

the polarization are high, the spin precession frequency depends on the polarization.⁷ The new magnetometer avoids that potential source of decoherence by operating quasi-statically near zero field. As figure 2 illustrates, the polarization of the optically pumped potassium vapor, initially aligned in the direction of the pump beam (the z direction), is rotated in the xz plane due to the torque from the y -component of the magnetic field. The linearly polarized probe beam, traveling in the x direction, undergoes optical rotation as it traverses the cell: The beam's polarization is rotated by an angle proportional to the x -component of the spin magnetization. The angle of rotation is effectively detected by passing the probe beam through a linear polarizer. Only the perpendicular polarization induced in the probe beam is detected by the photodiode array.

Atomic magnetometers can be susceptible to another major cause of spin relaxation: collisions with the cell wall. Paraffin coatings are often used to reduce wall-induced spin decoherence; the Princeton–Washington group instead filled their magnetometer cell with several atmospheres of helium-4 buffer gas. At that pressure, the diffusion of potassium atoms is severely reduced, so that the atoms typically diffuse only a few millimeters during the polarization lifetime.

The short diffusion length has another important benefit: Since the spins drift so little during a measurement, different slices of the magnetometer cell can be used for simultaneous, essentially independent multichannel measurements. The effective volume of the magnetometer is thus only about 0.3 cm^3 , much smaller than the 1000 cm^3 or so typically

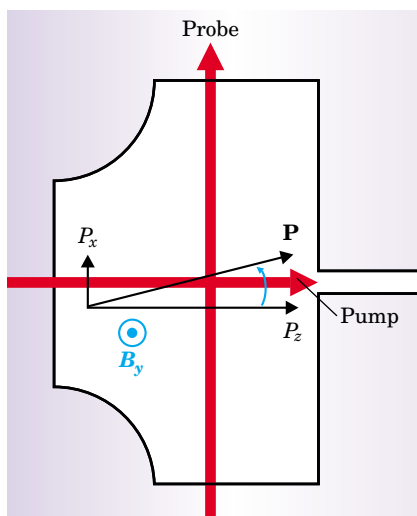


Figure 2. Optical rotation is used to measure B_y , the component of the magnetic field perpendicular to both the pump and probe laser beams. That field component rotates the potassium polarization $\mathbf{P}$, giving it a projection P_x onto the x -direction. The polarization angle of the probe beam is rotated by an angle proportional to P_x . (Adapted from ref. 1.)

found for other atomic magnetometers. The photodiode detection array, with seven elements separated by about 3 mm, illustrates the potential of the device: The array provides a one-dimensional map of the magnetic field in the cell. By numerically combining the signals from different channels, background magnetic noise can be rejected, and first- and higher-order field gradients can be obtained.

One inescapable constraint of the new magnetometer is that, to be in the requisite limit of fast spin exchange, the background field needs to be very

small, well below 100 nanotesla (1 milligauss) or so, orders of magnitude below Earth's field. Screening is therefore required. Furthermore, variations in the laboratory and Earth's field can be on the order of 100 picotesla, and can thus dwarf the extremely small fields sought in the most sensitive experiments. Romalis and company utilized several magnetic shields made of so-called mu-metal, a high-permeability alloy, to screen their experiment from background fields; three orthogonal sets of Helmholtz coils within the shielded enclosure were used to further control the field.

Thermally induced currents in the magnetic shields were the largest source of noise in the initial demonstrations of the magnetometer; they limited the sensitivity to about $0.5 \text{ fT/Hz}^{1/2}$. Romalis notes that through optimization—using superconducting magnetic shields, for instance—the magnetometer should be able to get much closer to its theoretical shot-noise sensitivity limit of $0.01 \text{ fT/Hz}^{1/2}$.

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Experiments Vindicate a 50-Year-Old Explanation of How Liquid Metals Resist Solidification

A metal's density barely falls on melting. One might guess, therefore, that metal atoms in the liquid phase pack together with almost the same efficiency and with almost the same order as in the solid phase. And—to continue this line of speculation—if one tried to cool a liquid metal below its equilibrium melting point, the few disorderly atoms would easily fall into line with the ordered majority and the liquid would promptly solidify.

In fact, as David Turnbull and Robert Cech showed in 1950, liquid metals can be cooled tens to hundreds of degrees below their equilibrium

Diffracted x rays reveal a sequence of structural changes in a levitated drop of metal as it cools and freezes.

melting temperatures without solidifying.¹ The trick is to prevent any impurities or other extraneous components from nucleating the nascent solid.

According to classical nucleation theory, a liquid solidifies when thermal fluctuations push it over an energy barrier. This nucleation barrier, W , depends on ΔG , the difference between the free energy of the liquid and solid phases. Specifically, $W \propto \Delta G^{-2}$. As a liquid cools, ΔG increases and

lowers the nucleation barrier.

But classical theory also has W proportional to γ^3 , where γ is the energy of the interface between the liquid and solid phases. Turnbull and Cech could undercool their samples because, for metals, the interfacial energy is far higher than one might expect based on density alone.

In 1952, to account for the unexpectedly large γ , Charles Frank put forward a now classic hypothesis.² It's

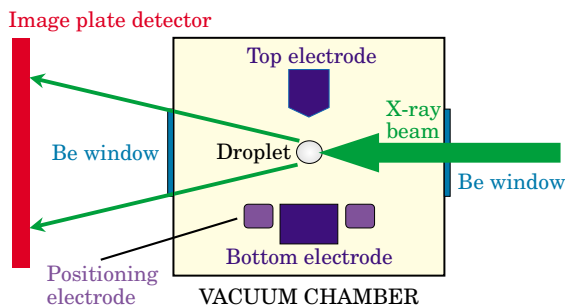


Figure 1. Schematic diagram of the electrostatic levitation chamber installed in an x-ray beamline. (Courtesy of Ken Kelton.)

possible to undercool metals, he argued, because of a fundamental mismatch in the way atoms arrange themselves in the liquid and solid phases.

According to Frank, atoms in the liquid possess a short-range order based on the icosahedron. One of Plato's perfect solids, the icosahedron has 20 triangular faces.

Frank picked icosahedral order because it's among the tightest and least energetic ways to arrange a small number of atoms. But because of their fivefold symmetry, icosahedral clusters can't combine to form a regular crystal. Frank saw that the energy cost of creating an interface between such structurally incompatible phases would be high.

When Frank published his paper, he didn't know about quasicrystals, some of which possess icosahedral order. But if he had known about them, he might have proposed the following test of his hypothesis:

Identify a material that has both a metastable quasicrystalline phase and a stable crystalline phase. Melt the material and let it cool. The falling

temperature lowers the nucleation barriers of both the quasicrystalline and crystalline phases. But because the liquid and quasicrystal phases have similar order—and hence a smaller γ —the quasicrystalline phase has the lower barrier and will solidify first. Eventually, the temperature drops to the point that the second barrier is low enough for the metastable phase to hop over and form the crystal.

Ken Kelton of Washington University in St. Louis, Missouri, didn't set out to perform this hypothetical task, but that's what he and his collaborators ended up doing. Their project, which involved levitating drops and using a state-of-the-art synchrotron, not only proves Frank's hypothesis, but also challenges theories of how crystals form.³

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Electrostatic levitation

Undercooling liquid metals is difficult. Even if a sample is free from impurities, any bump or crevice on the walls of the vessel that contains it can nucleate the solid phase at the equilibrium melting temperature.

Turnbull and Cech addressed the container problem by melting samples on flakes of amorphous silica. They assumed that the amorphous substrate would be a poor nucleator of crystalline structure. But ideally, one dispenses with a container. Thanks to surface tension, a drop of molten metal holds itself together. So, to achieve the containerless ideal, one levitates the drop and, for tracking structural changes, keeps it motionless in a beam of x rays or neutrons.

Several levitation methods exist.

Kelton opted for electrostatic levitation and, for help, turned to Jan Rogers of NASA's Marshall Space Flight Center in Huntsville, Alabama. Rogers and her coworkers Bob Hyers, Tom Rathz, and Mike Robinson developed the levitation chamber that appears on this month's cover and schematically in figure 1.

Before electrostatic levitation can begin, the initially solid drop is charged by induction. Electrodes above and below the drop create the levitation field, which, being electrostatic, lacks minima. Keeping the drop in place, therefore, is like balancing an upended broom: It requires an active feedback system. The Marshall feedback system uses cameras and computer control. With it, the 2-mm-sized drop can be held steady with a precision of 50 μm .

A laser melts the drop, which cools radiatively. The drop's thermal radiation spectrum provides the temperature diagnostic.

Recalescence

Kelton's original plan was to study titanium-zirconium-nickel. The alloy forms metastable icosahedral quasicrystals, but Kelton was focusing instead on the alloy's stable crystalline phase, a complex polytetrahedral arrangement called C14 Laves.

In preliminary levitation experiments at Marshall, Kelton and his Washington University colleagues Geun Woo Lee and Anup Gangopadhyay measured the temperature of a cooling drop of Ti-Zr-Ni. As figure 2 shows, the drop's steady decline in temperature is interrupted twice by two abrupt jumps. The jumps, termed recalescences, correspond to the release of latent heat at a phase transition.

Kelton suspected that the first recalescence signaled the formation of the alloy's metastable icosahedral phase, followed five seconds later by the formation of the C14 Laves phase. Viewing the metastable phase through an optical microscope confirmed its fivefold symmetry (figure 2). Here, Kelton realized, was a likely material for testing Frank's hypothesis.

Confirming Frank's hypothesis involves not only undercooling the right material, but also measuring its atomic structure. And that involved a trip to the Advanced Photon Source

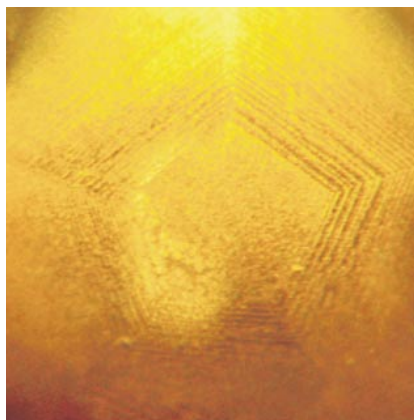
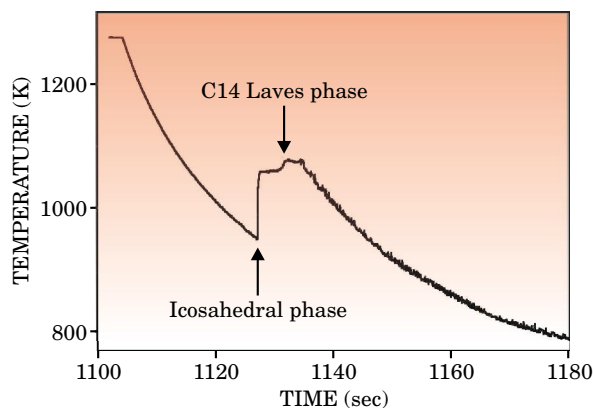


Figure 2. As a molten drop cools, its temperature rises sharply at two specific phase transitions (left). First, when the liquid forms the metastable icosahedral phase, which is quasicrystalline, and later when it forms the C14 Laves phase, which is crystalline. An optical micrograph (right) of the 2-mm-sized drop in its metastable state reveals pentagonal ridges. (Courtesy of Ken Kelton.)

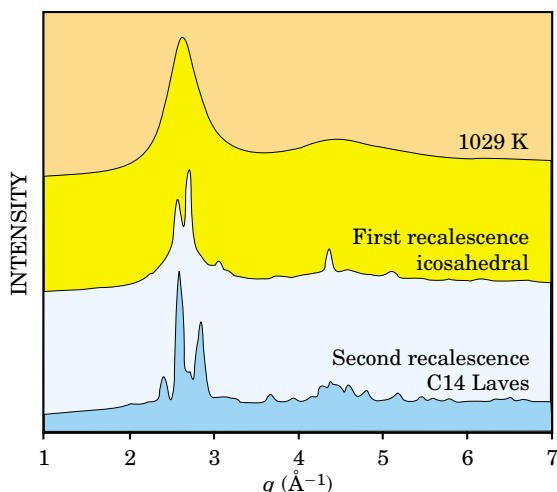


Figure 3. X-ray diffraction patterns capture the structural changes as the molten alloy (top) cools to solidify first into the icosahedral phase (middle) and then to the C14 Laves phase (bottom). The peaks occur at the predicted locations and are plotted as a function of the momentum transfer $q = 4\pi \sin\theta/\lambda$, where θ is the scattering angle and λ is the x-ray wavelength. (Adapted from ref. 2.)

at Argonne National Laboratory in Illinois. At the APS, Doug Robinson and Alan Goldman helped Kelton and his team to position the electrostatic levitation chamber in one of the synchrotron's beam lines.

A so-called third-generation synchrotron source, APS produces x rays of high brightness and high energy. Both qualities were invaluable for Kelton's experiment: The brightness made it possible to collect data with high signal-to-noise on the few-second timescale of the solidification, while the energies (125 keV, $\lambda = 0.99$ Å) made it possible to do a transmission experiment rather than a more difficult reflection experiment.

Figure 3 shows three representative diffraction patterns taken at different stages after the laser had melted the drop. The peaks appeared in the right places for both the solid icosahedral and C14 Laves phases. Frank was vindicated.

Nucleation theory

Figure 3 captures snapshots of the two solid phases, but Kelton and his colleagues could also obtain diffrac-

tion patterns at various points along the cooling curve. That's especially interesting for comparing experiment with theories of how crystals form.

Diffraction patterns depend on experimental setup. To compare experiment with theory, one calculates structure factors $S(q)$, where q is the momentum transfer. Constructing $S(q)$ from data involves modeling various aspects of the experiment, such as the transmission of the levitation chamber's beryllium windows. Constructing $S(q)$ from theory involves choosing an interatomic potential then doing either a large-scale computer simulation or an approximate theoretical analysis.

In the early 1980s, before the discovery of quasicrystals, Frank's ideas about local icosahedral ordering were applied to the formation of metallic glasses. Harvard University's David Nelson and his graduate student Subir Sachdev calculated temperature-dependent structure factors for glass-forming liquids.⁴ At large values of q , which probe short-range order, their $S(q)$ exhibits a pair of peaks and a shoulder that grows as the temperature drops. Kelton found the same features and the same temperature dependence in the $S(q)$ he derived from his data.

The existence of icosahedral order in the solidifying liquid has implications for classical nucleation theory. In that picture, nucleation starts, or fails to start, in small volumes. When the volume occupied by the nucleating phase exceeds the so-called critical volume, fluctuations favor the formation of the new phase.

From his data, Kelton derived both the size of the icosahedral clusters in the liquid and the critical volume. Both turned out to be a few nanometers across. The similarity of the two

scales suggests that a liquid metal isn't a structural blank slate. Structural correlations in the liquid could affect crystallization.

The small scale of the critical volume reveals a limitation of classical theory. When the crystallizing action takes place on the scale of a few tens of atoms, it's unlikely that a clear-cut, classical interface is appropriate. The challenge is to make nucleation theory more atomistic.

Other levitations, other systems

That a single system, Ti-Zr-Ni, was observed to form a quasicrystalline phase and then a crystalline phase was the key to proving Frank's hypothesis. But the 50-year-old theory had received impressive support from similar work done by other groups.

The first to study the structure of levitated drops were Dirk Holland-Moritz of the German Aerospace Research Establishment (DLR) in Cologne and his collaborators. The DLR team used electromagnetic levitation, which exploits an EM field to provide both levitation, through Lenz's law, and heating, through surface eddy currents.

Ten years ago, the DLR team showed that systems that have a high degree of icosahedral order in the solid phase can be undercooled further than systems that lack or have less icosahedral order.⁵

And last year, the DLR team and their collaborators from two French institutions—Paris-Sud University and the Center for Nuclear Studies in Grenoble—demonstrated for four elemental metals and three alloys that the further a liquid undercools, the greater its icosahedral order.⁶

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Stretchable Conductors Help Clear the Path to Skinlike Large-Area Devices

Sensitive skin" is the delicate name for a visionary technology: thin flexible large-area sensor arrays. With sensitive skin, one could endow robots with the information-gathering

tools they need to work in unstructured environments; one could clothe heart patients with shirts that monitor arrhythmia; one could equip food handlers with gloves that detect

Conducting stripes of gold foil can be stretched significantly when they're stuck to a rubbery substrate.