

case of small deviations from a collection of monodisperse spheres, the theoretical distributions of radii relative to the different systems are very different.

In conclusion, a collection of polydisperse spheres is, in principle, always distinguishable from a collection of monodisperse ellipsoidal particles because the resulting radial distribution functions are very different in the two cases.

However, such a distinction can be observed experimentally only when deviations from a system of monodisperse spheres are sufficiently large. In these cases, though the distinction still stands, the only way of interpreting experimental data is to fit different model distributions and choose the one giving the best agreement.

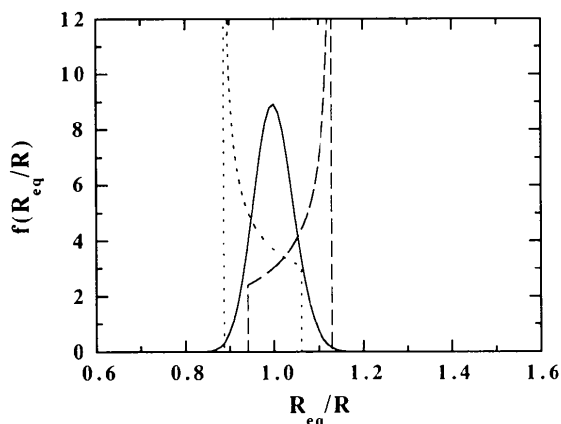


Fig. 4. Distribution functions of the equivalent radii, R_{eq} , of all orientations of ellipsoidal particles normalized to the radius, R , of the sphere of equivalent volume. The dotted line refers to monodisperse prolate ellipsoidal particles with axial ratio 1.2 and the dashed line to monodisperse oblate ellipsoidal particles with axial ratio 0.833. The Schulz distribution function (solid line) with $Z = 500$ is also reported.

The presence of heterogeneities in the scattering-length density of the particles, the smearing affecting the experimental data and the presence of a 'strong' structure factor, and/or the presence of polydispersity in both size and shape might make such a distinction impossible.

In some cases, such as those of micellar solutions or microemulsions, better information on anisotropic systems can be obtained by SAS by using a shear-aligned sample (Hayter & Penfold, 1984; Thurn, Kalus & Hoffmann, 1984). In this situation, an anisotropic scattering pattern is obtained from rodlike or disclike particles.

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Crystal handling at low temperatures. By THOMAS KOTTKE and DIETMAR STALKE, *Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, W-3400 Göttingen, Germany*

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Abstract

The cooling of a crystal in combination with the use of a protecting oil facilitates the handling and transfer to a diffractometer of even very sensitive material. The method is explained and the required device is described in this work. Basic advantages of the technique are simplicity and freedom of access to the sample without the need for sophisticated glassware. Therefore, this technique, suitable for crystal manipulation in the temperature range between room temperature and 193 K, is much more efficient than those involving the use of capillaries.

Introduction

The advantages of crystal structure determination at low temperature, compared to conventional room-temperature measurements, are well known (Rudman, 1976; Veith & Frank, 1988; Luger, 1989). Crystals that are unstable under ambient conditions, as well as liquids or gases, can be studied in the solid state. Many compounds cocrystallize with solvent. The vapor pressure of crystal solvent is still high and allows diffusion out of the lattice. Normally this destroys the crystal or, at least, causes changes in the intensities of the reflections during data collection. Cooling

of the crystal prevents the solvent from escaping from the lattice. Moreover, the problem of intensity decay with increasing $\sin \theta/\lambda$ is less severe when the crystal is cooled and so the quality of the data set is improved, resulting in a more accurate structure determination. At low temperature, the atoms vibrate more isotropically (Brock & Dunitz, 1990) and the residual electron-density map is less contaminated by the diffuse electron density arising from anharmonic behavior. Thus, the location of hydrogen atoms and electron-deformation-density work are facilitated.

There exist several home-made devices for maintaining the crystal in a cold environment while data are collected (Altona, 1964; Danielsson, Grenthe & Oskarsson, 1976; Bellard & Sheldrick, 1978; Hajdu, McLaughlin, Helliwell, Sheldon & Thompson, 1985; Zobel & Luger, 1990). Some devices are commercially available [Cosier & Glazer (1986) describe one and Enraf-Nonius, MSC and Siemens diffractometers can be obtained from their manufacturers with low-temperature devices]. However, to get the most out of low-temperature data collection, it is essential to handle the compounds at low temperature 'all the time', *i.e.* from crystallization up to and including data collection.

Method

The overall aim of developers of crystal-handling techniques should be to keep operations as simple as possible, so that they can readily be taught to beginners. This is the only way of guaranteeing that know-how will stay in an X-ray laboratory even though specialists may leave.

Many methods of selecting a crystal and transferring it to a diffractometer below room temperature have been employed by crystallographers [Veith & Bärnighausen (1974), Seebach, Amstutz, Laube, Schweizer & Dunitz (1985), Boese & Bläser (1989); the 'Hilgenberg apparatus' (The Hilgenberg Company, W-3509 Malsfeld, Germany)]. In addition to these techniques, that of *in situ* crystallization in a capillary on the diffractometer has been developed (van Nes & van Bolhuis, 1978; Brodalla, Mootz, Boese & Osswald, 1985; Blake, Cradock, Ebsworth & Franklin, 1990). One might get the impression that every crystallographer has a different way of handling crystals in a glove box and/or below ambient temperatures.

In our opinion, the sealing of crystals in capillaries at low temperature does not accord with the overall aim of simplicity. The manipulation of capillaries at low temperature requires sophisticated glassware that is not commonly available to the working synthetic chemist. Furthermore, these manipulations need months or years of practice.

Because of this, we have not used capillaries at all in the last five years. Instead, we constructed, from easily available parts, a low-temperature device which, combined with the oil-drop mounting technique pioneered by Hope (1987, 1988), enables the crystallographer to investigate the crystal quality using a polarizing microscope, as well as to mount the crystal at a fixed temperature ranging from room temperature to 193 K. Fig. 1 shows the device.

Boil-off from liquid nitrogen is directed through glass tubing towards the microscope slide on which the sample resides. At the beginning of crystal manipulation, the sample is located in an ordinary Schlenk flask, as generally used in a chemical laboratory. The whole batch of crystals in their

mother liquor and the flushing gas is cooled down. The Schlenk flask, with the sample, is almost entirely immersed in the cooling agent (normally ethanol/dry ice), which prevents the vessel from icing on the outside. Through the neck of the flask, a small spoon is allowed to cool down in the mother liquor. Afterwards, a portion of crystals is scooped up and covered with cold inert oil from a syringe. (If the crystals dry up very quickly, this can be done even within the mother liquor, preventing the crystals from being dried by the cold Schlenk gas.)

In Fig. 2, the nozzle of the mounting device can be seen in more detail. The microscope slide is provided with a small depression. This indentation is filled with oil and cooled by the gas stream. The crystals on the small spoon are now rapidly transferred to the microscope and immersed in the oil. The cold inert gas atmosphere and the surrounding oil prevent the crystals from being attacked by moisture and/or oxygen.

The oil allows washing, splitting and selection of crystals of suitable quality. When a suitable crystal has been selected, an electrical pistol drill is used to drill a hole into a dry-ice block. With a fibre that is already fixed on a goniometer pin, the crystal is picked out of the oil, captured on the tip of the fibre and transferred into the hole in the dry-ice block (Fig. 3).

At 195 K, most crystals survive the transportation over 2 m to the low-temperature nozzle at the diffractometer. There, the crystal mount can easily be detached from the dry-ice block and screwed onto the goniometer head. If



Fig. 1. The low-temperature device.



Fig. 2. The nozzle at the microscope slide.

lower temperatures are required, a small portable liquid-nitrogen evaporator can be used. When subject to the lower temperature of the diffractometer cooling device, the oil freezes and the crystal orientation is fixed.

This technique has several striking advantages when compared with the use of capillaries: the experimenter has free access to the sample (no limitations are imposed by glass joints, rubber stoppers *etc.*); the crystal does not experience mechanical stress through being pushed down into a capillary; there are no fixing problems (since we started using the technique, we have never 'lost' the orientation matrix); and the crystal cannot dry up because there is no capillary volume that can be filled with crystal solvent.

Two kinds of oil, of different viscosities, are used in our laboratory. Both are polyfluorinated polyethers (Riedel-de Haën, Seelze, Germany); the less viscous is Hostinert 216^u, the more viscous is RS 3000^u. The polyethers can be regarded as 'liquid teflon'; neither reaction with a compound nor miscibility with a solvent has been observed so far. These two oils are miscible with each other in any ratio, therefore a mixture suitable for crystal manipulation in the temperature range between room temperature and 193 K can be obtained. Fig. 4 illustrates the properties related to the viscosity for a given mixing proportion *versus* the temperature of the mixture. The upper graph represents the transition to a viscous phase; the lower graph indicates the freezing point (the recommended temperature of data collection is 10 to 20 K below this temperature).

The high transparency of both oils even allows the employment of a polarizing microscope to facilitate the investigation of crystal quality in the whole temperature range.

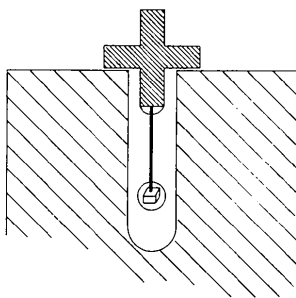


Fig. 3. The crystal in the dry-ice block.

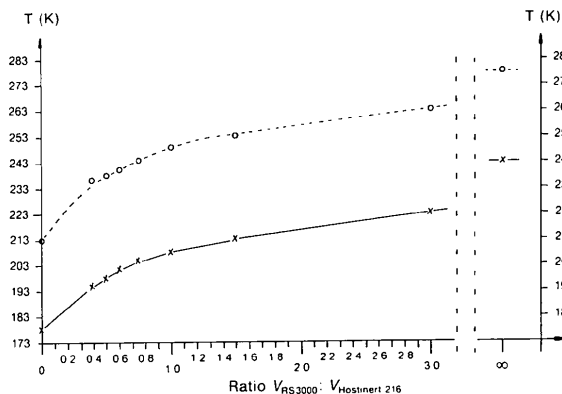


Fig. 4. Viscosity properties of the polyfluorinated polyethers.

The device

A schematic overview is given in Fig. 5. Cold nitrogen gas is generated from liquid nitrogen stored in a 7 l glass dewar. The main heater immersed in the liquid nitrogen causes nitrogen to evaporate. The gas flows through double-walled glass tubes with silvered vacuum jackets and is directed towards the microscope slide *via* a teflon nozzle.

The nitrogen gas is generated in a glass bottle without a base. A circular groove and four indentations in the lower part of the glass bottle hold the main heater. The bottle is joined to the vertical glass tube by a pierced plastic screw cap and a silicon-rubber sealing ring. The tubes are connected with a teflon seal and held together by steel springs to prevent breakage of the glass (Fig. 6).

The nozzle is fixed to the horizontal glass tube. The shape of the nozzle causes the gas stream to flatten and to spread at the outlet. Hence, the whole slide is surrounded by cold gas (Fig. 7). The shape of the nozzle, the aerodynamically favorable shape of the sample immersed in a 'puddle' of oil and the relatively high flow rate of the cold gas stream prevent the sample from icing. The nozzle is fitted with an integrated heater, which prevents the outlet from icing. The nozzle heater consists of a thin insulated heating wire (electrical resistance *ca* 2 Ω), which is fixed to the outlet of the teflon nozzle and covered with aluminium foil to guarantee sufficient distribution of heat (Fig. 2).

The basic structure of the main heater consists of a teflon ring (thickness 5 mm, width 10 mm). The diameter is adjusted to the inner diameter of the glass bottle (it should be noted that teflon shrinks when exposed to liquid nitrogen). An insulated heating wire is fitted onto the teflon ring *via* the screws (Fig. 8), forming a net (electrical resistance *ca* 10 Ω). To avoid bending, a steel cross (thickness 1 mm, width 10 mm) is screwed onto the opposite side of the ring. The whole device is supplied with direct current from an AC-DC transformer. The main heater and the nozzle heater are connected in series. The stream heater, a thin insulated heating wire bent to a spring (electrical resistance *ca* 5 Ω), is part of a second circuit; it is positioned inside the horizontal glass tube (Fig. 5). The electrical parts are protected against overheating by a level sensor

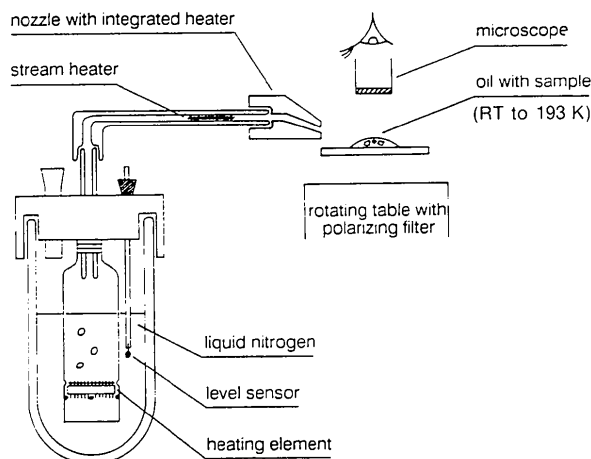


Fig. 5. Schematic overview of the low-temperature device (RT = room temperature).

integrated in a safety-circuit arrangement. The level sensor consists of a resistor with negative temperature coefficient (NTC) taped with an insulated heating wire. The safety circuit guarantees that the power supply will be switched off if the nitrogen level becomes too low. The nitrogen flow rate and the temperature of the stream heater are adjusted by two potentiometers.

In our experience, the mounting device is easy to make and even easier to maintain. With a single filling it can be run for up to 5 h, usually long enough to find a suitable crystal. It is refilled simply by adding liquid nitrogen without interrupting the work.

Experience

The device described above has been used for two years now and crystals of around 80 compounds have been mounted at low temperatures in the above manner. The design of the

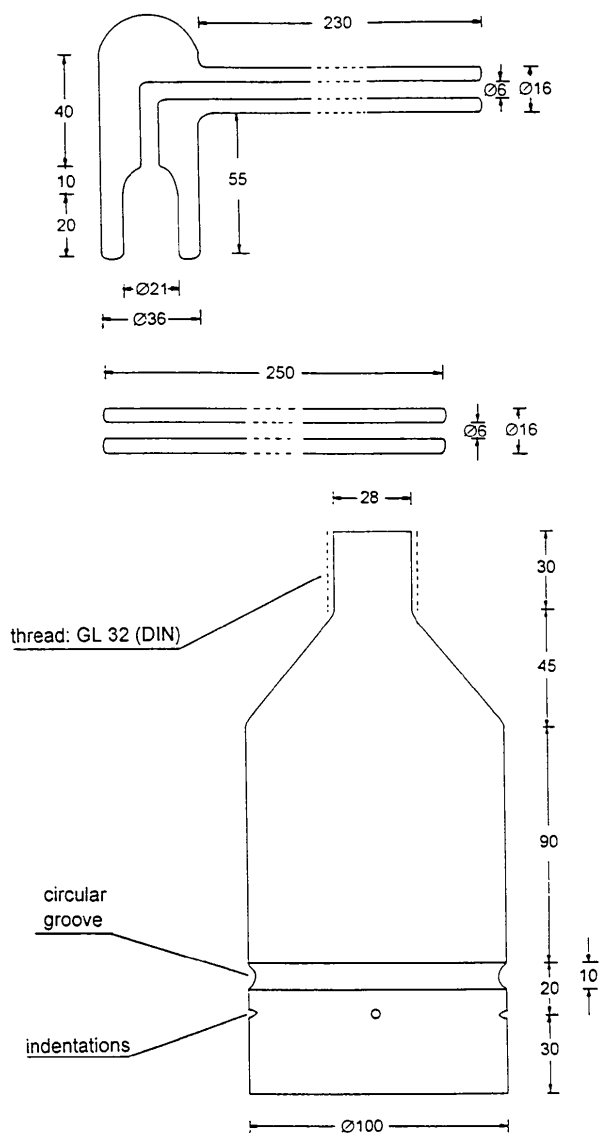


Fig. 6. The glass tubes (top) and the glass bottle.

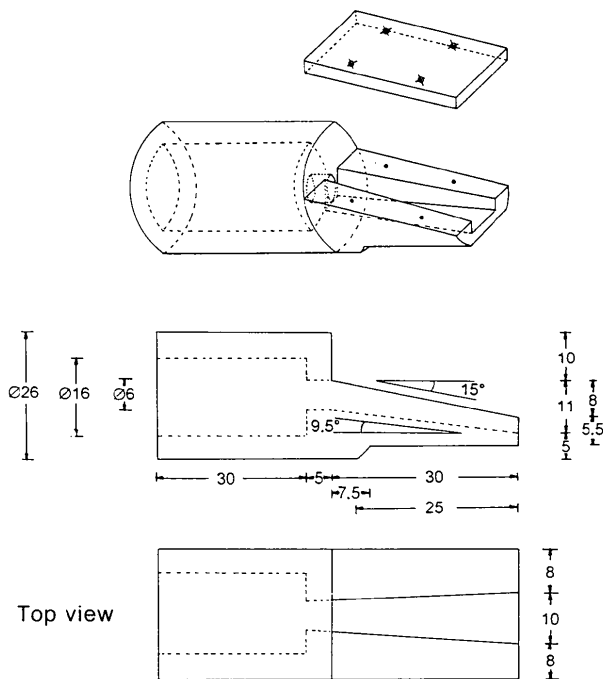


Fig. 7. The teflon nozzle.

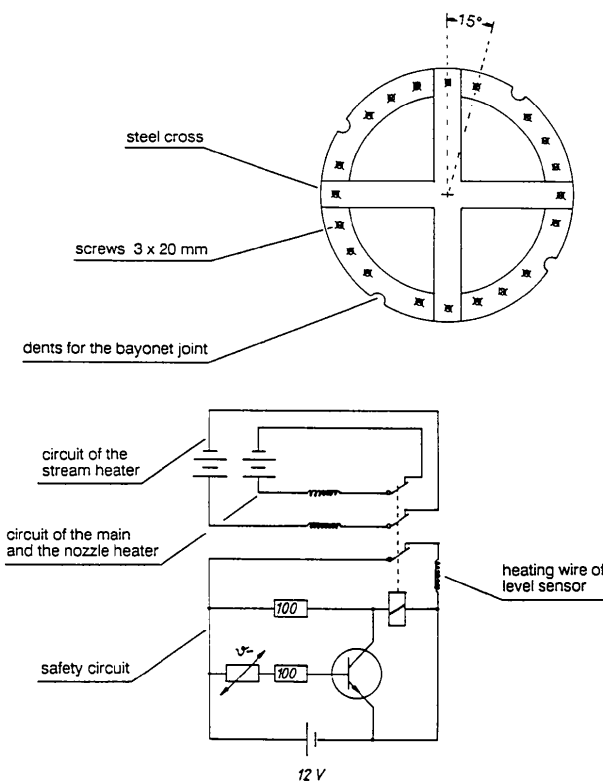


Fig. 8. The main heater (top) and the safety-circuit arrangement. Electrical parts: one relay (12 V, 100 mA, coil resistance ca 300 Ω), with three connections; one NTC resistor ($R_{298 K} \approx 1000 \Omega$); two resistors (100 K, 100 mW); and one transistor (NPN K8927).

nozzle with the integrated heater prevents the whole microscope slide from icing and, therefore, even very sensitive crystals can be selected without haste. The recently determined structure of $(n\text{-BuLi})_6$ may illustrate this. n -Butyllithium is known to be pyrophoric even as a hexane solution. The solvent-free crystals are even more difficult to handle, because their melting point is 239 K [197 K according to Wakefield (1974)].

The structure of $(n\text{-BuLi})_6$ consists of six Li atoms in a trigonal antiprismatic (distorted octahedral) conformation (approximately D_{3d} symmetry) containing six short (2.43 Å on average) and six long (2.94 Å on average) Li–Li distances. Analogous to cyclohexyllithium (Zerger, Rhine & Stucky, 1974), six faces of the octahedron are each capped by a single $n\text{-Bu}$ unit; the two almost equilateral (and opposite) faces with the longest triangular sides remain unoccupied (Fig. 9). Further structural details will be reported elsewhere (Kottke & Stalke, 1993).

Concluding remarks

The combination of the cooling of the sample and the use of the oil-drop mounting technique facilitates the handling of very sensitive crystals. With some practise, the transfer of the crystal from the mother liquor to the diffractometer can be realized within a minute. It is very easy for beginners to learn the technique (much easier than it is for them to learn how to mount crystals in capillaries) and, therefore, it is accepted in the laboratory. There are now crystallog-

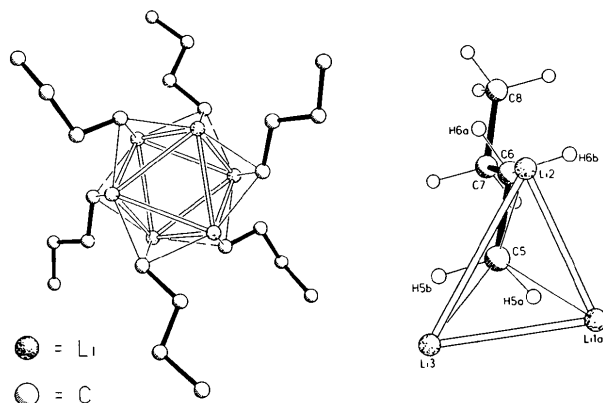


Fig. 9. The single-crystal structure of $(n\text{-BuLi})_6$.

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A 10^9 Pa high-pressure cell for X-ray and optical measurements. Erratum. By M. LESZCZYNSKI, S. PODLASIN and T. SUSKI, *High Pressure Research Centre UNIPRESS, Polish Academy of Sciences, Sokolowska 29/37, 01 142 Warsaw, Poland*

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Abstract

In the paper by Leszczynski, Podlasin & Suski [*J. Appl. Cryst.* (1993), **26**, 1–4], the value of the GaAs bulk modulus $B_0 = 1.1(0.2) \times 10^{11}$ Pa cited from the paper by Besson, Itie, Polian, Weill, Manssot & Gonzalez [*Phys. Rev. B*

(1991), **44**, 4214–4234] was misread from the figure. The correct value, as given by Itie [*Phase Transit.* (1992), **39**, 81], is $B_0 = 0.85 \times 10^{11}$ Pa and $B' = 4.5$ in a Murnaghan equation of state.

raphers in our laboratory who have never had the experience of mounting a crystal in a capillary. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support and Dr F. Koch (Riedel-de Haën, Seelze, Germany) for providing the perfluorinated polyethers.

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All relevant information is given in the *Abstract*.