# Throwing light on the undercooling puzzle

Undercooling was discovered in 1724 by Fahrenheit while observing that water droplets stay liquid below 0°C. However numerous questions about the underlying mechanisms remain nowadays still open. In the 1950's, theoricians postulated the structure at the atomic level to be incompatible with crystallization. This led to the speculation that the atoms in the liquid could locally arrange in icoahedra characterized by a five-fold symmetry. Fifty years after, *ab initio* molecular dynamics simulations revealed for the first time five-fold coordinated clusters (pentagons) in pure liquid metals as well as liquid alloys, some of them being known to form quasicrystalline phases upon rapid solidification [1, 2].

Using *ab initio* molecular dynamics simulations, a new remarkable undercooling phenomenon has been explained [3], namely an undercooling as deep as 350°C for Gold-Silicon eutectic alloy in contact with a specially decorated silicon (111) surface where the outermost layer of the solid featured pentagonal atomic arrangements. Such a five-fold coordinated surface influences the short-range order and the metastability of the liquid, favoring the existence of pentagons in this phase. This result has wide. For instance it should lead to important technological applications in the field of nanowire growth for which the eutectic alloy act as a catalyst. It is also speculated that the containerless techniques required today to obtain undercooling could be in the future be replaced by icosahedrally coated solid containers.

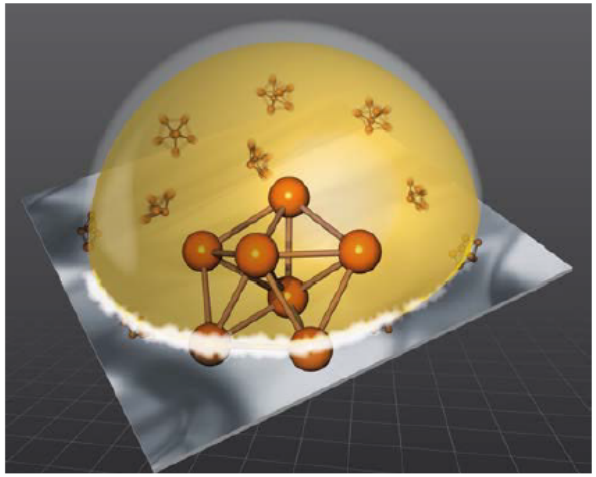


*Figure 1: Pentagonal arrangements in the gold-silicon eutectic droplets are stabilized by a decorated silicon (111) surface.*


[1] *N. Jakse and A. Pasturel, Phys. Rev. Lett. 91, 2003, 205702.*

[2] *N. Jakse, O. LeBacq and A. Pasturel, Phys. Rev. Lett. 93, 2004, 207801.*

[3] *T.U. Schulli, R. Daudin, G. Renaud, A. Vaysset, O. Geaymond and A. Pasturel, Nature 464, 2010, 1174.*


National and international collaborations: ESRF, RTRA Nanosciences, TU Wien


Contacts: A. Pasturel , N. Jakse, TOP

# The electromagnetic phase separation technique in the determination of solid / liquid equilibria in multicomponent systems

The knowledge of liquid/solid equilibria is of particular interest in the development of special materials with high characteristics, or in solidification process applications. The electromagnetic phase separation (EPS) technique, developed at the laboratory a few years ago, constitutes a powerful and viable technique to establish phase relationships in the solid/liquid range of a large variety of metallic systems, by maintaining long time annealing at high temperature, and thus to achieve the constitution of solid and liquid phases in equilibrium at selected temperatures and compositions. The method is appropriate for systems with volatile and reactive components to be studied at relatively high temperature.

Fe-W-C and Fe-Ti-B ternary systems and Al-based systems have been investigated successfully to determine equilibria involving a liquid phase. In the case of the Fe-W-C system, the link between DTA- determined temperatures and micrographs is not direct and the settling effect of WC carbides has to be taken into account. The EPS technique allows to determining the equilibrium states involving the liquid phase between 1423 K and 1543 K and to specifying the position of the liq./ WC+gamma and liq./WC+$M_6C$ univariant lines.

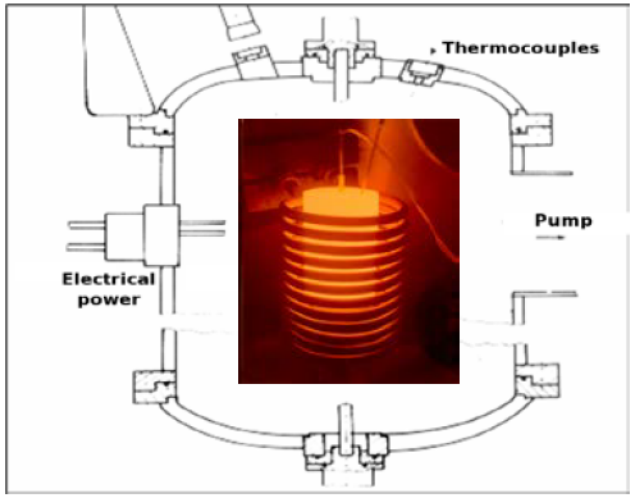



*Figure 1. Medium frequency induction furnace (10 kHz*

National collaborations: ANR ADRERA project
Contacts: A. Antoni-Zdziobek, TOP

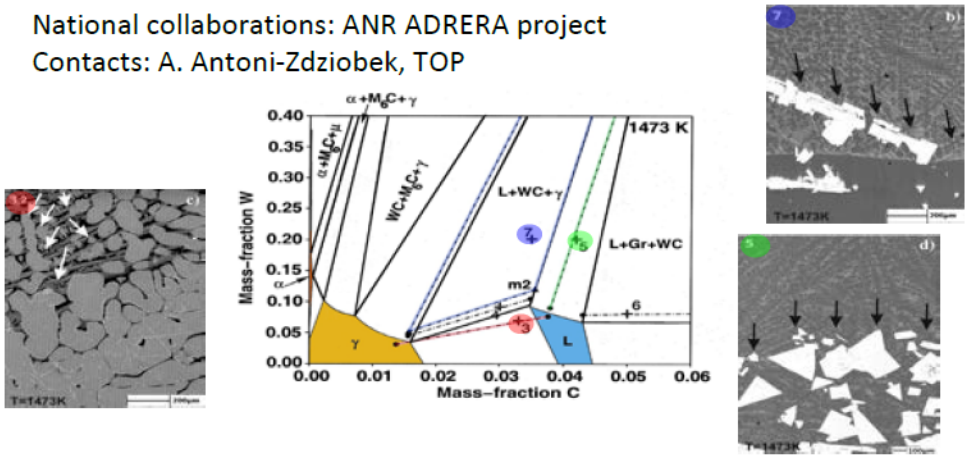



*Figure 2. Composition of phases in equilibria corresponding to tie-lines and tie-triangles on the isothermal section at 1473 K of the C-Fe-W system.*
*The arrows indicate a boundary limiting a liquid area. The coarse solid phases are located below this boundary.*

## Thermodynamic and kinetics of interfacial interactions in microelectronic packaging

In order to reply to the growing industrial demand of downscaling electronic devices, die to die or die to wafer interconnects (3D integration) are now considered as majors alternatives integration strategies and still need further decrease in size. The most used lead-free solders in the microelectronic industry are Sn-Ag-Cu alloys. In this framework, molten interconnects based on micro-bumps of 25um diameter become now widely used (Fig. 1). This technique using micro-bumps requires a reflow step during which intermetallic compounds (IMC) grow at the Cu/solder interface ($\eta$-$Cu_6Sn_5$ and $\varepsilon$-$Cu_3Sn$ layers). Even if these IMC evidences a good adhesion between Cu and solder alloy, their brittle nature and high resistivity is detrimental to the IC's. Moreover standard processes often requires up to five reflow steps, during which morphological and microstructural evolutions occur within micro-bumps as well as at the interface. Each reflow starts from melting of solder, continues by fast growth of scallops of $\eta$-$Cu_6Sn_5$ followed by the growth of $\varepsilon$-$Cu_3Sn$ compound and ends with solidification of unreacted molten solder.

Therefore, there are mainly three fundamental issues concerning these systems: (i) Interfacial interactions between liquid solder and substrate (wetting and reactivity [1]), (ii) effect of metallic substrate on the undercooling degree of the liquid solder and (iii) solidification of the solder alloy (nucleation and its role on the bulk microstructure). These topics are studied from both experimental and theoretical point of view and developed principally in the framework of two PhD thesis (in collaboration with StMicroelectronics, CEA-Leti Grenoble and Cherkasy University (Ukraine) - Prof. A. Gusak.

Experimental studies are mainly focused on the microstructural and morphological evolution of Cu/Sn-3.5Ag-0.7Cu (SAC 357) system during different stages of manufacturing process but also of other Sn-based solders [2]. Moreover, since Ni barrier is evaluated as a potential solution for limited IMC growth, they are extended to the case where an additional Ni layer is added between Cu and alloy. The effect of the system size, the solder composition and of the isothermal treatments on the microstructure of the solder ball and interfacial system are studied (Fig. 2). A thermo-kinetic model on the growth kinetics of IMC formed at Cu or Cu-Ni/solder interface has been developed. It shows that the significant difference observed between the growth kinetics of $\eta$ phase on Cu and Cu-Ni substrates can be explained by the difference in the driving forces of diffusion [3].

It is shown that the undercooling of the liquid solder depends on composition, solder size and cooling rate. Moreover the undercooling degrees are significantly higher in soldering configuration compared to solder balls alone (Fig. 3). This decrease in undercooling degree is most likely due to the presence of $Cu_6Sn_5$ compound at liquid solder/copper interface which promotes the heterogeneous nucleation on this compound [4]. Indeed, the possibility of solder-spreading transitions in solidification of solder at a rough rigid intermetallic surface is proven theoretically by a nucleation model developed recently [5]. Depending on the misorientation of scallops on the interface, one can observe a two-dimensional spreading transition over the scallops or a one-dimensional spreading transition along the triple-junction of two intermetallic compound scallops and liquid solder (Figs. 2 and 4).

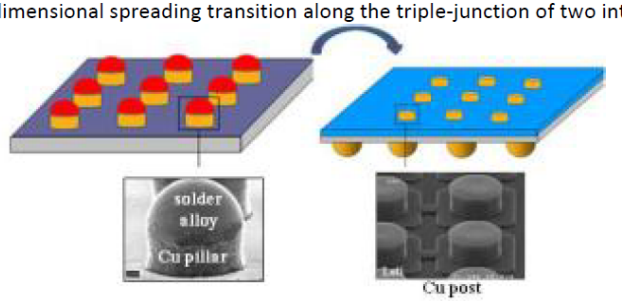



Figure 1 Schematic presentation of interconnects based on micro-bumps of 25um in diameter.

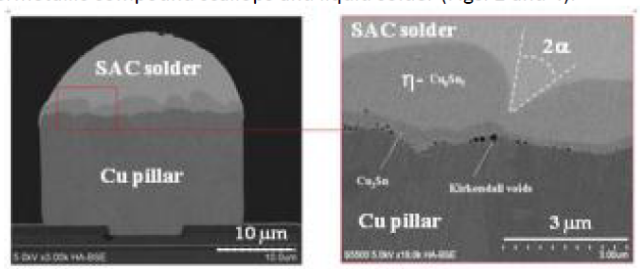
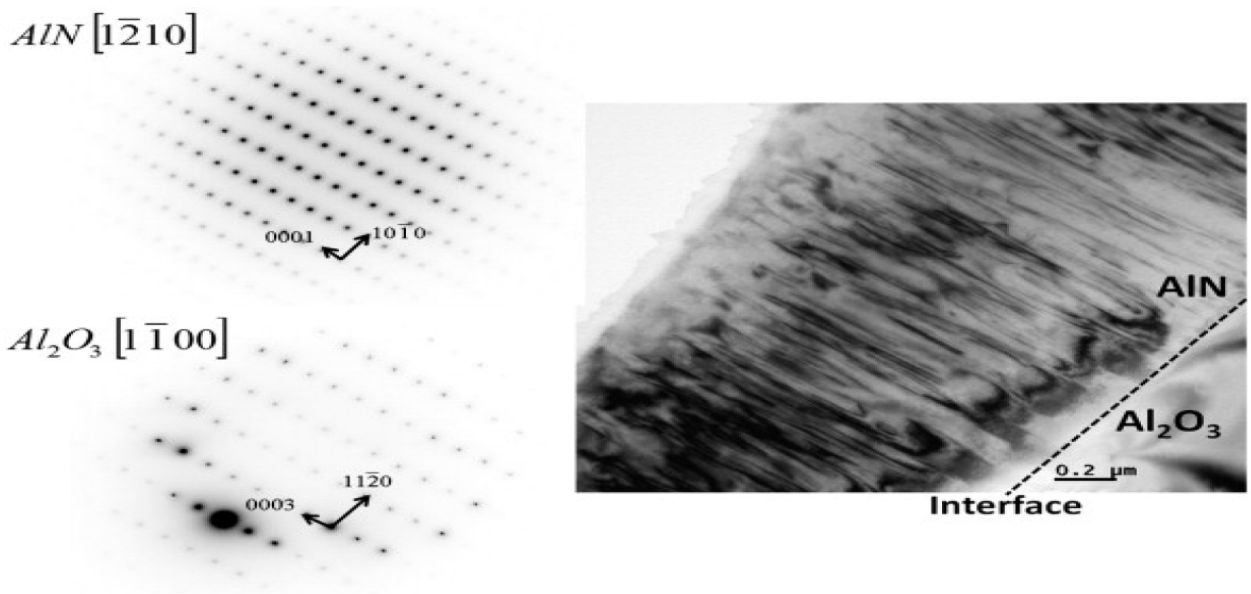



Figure 2 SEM micrographs of a Cu-pillar cross section after reflow of a SAC305 alloy deposed on the top of Cu-pillar.

# Epitaxial growth of AlN on c-plane sapphire by High Temperature Hydride Vapor Phase Epitaxy

*R. Boichot, N. Coudurier, F. Mercier, S. Lay, A. Crisci, S. Coindeau, A. Claudel, E. Blanquet, M. Pons*
*Surface and Coatings Technology* ***237***, *118 (2013)*

*AlN is epitaxially grown on c-plane sapphire by High Temperature Hydride Vapor Phase Epitaxy (HT-HVPE) at constant growth rate and thickness, while varying the N/Al ratio in the gas phase at 1500 °C. The influence of an additional low temperature (1200 °C) protective layer on AlN crystal quality is also assessed. The experiments and thermodynamic calculations show that the sapphire substrate is unstable at high temperature under hydrogen and ammonia while it is stable at low temperature or under a few hundred nanometers of AlN protective layer even at high temperature. In terms of AlN crystal quality, the optimal process developed here consists in depositing a 170 nm low temperature protective AlN layer with N/Al = 3 followed by a high temperature thick AlN layer grown with N/Al = 1.5. In this case, the interface between AlN and sapphire remains continuous (no etching) and the stress in the grown layer at room temperature is minimized by a balance of the growing tensile stress with the cooling compressive stress.*

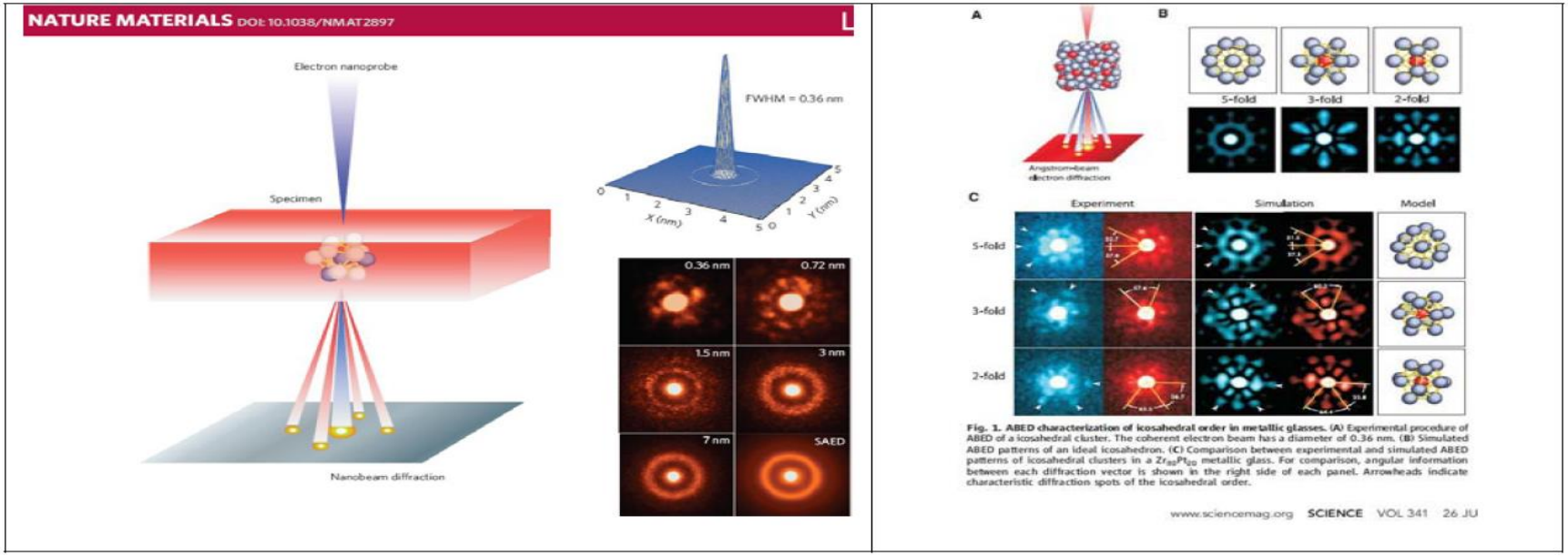



*Annotated TEM diffraction patterns (left) and interface bright field image (right) of the AlN two step grown layer on sapphire. Surface and Coatings Technology* ***237***, *118 (2013)*

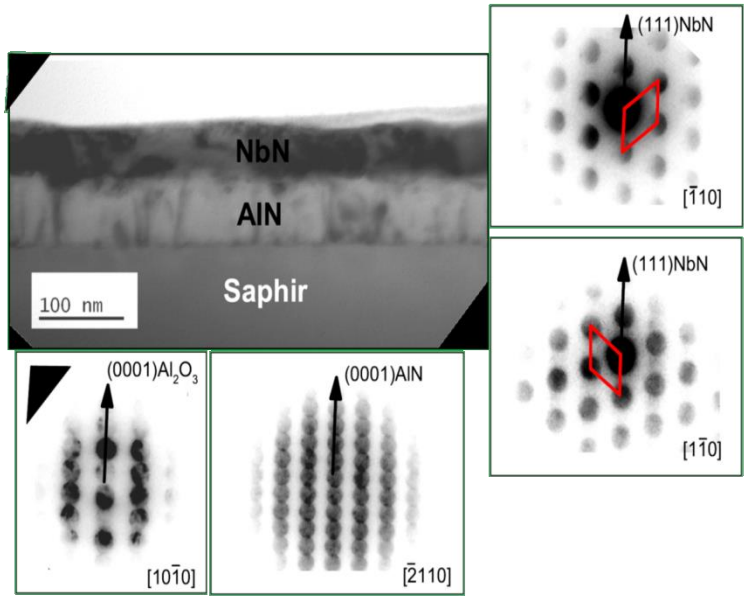
# L'observation directe de l'ordre atomique local dans les métaux vitrifiés

*A.R. Yavari et al. Science 341 (2013) 376-379, Nature Materials 10 (2011) 28-33*

*La détermination de la configuration atomique métallique est un problème de longue date dans la science des matériaux et la physique de l'état solide. Bien que différents modèles de structures atomiques aient été proposés depuis cinquante ans (notamment en France par exemple par Sadoc, Dubois et Le Caër, et en Angleterre par Gaskell et Dubois), une observation directe de la structure atomique locale des matériaux désordonnés n'a pas été possible. Grâce à l'avancement des nanotechnologies liés à la focalisation des faisceaux d'électrons à une section sous-nanométrique (voir figure à droite), dans le cadre d'une collaboration avec les chercheurs japonais et chinois, nous avons pu observer directement, pour la première fois, les clusters qui constituent la structure des verres métalliques à l'échelle atomique.*



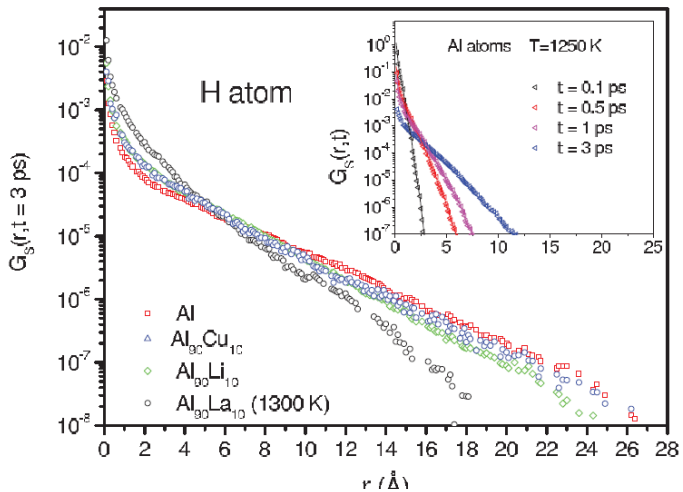
# Ultrathin monocrystalline layers of nobium nitride by high temperature vapor deposition

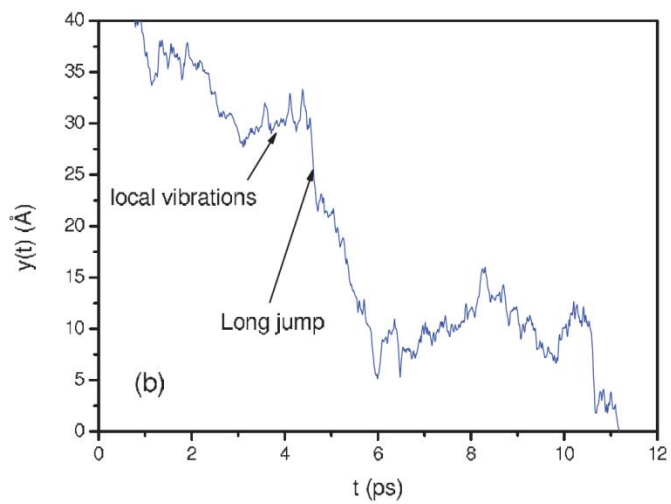



Synthesis of thin niobium nitride (NbN) layers by High Temperature Chemical Vapor Deposition (HTCVD) is presented and the crystallographic orientations are investigated during heteroepitaxial growth on (0001)$Al_2O_3$, (0001)AlN template and (11-20)$Al_2O_3$. The HTCVD NbN layers are ex-situ characterized by means of X-ray diffraction (XRD) methods, Raman spectroscopy and Transmission Electron Microscopy (TEM). Depending on the deposition temperature, hexagonal NbN or fcc NbN (face-centered cubic) is obtained. Orientation relationships between the fcc NbN layer with respect with the substrates are given. We discuss the role of an AlN layer as a possible protective layer of the sapphire for the synthesis of fcc NbN.

F. Mercier et al. Surface and Coatings Technology 260, 126 (2014)

# Hydrogen diffusion in liquid aluminum and its alloys from *ab initio* molecular dynamics




We study the hydrogen diffusion in liquid aluminum alloys through extensive ab initio molecular dynamics simulations. At the microscopic scale, we show that the hydrogen motion is characterized by a broad distribution of spatial jumps that can exceed 15 times the interatomic AlH distance. To determine the self-diffusion coefficient of hydrogen in liquid aluminum alloys, we develop a generalized continuous time random walk model. We show that the hydrogen motion does not follow a Brownian motion caused by a broad distribution of spatial jumps. This breakdown is also evidenced in the calculation of the self-part of the van Hove distribution function that is not the Gaussian expected for a Fickian process. Computed self-diffusion coefficients of H in liquid aluminum are in good agreement with experimental ones. In particular, we show that the model successfully accounts the effects of alloying elements on the hydrogen diffusion in agreement with experimental features. Tuning hydrogen diffusion with additional alloying elements in order to avoid porosities during solidification processes is a challenge for further experimental and theoretical studies.

N Jakse, A Pasturel, Applied Physics Letters 104 (15), 154101 (2014) ; The Journal of chemical physics 141 (9), 094504 (2014); Physical Review B 89 (17), 174302 (2014)

Self-part of the van Hove function at a function of distance for H atoms for aluminum and alloys Al90Cu10, Al90Li10 at *T* = 1000 K and Al90La10 at *T* = 1300 K and for time *t* = 3 ps. Inset: self-part of the van Hove function at a function of distance for Al atoms at *T* = 1000 K (top). Time evolution of coordinates (bottom).