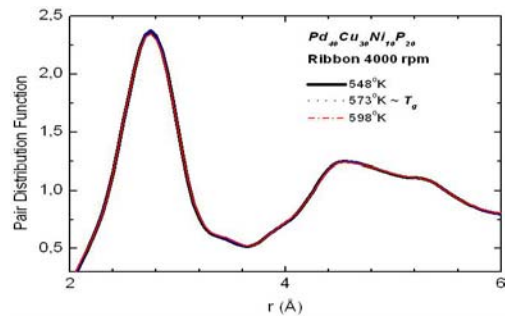
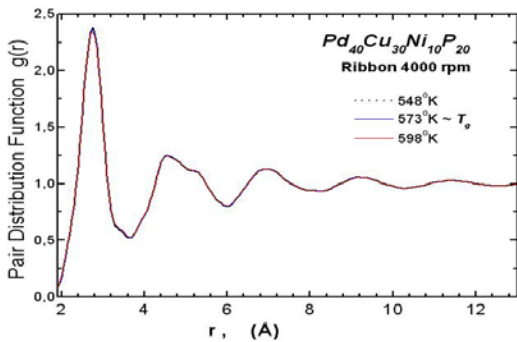
	Experiment title: STUDY OF THE GLASS TRANSITION IN BULK METALLIC GLASSES BY DIFFRACTION METHODS	Experiment number: ME-544
	Beamline: ID11/ID15	Date of experiment: 2003/I to 2004/II
Shifts: 66	Local contact(s): Dr Gavin Vaughan, Dr Marco Di Michiel	
Names and affiliations of applicants (* indicates experimentalists): A.R. Yavari*, CNRS- Institut National Polytechnique de Grenoble, France A.L. Greer, University of Cambridge, UK A. Inoue, University of Tohoku, Japan W.J. Botta*, Institut National Polytechnique de Grenoble France and Univ. Federal de Sao Carlos Brazil		

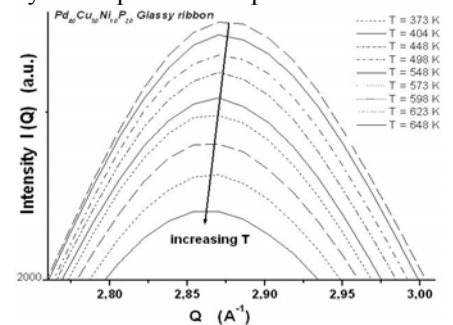
Report: The project is part of an on-going European RTN Network MRTN-CT-2003-504692 entitled “Ductile BMG Composites” (2004-2007) with a postdoc for the participating ESRF Materials Science group and coordinated by the main proposer (A. R. Yavari) please see < <http://www.inpg.fr/BMG-RTN/>>. It is also supported by the “International Frontier Centre on Advanced Materials IFCAM” (Japan-Europe) coordinated by the co-proposer A.L. Greer.

As in oxide glasses such as window glass and pyrex, the kinetics of diffusive atomic motion in metallic glasses can be modeled using a dispersion of “holes” or “free volume” in much the same way as “vacancies” in a crystal. Below a glass transition temperature T_g , free-volume V_f becomes negligible and the atoms freeze into a glassy state. However, as the quench rate is increased, some of the liquid’s free volume is trapped into the glassy state.



While very small changes in XRD can be observed during structural relaxation, the most important feature of pair distribution functions PDFs that we have measure (see above) is their similarity regardless of the temperature (not fully relaxed below T_g and fully relaxed at or above T_g). The above results confirm that the packing structure of bulk metallic glasses is nearly the same above T_g and below T_g and that as modeled previously, free volume is what distinguishes the glassy and supercooled liquid states.

However, PDFs cannot be used to derive volume or density variation (less than or near 0.5%) as the density ρ_0 is an input for PDF derivation. In view of the above results we treat the glassy state as a rigid isotropic solid up to T_g . In this approach, the successive broad maxima and Q_{max} corresponding to $I_{max}(Q)$ will elastically move to lower Q values with increasing temperature (see figure) as a result of thermal expansion and reversibly return to their initial Q_0 position upon cooling. Any deviation from this reversibility would then be discussed in terms of structural relaxation. In order to search for irreversible phenomena, we use the Ehrenfest relation $Q_{max} = 4\pi \sin\theta_m / \lambda = 1.23(2\pi/a)$ which is obtainable from the Debye formula for the scattering intensity $I(Q)$ and which yields a characteristic atomic dimension “ a ” and it follows that:



$$\left\{ \frac{Q_{max}(T^0)}{Q_{max}(T)} \right\}^3 = \left\{ \frac{V(T)}{V(T^0)} \right\} = \left\{ 1 + \alpha_{th}(T - T^0) \right\} \quad (1)$$

where α_{th} is the volume coefficient of thermal expansion. From theory the proportionality constant relating $Q_{max}(T)$ to $V(T)$ in Eq.(1) can change if the structure of the glass (chemical bonding) changes significantly. How precisely changes in Q_{max} allow measurement of changes in free volume content during relaxation annealing has not yet been established. The next figure shows plots of eq.(1) as-quenched $Pd_{40}Cu_{30}Ni_{10}P_{20}$ glass during in-situ thermal cycling. During initial heating the slope α_{th} is constant with the same value as measured by dilatometry. From about $T = 425$ K the plot dips until reaching $T_g = 590$ K. Subsequent heating and cooling shows only reversible dilatation. As expected, a slope change occurs at T_g as the glass goes over to the supercooled liquid state. The volume difference between the initial as-quenched state and the relaxed state is about 0.2%

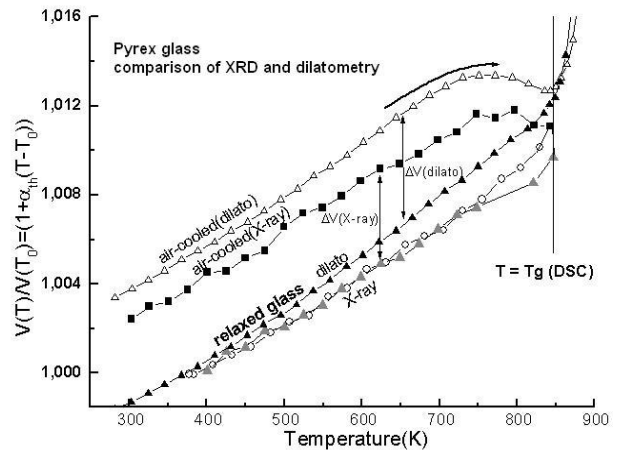
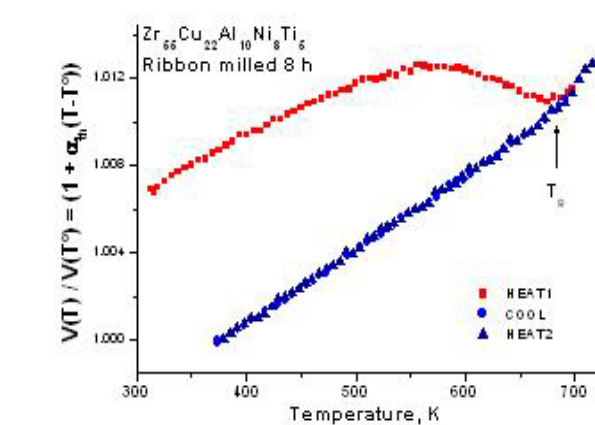
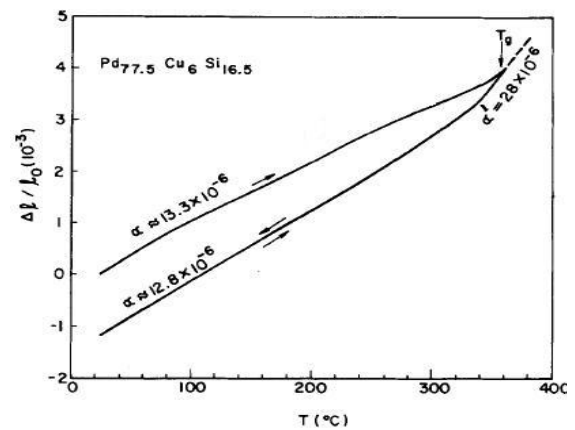
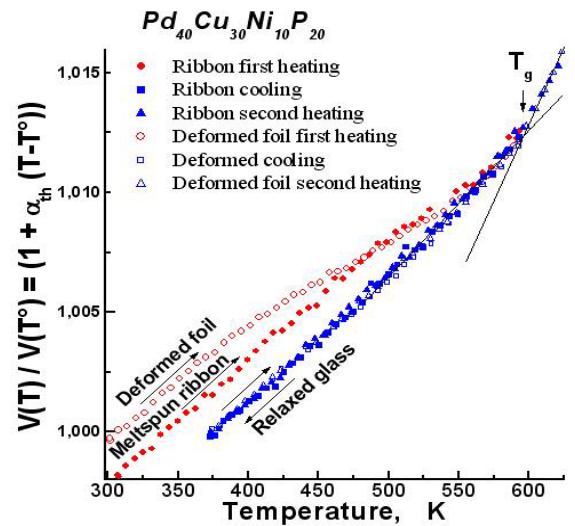
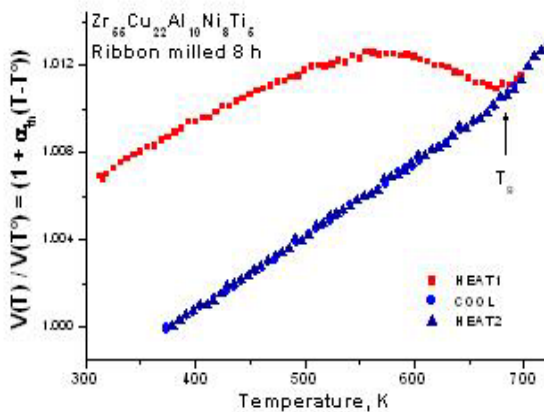
which corresponds well to densification of other melt-spun metallic glasses as measured by dilatometry (see next figure). Also shown are cycling experiments on the glassy ribbon after severe plastic deformation (corresponding to a thickness reduction of 90% to 97%). This comparison highlights several interesting findings. Firstly, the difference between the first heating to above $T > T_g$ and subsequent thermal cycling of the highly deformed foils now corresponds to a densification of about 0.4% of volume per atom indicating heavy deformation results in free-volume generation to a level double that of the as-quenched state. Secondly, the relaxed states of the material after rapid quenching and after heavy deformation exhibit exactly the same behavior with T_g detectable at the intersection of the four curves for the as-quenched, deformed, relaxed glass and supercooled liquid. Similar results have been obtained for Zr-based metal-metal glasses (next figure) and oxide glasses such as pyrex (next figure).

In crystalline materials, lattice expansion as measured by diffraction methods

differs from the expansion of the sample dimensions as measured by dilatometry due to contribution of thermal vacancies to the latter. We find that in glassy materials and metallic glasses in particular, this is not the case for the contribution of free volume. This finding is the first direct confirmation of simulation results indicating that atomic size holes are unstable in glasses and free volume is dispersed randomly. It allows direct measurement of excess free volume using diffraction in place of dilatometry which is difficult to use near T_g and above. For the first time, these measurements also allow studies of the kinetics of relaxation and thermal annealing-out of the free-volume by isothermal XRD (see last figure below right) using:

$$dV_f(T, t)/dt = -F(V_f)K_0 e^{-E/RT}$$

The method yields a temperature-dependent E for free-volume annihilation (in this case E increases from 92 kJ/g.at near 400 K to 114 kJ/g.at near 500 K).



Sample publications (others including ID15 staff have been submitted):

- * A.R. Yavari, M. Tonegaru, N. Lupu, A. Inoue, E. Matsubara, G. Vaughan, Å. Kvick and W.J. Botta, *Mater. Res. Symp. Proc.* **806** (2004) 203-208.
- * A.R. Yavari, A. LeMoulec, N. Nishiyama, G. Vaughan, Å. Kvick and W.J. Botta, *J. Metastable & Nanocryst. Mater.*, **20-21** (2003) 23-28
- * A.R. Yavari, J.L. Uriarte, N. Nishiyama, T. Zhang, A. Inoue, G. Heunen, *Mater. Sci. & Eng. A*, in press 2004.
- * J. L. Uriarte, A.R. Yavari, N. Nishiyama, G. Heunen, G. Vaughan, Å. Kvick and A. Inoue, *Scripta Mater.* **48** (2003) 809-812.
- * K. Ota, W.J. Botta, G. Vaughan, A.R. Yavari, *J. Alloys & Compounds*, 2004
- * E. Levchenko, N. Lupu, A. LeMoulec, E. Matsubara, G. Vaughan, Å. Kvick, A. Inoue, A.R. Yavari, *J. Metastable & Nanocryst. Mater.* In press 2004
- * "K. Hajlaoui, T. Benameur, G. Vaughan and A.R. Yavari, *Scripta Mater.*, **51** (2004) 843-848.

