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Fluorinert as a pressure-transmitting medium for high-pressure diffraction studies

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Fluorinert is a liquid pressure-transmitting medium that is widely used in high-pressure diffraction work. A systematic study of five different fluorinerts was carried out using single-crystal x-ray diffraction in a diamond-anvil cell in order to determine the pressure range over which they provide a hydrostatic stress state to the sample. It was found that none of the fluorinerts studied can be considered hydrostatic above 1.2 GPa, a lower pressure than reported previously. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1611993]

For high-pressure diffraction experiments (either single-crystal or powder), it is often necessary to ensure that the force applied to the sample crystal(s) is homogeneous and that the sample is free of any differential stress or shear strain. To achieve this, the crystal(s) within the pressure chamber must be immersed in a medium that displays hydrostatic behavior, for example, a liquid or gas, under all conditions of interest. Nonhydrostatic stress leads to significant broadening and shifts in the position of the diffraction peaks from the sample and, thus, inaccurate unit cell data.[1–4] It can also promote or suppress phase transitions.[5–9] Although the degree of line broadening depends sensitively upon a number of factors, including the physical state and the elastic constant tensor of the sample, this limitation of the cell/medium invariably degrades the quality of the resulting diffraction pattern by means of a loss of effective instrumental resolution.[10] The practice of neglecting the nonhydrostatic compression effect and taking the lattice parameter as the average of the lattice parameters calculated from the measured *d* spacings of the observed reflections results in an overestimation of the lattice parameter and the standard deviation in the lattice parameter.[4] Furthermore, the apparent pressure registered by internal pressure standards can also be affected by nonhydrostatic stresses,[2,3,11–14] resulting in incorrect equation of state parameters being determined from pressure–volume data.

One of the most commonly used pressure media for single-crystal diffraction studies is the 4:1 methanol:ethanol mixture, which is generally believed to remain at least quasi-hydrostatic to its glass transition at 10.4 GPa.[11] Miletich *et al.*[15] gave an overview on the most frequently used pressure-transmitting media. If alcohol is known to react or dissolve the sample, then a number of alkane-based fluids can be used, such as petroleum ether or a mixture of pentane and isopentane.[15–17] However, while all of these compounds can be used for x-ray diffraction measurements, they are all hydrogenated and thus give rise to incoherent scattering and high backgrounds in neutron diffraction experiments.

Fluorinerts, the brand name for a range of products supplied by 3M (St. Paul, MN), are completely fluorinated aliphatic compounds, contain no hydrogen and, thus, are ideal for neutron diffraction experiments. They also have the advantage that they are chemically inert and can, therefore, be employed with a wide variety of samples that may dissolve or react with the more commonly used pressure media. Fluorinerts thus became widely used as pressure-transmitting medium in high-pressure neutron diffraction experiments, especially in pressure cells of the Paris–Edinburgh design.[18,19] In this particular cell design, the nonhydrostaticity of the pressure medium also served to reduce stress on the anvils; in its original configuration maximum pressures of only 2–3 GPa could be achieved with hydrostatic pressure media compared to 9–10 GPa with fluorinert.[10]

Recent experiments suggest that fluorinert is hydrostatic to 0.6 GPa,[20,21] but evidence for a low hydrostatic limit of fluorinert goes back at least to the work of Decker *et al.*[22] They showed that use of fluorinert completely suppresses the monoclinic-to-rhombohedral phase transition in lead phosphate that normally occurs at 1.8 GPa and had therefore transmitted shear stresses to the lead phosphate sample that stabilized the monoclinic ferroelastic phase. More recently, line broadening in high-pressure neutron powder diffraction experiments has been attributed to the nonhydrostaticity of fluorinert, but estimates of the pressure range at which broadening starts range between 0.7 and 5 GPa.[17,23–26]

Part of this variation may be due to the many types of commercially available fluorinerts, of which the grades FC-70, FC-75, FC-77 and sometimes a mixture of FC-70 and FC-77, have been used for high-pressure studies. But there has been no systematic determination of the maximum pressure to which they provide hydrostatic pressure conditions. We have, therefore, performed experiments on five different grades of fluorinert in order to determine the pressure range that can be considered hydrostatic. This was achieved by compressing a quartz single crystal using each of these fluo-

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[a)] Electronic mail: tamas.varga@chemistry.gatech.edu rinerts as a pressure medium in a diamond-anvil cell (DAC) and monitoring the changes in the positions and widths of the diffraction peaks as a function of pressure.

Fluorinert samples were obtained commercially; FC-40, FC-70, FC-72, and FC-75 from Acros Organics (Fisher Scientific) (Pittsburgh, PA) and FC-77 from Sigma-Aldrich (St. Louis, MO). Gem-quality single crystals of twin-free natural quartz were obtained commercially. The same quartz sample was used for all of the fluorinerts. ‘‘BGI’’ (Bayerisches Geoinstitut, Bayreuth, Germany) and ‘‘ETH’’ (Swiss Federal Institute of Technology, Zurich, Switzerland) designs of diamond-anvil cell[15,27] were used.

Single-crystal diffraction measurements were performed at room temperature and high pressures using Huber four-circle diffractometers with Eulerian cradles, one at Virginia Tech (Blacksburg, VA) and one at the Bayerisches Geoinstitut (Bayreuth, Germany). The physical parameters of the diffractometer at Virginia Tech are very similar to that in Bayreuth.[28] Of particular importance is that the instrument configurations lead to a full width at half maximum (FWHM) of the individual components of the $\alpha_1-\alpha_2$ doublet of the diffracted beams from the quartz sample of approximately 0.05° under hydrostatic conditions. This means that broadening of the peaks due to strain or any other cause is readily detectable. Both diffractometers were driven by the SINGLE program.[29] The algorithm used for centering diffraction peaks is described in full in an earlier work of Angel *et al.*[28] The final step scan of a diffraction peak is performed with the ω circle and the resulting profile is fitted with a constrained pair of pseudo-Voigt functions that represent the contribution of the $K\alpha_1$ and $K\alpha_2$ components of the x-ray spectrum.[29] This refinement procedure provides the peak position of the $K\alpha_1$ component to a precision better than 0.01°, as well as the refined FWHM of the individual components. Each diffracted beam was centered in eight positions on the diffractometer, and the setting angles were determined following the method of King and Finger[30] to eliminate the effects of diffractometer circle zero offsets, crystal offsets, and aberrations in the diffractometer alignment. The 2θ value of the quartz 101 and 10-1 peaks determined in this way allowed pressure determination with a precision of better than 0.01 GPa via the known variation of the cell parameters with pressure.[28] The reported peak widths at each pressure are the average of the widths refined at each of the eight positions and the estimated uncertainty is calculated as the standard deviation of these values.

The five different fluorinerts that were studied essentially cover the entire range of physical properties available with this class of compounds (Table I). With each fluorinert, the pressure in the DAC was gradually increased until significant peak broadening was observed (typically amounting to a doubling of the peak width), and then gradually released until the initial peak width was recovered. Diffraction data were collected at several pressure points during both compression and release. All fluorinerts studied led to significant peak broadening beginning from a pressure of around 1 GPa or lower. A typical set of results is shown in Fig. 1. Upon increasing the pressure, the widths of the diffraction peaks from the quartz sample initially remain the same as at room pressure. Above a given pressure, the peak widths increase with increasing pressure, up to a point at which it is no longer possible to reliably determine either their widths or positions. We associate a nominal ‘‘hydrostatic limit’’ with either the first detection of broadening, or the pressure at which the broadening is extrapolated back to zero (Table I). We observed two types of behavior on pressure release that may also affect the apparent hydrostatic limit of these pressure media. For some samples (FC-72, FC-75, and FC-77), the peak width recovers upon pressure reduction, indicating that the mechanism of broadening is essentially reversible on the time scale of a few hours of the experiments. By contrast, for FC-70, which was the most viscous fluorinert with the highest boiling point, upon releasing pressure for the first time, an increase in peak width was observed at about 0.85 GPa (Fig. 2). When compressed for the second time, the sample displayed two significant peak width increases, but the sudden jump during pressure release was absent. Similar, but less pronounced, behavior was also observed with FC-40, the second most viscous fluorinert. This nonreversibility

TABLE I. Typical physical properties (from the selection guide for 3M™ Fluorinert™ electronic liquids) and observed hydrostatic limits of the fluorinert grades studied. A nominal hydrostatic limit was associated with either the first detection of broadening or the pressure at which the broadening was extrapolated back to zero.

Fluorinert grade	FC-72	FC-77	FC-75	FC-40	FC-70
Hydrostatic limit (GPa)	~1.05	~0.95	~1.20	~0.95	~0.55
Average molecular weight (g/mol)	340.0	415.0	420.0	650.0	820.0
Typical boiling point (°C)	56.0	97.0	102.0	155.0	215.0
Density (g/cm^3)	1.68	1.78	1.77	1.87	1.94
Kinematic viscosity (cs)	0.4	0.8	0.8	2.2	14.0
Vapor pressure (Torr)	232.0	42.0	31.0	3.0	<0.1

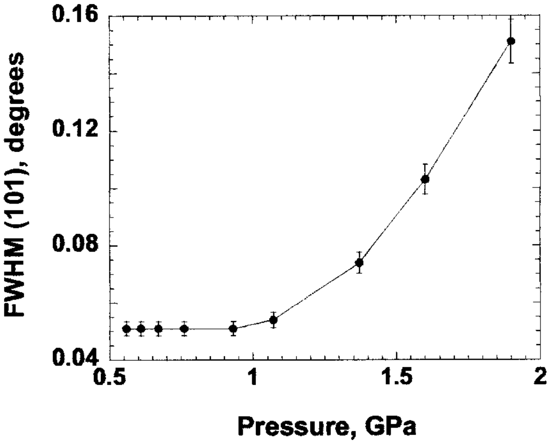

FIG. 1. Change of average peak width (FWHM) of the quartz (101) reflection with pressure for fluorinert FC-72 upon compression. This tendency of peak broadening at around 1 GPa was found to be typical for all of the fluorinerts studied. The straight lines drawn between the points serve as a guide for the eyes.

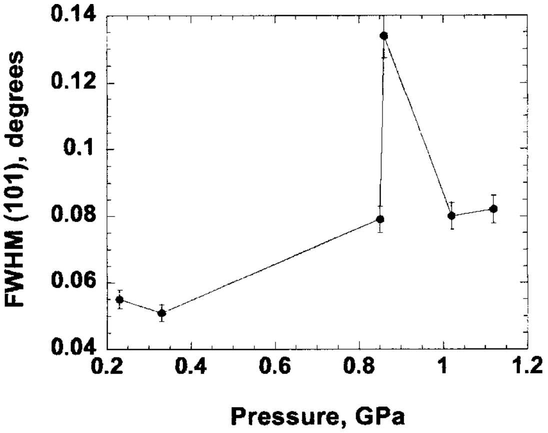

FIG. 2. Change of average peak width (FWHM) of the quartz (101) reflection with pressure for fluorinert FC-70 during pressure release. An increase in peak width was observed at about 0.85 GPa suggesting that not all of the broadening is immediately reversible upon pressure release at room temperature. The straight lines drawn between the points serve as a guide for the eyes.

seems to be more pronounced in the more viscous fluorinerts, which suggests that it may be alleviated by temperature annealing. Without such annealing, it means that the hydrostatic limit on subsequent pressure cycles may be lower than that observed on the first pressurization.

The precise mechanism of peak broadening due to nonhydrostatic pressure media in a single-crystal diffraction experiment is not fully understood, although it is clear that it must differ from that in a powder diffraction experiment.[4] Furthermore, the degree of broadening is presumably also a function of the components of the elastic tensor of the sample crystal, its orientation with respect to the stress field of the pressure medium, and the stress state of the medium. Nonetheless, the detection of peak broadening in a single-crystal experiment is proof that a nonhydrostatic stress has been applied to the sample crystal. The absence of broadening, however, does not prove that the medium is truly hydrostatic. The pressures that we found for the onset of broadening are, therefore, upper limits on the pressures to which the various fluorinert compounds remain hydrostatic pressure media at room temperatures. Our results show that all of the fluorinerts that we studied become nonhydrostatic at pressures of less than 1.2 GPa, that being the limit observed for the FC-75 grade, while the FC-70 grade becomes nonhydrostatic below 0.6 GPa. However, there does not appear to be a strong correlation between the physical properties and the hydrostatic limit of these fluorinerts. We also note that not all of the broadening is immediately reversible upon pressure release at room temperature.

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