that as R was reduced they might first relax into periodic oscillations before the unsteady motion ceased at $R = R'_w$; but no such behaviour was detected experimentally.

The transition has great sensitivity to end effects; but in contrast another, more easily recorded property was found to be surprisingly insensitive to them. Expressed as a multiple of Ω, the angular speed ω/n of the observed travelling waves turned out to be nearly independent of R, as shown in Fig. 2 which includes values of $\omega/n\Omega$ from all our measurements of frequency. The mean value is about 0.32, which is unexpectedly close to corresponding values found previously by others from observations in apparatus with Γ an order of magnitude larger, for example the value 0.34 found by Coles[9]. Considered alone, this property might thus be deceptive as regards the overall importance of end effects.

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1. Taylor, G. I. *Phil. Trans. R. Soc.* **A223,** 289–343 (1923).
2. Fenstermacher, P. R., Swinney, H. L. & Gollub, J. P. *J. Fluid Mech.* **94,** 103 (1979).
3. Walden, R. W. & Donnelly, R. J. *Phys. Rev. Lett.* **42,** 301–304 (1979).
4. Ruelle, D. & Takens, F. *Commun. Math. Phys.* **20,** 167–192 (1971).
5. Benjamin, T. B. *Proc. R. Soc.* **A359,** 27–43 (1978).
6. Benjamin, T. B. & Mullin, T. *Phil. Trans. R. Soc.* A (submitted).
7. Benjamin, T. B. *Proc. R. Soc.* **A359,** 1–26 (1978).
8. Schaeffer, D. G. *Math. Proc. Camb. Phil. Soc.* **87,** 307–337 (1980).
9. Coles, D. *J. Fluid. Mech.* **21,** 385–425 (1965).
10. Snyder, H. A. *J. Fluid. Mech.* **35,** 273–298 (1969).
11. Cole, J. A. *J. Fluid. Mech.* **75,** 1–15 (1976).
12. Eagles, P. M. *J. Fluid. Mech.* **49,** 529–550 (1971).
13. Markho, P. H., Jones, C. D. & Mobbs, F. R. *J. Mech. Engng Sci.* **19,** 76–80 (1977).

Complete vitrification in pure liquid water and dilute aqueous solutions

Peter Brüggeller & Erwin Mayer

Institut für Anorganische und Analytische Chemie, Universität Innsbruck, A 6020 Innsbruck, Austria

Pure water can only be vitrified by the very slow condensation of vapour on a metal surface maintained at very low temperatures[1,2]. Attempts to form vitreous ice by rapid cooling of liquid water invariably lead to formation of ice I_h (ref. 3). (Pryde and Jones[4] did report a heat capacity change of rapidly cooled water at 126 K which they attributed to a glass transition, but could not reproduce this result in subsequent experiments.) Dilute aqueous solutions in contrast to concentrated aqueous solutions[5] behave similarly to water and separate during freezing, even with the highest cooling rates available, into pure ice and concentrated solute[6]. We report here that macroscopic parts of samples of pure liquid water and of dilute aqueous solutions can be vitrified completely by jet-freezing of micrometre-sized aqueous droplets distributed in n-heptane as an emulsion—the resulting supercooling effect of ~40 K being essential for vitrification[7].

The formation of vitrified ice from pure liquid water is demonstrated by the differential thermal analysis (DTA) warm-up curve of a jet-frozen emulsion of pure water (Fig. 1b). The exothermic peak at 150 K occurs at the temperature reported for the devitrification of amorphous ice prepared from water vapour[8]. The endothermic peak at 183 K is due to an n-heptane impurity. Jet-frozen 0.10 M $CuCl_2$ solutions (chosen for ESR requirements) gave similar warm-up curves with the exothermic peak also occuring at 150 K. We have not observed clearly a glass transition. Only a faint endothermic inclination at ~138 K in warm-up curves of jet-frozen water and of 0.10 M $CuCl_2$ solutions might come from the glass transition of the vitreous phase which compares well with the glass transition temperature of vapour deposited amorphous ice[8]. The glass transition will be unmistakable only in vitreous samples with little or no crystalline impurity, and investigations of vitreous ice formed from water vapour seem to confirm this[8].
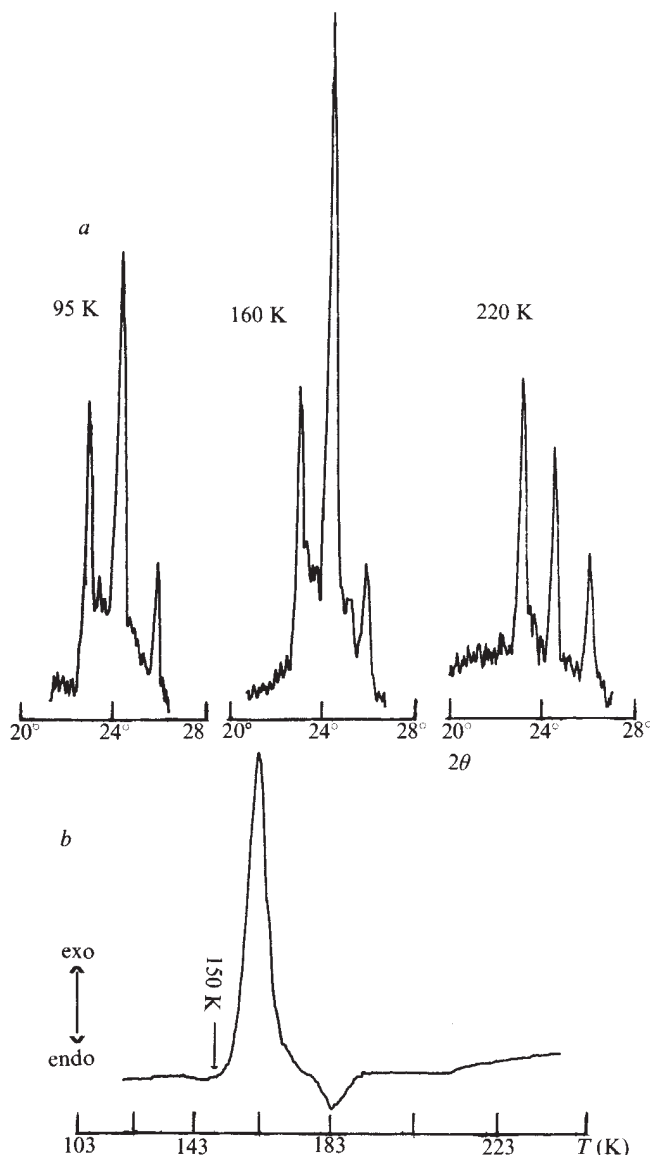

Fig. 1 a, X-ray diffraction pattern (Cu Kα) of a jet-frozen emulsified 0.10 M $CuCl_2$ solution, heated consecutively from 95 K to 160 and to 220 K. b, DTA warm-up curve of jet-frozen emulsified pure liquid water. Heating rate 6° min^{-1}. The low-temperature DTA apparatus was similar to that used by Rasmussen[9]. The NiCr–Konstantan combination was used as thermocouple and the bottom parts of thin-walled 10-mm diameter NMR tubes were used for sample and reference, and for temperature measurement. About 100 mg of sample were diluted with 300 mg $CaCO_3$ and transferred quickly into the precooled DTA apparatus. $CaCO_3$ was used as inert reference and in the tube for temperature measurement. Samples were prepared as follows: the emulsion was prepared by dissolving 0.030 g Span 65 (sorbitan tristearate) in 9 ml n-heptane, adding 1 ml pure liquid water (b) respectively 1 ml 0.10 M aqueous $CuCl_2$ solution (a) and sonifying the mixture. Droplet size depends strongly on sonifier energy and was adjusted to 1–5 μm (larger droplets supercool insignificantly[7] and the ESR spectra indicated strong aggregation). 5 ml emulsion were jetted through a thick-walled glass tube with a 50 μm aperture, using 100 atm working pressure, into 120 ml of vigorously stirred liquid ethane cooled to ~90 K. We preferred ethane to propane as cryomedium because ethane can be pumped off quantitatively at 120 K. For DTA and X-ray experiments n-heptane was removed nearly completely by washing the frozen droplets several times with liquid ethane at 110 K. After pumping off the remaining ethane at 120 K the frozen droplets were transferred quickly with a liquid-nitrogen cooled spoon into the precooled apparatus. During the whole procedure the droplets were warmed at most to 130 K. At liquid-nitrogen temperatures special care has to be taken to prevent accumulation of liquid oxygen in the cryomedium.

The amount of the vitrified material was determined by calibration with a 50% w/v vitrified glycerol solution. Devitrification of a 50% w/v glycerol solution produces according to Rasmussen and Luyet[9,10] a 73% w/v glycerol solution. We obtain an estimate by comparing the peak areas. To reduce errors both standard and sample were diluted equally with $CaCO_3$ and an amount of vitrified glycerol was chosen with a similar signal intensity to our vitrified samples. We found that jet-frozen water/heptane emulsions contain 13% vitrified ice. For jet-frozen emulsified 0.10 M $CuCl_2$ solutions a slightly higher value of 16% devitrified ice was obtained after several determinations. This only slightly higher value indicates that the freezing behaviour of a 0.10 M solution is comparable with the freezing behaviour of pure water, the small amount of additional devitrification coming from more concentrated vitrified parts of the solution.

We also investigated the vitrification of aqueous emulsions by X-ray diffraction and ESR spectroscopy. The X-ray diffraction pattern of ice allows us to differentiate between the phases I_h and I_c and mixtures of these, by the relative intensities of the three strong reflexes of ice I_h (for Cu Kα: $2\theta = 22.8°$, $24.3°$ and $25.9°$) and the strong reflex of ice I_c ($2\theta = 24.3°$)[11,12]. The presence of vitreous components in a partially crystalline sample can be followed by the formation of ice I_c at the devitrification temperature and the relative increase of the reflex of ice I_c at $2\theta = 24.3°$. Figure 1a shows the characteristic part of the X-ray diffraction pattern of a jet-frozen 0.10 M $CuCl_2$ emulsion. The diffraction pattern at 95 K indicates a mixture of ice I_h and I_c. At 160 K a drastic increase of the reflex at $2\theta = 24.3°$ indicates the formation of ice I_c by devitrification of an amorphous phase. At still higher temperatures, ice I_c transforms to ice I_h and at 220 K only the reflexes of I_h are visible. Our experimental conditions inevitably lead to contamination of the original jet-frozen sample by ice I_h due to condensation of water vapour during the preparation and transfer of the sample to the X-ray camera, therefore, the resulting X-ray diffraction pattern at 95 K will contain an unknown amount of ice I_h.

The freezing behaviour of the solute in a dilute solution was studied by ESR spectroscopy. Whereas most other spectroscopic techniques are only sensitive to short-range order (that is,
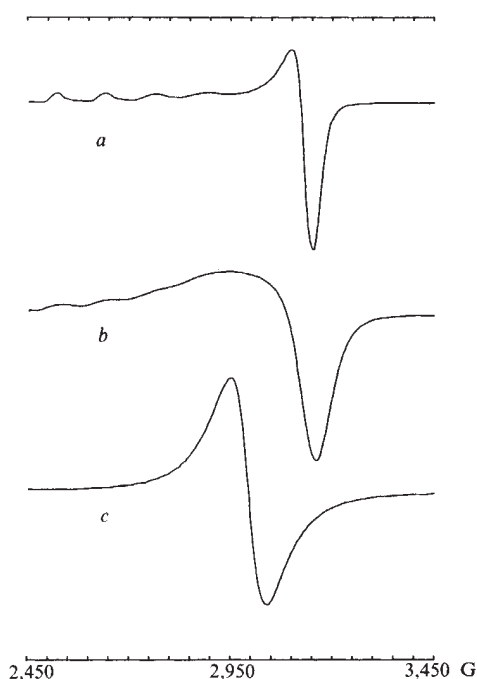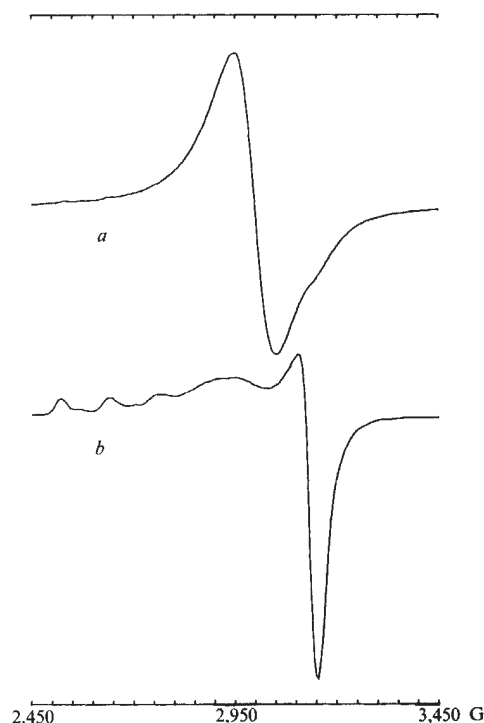
Fig. 3   Low temperature (113 K) ESR spectra of: *a*, 0.10 M $CuCl_2$ solution spray-frozen into liquid propane cooled to ~80 K. The reported technique[15] was slightly modified: the solution was sprayed into 50 ml of stirred propane and the suspension filtered at 90 K. *b*, A jet-frozen 0.10 M $CuCl_2$ emulsion using optimized conditions as described in Fig. 1.

the first hydration sphere), ESR is sensitive to comparatively long range order effects due to the $1/r^3$ dependence of dipolar interaction[13]. With our system we can differentiate clearly between a 0.10 and a 1.5 M vitrified solution (Fig. 2a,b). We used ESR spectroscopy to maximize the various parameters such as cooling conditions and droplet size and found the spectra invaluable for assessing qualitatively the relative amounts of phase separated crystalline and of vitrified material. We used a 0.10 M aqueous $CuCl_2$ solution as our ESR test system because: (1) the spectra representing the two extremes—perfect vitrification and complete phase separation—are shown in Fig. 2a and c and are separated sufficiently for evaluation. (2) At a concentration of 0.10 M the ESR spectrum was the most sensitive to the segregation of ice during the freezing process. At higher concentrations the ESR signal begins to broaden due to dipole–dipole interactions as shown in Fig. 2b. At lower concentrations the spectra of glycerol vitrified solutions are nearly identical to the ESR spectrum in Fig. 2a. Therefore even drastic segregation of ice from a very dilute solution such as 10^{-3} M, resulting in a dramatic increase of the solute concentration, will not show up in the ESR spectrum. Figure 3b shows the ESR spectrum of a jet-frozen emulsion in the 'best' conditions for vitrification. These conditions were identical with the freezing conditions of the pure liquid water sample in Fig. 1b. The ESR spectrum is very similar to the spectrum of the perfectly vitrified solution in Fig. 2a. Some aggregation of $CuCl_2$ is indicated by a broad hump at 2,940 G.

The ESR spectra of jet-frozen 0.10 M $CuCl_2$ emulsions display drastic spectral changes with increasing temperature which are irreversible. In Fig. 4 the ESR spectra of a sample warmed for 30 min consecutively to 153 K (*b*), 173 K (*c*) and 193 K (*d*) have to be compared with the spectrum of the original sample at 113 K (*a*). At 153 K the ESR signal starts to broaden approaching within 30 min the width of a 1.5 M vitrified solution (compare with Fig. 2b). The increase of the signal at 2,940 G indicates the formation of a highly concentrated $CuCl_2$ phase.

Fig. 2   Low temperature (113 K) ESR spectra of: *a*, 0.10 M $CuCl_2$ solution, containing 50% (v/v) glycerol for vitrification; *b*, 1.5 M $CuCl_2$ solution vitrified as above; *c*, 0.10 M $CuCl_2$ slowly frozen by immersion in liquid nitrogen.

At higher temperatures the amount of concentrated $CuCl_2$ increases. Evidence from DTA warm-up curves and from the X-ray diffraction patterns of Fig. 1a clearly indicates the process causing the irreversible change of the ESR spectra with temperature. The start at 153 K correlates well with the devitrification temperture determined by DTA. At this temperature ice I_c (shown by the X-ray diffraction pattern) starts to separate from the vitrified solution, the remaining $CuCl_2$ becoming more and more concentrated.

From the theory[3] of the homogeneous nucleation of freezing, the cooling rate necessary for vitrifying a μm-sized droplet of water was estimated to be $>10^{10}$ K s^{-1} and was considered to be unattainable in practice. To compare our technique with others and to obtain some idea of the relative effects of emulsification and of jet-freezing we investigated the freezing methods usually applied in freeze etching. These methods were too slow to give observable DTA devitrification peaks, and we therefore used ESR spectroscopy. Dropping of 1 μl droplets into liquid Freon at 120 K (the "standard freezing method"[14]—cooling rates up to 10^3 K s^{-1}), yields complete aggregation and the ESR spectrum of a frozen 0.10 M $CuCl_2$ solution is identical with the spectrum in Fig. 2c. Even the much faster cooling methods developed by Bachmann and Schmitt[15] (spray-freezing and jet-freezing into liquid propane at 77 K, estimated cooling rates of 10^5 K s^{-1}) do not prevent segregation of the solute from the solvent. The ESR spectrum of a spray-frozen 0.10 M $CuCl_2$ solution in Fig. 3a shows mainly aggregated $CuCl_2$ and only a minor amount of less concentrated $CuCl_2$ is indicated by the shoulder at 3,150 G. Jet-freezing of a 0.10 M $CuCl_2$ solution through a 20 μm aperture with 10 atm working pressure into liquid propane gives similar results to spray-freezing. We also tried to obtain a comparison with the cooling methods applied in splat-cooling of liquid metals and alloys[16] by jetting a 0.10 M $CuCl_2$ solution through a 10 μm aperture with 100 atm working pressure onto a copper plate cooled to 77 K. The jet was moved as quickly as possible over the surface of the cooled copper plate and its speed was calculated to be ~100 m s^{-1} from the diameter of the aperture and consumption of liquid. Although this experiment was not performed using strict splat-quenching conditions we

believe it to be comparable with the 'gun-technique'[16] because of the high speed and small diameter of the jet. The ESR spectrum of the resulting frozen solid indicated complete aggregation. Apparently splat-cooling techniques give very low cooling rates for water and dilute aqueous solutions due to the low conductivities of water and ice.

We estimated our cooling rate by jet-freezing a non-emulsified 0.10 M $CuCl_2$ solution, using otherwise identical conditions (glass capillary with 50 μm aperture, 100 atm working pressure into liquid propane at 77 K). The ESR spectrum shows a clear improvement over the ESR spectrum of a spray-frozen sample in Fig. 3a, the signals at 3,050 and 3,150 G being of equal size. We therefore assume the cooling rate to be between 10^5 and 10^6 K s^{-1}. The further improvement with emulsified solutions in Fig. 3b demonstrates clearly the importance of emulsification and of the resulting supercooling effect for the vitrification of water and dilute aqueous solutions.

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1. Burton, E. F. & Oliver, W. F. *Proc. R. Soc.* A153, 166 (1935).
2. Venkatesh, C. G. & Rice, S. A. *Science* 186, 927–928 (1974).
3. Fletcher, N. H. *Rep. Progr. Phys.* 34, 913–994 (1971).
4. Pryde, J. A. & Jones, G. O. *Nature* 170, 685–688 (1952).
5. Angell, C. A. & Sare, E. J. *J. chem. Phys.* 49, 4713–4714 (1968); 52, 1058–1068 (1970).
6. Wolstenholme, G. E. W. & O'Conner, M. *The Frozen Cell* (Churchill, London 1970).
7. Rasmussen, D. H. & MacKenzie, A. P. *J. chem. Phys.* 59, 5003–5013 (1973).
8. McMillan, J. A. & Los, S. C. *Nature* 206, 806–807 (1965).
9. Rasmussen, D. & Luyet, B. *Biodynamica* 10, 319–331 (1969).
10. Luyet, B. & Rasmussen, D. *Biodynamica* 10, 167–191 (1968).
11. Dowell, L. G. & Rinfret, A. P. *Nature* 188, 1144–1148 (1960).
12. Olander, D. S. & Rice, S. A. *Proc. natn. Acad. Sci. U.S.A.* 69, 98–100 (1972).
13. Abragam, A. *The Principles of Nuclear Magnetism*, 126 (Clarendon, Oxford, 1973).
14. Moor, H. & Mühlethaler, J. *J. Cell Biol.* 17, 609–628 (1963).
15. Bachmann, L. & Schmitt, W. W., *Proc. natn. Acad. Sci. U.S.A.* 68, 2149–2152 (1971); in *Freeze Etching*, (eds Benedetti, & E. L. & Favard, P.) 73–79 (Soc. Franc. Microsc. Electron, Paris 1973).
16. Jones, H. *Rep. Progr. Phys.* 36, 1425–1497 (1973).

Lu–Hf total-rock isochron for the eucrite meteorites

P. J. Patchett*† & M. Tatsumoto*

* US Geological Survey, Denver Federal Center, Denver, Colorado 80225
† Colorado School of Mines, Golden, Colorado 80401

The isotope ^{176}Lu (2.6% of natural lutetium) decays by β^- to ^{176}Hf, with a long half life. We present here the first Lu–Hf isochron. The eucrite meteorites, a suite of planetary igneous rocks of known age, 4,550 Myr, define a 10-point total-rock isochron with a slope of 0.0934±40, leading to a value of $3.53\pm0.14\times10^{10}$ yr for the β^--decay half life of ^{176}Lu. The isochron intercept of 0.27973±12 gives the initial ^{176}Hf/^{177}Hf for the inner Solar System at the time of accretion.

Previous geochronological use of the ^{176}Lu–^{176}Hf decay scheme involved REE-rich minerals[1,2] in attempts to determine the half life. Faure[3] summarized all physical determinations and suggested a best estimate of $3.5\pm0.2\times10^{10}$ yr. However, because ^{176}Lu is an odd Z-odd N nuclide, then a branching decay is theoretically possible. Dixon et al.[4] set an approximate upper limit of 3% on the electron capture to ^{176}Yb, but to date this possible decay has been neither clearly substantiated nor disproved. It has also not been clearly shown that the Lu–Hf method can be used in isotope chronology and geochemistry.

Using a wide variety of petrological and geochemical criteria, the eucrites constitute a coherent group of cumulate and noncumulate igneous rocks (brecciated to varying degrees), which may have come from a single-parent asteroid[5-7]. In isotope geochemistry, the eucrites are important because they seem to have been produced during a major planetary differentiation 4,550 Myr ago, and to have been isotopically mainly
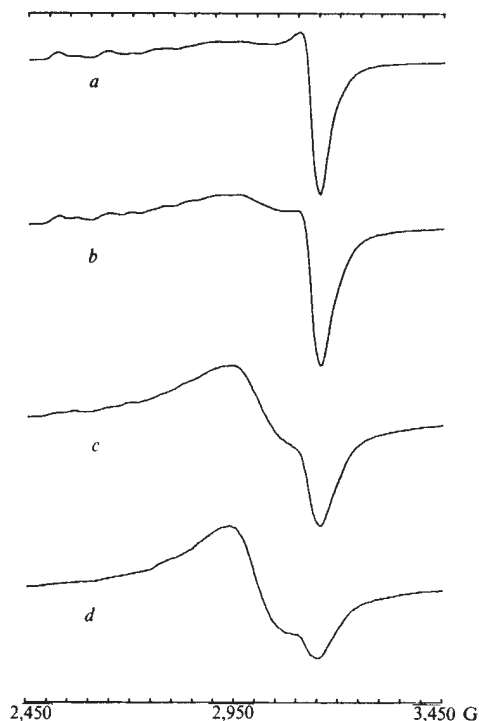

Fig. 4 Low temperature (113 K) ESR spectra of a jet-frozen 0.10 M aqueous $CuCl_2/n$-heptane emulsion: *a*, warmed at most to 113 K; *b, c* and *d* warmed consecutively for 30 min to 153 K, 173 K and 193 K respectively.