A&A 386, 1103–1105 (2002)
DOI: 10.1051/0004-6361:20020333

Astronomy
&
Astrophysics

Research Note

The low temperature crystallization effect reevaluated

W. A. Schutte[⋆]

Raymond and Beverly Sackler Laboratory for Astrophysics, Leiden Observatory, PO Box 9513,
2300 RA Leiden, The Netherlands

Received 7 February 2002 / Accepted 4 March 2002

Abstract. We reevaluate the Low Temperature Crystallization (LTC) effect reported by Moore et al. (1994) for ices condensed on a layer of amorphous silicate smoke on an aluminum substrate at <20 K. We consider the possibility that the observations put forward by Moore et al. in support of the LTC phenomenon could result from poor thermal conductivity in the fluffy smoke layer causing the temperature of the smoke particles to be well above that of the aluminum substrate. We conclude that there is currently no persuasive evidence for LTC in the Moore et al. experiments.

Key words. ISM: dust, extinction – infrared: ISM – ISM: general

1. Introduction

The presence of crystalline ices in interstellar environments is generally considered exclusive evidence for thermal annealing. Indeed, when gases such as H_2O and CH_3OH are deposited at 10–20 K, temperatures representative for the dust in the interstellar medium, this results in the formation of amorphous ices (e.g., Hudgins et al. 1993). Crystallization only occurs after warm-up to $>\sim 150$ K in the laboratory. However, Moore et al. (1994) observed the formation of crystalline ice when H_2O, CH_3OH or NH_3 ices were condensed on a layer of amorphous silicate smoke which was deposited on a <20 K aluminum substrate. The authors named this phenomenon Low Temperature Crystallization (LTC). They hypothesized that active defect sites on the grains which constitute the smoke layer could cause the crystallization.

It is clear that the occurrence of LTC would have far reaching implications for the interpretation of interstellar ice observations. Generally, the OH stretching mode absorption feature of H_2O ice observed towards high and low mass protostars indicates that the ice is predominantly amorphous (Smith et al. 1988; Whittet et al. 1988). However, the emission from the disk surrounding the young star HD 100546 shows a feature at 60 μm, clearly indicating the presence of crystalline ice (Malfait et al. 1998). So far these observations have been interpreted in terms of the thermal history of the ices, but if LTC occurs, this would imply that crystallization of the ice relates to the nature of the silicate dust onto which it is condensed.

Which physical mechanism could cause the LTC effect is unclear. As noted by Moore et al., it is possible that the interaction between the smoke particle surface and the condensing gases could cause the first 1 or 2 monolayers to crystallize at low temperature, but it is hard to understand why any such surface reactivity would extend further into the ice sample. Thus the possibility that the LTC was caused by an experimental effect deserves close consideration. In particular, because of the fluffy nature of the smoke and because of the close correspondence of the composition of the smoke with quartz glass, a material known for its low thermal conductivity, the cooling of the smoke layer by the transportation of heat to the underlying aluminum substrate may have been very inefficient. The top of the layer is constantly heated by thermal radiation emanating from the room temperature set-up walls. This may have caused the smoke layer to have a temperature well in excess of the 20 K aluminum surface.

In this short communication we investigate whether the various results put forward by Moore et al. in support of the LTC phenomenon can also be explained by the effects of a steep temperature gradient in the smoke layer resulting from its low thermal conductivity.

2. Evaluation

To exclude the possibility of crystalline condensation due to elevated temperatures in the smoke layer, Moore et al. relied on a number of experimental results. First, it was

---

[⋆] e-mail: schutte@strw.Leidenuniv.nl

noted that crystalline ices form on all smoke layers, irrespective of the layer thickness or the nature of the gas. Second, they found that CO and CH_4 also condense, indicating temperatures below 50 K. Third, the temperature dependent sublimation behaviour of the ices deposited on the smoke layer "appeared to be the same" as that of ice films that were directly deposited on the aluminum substrate.

We now consider the possibility that each of these observations could be explained in terms of condensation of gases on a smoke layer with a steep vertical temperature gradient. Such a temperature gradient could result from a low thermal conductivity of the smoke layer. The top of the layer is constantly heated by the absorption of radiation from the substrate walls, while at the bottom the layer is cooled by its contact with the cold (<20 K) finger. If the thermal conductivity of the smoke layer is low, a steep temperature gradient would be required to allow transportation of the absorbed heat to the aluminum substrate. (It must be noted that at the deposition rates used by Moore et al. ($\sim 10^{20}$ molecules hr^{-1}), the heat of condensation is small relative to the energy absorbed from the thermal radiation by the $\sim$290 K walls of the set-up). Considering this possibility, the first observation by Moore et al. can be understood in terms of inward diffusion of the gases through the upper warm regions of the smoke layer, until they reach a region where the temperature is just low enough for them to condense. Since in this picture the condensation will always take place at the temperature which is just sufficient for condensation, irrespective of smoke layer thickness and the nature of the gas, this process will always result in the formation of crystalline ice. The condensation of very volatile gases like CO can be understood if these gases diffuse through the warm smoke layer until they reach the cold aluminum substrate itself. Finally, the similar vaporization behaviour during warm-up of a sample deposited on smoke on top of aluminum or deposited directly on the aluminum substrate can be understood in terms of a sublimation and recondensation sequence. After their initial sublimation, the molecules can, through a random walk, diffuse down to slightly colder regions, where they recondense. Going through this cycle a number of times, the gases could eventually diffuse all the way down to the aluminum substrate, and will only be finally lost when the substrate itself becomes sufficiently warm. We conclude that all the observations by Moore et al. in support of the LTC phenomenon may be explained by the presence of a temperature gradient in the smoke layer.

To investigate the possible influence of the thermal conductivity of the substrate material on the physical state of a condensed ice layer, we have performed an experiment in which H_2O ice was deposited on a quartz window. For details on the experimental procedure we refer to Gerakines et al. (1995). We note that the composition of quartz is very similar to that of the silica smokes in the Moore et al. experiments. It is expected that for a material with a low thermal conductivity such as quartz a thermal gradient could arise from the center to the edge of the substrate. At the edge the substrate is in intimate contact with the 12 K coldfinger through the use of an indium seal, and therefore will be at 12 K as well. The positive thermal gradient towards the center, where the substrate temperature may be considerably higher, allows the transportation to the cold finger of the heat which results from the absorption by the substrate of the radiation from the set-up walls.

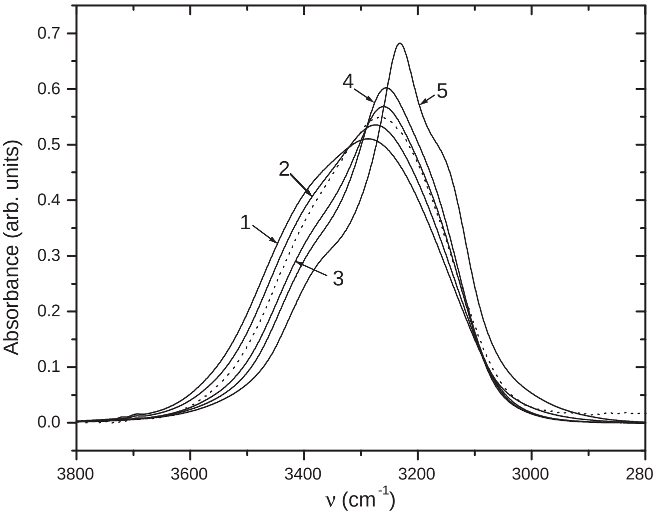

Fig. 1. The OH stretching mode of a sample of pure water ice as deposited on the quartz substrate with the cold finger at 12 K (dashed line), compared with the spectra of water ice deposited on a CsI substrate: 1) after deposition at 12 K; 2) after warm-up to 50 K; 3) to 80 K; 4) to 120 K, 5) to 160 K.

Figure 1 shows the spectrum of a sample of pure H_2O deposited on a quartz substrate mounted on a 12 K cold finger. We used a low deposition rate (10^2 monolayers hr^{-1}), analogous to the deposition rates reported by Moore et al. By comparison to an H_2O sample deposited on a standard CsI sample, it can be seen that the sample on the quartz window is somewhat annealed, analogous to an ice sample after warm-up to 60–70 K on the CsI substrate. This clearly shows that low thermal conductivity causes the temperature on the quartz window to be considerably higher than that of the cold finger itself. To verify that the annealing is caused by the temperature and not by some kind of LTC effect, we also deposited CO on the substrate. It was observed that, following deposition, the CO ice gradually evaporates. The sublimation rate obtained from the decrease of the 2140 cm^{-1} CO stretching mode was equal to 1.6×10^{13} molecules s^{-1}, corresponding to a temperature of 30 K (Sandford & Allamandola 1988). We note that the difference in the temperature obtained from the CO sublimation rate and the degree of annealing of the H_2O ice can be easily understood when considering the temperature gradient over the substrate. Since CO is a highly volatile species, it will not be able to condense on the warmest regions of the substrate, i.e., near the center. Therefore the CO ice will, on the average, have a lower temperature than the H_2O ice, which can condense also at the center of the substrate where the temperatures are highest.

The experimental results emphasize that low thermal conductivity is a major concern when attempting to obtain cryogenic temperatures with materials of chemical composition similar to quartz. We note that these problems will be greatly enhanced when using a loose agglomerate of particles like the fluffy smokes in the Moore et al. experiments.

In summary, all experimental results by Moore et al. can be rationalized in terms of poor thermal conductivity through the smoke layer and the resulting high temperature of the particles. To exclude this possibility, a careful measurement would need to be made of the thermal conductivity of the smoke layer in the Moore et al. experiments, followed by modelling of the equilibrium between absorption of thermal radiation and cooling by heat transport to the cold finger to determine the temperature structure of the smoke layer. Only after such an analysis has clearly shown that the temperature throughout the smoke layer is below the crystallization temperature of H_2O ice ($\sim$130 K), low temperature crystallization can be considered a viable explanation. We conclude that there is currently no persuasive experimental evidence that low temperature crystallization occurs in the Moore et al. experiments.

Acknowledgements. This research would not have taken place without the encouragement of Rens Waters. We thank Thomas Henning for sharing his knowledge on the nature of quartz glass. A thorough review of the manuscript by Helen Fraser provided some important new insights into the subject.

References

Gerakines, P. A., Schutte, W. A., Greenberg, J. M., & van Dishoeck, E. F. 1995, A&A, 296, 810

Hudgins, D. M., Sandford, S. A., Allamandola, L. J., & Tielens, A. G. G. M. 1993, ApJS, 86, 713

Malfait, K., Waelkens, C., Waters, L. B. F. M., et al. 1998, A&A, 332, L25

Moore, M. H., Ferrante, F. R., Hudson, R. L., Nuth III, J. A., & Donn, B. 1994, ApJ, 428, L81

Sandford, S. A., & Allamandola, L. J. 1988, Icarus, 76, 201

Smith, R. G., Sellgren, K., & Tokunaga, A. T. 1989, ApJ, 344, 413

Whittet, D. C. B., Bode, M. F., Longmore, A. J., et al. 1988, MNRAS, 233, 321