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To: Prof. Dominik Munzar
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Masaryk University, Brno, Czech Republic

Handled by
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Date
Aug. 30th, 2021

Our reference

Subject
Review of Habilitation of Dr. Jiri Orava

Review of Habilitation Thesis of Dr. Jiri Orava entitled:
What Drives the Lability of Glass-Forming Liquids to Crystallize?
Applications in Electronic, Structural and Optical Materials.

The current reviewer is in a good position to evaluate the work of Dr. Orava. The primary reason is that we both can be considered (world-class) experts on ultrafast differential scanning calorimetry (UFDSC) of phase-change materials (PCMs). I started with research on PCMs in 2001, employing transmission electron microscopy (TEM) to study PCMs, resulting in a first published paper in 2002. To date I am still active in studying PCMs with extended resources (infrastructure and PhD student projects). Dr. Orava started to work in this field at least (shortly) before 2012 when he was first author of a seminal paper in which for the first time UFDSC was used to analyse the crystal growth rate over a wide temperature range of a PCM (actually the most studied one: Ge2Sb2Te5). Since then Dr. Orava has been working continuously on PCMs, in particular chalcogenide glasses and also on metallic glasses with main focus on studying the crystallization in both types of glass-forming liquids. The current habilitation thesis is centred around this main focus. In the period 2014-2018 the present reviewer also published 5 papers employing UFDSC for studying chalcogenide glasses. Importantly, I can still be considered an independent reviewer of the work of Dr. Orava since we have not any joint publication (but referred extensively to each other's work).

Currently, I am full professor and group leader of the research unit "Nanostructured Materials and Interfaces" within the Zernike Institute for Advanced Materials, Faculty of Science and Engineering of the University of Groningen, Netherlands. My general research focus is on structure-property relations of nanostructured materials, thin films and optoelectronic materials, in particular phase-change materials and chalcogenides. My main expertise is employing Transmission Electron Microscopy in my research. I have published about 230 papers in peer-reviewed scientific journals (H-index 51 Google Scholar).

The habilitation thesis of Dr. Orava is very impressive and is rated as excellent because of several reasons: (1) it is based on a lengthy series of very high quality papers published in high impact journals, (2) the series of papers shows both very nice coherence and evolution over the years (2012 till today) showing the systematic manner in which Dr. Orava has worked on sequential research topics, (3) the habilitation thesis is not just a sequential list of papers (with an introduction to put them into context), but it is actually a new review, of course mostly centred around own earlier work, but also being open to relevant developments and papers of other groups in the field to make it really an up-to-date review for 2022.

In 2012 Orava et al. published a truly groundbreaking paper in Nature Materials where the crystal growth rate in supercooled-liquid Ge2Sb2Te5 was derived from UFDSC data at higher temperatures beyond the glass-transition temperature (Tg) than was measured in earlier work. In earlier work only slow growth close to Tg was measured and then always Arrhenius type dependence between growth rate G and temperature T was observed, i.e. a linear dependence between ln(G) and 1/T. At higher temperatures Orava et al. observed clear deviations from this linear dependence. This non-linearity could be explained well by considering supercooled-liquid Ge2Sb2Te5 as a fragile liquid. Although experts in the field of (crystallization in) glass-forming liquids were at that time already well aware of the concept of fragility, this was new for the field of PCMs. For the first time this explained properly why the activation energy for crystal growth can be high close to Tg and much lower at high temperature still well in the regime where the growth rate is limited by atomic mobility (viscosity) and not by driving force (which is the limiting factor close to the melting point). It also explained the exceptional crystallization kinetics of PCMs making them suitable for memory applications: combining very good data retention (i.e. ‘stable’ amorphous phase) at low temperatures, but still very high switching speeds (i.e. crystallization rates) at high temperature for a relative large temperature range (i.e. making it rather easy and robust to operate in this window). Although the published work in Nature Materials contained an important series of (also debatable) assumptions to couple the UFDSC data to the crystal growth rates, still the impact of this paper on the field of PCMs, particularly introducing the concept of fragility, was tremendous. This is also clearly evidenced by the many citations this work has received till now for a relatively limited research field: 430 according to Google Scholar.

In a follow-up work Orava et al. studied the effect of sandwiching the Ge2Sb2Te5 film between thin dielectric layers as is the case in actual memories (both optical disks and electrical memories). It was observed that capping layers reduce crystal growth rate (particularly in the supercooled-liquid close to Tg), which was attributed to crystallization induced stresses retarding crystal growth. At high heating rates and thus higher temperatures this retarding effect disappears, because the stresses can relax.

When switching from the nucleation dominant Ge2Sb2Te5 to the growth dominant AgInSbTe alloy it turned out that the large temperature range in which Arrhenius behaviour is observed makes it impossible to fit the experimental data assuming a single fragility phase-change liquid. In two ways this issue can be resolved. The first one is that the Arrhenius behaviour still occurs in the glassy phase as was proposed by Salinga et al. [Nature Commun. 4, 2371 (2013); DOI: 10.1038/ncomms3371]. However, this would require a very high, likely unrealistic value for Tg. Then, based on their own UFDSC data, Orava et al. came with another solution. The data can be explained well when there is, upon cooling, a fragile to strong crossover in the liquid (and upon further cooling there is a differently sloped Arrhenius behaviour below Tg in the glass). Indeed, this elegantly explained the observed behaviour. Also this work, introducing the concept of the fragile to strong crossover, sparked significant work in other groups explaining their data using this concept.

More (follow-up) papers can be addressed, here, but the above ones should sufficiently highlight the excellence of the work of Dr. Orava, he reviews also very well in his habilitation thesis. Also to the field of metallic glasses Dr. Orava has made substantial contributions. The present reviewer is less involved in this field and therefore does not put emphasis on these contributions. Still, the present reviewer has no doubts that the work of Dr. Orava in the field of glass forming melts is of generic importance and therefore emphasizing the distinction between different types of glasses, e.g. based on chalcogenides or metals, is not doing full justice to the work of Orava et al..

The track record of Dr. Orava makes sufficiently clear that he has developed into a mature and independent researcher who is also very well capable to choose his own high impact research directions and to guide students working along these directions and to publish joint papers. His track record also shows that Dr. Orava can be productive in quite different research environments which is rated positively in the context of the present review of his capabilities.

Jiri Orava has given inspiring presentation at the EPCOS and MRS Spring meetings which are the two major annual conferences of the PCM community. At these instances I had the pleasure to be in the audience when Dr. Orava gave (invited) oral presentations. Therefore, I can provide my opinion, which is probably generally supported, that Dr. Orava is a very good presenter. He is giving well-structured talks, is convincing and is able to convey a relative complex message clearly to his audience. His presentations demonstrated that Jiri Orava should also have good didactical skills. So, although I do not have any information regarding his teaching skills and how his teaching is evaluated and rated by his students, I am convinced that Dr. Orava should be a good lecturer and teacher.

The above description now (hopefully) provides sufficient examples and arguments to finalize and summarize this review such that in the following bulleted points my overall judgement of the performance of Dr. Orava can be given:

- Excellent track record in research;
- Author and co-author of highly cited papers;
- Consistent and coherent research focus, later work builds excellently on previous insights;

- Predominant focus on publishing high-quality research rather than on producing a large numbers of papers;
- Original and creative researcher, who can come up with new ideas and solutions that provide important progress in research;
- Well known in the PCM community.
- Very good speaker who can convince his audience.

Conclusion:

The habilitation thesis entitled "What Drives the Lability of Glass-Forming Liquids to Crystallize? Applications in Electronic, Structural and Optical Materials" by Jiří Orava fulfils requirements expected of a habilitation thesis in the field of Condensed Matter Physics.

Sincerely,

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