatures (4.2 K) are also possible [23] for further materials, not restricted to heavy-duty alloys. All that is at first needed are experimental indentation loading curves for their correct analysis.

## Conflicts of Interest

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

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