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Hydrostatic limits of Fluorinert liquids used for neutron and transport studies at high pressure

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Abstract

We determined the hydrostatic limits at room temperature for a number of Fluorinert liquids: FC70, FC75, FC77, FC84, FC87 and their mixtures. Pressure exceeding this limit produces pressure gradients in the sample, which are retained at low temperature. The maximum hydrostatic limit (2.3 GPa) was found for a (1:1) mixture of FC84/87.

Fluorinert liquids (the brand name of products supplied by 3M, St Paul, MN) are the analogues of hydrocarbons in which hydrogen is substituted by fluorine. These liquids are widely used for neutron studies at high pressure as pressure-transmitting media, since they exhibit very small incoherent scattering of neutrons. Fluorinerts, especially the mixture (1:1) FC70/77, are also widely used for magnetic and transport studies up to 2 GPa in piston–cylinder cells and up to 8 GPa in multianvil cubic pressure cells. Shear stresses, developed in a liquid, when it solidifies at high pressure—above the hydrostatic limit—may strongly influence the properties of a single crystal immersed in it. For this reason knowledge of the hydrostatic limit of the liquid in use is important for interpretation of the experimental results. The influence of pressure gradients in a solidified liquid is of special importance in the case of soft noncubic crystals, cubic crystals with magnetic domain structure and crystals with anisotropic magnetic interactions. For these materials neglecting the nonhydrostaticity of the surrounding medium may depreciate the results of expensive and time-consuming experiments made with the use of excellent neutron facilities. It is important to have a guide for the choice of suitable liquid from a variety of available grades. In the sequence of Fluorinert liquids FC70/75/77/84/87 one can see a systematic decrease of average molecular weight, density and kinematic viscosity and increase of vapour pressure[1]. It is natural to expect that more volatile and less viscous liquids (right side of the sequence) will became very viscous and finally solidify at higher pressures than those taken from the left side of this sequence. An additional increase of the hydrostatic limit (solidification pressure) of a liquid may be achieved by mixing two similar liquids. In this case the pressure-induced crystallization is suppressed and glass forming at

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[1] 3M^{TM} Fluorinert^{TM} liquids for Electronics Manufacturing (selection guide).

higher pressure is observed. Typical examples are mixtures of methanol and ethanol (4:1) and pentane and isopentane (1:1), which have glass transitions and hydrostatic limits at pressures of 10.4 and 6.5 GPa respectively [1]. Some Fluorinert liquids were studied earlier [2], but all of them exhibit a hydrostatic limit less than or equal to ∼1.2 GPa. Thus, the problem of finding a liquid with a small incoherent scattering of neutrons that is hydrostatic in the medium range of pressures (up to ∼2.5 GPa) remains. Different methods of probing the hydrostatic limit of a liquid at high pressure can be used. Broadening of the ruby fluorescence line [1] or broadening of the x-ray diffraction line of a quartz crystal immersed in a liquid [2] signal that pressure gradients appear in the sample as a result of solidification of the surrounding liquid. We used another method [3], based on the measurements of electrical resistance of two manganin pressure gauges immersed in a liquid. Manganin, an alloy of Cu, Ni and Mn, is an excellent secondary pressure gauge whose resistance nearly linearly increases with pressure even in the multi-GPa pressure range. If we prepare two similar flat zig-zag coils made of manganin, put them in a capsule filled with liquid, and compress this capsule in a high-pressure device with uniaxial application of force, then both gauges will exhibit identical increase of the resistance independent of their orientation relative to the loading axis if the liquid around is still hydrostatic and cannot support shear stresses. Solidification of the liquid results in different responses of the gauges on further pressure increase. For a gauge oriented perpendicular to the loading axis (horizontal gauge), the resistance continues to increase, whereas it can even decrease for a gauge oriented along the loading axis (vertical gauge). A plot of $P_V(P_H)$ will have a kink at pressure P_C, corresponding to the hydrostatic limit of the surrounding liquid. This method is very fast and was used to check a variety of pure liquids and their mixtures. A toroidal anvil device supplied with a Teflon capsule and lithographic stone gasket [4] was used for these room-temperature experiments. The method of monitoring the broadening of neutron diffraction lines for a single crystal of NaCl immersed in Fluorinert liquid confirmed the results of the manganin gauge method. Diffraction lines start to broaden relative to their natural instrumental width just after solidification of the Fluorinert liquid determined by the manganin gauge. We have found the hydrostatic limits at room temperature for a number of Fluorinert liquids: FC70, FC75, FC77, FC84, FC87; four binary mixtures: FC70/75, FC70/77, FC75/77, FC84/87 (all 1:1 by volume); and one ternary mixture FC75/77/87 (1:1:2 by volume). Typical plots of $P_V(P_H)$ are shown in figure 1. One should remember that above P_C the resistance of the manganin gauge is not directly proportional to pressure and P_V and P_H in the plot is only tentative.

Figure 2 shows the x–P_C diagrams of binary mixtures for different Fluorinert liquids. Nonmonotonic dependences of $P_C(x)$ were found in the systems FC75/77 and FC84/87, with the hydrostatic limit P_C of 1:1 mixture being higher than those of the pure liquids. A 1:1 mixture by volume of FC87 and FC84 exhibits the highest hydrostatic limit (2.3 GPa) of all liquids studied, and can be recommended for neutron studies at high pressure. We also tested one ternary mixture, FC87/77/75 (2:1:1 by volume), which was composed of FC87 and the best liquid in the system FC77/75 (1:1 by volume). The hydrostatic limit of this liquid (2.18 GPa) was, however, slightly lower than P_C for pure FC87. The hydrostatic limits for FC70, FC75 and FC77 were determined earlier [2] and coincide well with our experiments in the case of FC70 and FC75. For FC77, however, our determination gives higher $P_C \sim 1.5$ GPa, compared to $P_C \sim 1$ GPa found in [2].

Low-temperature neutron diffraction experiments give information on the magnetic properties of materials that cannot be obtained at room temperature. On cooling the pressure cell, which contains the sample immersed in Fluorinert, one should cross the solidification point of this liquid, even if the room temperature pressure was lower than the hydrostatic limit. The long experience of researchers exploring quantum oscillations of transport and magnetic

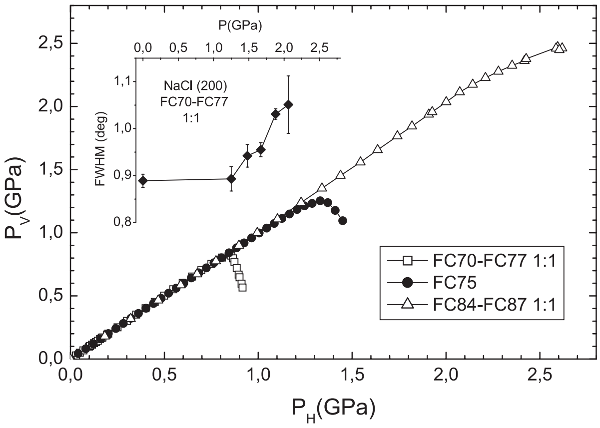

Figure 1. Typical experimental scans of vertical versus horizontal manganin pressure for FC70/75 1:1 (squares), FC75 (circles) and FC84/87 1:1 (triangles). Solidification of liquid takes place at the point where the relation $P_H = P_V$ is broken. The inset shows the average width (FWHM) of the NaCl single crystal (200) peak (diamonds) compressed in FC70/77 1:1. All measurements were done at room temperature.

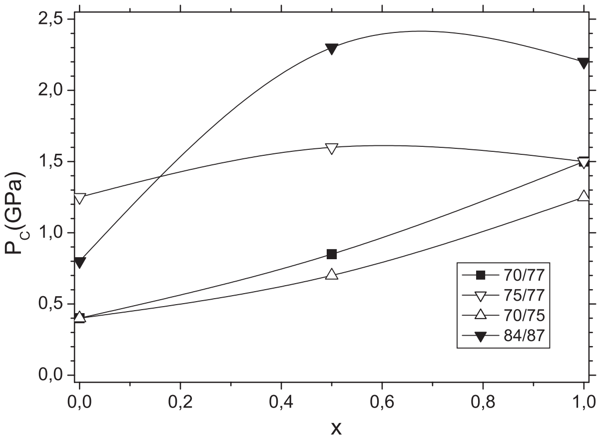

Figure 2. Concentration (x) dependences of the hydrostatic limit for the systems FC70/77, FC70/75, FC75/77 and FC84/87. Increase of x means adding more liquid with a higher number of Fluorinert grade.

properties of single crystals, which are rather sensitive to the presence of nonhydrostatic components of pressure, shows that slow cooling of the pressure cell with a liquid pressure medium is needed [5, 6]. Recommended cooling rates are $\sim 1\ \mathrm{K\ min^{-1}}$ between room temperature and 77 K. At lower temperatures the thermal contraction of the pressure cell, sample and solidified liquid becomes small and does not produce appreciable shear stresses in the sample. Following these recommendations, we tested how pressure gradients appear at low temperature when Fluorinert FC75 was used as the pressure-transmitting medium. We performed electrical resistance measurements on a lead sample with the use of a small clamped toroidal anvil cell, supplied with a gasket and Teflon capsule filled with FC75. The superconducting transition temperature T_C of lead decreases nearly linearly with pressure and served as a low-temperature manometer [7]. The appearance of pressure gradients at

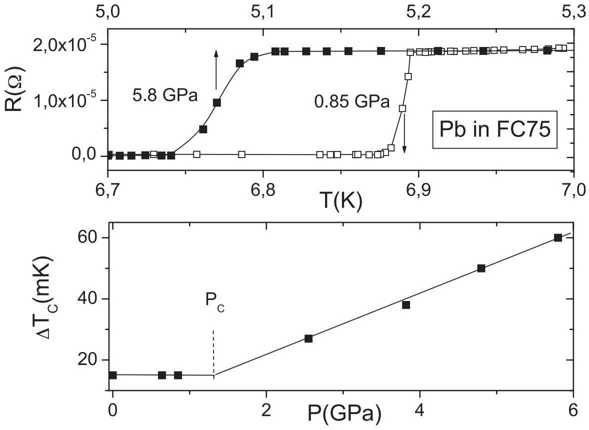

Figure 3. Superconducting transitions in lead sample compressed in Fluorinert FC75 (upper panel). Broadening of the transition indicates the presence of pressure gradients in the sample. Pressure dependence of the superconducting transition width for a lead sample in Fluorinert FC75 (lower panel). The transition width ~30 mK corresponds to 0.1 GPa pressure gradient. The pressure-independent transition width ~15 mK below 1 GPa is an 'instrumental width'. Increased broadening of the transition above 1.2 GPa is due to solidification of FC75 on compression.

low temperature results in a broadening of the resistive superconducting transition. Figure 3 shows that this broadening starts to develop at a pressure $P > P_C$ for FC75. In other words, hydrostatic pressure can be retained in the cell at low temperature if the room-temperature pressure is below the hydrostatic limit and the cooling rate is small (~1 K min^{-1}).

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