the target range for DRAM applications (1–5 × 10^{-7} A cm^{-2}). At this composition, we find \( \varepsilon_r = 62.5 \) and the FOM is 24.3 μC cm^{-2}.

These results should be contrasted with those of bulk crystalline \( \text{Zr}_x\text{Sn}_{1-x}\text{Ti}_2\text{O}_7 \) (where \( x + y + z = 2 \)) (ref. 12). A single homogeneous solid-solution phase, isomorphic with the orthorhombic \( \alpha\text{PbO} \) structure, was found near the composition \( \text{ZrTiO}_3 \) as indicated in Fig. 2. The remainder of the \( \text{Zr}_2\text{Sn}_{1-x}\text{Ti}_2\text{O}_7 \) phase diagram consists of multiphase ternary systems and the endmembers. \( \text{ZrSnTiO}_4 \) is known for their superior microwave properties, including a moderate dielectric constant, very low dissipation factor, and low temperature coefficient of permittivity.\(^{15}\) The properties of \( \text{Zr}_{0.95}\text{Sn}_{0.05}\text{Ti}_2\text{O}_7 \) for example, were studied carefully as a function of doping and sintering. A permittivity of \( \varepsilon_r = 36 \) and a dissipation factor (tan \( \delta \)) of \( 10^{-3} \) were obtained. The indicated composition is typical of those used for applications, which are invariably chosen to be within the homogeneous phase field. Note that the optimum compositions in our amorphous films are outside this composition field that yields homogeneous crystalline phases.

Amorphous thin films of \( \text{ZrSnTiO}_4 \) with a particular but unspecified \( \text{ZrSn} \) composition have been studied;\(^{16}\) a value of \( \varepsilon_r = 27 \) was inferred in amorphous films prepared by radio frequency magnetron sputtering at \( 200 \) °C; a value of \( \varepsilon_r = 38 \) was found in crystalline films, that is, the bulk value. For approximately the same composition, however, we observe \( \varepsilon_r = 50 \). This is a very substantial difference. At present we cannot explain the discrepancy between our data and those described in ref. 14. We do observe a decrease in the dielectric constant for deposition at higher temperatures, namely for films with a presumably greater degree of local order so perhaps the films deposited by Nakagawa et al.\(^{14} \) also have a higher degree of order than our films.

This work demonstrates the value of the GCS technique in the search for metastable materials whose properties are sensitive to preparation conditions. Many issues regarding the development of this material for practical application remain to be addressed. For example, fully optimized uniform films need to be made using a single target with on-axis sputtering (or using CVD), and the properties of films \( \sim 10–20 \) nm thick (one fifth the present value) must be evaluated. Also, conditions that lead to lower leakage current must be found and capacitors made using standard electrodes (for example, TiN) must be subjected to standard post-processing and evaluated for reliability using accelerated testing. Although \( \text{ZrSnTiO}_4 \) films must be further developed, our preliminary results are encouraging.

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14. Nakamura, O. et al. Electrical properties of \( \text{Zr}_{0.95} \) \( \text{Sn}_{0.05} \) \( \text{Ti}_2 \) \( \text{O}_7 \) thin films fabricated by pulsed laser deposition. J. Appl. Phys. 83, 89–902 (1996).

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**Decompression-induced melting of ice IV and the liquid–liquid transition in water**

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Although liquid water has been the focus of intensive research for over 100 years, a coherent physical picture that unifies all of the known anomalies of this liquid is still lacking. Some of these anomalies occur in the supercooled region, and have been rationalized on the grounds of a possible retracing of the liquid–gas spinodal (metastability limit) line into the supercooled liquid region or alternatively the presence of a line of first-order liquid–liquid phase transitions in this region which ends in a critical point. But these ideas remain untested experimentally.
in part because supercooled water can be probed only above the homogeneous nucleation temperature $T_N$ at which water spontaneously crystallizes. Here we report an experimental approach that is not restricted by the barrier imposed by $T_{1b}$ involving measurement of the decomposition-induced melting curves of several high-pressure phases of ice in small emulsified droplets. We find that the melting curve for ice IV seems to undergo a discontinuity at precisely the location proposed for the line of liquid–liquid phase transitions. This is consistent with, but does not prove, the coexistence of two different phases of (supercooled) liquid water. From the experimental data we calculate a possible Gibbs potential surface and a corresponding equation of state for water, from the forms of which we estimate the coordinates of the liquid–liquid critical point to be at pressure $P_c = 0.1$ GPa and temperature $T_c = 220$ K.

In the liquid–liquid hypothesis for the anomalies of supercooled water, the liquid can exist in two phases of different densities, here denoted the high-density liquid (HDL) and low-density liquid (LDL) by analogy with the known high-density amorphous (HDA) and low-density amorphous (LDA) phases of ice. To explore the region of the phase diagram in which this transition is supposed to occur, we have studied water confined to droplets with diameters of the order of 1–10 μm and exposed to high pressures (Fig. 1a). In such small volumes, nucleation of secondary ice phases following melting in the supercooled regime is kinetically suppressed. This procedure is especially useful in detecting metastable melting curves (Fig. 1b, c) and, as it is not affected by the presence of the line of homogeneous nucleation temperatures $T_{1b}(P)$ (ref. 16) (below which melting is immediately followed by freezing), can be applied to provide a partial test for the hypothesis that there exists a line $L_1$ of liquid–liquid first-order phase transitions somewhere in the region of the $P$–$T$ plane below the line $T_{1b}(P)$. Any metastable melting line that crosses $L_1$ should display discontinuous behaviour at $L_1$ (such as ice IV shown in Fig. 1d) because the melting behaviour of the ice would be different for the two liquids that coexist at $L_1$. We confine 1 cm$^3$ of water emulsion in an indium capsule and we compress (and decompress) it at a constant rate by a piston cylinder apparatus (Fig. 1a). We measure $T$ using a thermocouple throughout the compression and decompression cycle. As an exothermic (or exothermic) transition results in a change in temperature (Fig. 1b), we can determine with high accuracy the location of the CIMP (compression-induced melting) and DIM (decomposition-induced melting) lines. The present experiments reveal that discontinuous behaviour does occur on melting (Fig. 2). In the region of overlap, the DIM line agrees with the previously reported melting lines (18), confirming that they are indeed the equilibrium stable melting line and the equilibrium metastable melting line. Moreover, there do not appear to be an emulsion-carrier sample without water. We confirm the production of the supercooled liquid on further decompression by finding an exothermic transition at the $T_{1b}$ line below 0.2 GPa, which indicates freezing of the liquid. Crystalline ice appears to form probably due to immediate freezing after melting occurs (below $T_{1b}$); the transition to another crystalline phase should occur on the DIM line because the liquid produced by DIM should crystallize homogeneously below this temperature.

We extend the $T_{1b}$ line to 1.5 GPa by compressing the supercooled liquid and detecting its freezing on the $T_{1b}$ (Fig. 2a, centre panel). We also observe the CIMP line for ice IV, consistent with previous results (note that we replace the nominal pressure reported in ref. 16 by the real pressure). We find the crystallization lines $T_{X}$ of emulsified HDA is higher by $\sim 20$ K than that of bulk HDA around 1.5 GPa; only the results are shown in Fig. 2a, right panel. The long-dashed line and the horizontal "error bar" around 0.2 GPa in Fig. 2a, right panel, indicate the proposed (20) and the experimentally obtained (21) location of the LDA/HDA "equilibrium" boundary. The long-dashed line around 0.5 GPa indicates the extrapolated $T_{X}$/HDA "equilibrium" boundary.

We also find what appear to be two "possible new phases" (PNP), denoted PNP-XIII and PNP-XIV. The DIM line for PNP-XIV is useful because it serves as a "control" for the discontinuous

Figure 1 Overlap of the present experiment. This experiment is designed to probe the region of the temperature-pressure phase diagram—below the nucleation temperature $T_N$ and above the crystallization temperature $T_c$—where the line $L_1$ of liquid–liquid phase transitions might exist separating a low-density liquid phase from a high-density liquid phase. a, The experimental setup. The sample, volume $\sim 10^{-2} \text{cm}^3$, consists of 40% v/v of deuterated water in a hydrogenated methyl ester selected so that the liquid–liquid transition occurs at $T = 10$ K (ref. 19). Pressure $P$ is applied, keeping the cylinder at a nearly constant low temperature, using a hydraulic piston pump with a relative accuracy of $\sim 2$ MPa at 0.1 GPa and 10 MPa at 1 GPa. The temperature $T$ of the sample is monitored by an automatic thermocouple with a relative accuracy of $\pm 0.02$ K (ref. 19). The compression (and decompression) rate is held constant at $dP/dt = 0.2$ GPa/min$^{-1}$ even during transitions. Also shown is a diagram illustrating the case of compression-induced melting from crystal (X) to liquid (L), b, The endothermic temperature response of the sample during CIMP (compression-induced melting) and DIM (decomposition-induced melting) during both CIMP and DIM, the crystal X is forced by the pressure, which reduces the sample temperature because the melt absorbs the latent heat quasi-adiabatically. The cooled sample melts only the compression or decompression. The diagram shows: the endothermic temperature response to a sequence of four infinitesimal pressure increments during CIMP and a corresponding temperature response to a sequence of four infinitesimal pressure decrements during DIM. After the entire sample is transformed, the temperature returns to the cylinder temperature. The phase diagram is a typical phase diagram showing two stable melting lines (solid curve), denoted Z, separating two stable crystalline phases $X_1$ and $X_2$ from the stable liquid (the hatched region). Also shown are two metastable melting lines (dashed curve, denoted Z), one of which can be located using DIM and the other using CIMP. Use of an emulsion suppresses the direct $X_1$/$X_2$ transitions, d, Schematic illustration of the present experiments. We measure the DIM line of ice IV, and search for a kink. We choose ice IV (ref. 20) because its metastable melting line is readily measurable by DIM; it appears to extrapolate to the region of the hypothesized line $L_1$ of liquid–liquid (LDL/HDL) transitions located between $T_N$ and $T_{1b}$ and terminating at an apparent critical point (the black point).
behaviour shown by the DIM line of ice IV. We obtain PNP-XIII by the decompression-induced transition of the PNP-XVII emulsion annealed around 250 K. We obtain PNP-XVII (1) by heating emulsified EDA above T_{12} around 1.5 GPa, (2) by compressing supercooled liquid beyond the T_{12} line around 230 K or (3) by cooling the liquid below T_{12} above ~1 GPa.

The smoothness of the PNP-XIV DIM line above T_{12} implies that L_{12} if it exists, lies in a different region of the P-T diagram traversed by the DIM line of PNP-XIV. PNP-XIV may have a rather ordered structure because of the endothermic nature of the melting and immediate freezing transition below T_{12} (Fig. 2b, left panel) which indicates that the transition is apparently from a relatively ordered crystalline phase to a more disordered crystalline phase with net heat absorption.

We note that the DIM line of ice IV shows a sharp kink at 0.1 GPa and 215 K. To interpret this sharp kink, we calculate the Gibbs potential surface for liquid water, G_{L}(P,T), and we consider if this surface is consistent with the possible existence of L_{12}. We shall see that the kink in the DIM line of ice IV may occur precisely at the line L_{12} of the hypothesized liquid-liquid transition. As with all phase-transition data, our data are also consistent with the possibility of no singularity at all, rather than with a sharp but continuous change in the behaviour of the relevant quantities—as there must be experimental error bars on data points (and since the number of data points is

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**Figure 2** Data obtained in the present experiment. a. The left panel shows the measured DIM temperature response of the ice emulsion during decompression; the centre panel shows the measured DIM temperature response during each compression. The right panel shows the melting lines that are extracted from the data shown. The DIM line of ice IV shows a kink at P = 0.1 GPa and T = 215 K, and it is followed by the line of broad endothermic transitions (the wavy hatched region). We note also that the kink appears well below the homogeneous nucleation line T_{n}(P), so the possibility that the kink is due to T_{n}(P) seems unlikely. The right panel also shows the melting lines of the other ices and the LDA-PDA and PDA-PDA transition lines (the long-dashed lines). The horizontal bar indicates the range of metastability found for the LDA-PDA transition.b. Enlargement of the region in which the kink in the DIM curve of ice IV occurs (compatible with the temperature responses forms the DIM lines of L_{12}).

**Figure 3** Gibbs potential surface for liquid water probed in the present experiments for both its stable and metastable regions. a. Schematic Gibbs potential of liquid water relative to that of ice I_{h}, LG = G_{L} - G_{I_h}. The intersection line of LG and the basal plane defines the melting line of ice I_{h}. b, Gibbs potential of a typical high-pressure ice relative to that of ice I_{h}, LG = G_{Ih} - G_{Ih}. The melting line for the high-pressure ice, defined by the intersection between the Gibbs potential surface of the liquid and that of the high-pressure ice. We obtain numerically the LG along the melting line which equal LG along the melting lines. c, Schematic construction of the LG surface (the dark region) by smooth graphical interpolation between the LG potential along the melting lines for different ices (the thick solid lines). Each of the nearly vertical thick solid lines is a melting line. The horizontal line is the melting line of ice I_{h} where the LG is zero (a). These lines locate on a surface (the LG surface, the dark region). Once we know the LG surface, we calculate the LG plane for PNP-XIII and PNP-XIV following the reverse procedure using the melting lines of PNP ice. We also estimate, and show by the thick dashed lines, the LG potential along the melting lines of PNP ices on these LG planes.
finite, not infinite) there is no a priori way to distinguish a function with a sharp discontinuous 'step' from a continuous function with a sharp but still continuous behaviour that merely resembles a step. An example of such a function is \( y = \tanh(10x) \) which appears to jump discontinuously from \(-1\) for negative \( x \) to \( +1 \) for positive \( x \), yet in fact is a continuous function.

The general procedure we shall follow is based on the fact that along the melting line of any solid ice phase (ice I\(_{h}\), or any of the high-pressure ice phases), the Gibbs potentials of the coexisting ice and liquid phases must be identical. Hence we can obtain the Gibbs potential of the liquid phase along the melting line of each ice phase by evaluating the Gibbs potential of that ice phase along its melting line.

The Gibbs potential has no natural zero; in this study, we construct \( \Delta G \equiv G - G_{0} \), the Gibbs potential of the liquid relative to that of ice I\(_{h}\). (Fig. 3a). Hence the slope of this surface with respect to \( P \) must be the difference in specific volumes of the liquid and ice I\(_{h}\), and the slope with respect to \( T \) must be the difference in entropies of the liquid and ice I\(_{h}\). One advantage of this construction is that the melting line of ice I\(_{h}\) is a curve that is constrained to lie in the plane \( \Delta G = 0 \) (Fig. 3a).

We now consider the Gibbs potential of one of the high-pressure ices relative to that of ice I\(_{h}\), \( \Delta G_{hl} \equiv G_{hl} - G_{0} \) (Fig. 3b). We can obtain the \( \Delta G_{hl} \) surface by noting that to a good approximation it is a plane because (1) the difference in specific volume between the high-pressure ice and ice I\(_{h}\), \( \Delta V \equiv V_{hl} - V_{h} \), is small and constant over the relevant pressure range (0.1-1.5 GPa and 77-300 K), and (2) the difference in entropy between the high-pressure ice and ice I\(_{h}\), \( \Delta S = S_{hl} - S_{h} \), is relatively small (so the pressure at the phase boundary between the high-pressure ice and ice I\(_{h}\) is roughly constant and independent of temperature, and hence the line of intersection with the basalt plane is approximately parallel to the \( T \) axis). This plane can be determined by knowing any three points on, or equivalently, by knowing one point—say, the pressure at the plane's intersection with the basalt plane—and the slopes of the plane in the temperature and pressure directions. We therefore calculate the \( \Delta G_{hl} \) plane from its slope and the pressure at the intersection; we take the slope, \( [\partial(\Delta G_{hl})/\partial P]_{T} = \partial V_{hl} - \partial V_{h} \), from ref. 24, and the pressure from that at the intersection between the melting line of the high-pressure ice and that of ice I\(_{h}\) (Fig. 2a, right panel); this is the pressure of the triple point at which three phases (liquid, ice I\(_{h}\), and the high-pressure ice) coexist.

Figure 3c shows how we calculate \( \Delta G_{hl} \) along the melting line from the known \( \Delta G_{hl} \) plane and the known melting line of a given high-pressure ice phase—because \( G_{hl} = G_{0} \) along this line. We can

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**Figure 4** Application of data obtained in the present experiment to reconstruct the Gibbs potential surface and the thermodynamic equation of state \( V = V(P,T) \). a, Comparison of the \( \Delta G_{hl} \) surface evaluated by the method of Fig. 3d (the dark region) with (1) the Gibbs potential surfaces of LDA and HDA relative to that of ice I\(_{h}\), and (2) the \( \Delta G_{hl} \) at 1 bar. The LDA Gibbs potential at 10 K and 1 bar is known experimentally to be \( +1 \pm 0.1 \) kJ mol\(^{-1}\). Also shown are \( \Delta G_{hl} \) along the melting lines of all RN1 ices. We find a RN1 with a density of 1.2 g cm\(^{-3}\), while for RN1 with a density of 1.2 g cm\(^{-3}\). The value of \( \Delta G_{hl} \) at 1 bar for \( T > 25 K \) (the thick solid line) is obtained from ref. 28, and we assert that this Gibbs potential at 1 bar is connected with the LDA potential via the possible low-density liquid (LDL) state—because the LDL above 25 K, cooled extremely rapidly at 1 bar, becomes a glass which resembles LDA/P. b, The \( \Delta G_{hl} \) surface in the 80-270 K and 0-4 GPa region with constant \( P \) and constant \( T \) lines at 50 K and 10 K intervals, as evaluated from experimental data. c, Dependence of \( \Delta G_{hl} \) on pressure at some fixed temperatures (also evaluated from experimental data), which may be read in conjunction with b; the thin solid lines in b correspond to the lines in the figure. The filled with a reverse-Arends direction. The filled circles at 0 GPa correspond to the measured and estimated potentials at corresponding temperatures at 1 bar. The LDA Gibbs potential at 1 bar is the experimental value. We can draw smooth lines by interpolation between the Gibbs potential points of the ice phases, and so can construct an accurate \( \Delta G_{hl} \) surfaces. To connect the \( \Delta G_{hl} \) at high pressure with that at 1 bar, a rapid slope change (corresponding to our possible liquid-liquid phase transition) should appear below \( 220 K \). d, Possible qualitative equation of state \( V(P,T) \) of liquid, given by the partial derivative \( \partial V_{hl} / \partial P \), and by adding the specific volume of ice I\(_{h}\). The specific volumes of the amorphous phases are known for the region below 7 K (ref. 21) and for the stable high-temperature liquid. Solid lines are the specific volume along the melting lines of ice I\(_{h}\) and RN1. The high-temperature liquid appears to separate into two low-temperature liquid phases just below the critical point located at around 0.1 GPa and 220 K. We emphasize that the data cannot locate the coordinates of the critical point, denoted \( \Delta G_{hl} \) with high accuracy, owing to the possibility that the phase transition line might have a "hook" in it. These two liquid phases are continuous with the two amorphous phases that are known to exist below \( 150 K \). We note that this phase transition surface differs from that of a typical liquid only in the presence of this critical point—which in turn arises because below the line of density maxima the fluctuations in specific volume and in entropy are anticontinued by definition.
repeat this procedure for each of the high-pressure ice phases, and thereby obtain values of the Gibbs potential along an entire family of lines (Fig. 3d). Using this family of lines, we then construct the $\Delta G_i$ surface (Fig. 3d) by interpolation between the known values of $\Delta G_i$ along this family of lines.

Figures 4a shows a portion of the $\Delta G_i$ surface. As an accuracy check, we note that this surface includes on it the previously reported line at 1 bar. Also shown are the $\Delta G$ surfaces of LDA and HDA. Thus we can calculate the entire $\Delta G_i$ surface by connecting these individual lines, and taking the slopes of the LDA phase and the hypothesized LLD phase to be similar (compare the hatched area of Fig. 4a).

In this way, we find that the LDA and HDA Gibbs potential surfaces satisfy, that they are planes and that the $L_i$ -- $HDA$ equilibrium transition pressure is 0.5 GPa and the LDA/ HDA equilibrium pressure is 0.2 GPa (refs 20, 21). The slope [$\Delta G = \frac{\partial G}{\partial P}$] of LDA and HDA we obtain from their known specific volumes.\textsuperscript{15} We note that the LDA plane is almost parallel to the basal plane because the specific volume of LDA and that of ice II are essentially the same.\textsuperscript{25} The thick solid lines in Fig. 4a (except the line at 1 bar) are $\Delta G_i$ along the melting lines of high-pressure ices, and the thick broken lines (except the line at 1 bar) are those of the NPN ices. The error in the Gibbs potential is much less than 0.1 kJ mol$^{-1}$.

Figure 4b shows the detailed calculation of the $\Delta G_i$ surface for $T$ between 80 and 270 K and $P$ between 0 and 5.0 GPa. We note that the intersection between the nearly flat LD 111 surface and the slope of the H11 Gibbs potential makes a distinct "crease" which starts at the LDA/HDA boundary and continues to a point with coordinates $P = 0.1$ GPa and $T = 220$ K. This behaviour is consistent with the presence of a first-order transition line, as the specific volume of the derivative of the Gibbs potential is discontinuous across the crease.

To further test this possibility, we show in Fig. 4c the pressure dependence of $\Delta G_i$ at fixed $T$. For $T > 235$ K, the $\Delta G_i$ at high $P$ extrapolates smoothly to the independently calculated $\Delta G_i$ at 1 bar. For the 220 K isotherm, the slope changes rapidly around 0.1 GPa in order to connect the 1 bar value of $\Delta G_i$ while at 215 K a crease in the surface must occur if the values of $\Delta G_i$ at 1 bar and 0.1 GPa are to be on the same curve.

We note that this point (0.1 GPa, 215 K) is precisely the point where the melting curve of ice IV undergoes a sharp discontinuity, so $\Delta G_i = \Delta G_{IV}$. Although this could be a coincidence, it could also arise because of the presence of a first-order liquid-liquid phase transitions.

In Fig. 4d we show a possible composition of state $Y = Y(P, T)$ that is consistent with experimental data. The specific volumes of the two liquid phases LDA and HDA appear to be continuous with the specific volumes of LDA and HDA. Further, the anomalous behaviour of supercooled D$_2$O in terms of both liquid structural\textsuperscript{26} and molecular relaxation\textsuperscript{26} are also consistent with the existence of a critical point with approximately the same coordinates.

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\[ \text{1. Debernardi, R. G. M. J. Chem. Phys. 1997.} \]
\[ \text{2. Angell, C. A. Formation of phases from liquids and supercooled processes.} \]
\[ \text{3. Fouchet, C. A. The role of molar volume and} \]
\[ \text{4. Sivret, G. A. Isothermal compressibility of supercooled water and evidence for a} \]
\[ \text{5. Speedy, R. J. & Angell, C. A. Isotopic compressibility of supercooled water and evidence for a} \]
\[ \text{6. Speedy, R. J. & Angell, C. A. Isothermal compressibility of supercooled water and evidence for a} \]
\[ \text{7. Speedy, R. J. & Angell, C. A. Isothermal compressibility of supercooled water and evidence for a} \]

Direct measurement of tropospheric ozone distributions from space

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The role of ozone in absorbing ultraviolet solar radiation is well known. Ozone also makes a significant contribution to the radiative balance of the upper troposphere and lower stratosphere, such that changes in the distribution of ozone in these atmospheric regions will affect the radiative forcing of climate.\textsuperscript{1,2} Furthermore, tropospheric ozone is the source of the hydroxyl radical which controls the abundance and distribution of many aerosol species, including greenhouse gases such as methane and hydrochlorofluorocarbons. Tropospheric ozone is produced photochemically in situ and is also transported down from the stratosphere, but the relative importance of these two sources to its global budget is poorly understood. High-quality tropospheric and lower-stratospheric ozone profile measurements are available from sondes and lidar techniques, but their geographical sampling is very limited. Complementary satellite measurements of the global ozone distribution in this height region are therefore required to quantify ozone’s tropospheric budget and its participation in climate-forcing and tropospheric...

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