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Annex No. 10 to the MU Directive on Habilitation Procedures and Professor Appointment Procedures

HABILITATION THESIS REVIEWER'S REPORT

Masaryk University	
Applicant	Ing. Jiří Orava, Ph.D.
Habilitation thesis	What Drives the Lability of Glass-Forming Liquids to Crystallize? Applications in Electronic, Structural and Optical Materials
Reviewer	Prof. Richard J Curry, PhD, BSc, CEng, FInstP
Reviewer's home unit, institution	University of Manchester

The preface contextualises the thesis well. It provides a high-level overview of the central thesis subject matter and its relationship to the development of an understanding of the material systems of study. The thesis structure is outlined, followed later by a useful presentation that outlines the key contributions of the author to the topics covered in relevant publications.

The introduction begins with a summary of the highly-complex nature of glass forming. This is handled well and clearly illustrates why this subject matter remains of academic interest. The landscape is exceptionally broad and has been the subject of experimental, theoretical and simulation studies for decades. In order to allow insight the author has identified two exemplar systems, phase-change systems and metallic glasses, and the process of thermal cycling as means of controlling glass properties. The exemplar system of phase-change glasses is particularly noteworthy as they relate to technologically important materials which underpin many data-storage media. The author then turns attention to the key processes of nucleation and crystallisation. It is immediately apparent that the author has an authoritative grasp on these topics in relation to glass systems. The summary is comprehensive, illustrating insight, and not for the faint hearted! To obtain this level of understanding and the ability to make connections across a wide range of glass families (and show awareness of those which stand out) demonstrates the time devoted to developing an intimate knowledge of the subject matter.

Chapter 2 continues the detailed consideration of kinetic vs thermodynamic interactions in crystallisation. Through taking a broader view of all materials systems, from metallics through to organics, it is possible to draw some conclusions of interest. For example, plotting T^U_{max}(K) against T_g(K) a linear relationship is found as we demonstrated in the author's previous work. This is noteworthy when trying to draw general conclusions on the topic of glass formation. It is further developed through the consideration of the relationship with the 'fragility corrected' reduced glass transition temperature. Through the analysis presented it is argued, supported by the available data, that there are a set of common underlying behaviours that apply irrespective of the glass forming system.

Chapter 3 introduces the key experimental characterisation techniques available for the study of crystallisation (and other processes). It focuses on the technique of fast differential scanning calorimetry (FDSC) that is to be relied upon later to study phase-change systems and provides an overview of relevant approximations that can be applied. The use of simulation to study these systems is discussed and its ability to extract qualitative and quantitative information relating to key parameters.

The focus narrows in on phase-change materials in chapter 4, in particular the $Ge_2Sb_2Te_5$ (GST) system. The use of FDSC to shed additional insight into this class of materials (in thin film form) is discussed with the variation in T_g and the implication this has for interpreting data and models discussed. The text then goes on to present systems that do not display a single-fragility liquid nature with the detailed work of the author on the AIST system (and others) described. The prediction and subsequent experimental observation of a fragile-to-strong crossover is discussed for AIST in light of the remaining uncertainty over its T_g. FDSC is then used to shed light on the liquid nature of non-phase-change $Ge_{15}Te_{85}$ and phase-change GeTe systems, linking crystallization, viscosity and evolution with temperature. The chapter then goes on to discuss 'priming' of phase-change systems and how the presence (or lack of) a crossover may or may not impede the use of this methodology for increasing the write speed of memory. Finally, the inclusion of a brief diversion into filamentary systems as future memory media is certainly relevant and of course shows awareness of the continuing wider research environment in which the major work reviewed resides.

Metallic glasses are turned to in chapter 5. These systems lend themselves to in-situ study in x-ray and electron beams enabling dynamic studies with very high resolution. As such significant insight into the dynamics governing phase change is obtained, which then enables models to be tested with greater detail. This interesting work (ongoing) is utilising state-of-the-art facilities including synchrotron light sources and shows potential to provide fundamental insight into these systems at a level where direct comparison with ab initio studies (performed using similar volume scales) can be made.

The nature of amorphous-amorphous transitions and athermal behaviour are explored in chapter 6. The origin of well-known, though not always well-understood, effects such as photodarkening etc. are discussed in relation to structure and bonding in chalcogenide systems. The observation of contrasting reversible/irreversible behaviour within the same system but deposited using different methods is discussed and the observation/measurement of phenomena such as photoamorphisation. Ongoing work is then discussed relating to the effect of light intensity on crystallization/amorphisation within the same material. Whilst presented within the framework of 'athermal' behaviour work still remains to fully understand this behaviour. Clearly, there will be some phonon coupled interactions taking place which may at least contribute to what is physically taking place within the material to enable the observed behaviour.

In summary the presented work clearly outlines a candidate who is in full command of their area of expertise. The level of understanding expressed is impressive, and admittedly complex in places for the reader to fully appreciate the full picture that the dedicated work of the candidate has been able to assemble to date through their career. I have no doubt that they will continue to excel as a leader in this field, and through the intricate connections made between the fundamental behaviour of these systems and their application in technology new advances and opportunities will be realised.

Reviewer's questions for the habilitation thesis defence (number of questions up to the reviewer)

Relating to the work on nanoscale systems (e.g. Chapter 5) I note that the doping of these (e.g. during colloidal chemical synthesis) is particularly challenging as the dopants are often 'pushed' towards the surface as they represent an impurity with higher local energy. It might therefore be expected that once nanocrystallites are formed within glasses the same occurs, and that this might lead to irreversible crystallisation and bi-phasic regions forming. Is there any evidence of this or does the surrounding matrix frustrate phase separation occurring? What do you think might be the implications for allowing stable low (|e.g.1%) doping with optically active species?

Relating to the current work described in Chapter 6, can you comment on why light intensity alone (i.e. without any thermal/phonon interactions) might lead to the observed ability to transition between the two states? If you do not invoke any non-linear (i.e. multiphoton) photonic interactions then why should light intensity drive the different bonding re-arrangements required?

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.

Date: 26th July 2022 Signature: