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About the Cover

NASA photograph of Callisto, one of the two largest moons of Jupiter, showing the Valhalla region (large crater surrounded by circular cracks). The darkish surface is about what most astronomers expected to see on the basis of their Earthbound observations. Ganymede, the twin of Callisto in most respects, looks strikingly different. The article on p. 1 discusses our measurements of the strength of ice under extreme conditions, undertaken to help us model the evolution and current state of these icy moons.

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Synchrotron-Radiation Research Project

Synchrotron-radiation x-ray sources provide intense x-ray beams with very desirable characteristics. The x-ray beams are continuously variable in energy and come in repetitive short bursts, are highly collimated, and have a high degree of linear polarization. This unusual combination of characteristics makes them valuable for a wide range of research fields, affecting virtually all of our Laboratory research programs.

In December 1982, in collaboration with several campuses of the University of California, the Los Alamos National Laboratory, and the Sandia National Laboratories, we proposed construction of two synchrotron-radiation beam lines at the Stanford Synchrotron Radiation Laboratory (SSRL). These beam lines would be used for both fundamental and applied research. Our proposal received a favorable review by SSRL's review panel last spring and was accepted by SSRL on September 27, 1983.

Funding to begin the project has been approved by the U.S. Department of Energy and Congress, and design preliminary to construction has begun. We expect to complete the building that will accommodate the beam lines this summer and to have the beam-line components ready for installation by next summer (1985).

One beam line will extend from a bending magnet on the SSRL electron storage ring and initially will have one experiment station at 5- to 150-eV photon energy. It will be used largely for studies in chemical and surface sciences. Provision also will be made for two possible additional stations, one for hard x rays in the energy range from 3 to 40 keV and the other for white light in the 5- to 40-eV energy range.

The second beam line will extend from a wiggler in a straight section of the storage ring. A wiggler is a series of magnets that oscillates the electron beam without producing any net deflection. This is equivalent to many bending magnets in series, and thus the wiggler can produce x-ray beams of unusually high intensity.

Our wiggler line will be one of the most powerful x-ray sources in the world. In the energy range from 0.1 to 10 keV, it will produce more than 10^{15} photons per second per horizontal milliradian in an energy bandwidth of 1%. It will have two experiment stations, one for soft x rays (from about 0.1 to 2 keV) and one for hard x rays (from about 1.5 to 50 keV). We expect it to be useful for research in biology, atomic physics, chemical and materials sciences, x-ray diagnostics, and new x-ray instrumentation.

With the completion of these beam lines, the Laboratory will have a new, world-class research capability. Together with the other members of the team, we look forward to years of fruitful research at SSRL.

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Briefs

Raman Spectroscopy of Shocked Water

We have performed the first measurements of spontaneous Raman spectra emitted from water shocked to high pressure (7 GPa) by the impact of a projectile from our two-stage light-gas gun. Water is one of the detonation products of many explosives. This technique enables us to explore the physics and chemistry of various detonation products to better understand the detonation process.

In the spontaneous Raman effect, a photon of a known frequency is absorbed by a molecule and reemitted (scattered) at a different frequency. The amount of the change in frequency corresponds to a vibrational frequency of the molecule. Hence, we can study the structure of the scattering molecule (i.e., measure its various vibrational frequencies) by analyzing the scattered light with a spectrograph.

We used a frequency-doubled neodymium:yttrium-aluminum-garnet laser (wavelength of 532 nm, pulse length of 10 ns) to probe a sample of water shocked to a pressure of 7 GPa and a temperature of about 640 K. A lens

Fig. 1

Spontaneous Raman spectrum of shocked water (7 GPa, 640 K). Probe laser light is confined to the narrow line at 532 nm. The broad peak is Raman-scattered light displaced from the laser line by the OH-stretch vibration of the water molecule. The broad continuum (below the band) arises from light emitted by hot gases in the target chamber.

system collects the spontaneous Raman light scattered at right angles to the probe laser beam and sends it to a spectrograph. Although the signal is extremely weak (only about 20 pJ), we can record a spectrum covering wavelengths from 400 to 700 nm during the laser pulse by using a high-gain, gated, microchannel-plate image intensifier at the focal plane of the spectrograph. The output of the intensifier is recorded on sensitive photographic film.

The Raman spectra of most molecules feature narrow, well-defined lines. The Raman spectrum of the OH-stretch vibration in water is broad, however, because of the influence of weak O-H bonds between some of the water molecules.

In our spectrum of shocked water (Fig. 1), the OH-stretch band is roughly 20% narrower than it is for unshocked water. We also observe a small shift in the peak ($+15 \text{ cm}^{-1}$) that may be due to compression of the molecule. We believe that under the shocked conditions, some of the weak O-H bonds between water molecules break, reducing their contribution to the bandwidth and narrowing the band.

This combination of shock-wave techniques with sensitive spectroscopy yields new information about the dynamic chemical processes occurring in shocked substances. In future experiments, we hope to observe the theoretically predicted formation of molecular ions in water ($2\text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}_3\text{O}^+$) and to obtain spectra from other materials such as hydrogen, nitrogen, and hydrocarbons.

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The Strength of Ice

To model the evolution and current state of Jupiter's two largest moons, which are very cold and about 75% ice by volume, we need to understand the flow properties of ice under extreme conditions. With our new testing apparatus, we have determined that ice is much weaker at low temperatures (below 160 K) than had been believed.

It has long been known that Jupiter's two largest moons, Ganymede and Callisto, have about the same composition (mostly ice) and surface temperature (about 100 K). One possible projection of what their surfaces might look like is based upon a direct extrapolation of known data. Over temperatures from 220 to 273 K and pressures from 0 to 20 MPa, the rheology and general physical properties of ice are extremely well known, better, in fact, than those of any other kind of rock (see the box on p. 4). Therefore, astronomers had a fair idea of what to expect from actual close-up pictures of these moons, although they were prepared for the unexpected.

When the Voyager spacecraft sent back pictures of Callisto and Ganymede, in 1979, astronomers received a pleasant surprise—a new mystery to unravel. Callisto looked about as expected, with a dark surface and many craters. The surface of Ganymede, however, was characterized by about equal proportions of dark, heavily cratered patches and bright, lightly cratered bands, evidently fresh material that had flowed in long after the original surface had formed (Fig. 1). Furthermore, close examination revealed that the craters on both Callisto and Ganymede had slumped, as though

the crust was viscous. According to extrapolations from the best available information, ice would not have behaved in that way. Either the surfaces of these moons were not made entirely of ice or the existing information was wrong.

Before we attempt to unravel this mystery, let us first consider what was known about Jupiter's moons at that time. Ganymede and Callisto have been under observation for centuries. Their masses, densities, color (darkish white), albedo, surface chemistry, and surface temperatures have been measured repeatedly. All evidence pointed to a chemistry similar to that of a dirty snowball.

Just what the "snow" consists of presumably was settled by considering how solid bodies condense from the solar nebula. The only likely candidates (plentiful, simple, low-density compounds with freezing points in the right range) are water, ammonia, and methane. Neither ammonia nor methane could condense at the temperatures and pressures in the solar nebula at the orbit of Jupiter (although they could at the orbit of Saturn). Hence, the low densities of Ganymede and Callisto (less than 2 Mg/m^3) indicate that only about half of their mass is silicate rock and the rest is water ice, perhaps with traces of

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Fig. 1

The surface of Ganymede, photographed by the Voyager 2 spacecraft in 1979 from a distance of 312 000 km. The width of the surface shown here is about 1200 km. The darker cratered surface, evidently older, appears to have cracked and spread apart or partially foundered and filled either with magma (water) or with viscous, flowing fresh ice. Furthermore, on close examination, the craters appear to have slumped. According to the best information available at the time this picture was taken, ice should be too strong at the measured surface temperatures (100 K) to flow in this way. Our recent measurements, however, indicate that ice at low temperatures is much weaker than predicted.

dissolved ammonia and methane. By volume, the proportion of ice must be close to 75%.

Knowing this much about the overall composition of these Jovian moons, what can we deduce about their surfaces? No one really knows what the structure of these bodies was when they first formed. In one theory, a rocky core solidified first and, when it had cooled enough, water and then ice condensed onto it. In another theory, all the ice and rock condensed into small particles before there were any moons or planets. Then, these small particles clumped together, forming the larger bodies, with the result that the ice and rocky material would be homogeneously mixed throughout.

As it happens, the current state of these moons does not require us to choose between these two theories. Most astronomers agree that, after the first 500 million years (still several billion years ago), the end result would be much the same. To convince ourselves of this,

let us follow the evolution of the homogeneous (second) model over its first 500 million years and see what may have happened (Fig. 2a). First of all, we must assume that rocks on Callisto and Ganymede (just like those on Earth) contain heat-generating radioactive isotopes such as potassium-40 and thorium-232. Heat was being generated and hardly any being radiated away; with a surface temperature of 100 K, the radiation efficiency is exceptionally poor. Thus, the interior temperatures must have begun to rise rapidly. There probably was enough heat to melt the interior ice, just as there apparently was enough heat to melt the rocks on Earth.

Heat-flow calculations and the phase diagram for ice (Fig. 3) suggest that the first melt would have occurred several hundred kilometres below the surface. The silicate particles liberated by melting then would sink, swiftly converting their gravitational potential energy to heat, causing further melt, and, in turn, causing more gravitational heating and so on. This would result in a major rearrangement of the moon's interior. All the rocks would sink to the center, and the melting probably would have risen to within a few kilometres of the surface.

The situation of the remaining crust would be delicate, to say the least. The crust would be too heavy to float (since it would still contain rocky particles), but, as long as it remained a relatively uniform layer, it might be rigid enough to stay up. Any substantial break, as from a major meteor impact, for example (these were frequent in that era), would cause the crust to break up and slide into the depths.

Upon break up of the crust, the water would be suddenly released from pressure and exposed to vacuum (neither Callisto nor Ganymede has an appreciable atmosphere); it would boil briefly and then freeze solid to a great depth. This ice would form from clean water, however, since all the heavy particles would long since have settled out of it. Therefore, the homogeneous model produces the same configuration as the heterogeneous model, namely, a small rocky core surrounded by a thick layer of ice and maybe some water.

What happens next depends strongly on how ice flows under stress (Fig. 2b). Ice that flows easily would be able to dissipate the heat of radioactive decay by solid-state convection. Ice near the rocky core would be warmed by the radioactive decay in the core and could rise close enough to the surface, warming the surface a few degrees and making it a better radiator. This would keep the interior of the moon cold enough that it would remain completely frozen. Conversely, ice too strong to flow would increase the likelihood that liquid water remains deep in the interiors of Callisto and Ganymede.

Thus, we have a coherent theory of why we should expect the outer layers of both of these moons to be mostly water

ice. The question remains, however: why are the surfaces of Ganymede and Callisto so different? To find an answer, we investigated the properties of ice in a joint project with the U.S. Geological Survey, Menlo Park, California, to model the physical processes, past and present, within these bodies.

Preparing the Ice Samples

For our experiments, we require polycrystalline ice specimens of uniform composition and dimensions. These samples then are subjected to uniform hydrostatic compression, and we measure their strength under axial compression loading. We mold the ice samples using special precautions to avoid strains and voids and cut them to

(a) The first 500 million years

(b) The next 4 billion years

Fig. 2

Stages in the evolution of Ganymede and Callisto, the two largest moons of Jupiter, assuming that they started with uniform composition (dirty snow). The Roman numbers refer to the different ice polymorphs (high-pressure forms). (a) The first 500 million years. Radiogenic heating converts all of ice VIII into ice VI and most of ice II into ice V, and melting occurs at the boundary between ice V and ice VI. Gravitational heating, caused by the fall of rocks released by melting, then melts all of the ice except a thin crust. (b) The next 4 billion years (to the present). There are two alternative scenarios, depending on the (unknown) strengths of the various ice polymorphs. If the ice is weak enough to rise when heated and fall when cooled, it could carry away enough heat to freeze all the water beneath it. If not, there may be a thick ice crust and then, below the crust, an ocean hundreds of kilometres deep.

a standard size. Each sample is encased in a thin-walled indium jacket (whose strength is negligible in comparison with that of ice); this permits us to constrain the specimen from the outside as it would be if the pressure were being applied by surrounding ice.

The molding process begins with the production of ice seeds as we crush clear ice taken from a vat of partially frozen deaerated distilled water. We pack the seed ice into stainless steel tube molds and evacuate these for about 30 minutes at 248 K to degas the ice surfaces. Then, we add ice-cold distilled water, degassed by boiling and then cooling under its own vapor, and allow it to saturate the molds for about 5 to 10 minutes. Next, we set the molds on a copper plate at the bottom of a deep freezer, insulating the sides of the molds with styrofoam. Freezing thus proceeds upward from the bottom of the molds, concentrating the strains of freezing (and any resulting voids) into a discardable seed-free region at the top of the mold. Finally, we remove the samples by gently warming the tubes and pushing the ice cylinders out. By starting with ice seeds, we ensure that the finished specimen will have uniform granules and no preferred crystal orientation.

(Obviously, the ice on Callisto and Ganymede formed without these

precautions and so probably differs from our samples. However, pure ice offers a logical starting point. After we have established its properties, we plan to extend our experiments to include the effects of impurities, nonuniform grain size, and nonrandom grain orientation, thereby more closely approximating the ice of these moons.)

As molded, the ice cylinders are 25 mm in diameter. We shave the ends of each cylinder flat and perpendicular to its long axis to a length of about 64 mm. Then, we seal each sample into the thin-walled (0.5-mm) indium tube capped at each end by a 19-mm-thick stainless steel disk coated with indium, using a soldering iron and keeping all constituent parts (ice, tube, and end caps) cold (195 K) in a dry ice/alcohol bath.

Deformation Apparatus and Testing

At the heart of the experimental apparatus is a 600-MPa triaxial pressure vessel (Fig. 4) surrounded by a cryostatic tank. A tensile reaction frame connects

The Kinds of Ice

Everyone is familiar with the three different states of water: vapor, liquid, and solid (ice). What may be less familiar is the notion of different kinds or polymorphs of ice. All the ice we will ever encounter on Earth is of one type, called ice I_h (Fig. 3). Ice I_h is a remarkable material, unique in many properties. Water is one of the few liquids that expands when it is cooled to near its freezing point and expands even more when it freezes. Thus, ordinary ice (ice I_h) floats. This property of water is one of the factors that makes the Earth habitable, since, without their insulating blankets of ice, the polar seas would freeze solid and never thaw, producing a permanent ice age.

A corollary of this property is that high compression can melt ordinary ice, even below its normal freezing temperature, as indicated by the slope of the upper boundary of the ice I_h region in Fig. 3. This is why ice skaters can glide without friction; their weight compresses

Fig. 3

Phase diagram for water. Dashed lines are extrapolations. The numbers in parentheses represent relative densities of the phases projected to 0.1 MPa and 98 K.¹ The dotted curve is a possible pressure-temperature profile for Ganymede and Callisto. Ices VII and VIII are higher-pressure polymorphs, off scale to the right. Ice IV is a metastable form within the Ice-V field. The shading denotes the region explored experimentally in this study.

the vessel to a screw-loading mechanism below it. Pressure is generated by a conventional separator-intensifier system using helium, nitrogen, or argon (depending on the desired temperature and pressure) and is measured with a Heise bourdon tube gauge.

For moderately low temperatures (273 to 160 K), we fill the cryostat with about 30 litres of alcohol and cool it by circulating chilled alcohol through a cooling coil as needed to maintain a constant temperature. For lower temperatures and occasionally for 195 K, we use various cryogenic mixtures. In these latter cases, thermal buffering by the latent heat of melting or vaporization provides temperature stability.

In most cases, we chill the vessel to test temperature before introducing the sample. To insert a sample, we unscrew the top nut and extract the top plug (containing the force gauge), allowing access to the sample chamber. After reclosing and pressurizing the vessel, we usually allow at least an hour for the sample to come to thermal

equilibrium and causes a small amount of melting, thereby lubricating their skate blades with a very thin film of water (temporarily melted ice). This property also enables glaciers to work their way around obstacles and creep to the sea.

Under extreme pressures, however, ice I_h changes into new kinds of ice. The ice molecules fall into more compact arrangements and the material acquires new properties. Each of these changes is accompanied by a change in volume. All of these ices (II through IX) are heavier than water (the numbers in parentheses in Fig. 3 are densities).

Although these heavy ices are found only in laboratory experiments on Earth, they are common elsewhere in the solar system. They are the normal state of ices below the surfaces of the icy moons of Jupiter, for example. The properties of these heavy ices must have strongly influenced how these bodies evolved and how they acquired their present form. Hence, to understand the features we observe on these moons, we must study the properties of all kinds of ice.

equilibrium. We always leave a small gap between the top of the jacketed sample and the force gauge to avoid preloading the sample.

To measure the strength of a sample, we compress it with the moving piston and measure the load as a function of time with the force gauge (whose sensitivity is better than ± 0.1 MPa). Because the force gauge is inside the vessel, friction along sliding seals introduces no error in the reading of the force gauge.

At the end of the run, we must test to see if the indium jacket is still leaktight, especially for samples that appear

Fig. 4

Our 600-MPa triaxial testing apparatus. Axial load on the sample is determined by measuring the elastic distortion of the force gauge; the measurement is unaffected by friction on the sliding seals. A cryostatic tank surrounding the apparatus may be filled with any of various refrigerants for experiments at different temperatures.

(a)

(b)

Fig. 5

Samples, still encapsulated in their indium jackets, exhibiting the two principal behaviors under compression. (a) Brittle fracture. The single fracture plane is inclined 46° with respect to the specimen axis. The inset shows a typical run record (stress difference vs time) for brittle behavior. The displacement rate of the piston was initially 2.2×10^{-2} mm/s and later changed to 2.2×10^{-4} mm/s (to the right of the dashed line). (b) Ductile flow. Originally, this sample and the one in (a) had the same height and diameter; this sample now is about 9 mm shorter and 1 mm larger in diameter at its widest point than the one in (a). The inset shows a typical run record for ductile behavior: The displacement rate was 2.2×10^{-3} mm/s. The confining pressures for brittle (σ_{UH}) and ductile (σ_{SH}) specimens also are shown.

weaker than normal. (Any leak would decrease the pressure differential forcing the jacket wall against the sample, thus reducing the confinement and permitting the sample to fail prematurely.) To test for leaks, we release the pressure, open the vessel quickly, and immerse the sample in cold alcohol (195 K). If any of the pressurizing gas has leaked into the sample, it will gradually seep back out, forming bubbles that plainly indicate even pinhole leaks too small to be seen. Most of the jackets remained leaktight and passed this test.

Mechanical Test Results

To date, we have subjected nearly 100 samples to constant-strain-rate compression tests. The shaded area in Fig. 3 represents the range of confining pressure and temperature in these tests. Pressures ranged from 0.1 to 350 MPa, temperatures from 77 to 258 K, and strain rates from 3.5 to $350 \times 10^{-6} \text{ s}^{-1}$. Most of these tests were in the ice I_h field, although a number of the more recent tests were in the ice II and ice III fields. The ice samples displayed three basic types of inelastic behavior—brittle, ductile, and pseudoductile.

In brittle fracture (Fig. 5a), an initially linear stress-strain curve suddenly drops at one or more points. These events are often accompanied by a loud report. The deformed samples display one or more macroscopic faults or a complex crush zone, develop no significant radial strains or barreling, and exhibit little or no work hardening or plastic flow.

Ductile flow (Fig. 5b) is characterized by a continuous stress-strain curve that exhibits a stress maximum after initial yield followed by a smooth decrease in stress with increasing strain. Beyond a few percent permanent strain, the stress supported by the samples usually stabilizes to a nearly steady value. Ductile samples show a relatively uniform radial expansion along their central two-thirds and taper near their ends. Small surface irregularities are typical.

Pseudoductile flow occurs only at confining pressures approaching 200 MPa. The stress-strain curve mimics that for ductile flow, but the mechanism

appears to be a progressive phase change from ice I_h to ice II.

The Brittle Field

At the three coldest temperatures (77, 113, and 143 K), we observed only brittle behavior. We encountered only ice I_h at these temperatures even though our run conditions actually put us into the ice II (or ice IX) stability fields (Fig. 3). The reason is that at temperatures below 200 K, any of these phase transformations requires either a large overpressure or an extremely long time.

Samples deformed at room pressure tended to crush near one end. In addition, their strength tended to drop in a series of small events, giving the load-displacement record a stair-step appearance. Those samples tested under higher confining pressure behaved quite differently, typically showing only one or two large fractures and having a single (usually audible) failure event involving a large strength reduction (20 to 50%).

The large fractures were invariably oriented near 45° to the loading direction, regardless of the magnitude of the (nonzero) confining pressure, and did not necessarily intersect the ends of the samples. The brittle strength of a sample was considerably higher with confining pressure than without (Fig. 6), but on up to about 50 MPa. Above 50 MPa, the brittle strength was independent of confining pressure.

We also observed brittle behavior at 158 and 195 K, but found that it could be suppressed by lowering the strain rate. Most of the range of pressure and strain rate accessible to us at 195 K was in the ductile field (Fig. 3). The qualitative character of brittle failure at 158 and 195 K was the same as at 143 K and below. Viewed across the temperature range from 77 to 195 K, brittle strength showed only a very weak negative temperature dependence (in contrast to that in the ductile field).

We inadvertently conducted one experiment on ice II at 158 K. This polymorph formed when we pressurized an ordinary jacketed sample of ice I_h to about 330 MPa, more than 150 MPa beyond the equilibrium boundary between ice I_h and ice II (Fig. 3). The

transition caused a sudden volume decrease, which we observed as a pressure drop. Also, our loading piston had to travel several millimetres farther than it did for ice I_h samples (i.e., the sample had shortened). We ran the test at our fast strain rate (about

$4 \times 10^{-4} \text{ s}^{-1}$). The sample failed by brittle fracture but was much stronger than the other brittle samples at 158 K (Fig. 6).

Because the failure strength of ice is independent of confining pressure (above 50 MPa), we can infer that the failure

Fig. 6

Strength vs confining pressure for the five coldest temperatures used in this study: (a) 77 K, (b) 113 K, (c) 143 K, (d) 158 K, and (e) 195 K. The squares represent tests at a strain rate of $3.5 \times 10^{-6} \text{ s}^{-1}$ and the triangles and circles represent tests, respectively, at strain rates 10 and 100 times greater. Solid points denote brittle behavior, open points represent ductile behavior, and half-open points indicate transitional behavior. The approximate location of the brittle-to-ductile transition is shown by vertical gray lines. Blue lines indicate the approximate location of the transition from ice I_h to ice II or to ice IX. Most runs produced a single data point. Differential stress in the ductile run at 180 MPa in Fig. 6d (the open square with vertical bars) showed anomalous up-and-down variations over the range indicated. Our first encounter with a polymorph other than ice I_h was the new-phase formation at 158 K (blue).

Fig. 7

Ductile strength vs confining pressure for the warmer temperatures used, 195 to 258 K. Most runs involved more than one axial load or strain rate, so they produced multiple data points. The symbol conventions are the same as in Fig. 6.

process requires no volume change before failure. If a volume change did occur, for instance from the creation of a few microfractures, some of the energy budget for failure would have to go toward doing work against the confining medium and the failure strength would increase with pressure. (This, in fact, is why the brittle failure of most ordinary rocks is pressure dependent.)

Any change in the shape of the sample can be resolved either as a volume strain or as a shear strain. If the volume strain component is absent, the failure must be fundamentally a shearing process. In an end-loaded cylinder surrounded by a uniform confining pressure, as in our tests, the maximum resolved shear stress lies on planes oriented at 45° to the long axis. Hence, although the brittle failure mechanism in ice seems to be unusual in comparison with that of most other rocks, the 45° fracture angle and the strength independent of confining pressure are, at least, self-consistent. We are now investigating the possibility that brittle failure in ice involves a local change of phase to either water or ice II.

The Ductile Field for Ice I_h

The behavior observed at 195 K and above was almost entirely ductile (Figs. 6e and 7). Ductile flow strength showed a strong positive dependence on strain rate and a negative dependence on temperature. At this point, we can resolve only a weak dependence upon confining pressure, which appears rather complex: ductile strength rises with increasing pressure to 80 MPa and then decreases. The relationship between strain rate, axial load, and temperature at fixed confining pressure (50 MPa) is shown in Fig. 8. Strain rate changes as the fourth power of the applied stress.

The temperature effect on strain rate is more complex. We have identified three regimes in which the temperature dependence can be summarized by a different activation energy. Above 243 K, the activation energy is about 91 kJ/mol; between 243 and 195 K, it is 61 kJ/mol; and below 195 K, it is only 29 kJ/mol.

Earlier work on polycrystalline ice, performed above 225 K, detected only

the first of these regimes.² When predictions of ice flow at very low temperatures were needed (for the study of the icy moons in particular), the high value of activation energy was generally presumed to apply. It now appears that such predictions vastly overestimated the strength of ice near the surfaces of the icy moons.

In tests done by other workers on single-crystal ice,² again generally at temperatures above 225 K, the measured temperature sensitivity was about 60 kJ/mol (near the value of our intermediate range of temperature sensitivity). It has been established that at the higher temperatures, where we find a high temperature sensitivity, the strength of ice is controlled by processes taking place along grain boundaries: sliding of grain-grain contact surfaces, aided perhaps by the formation of minute quantities of liquid water. Hence, the regime of intermediate temperature sensitivity may be the result of a change from inter- to intragranular control of

Fig. 8

Ductile flow data (differential stress vs the reciprocal of temperature) at a fixed confining pressure (50 MPa). On this logarithmic plot, the slope of the line at a constant strain rate is proportional to the activation energy, so that a break in the slope is often indicative of a change in mechanism. Open points represent actual data from Figs. 6a and e. The solid points represent data (interpolated in strain rate) from the literature.³ Dashed lines represent extrapolations to lower strain rates, based on our understanding of the low-temperature behavior. In this plot, we assume that the fracture strength is independent of strain rate.

plastic flow. We have, as yet, little information on what controls flow in the regime of low temperature sensitivity.

The Pseudoductile Field

At confining pressures near 200 MPa, we observed a radical change in behavior: the apparent strength decreased by a factor of five between 150 and 225 MPa. We even had one sample of essentially zero strength in a low-strain-rate run at 195 K and 200 MPa (Fig. 6e). By comparing displacement measurements during the runs with direct measurements of sample length afterward, we found that the samples exhibiting the anomalously low strength had expanded when the pressure was released. Since we had carefully eliminated voids in all samples, we conclude that the expansion came about as the result of a phase change from ice II back to ice I_h (which involves a 21% reduction in density, see Fig. 3), reversing a progressive phase change occurring while the load was being applied. This conclusion was fortified by the observation in three of the anomalously weak samples that the strength began to return as the transformation approached completion (Fig. 9).

The Ductile Field for Ice II and Ice III

Preliminary results of our measurements on ice II and ice III are given in Fig. 10. Again, we generated these samples by overpressurizing samples of ice I_h. However, we needed less overpressure at the warmer temperatures. At 248 K, for instance, the necessary pressure was 280 MPa,

about 70 MPa beyond the equilibrium transition pressure. We find that at equal temperatures and strain rates, ice II is stronger than ice I_h and its strength is only a little more temperature sensitive. Ice III is both much weaker and much more temperature sensitive.

We have not yet measured how the strengths of ice II and ice III depend on stress, but we have measured the pressure dependence. We found that, in contrast to ice I_h, ice II and ice III become steadily stronger with increasing pressure. This pressure-effect reversal mirrors the reversal of the pressure effect on melting temperature (Fig. 3). This finding lends credence to the speculation that there may be an empirical correlation between creep properties and melting temperatures in many materials.

Thin-Section Petrography

When we examine thin sections of the starting ice material, we see an equigranular texture with polygonal grain shapes and an average grain size of 1 to 2 mm (Fig. 11a). Optical measurements suggest that there is no preferred orientation of the individual grains. Although the whole specimens are clear, grain boundaries observed in thin sections are slightly cloudy and are decorated by arrays of small bubbles.

Figure 11b shows a sample that deformed by brittle fracture, developing a single fault inclined at about 46° to the load axis. In thin section, the fault zone is revealed as a complex structure involving microfracturing and fine recrystallized grains. The fault surface was still cohesive, but this may be due to annealing after deformation.

Fig. 9

Differential stress as a function of shortening for most of the runs plotted as open circles in Fig. 6e, illustrating the effects of the phase transition from ice I_h to ice II at higher pressures. Run 44 (100 MPa) is shown with dashed interpolations through two portions of the run where we slowed the strain rate to $3.5 \times 10^{-6} \text{ s}^{-1}$.

Figure 11c shows the result of ductile deformation at 195 K. The texture in this sample has been modified by partial recrystallization to smaller grain size with grain shapes that are more irregular than the original polygonal grains. This texture, a result of high-temperature recrystallization, is typical of rocks and ceramics deformed at temperatures greater than half their absolute melting temperatures.

Astronomical Implications

Our results concerning the rheology of ice I_h contribute little definitive data upon which to select one evolutionary model over the other. The data do, however, apply to processes occurring within the ice I_h layer. These include such tectonic activities as faulting, rifting, and viscous relaxation of impact craters, which are manifested in the surface topography recorded in such detail by the recent Voyager missions (see Fig. 1).

Fig. 10

Comparison of the steady-state strengths of ice I_h under a confining pressure of 50 MPa and ice II and ice III at 250 MPa and a constant strain rate of about $4 \times 10^{-4} \text{ s}^{-1}$. Ice II is stronger than ice I_h and its strength is only slightly more temperature sensitive. Ice III is much weaker than ice I_h ; it also is much more temperature sensitive.

(a) Starting material

(b) Brittle fracture

(c) Ductile deformation

Fig. 11

Thin-section photomicrographs of ice specimens, taken in transmitted light between crossed polarizing filters. (a) Starting ice material. Note the polygonal grains and the equigranular texture. (b) Brittle fracture, run at 158 K and 80 MPa. Note the fault inclined at 46° and the lack of textural

modification outside the recrystallized fault zone. This section is from the ice sample shown in Fig. 5a. (c) Ductile deformation run at 195 K and 50 MPa. Partial recrystallization is evident from the smaller grain size. This section is from the sample shown in Fig. 5b.

Taking a reasonable temperature profile for the ice I_h layer (Fig. 3) and extrapolating our strength data to lower temperature (Fig. 8), we can model the rheology of the upper 150 to 200 km of Ganymede and Callisto (Fig. 12). From this figure, for instance, we can determine the strain rate vs depth relationship required to maintain a constant differential stress through the ice I_h layer, or the stress vs depth relationship required to maintain a constant effective viscosity. (Effective viscosity is proportional to the ratio of differential stress to strain rate.)

As indicated earlier, our predicted viscosities at very low temperatures (Fig. 8) are many orders of magnitude lower than those predicted on the basis * of previous work. We realized, as a direct

result of our finding of a rather weak temperature sensitivity of flow (29 kJ/mol) below 195 K, that ice can be expected to be easily deformable over geologic periods near the surface on Ganymede and Callisto. However, the near-surface viscosities estimated to explain the observed features are a few orders of magnitude higher than those predicted in Fig. 12. We need more detailed calculations and better experimental resolution of the temperature sensitivity before we can determine whether the discrepancy requires us to postulate that the upper layers of the icy moons are made of something other than pure water ice.

Nonimpact fracture on Ganymede and Callisto must be restricted to depths of a few kilometres. Figure 12 indicates that a strain rate of about 10^{-9} s^{-1} (relatively rapid in geologic terms) is required to maintain a stress difference above 50 MPa (the lowest brittle strength of pure, intact ice as measured in this study) at a depth of 10 km on Callisto. Given the increasing temperature and pressure below 10 km, it seems unlikely that anything but a meteor impact could produce brittle failure (moonquakes) below that depth. If the rift pattern on Ganymede is suggestive of deeper faulting as some researchers have suggested,⁴ then the crust of that body may be a stronger material than we have been measuring here (perhaps a rock-ice mix). If interior temperatures were cooler in ages past, deep faults could have formed earlier in the evolution of the moons.

If the temperature-pressure profile in Fig. 3 is reasonably accurate, then Fig. 12 indicates that present-day large-scale convection involving any of the ice I_h layer would require stresses of the order of 1 MPa at depths of 100 to 200 km. We estimate that the rigid outer crust, whose lower limit is roughly defined by the point of strongest curvature in the lines of constant strain rate in Fig. 12, is only about 20 to 30 km thick. We must remember, however, that this conclusion hinges rather strongly on the arbitrary curvature of the temperature-pressure profile in Fig. 3 and on our experimental results below 195 K. Even if the

Fig. 12

Implications of our work for Ganymede and Callisto, calculated from Fig. 8 using the temperature-pressure profile in Fig. 3. Because Ganymede and Callisto have approximately the same temperature-pressure profile but not the same pressure-depth profile, individual horizontal scales are given in this figure. Given any two of the parameters (differential stress, strain rate, depth), the third can be determined from the figure. Also shown are values of effective viscosity, which is proportional to the ratio of differential stress and strain rate.

extrapolation of our results (Fig. 8) is valid, this estimate of crustal thickness could easily be off by a factor of two or three.

Since we have explored plastic flow mainly in ice I_h , we can shed little light on the likelihood of ductile flow of ice at depths below about 200 km on either Callisto or Ganymede where we would encounter higher ice polymorphs (see Figs. 3 and 12). In particular, we still can only speculate on the reasons why these two moons (which are so similar in size, temperature, and overall composition) should appear so different. However, our findings on the weakness of ice III suggest the possibility of large-scale runaway solid-state flow and thermal convection that may have been important in the evolution of Ganymede.

Summary

We have been investigating the strength and ductility of ice at temperatures down to 77 K and with confining pressures of up to 350 MPa, values typical of conditions within the larger moons of Jupiter. We observed both brittle and ductile behavior in ice I_h at temperatures below 195 K and ductile behavior alone (regardless of strain rate or pressure) at higher temperatures. We

also observed yielding that apparently is influenced by a phase change from ice I_h to ice II, accompanied by a large volume decrease, at pressures approaching 200 MPa. Additionally, we discovered temperature regimes in which ice I_h is much weaker than had hitherto been believed. Our preliminary measurements indicate that ice III is much weaker than ice I_h at comparable temperatures and strain rates. Our findings correlate roughly with and may help to explain apparent ice flow and viscous slumping of craters observed on the surfaces of Callisto and Ganymede. □

Key Words: Callisto; Ganymede; ice I_h ; ice II; ice III; planetary evolution; Voyager spacecraft.

Notes and References

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LLNL in the Developing Livermore Valley

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The Lawrence Livermore National Laboratory was established in 1952 in a tranquil and pleasant landscape of largely undeveloped grazing areas and crop lands. These surroundings are still to be seen to the south of the Laboratory, but in recent years urban development consisting of housing and light industry has been rapidly advancing from the west. If this trend continues as expected, within a few years even the land adjacent to the Laboratory will be filled with such developments. The aerial photographs presented here dramatically illustrate this pattern of gradual urban encroachment into the area surrounding the Laboratory.

Pressure to develop the flatter portions of the Livermore Valley has come from many sources. Among these are demands for new housing reflecting the continued growth of the city of Livermore, expanded commercial building to serve this growing community, and relatively high property values in the San Francisco Bay Area to the west. The Laboratory, located in the far eastern end of the valley, has been effectively isolated from development pressures in the past, but the extent of current plans indicates that private development of the land adjacent to both LLNL and Sandia National Laboratories, Livermore, is quite likely.

Partly as a result of these development pressures and partly because of the security needs of the times, the Laboratory is working with the Sandia National Laboratories, the Department of Energy, and the U.S. Congress, to acquire additional land on its borders. □

November 1936

The city of Livermore, looking northeast. The road leading from the downtown area toward the upper right corner of the photograph is East Avenue. Livermore High School, to the left of East Avenue, is near the eastern edge of the developed portion of the city.

1944

Livermore's new neighbor, the Livermore Naval Air Station. The two miles between the air base and downtown Livermore is almost exclusively agricultural. The air base was activated as a training station in 1943 and deactivated late in 1946.

March 1954

At right, the city of Livermore, looking northeast. The Laboratory (upper right corner) is only one and a half years old, and redevelopment of the air station has barely begun. A major housing development is underway on the Livermore end of East Avenue. Below, the city of Livermore (in the foreground), looking to the west. Highway 50 runs north of the city; the eight-lane Interstate 580 has not been built. Development of the valley between Livermore and Pleasanton is minimal.

March 1956

After three and a half years, the Laboratory is well established, with several major structures completed. The surrounding area remains rural and almost unchanged.

May 1969

A view of the Lawrence Livermore and Sandia laboratories (in the foreground) and the city of Livermore, looking west. Residential development on both sides of East Avenue has progressed significantly toward the laboratories.

April 1983

The Livermore Valley, looking toward the west. The Lawrence Livermore National Laboratory and Sandia National Laboratories, Livermore, are in the foreground. Residential and commercial developments are advancing rapidly toward the laboratories. The Livermore city limit was recently advanced to the Laboratory's western boundary and is expected to be at the north boundary in the near future.

September 1983

After thirty years, the Laboratory's mile-square site is almost fully developed. The eastern portion of the Laboratory, particularly the northeast (upper-right) quadrant, contains the few remaining sites suitable for large-scale development. The H-shaped buildings along the southwest (bottom-left) boundary are the barracks left from the days of the Naval Air Station; they are being removed as replacement facilities are made available elsewhere.

July 1963

This photograph and the one on the next page (composites of photographs of smaller areas) show development in the Livermore Valley over a twenty-year period. Both pictures show the cities of Livermore (on the right), Pleasanton, and Dublin (on the left). This photograph is cut off just short of the Laboratory's western boundary.

February 1982

In this composite photograph, the Laboratory is visible at the far right. By 1982, two new freeways cross the area, and extensive commercial and residential construction fills much of the once agricultural lands. Not shown in this picture are two recently begun industrial parks, one in Pleasanton and one north of LLNL near the freeway.

First-Principles Calculations of Materials Properties

Dramatic advances in electron-band theory (the quantum mechanical theory of electrons in solids and liquids) enable us to calculate reliably the thermodynamic properties of many materials from first principles.

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Many of our programs at the Laboratory require accurate and detailed information about the thermodynamic properties of materials over a wide range of temperature and pressure (up to 100 eV and 10 TPa). Over most of this range, reliable experimental data are unavailable so we must calculate the needed values from theoretical models. Although many simple theories (such as the semiclassical Thomas-Fermi models) have been highly successful, they often have severe limitations at the low temperatures and pressures where quantum-mechanical effects become important. In the past decade, electron-band theory has come to fill this gap, greatly improving existing calculations and opening up totally new vistas as well.

Electron-band theory is the modern quantum-mechanical theory of electrons in solids and liquids. As atoms condense to form a liquid or solid metal, the electrons in the more energetic outer orbits break away from their respective atoms (leaving them ionized) and move about freely. Because these "free" electrons behave like waves, they are scattered by the relatively stationary ions

much as water waves are scattered by pilings in a pier.

This wave nature of electrons in condensed matter, an essential aspect of quantum mechanics, is indispensable to an understanding of a vast array of materials properties of solids and liquids. With the aid of electron-band theory, we can now explain, for example, the large variations in equilibrium (zero-pressure) atomic volume throughout the periodic table, the rich optical and x-ray absorption spectra for solids, and why some materials are conductors and others are insulators.

The initial formulation of electron-band theory dates back to early work on crystalline solids in the 1930s.^{1,2} Although this work led to the development of many detailed formalisms, the calculations involved were so formidable that these techniques came into common use only after the advent of large computers in the 1960s. Even then, the tremendous expense in computer time severely limited the first-principles applications of electron-band theory and the materials properties that we could calculate.

Several conceptual developments in the past ten years have increased greatly

both the speed and applicability of these methods, with only slight losses in accuracy, thereby breaking this bottleneck. The result has been a surge in the use of electron-band theory and its successful application to calculational problems that were almost beyond reach a decade ago. Two such problems, which are of particular interest to LLNL programs, are equations of state and temperature-pressure phase diagrams.

The equation of state for a particular material is the unique relationship that exists among pressure, temperature, and the material's density. This equation specifies, for example, the pressure required at some particular temperature to compress a solid to a given fraction of its original volume.

Another effect of temperature or applied pressure can be an abrupt change in the microscopic packing arrangement of the atoms from one configuration to another, possibly disordered as in the case of the liquid phase. Although such structural phase transitions often have only a small effect on the equation of state, they may dramatically change other properties (for example, the loss of material strength at melt). The goal of structural phase-stability calculations is to determine the phase diagram of a given material, i.e., the boundaries in the temperature-pressure plane that separate regions where different crystal structures (or the liquid) are stable.

Although the greatest strength of electron-band theory today still rests with treating perfectly periodic crystals at cryogenic temperatures, significant progress has been made in dealing with the ion vibrations brought about by increasing temperature. It is now possible to calculate from first principles the vibrational or phonon spectrum of certain elemental solids and the corresponding thermal contribution to the total equation of state. The creation of lattice vibrations can also induce solid-solid phase transitions by lowering the total free energy of one crystal structure with respect to that of another. Thus the determination of the phonon spectrum is often an essential ingredient in calculating the equation of state of

a material and in completing the temperature axis of its phase diagram as well.

When the temperature is high enough, the solid melts (i.e., the ions free themselves from their equilibrium positions and begin to migrate). Although the electron-band theory for the liquid state is far less advanced than for the solid, it has recently become possible to make first-principles calculations of the thermodynamic properties of certain simple metal liquids, including the melting curve on the phase diagram.

Electron-Band Theory

At very low temperatures, the ion cores are essentially stationary and thermodynamic properties, such as total energy, are dominated by the behavior of the valence electrons (i.e., those electrons moving freely throughout the metal). To calculate the total energy, we must first determine the permissible quantum-mechanical states available for these valence electrons.

It would be an impossible task to determine simultaneously the quantum mechanical states of all the valence electrons because there are so many of these electrons, even in the tiniest bit of matter, and each interaction affects all the others. To get anywhere at all, therefore, it is necessary to make a seemingly drastic reformulation (which is, however, entirely rigorous theoretically).³ In this reformulation, the exact many-body quantum-mechanical problem is replaced by a one-electron Schrödinger equation that treats each electron as if it is moving in an average potential field created by all of the remaining positive and negative charges.

This is not enough, however. Although it can be shown theoretically that there exists a unique functional of the electron density that will give an exact solution for the total energy in this one-electron representation, and although some parts of this functional are known, the rest is unknown.³ We must make an approximation, substituting for the unknown part the functional calculated for a system of electrons in a uniform compensating

Fig. 1

Electron energy bands as a function of relative atomic volume (Ω/Ω_0) in aluminum. The electron energies are given relative to the Fermi level (horizontal line, $E/E_F = 1$), which is the energy of the most energetic electron in the metal at zero temperature. At large volumes (beyond the right side of the figure), all bands are narrow and approach the discrete levels of an isolated atom. Near normal solid density ($\Omega/\Omega_0 = 1$), the 1s, 2s, and 2p electrons are tightly bound (narrow energy bands) and only the 3s and 3p (valence) states are broad. At higher compression, the 3d and 4f states enter the picture from above and even the 1s, 2s, and 2p bands become quite broad and overlap the higher-lying bands.

positive background.⁴ This approximation is referred to as the local-density approximation, and electron-band theory often is called local-density theory for this reason.

The electron states calculated in the one-electron representation fall into continuous bands of allowed energy values, separated by energy gaps. Figure 1 shows the energy bands for aluminum as a function of relative atomic volume, Ω/Ω_0 . The Fermi energy, indicated by the horizontal line, is the energy of the most energetic electron in the solid. At zero temperature, electron states above this energy are empty while those below are occupied. Only the occupied states contribute to the total energy of the solid. All thermodynamic functions of interest may be directly calculated, once the total energy of the solid is known as a function of volume and temperature.

The electronic structure of real materials lies between two very simple limits, as suggested in Fig. 1. At very large volumes (e.g., in the vapor phase),

the coulomb attraction between an electron and its "own" nucleus is the dominant potential energy term, and the energy bands reduce to the discrete energy levels found with isolated atoms. Even uncompressed solid aluminum represents such a large volume for its 1s, 2s, and 2p core electrons (though not for the others), and so these bands become very narrow toward the right-hand side of Fig. 1. (For even larger volumes, the other bands also become extremely narrow.)

At very high compressions, on the other hand, the kinetic energy of the electrons becomes the dominant factor and both the core and the valence electrons behave as if they were free particles, characterized by broad overlapping bands. Since the 2p band overlaps both the 1s and 2s bands in energy at the left side of Fig. 1, there is an uninterrupted continuum of levels in this region beginning with the 1s band and extending upward in energy.

The electronic states in most solids at normal conditions are intermediate between these atomic and free-electron limits. Applied pressure not only broadens the electron bands but also rearranges them, as, for example, the bottom of the 3d band in Fig. 1 eventually drops below that of the 3s band. Since the occupation of electron bands of different angular momentum (s, p, d, f, etc.) and their degree of broadening contribute to the properties that differentiate among the simple, transition, and actinide metals, these pressure-induced changes in electronic structure also affect measurable thermodynamic properties.

The local-density approximation makes it possible to calculate the total energy and other thermodynamic properties using a variety of techniques, but only laboriously except in cases where the electronic structure simulates either the atomic or the free-electron extreme. Recently, however, dramatic progress has occurred in the development of powerful perturbation-expansion and muffin-tin-potential techniques, permitting computationally convenient solutions for a much broader class of materials. This has led to

renewed interest in the application of electron-band theory to materials physics.

Perturbation Theory Techniques

The free-electron limit mentioned above often is achieved at much larger volumes than might be expected from the preceding arguments. In aluminum, for example, the 3s and 3p valence electrons already behave at zero pressure as if they were only weakly perturbed by the ion cores. This occurs because, in aluminum, the positive and negative potentials almost cancel except close to each nucleus. Since the energetic valence electrons spend most of their time far from these core regions, they are only slightly affected by the deep ion-core potentials.

This phenomenon can be expressed mathematically by transforming the Schrödinger equation to an equivalent expression in which we replace the full electron potential with a weak effective potential, or pseudopotential. Then, we can carry out perturbation expansions in terms of the pseudopotential, with the free-electron gas as the unperturbed system, to obtain a simplified expression for the total energy. This approach is called pseudopotential perturbation theory.⁵

Similarly, the "free atom" limit often persists to much smaller volumes than one might naively expect from Fig. 1. For example, the d electrons in iron and copper (transition metals) retain their narrow energy bands in the condensed state. This is primarily an angular-momentum effect. The high-angular-momentum 3d electrons in iron or copper, for example, have energies comparable to those of the 4s and 4p electrons. Because of their smaller principal quantum number (3 vs 4), however, their wave functions are much more localized around the ion cores. Near any given site, such electrons are moving in a strong atomic potential plus a weak perturbing potential (or pseudopotential) due to the rest of the solid.

Approximate solutions to the Schrödinger equation also may be

based on the effective weakness of this perturbing potential. This latter approach is usually referred to as tight-binding theory, in reference to the "tightly bound" nature of the electrons it treats.

Within the past ten years, we have combined the pseudopotential and tight-binding methods into a generalized pseudopotential theory, or GPT,⁶ for both simple and d-band transition metals. It is also possible, in principle, to extend such methods to f-band metals like the actinides, and this is one goal of our future work.

The greatest practical strength of our GPT formulation is that it applies equally to the whole range of condensed matter, from perfect crystals at absolute zero to completely disordered liquid metals. This enormous flexibility arises because the perturbation methods allow us to treat analytically the structure dependence (i.e., the dependence on ion position) of all theoretical quantities. This important feature is evident in the case of the total energy, which we can express as a sum of effective pairwise (central-force) interactions between the ions plus a large volume-dependent constant. Knowledge of the volume-dependent (but structure-independent) pair potential allows us to calculate not only structural energy differences in the solid but also the phonon spectrum and liquid thermodynamic properties.

The weakness of this approach, however, is that it gives only an approximation to the total energy of a metal because it neglects multi-ion contributions arising from higher-order pseudopotential terms. In some cases, as in the large zero-temperature portion of the total pressure in the solid, these terms can combine to make a significant contribution to the total energy. The complementary muffin-tin approach, a nonperturbative method of solving the one-electron Schrödinger equation (discussed below), yields more accurate results for such low-temperature properties.

Muffin-Tin Approximations

An alternate way of solving the one-electron Schrödinger equation for perfect crystals² rests on the realization that the

space within a crystal can be divided into two distinct regions, each with its own characteristic potential. For an electron situated midway between neighboring nuclei, the opposing forces must nearly cancel, so that the potential should be nearly constant in this region. Very close to any particular nucleus, on the other hand, the potential should be nearly spherically symmetrical.

If we exaggerate the extent of the two limiting regions, employing the spherically symmetric potential out to a certain radius and then shifting to the constant potential, the result (for a two-dimensional crystal) resembles the familiar pan for baking muffins or cupcakes (Fig. 2), with a nucleus positioned at the center of each circular cup. There is now ample evidence that this approximation is quite accurate for close-packed solids, which include most metallic structures.

It is relatively simple to find wave functions that satisfy the one-electron Schrödinger equation within either of the two muffin-tin regions. However, it is difficult to find wave functions that are both continuous and differentiable across the boundaries between the two regions and that have the same symmetry as the crystal. This used to involve, in effect, a trial-and-error search, substituting one energy value after another into a large

matrix equation to locate those that correspond to the desired electron eigenstates for the crystal. With large digital computers, these methods^{2,7} have become feasible and have produced important results.⁸ Unfortunately, these methods are extremely time consuming, taking, in some cases, up to an hour of CDC 7600 time to compute a single equation-of-state point.

The key difficulty in an exact solution of the muffin-tin problem is that the energy being sought appears throughout the matrix equation, making it necessary to recalculate the entire matrix for each trial value of the energy. In 1975, however, it was discovered that the wave function could be approximated with a special energy-independent function.⁹ This technique, called the linear muffin-tin orbitals (LMTO) method, made it possible to construct the matrix once and then diagonalize it to obtain the desired eigenvalues nearly a hundred times faster than the older methods with only slight further loss of accuracy. We have been using this technique for the past five years and were among the first to apply it extensively to the calculation of low-temperature equations of state and phase stability.

These muffin-tin methods perform equally well regardless of the degree to

Fig. 2

Diagram of the muffin-tin-potential model used to simplify calculations using the electron-band theory. The cups represent the strong attraction of the ion core for electrons. The flat area among the cups represents the net weak attraction when an electron is midway between ionic cores.

which the electron states are localized or extended. Thus, they are immediately applicable to a wide range of solids, including simple, transition, and actinide metals as well as many insulators. On the other hand, muffin-tin methods require a high degree of crystalline symmetry and a relatively close-packed arrangement of the atoms. These conditions are generally well satisfied for low-temperature metals but deteriorate with thermal disorder of the lattice at high temperatures, where methods such as the GPT are more appropriate.

Equations of State

One of the most easily verified points on a zero-temperature equation-of-state curve for any material is the predicted density at zero pressure. This point also presents one of the more difficult calculational challenges because, in general, the lower the pressure, the less free-electron-like (i.e., less simple to calculate) the underlying electronic structure becomes. A good indication of how well these calculational methods perform, therefore, is given by the predicted zero-pressure volumes of the elements.

Figure 3 compares available experimental data from the open literature with muffin-tin calculations of zero-pressure volumes of the elements and with earlier Thomas-Fermi theoretical approaches. For clarity, we represent the experimental values by quasi-continuous solid lines and the theoretical predictions as data points. The two curves represent the Thomas-Fermi results, the only general methods previously available for such calculations.

The dramatic variation from element to element in the experimental zero-pressure volumes in Fig. 3 is a direct manifestation of the wave nature of electrons in solids. The band-theory predictions correctly follow these trends to within about 6% on average. The predictions of the two semiclassical Thomas-Fermi models fail completely to reproduce this behavior since they neglect the wave aspect of electron behavior. This is why the Thomas-Fermi models have been used mostly at higher pressures, where they are more accurate.

At lower pressures, the equation of state has been based, as much as possible, on experimental results.

For comparisons at higher pressure, we turn to room-temperature data obtained from diamond-anvil measurements.¹⁰ Figure 4 shows experimental data¹¹ and muffin-tin predictions for the zero-temperature pressure-volume curves of three very dissimilar elements: xenon, an insulator at low pressure, lanthanum, a rare earth metal, and aluminum, a simple metal. The experimental measurements were carried out at room temperature (or below, for xenon), but have been reduced to zero temperature by using simple model estimates for the small corrections (less than 1 GPa).

Because the band-theory methods involve approximations, there is inevitably some discrepancy in pressure or volume between theory and experiment. The offsets in volume shown in Fig. 4 are representative (1 to 8%), with that for aluminum somewhat better than the average and lanthanum among the worst. The semiclassical Thomas-

Fig. 3

Equilibrium zero-pressure atomic volumes of the elements as a function of atomic number. The observed experimental values lie along the quasi-continuous solid lines (black), whereas those calculated by first-principles muffin-tin band theory are represented by solid blue points. Thomas-Fermi calculations (TFC and TFD, blue lines), shown here far outside their normal range of application, reproduce none of the wide-ranging variability observed experimentally.

Fermi predictions (TFC and TFD in Fig. 3) would be far worse, however, on the order of 100%. The results in Figs. 3 and 4 support an important conclusion: given only the atomic number and the choice of crystal structure as input, electron-band theory can reproduce the dramatic differences in equations of state among the very dissimilar elements throughout the periodic table.

Pressures significantly higher than 50 GPa can be obtained only with shock compression experiments; our two-stage light-gas gun, for example, routinely achieves pressures of a few hundred gigapascals. However, shock compression strongly heats the sample being investigated. To calculate a pressure-

volume curve from such experiments, we also must account for the thermal contribution to the equation of state.

The thermal pressure is the difference at fixed volume between the pressure at some finite temperature and that at absolute zero. It has two components, one electronic and the other ionic. At elevated temperature, the electrons will no longer occupy the lowest energy states available but will be excited to higher lying states. This electronic-excitation contribution may be obtained by performing electron-band-structure calculations at finite temperature.

The ionic contribution, i.e., that due to the vibrational motion of the ion cores themselves, is the dominant thermal correction in the region probed by the two-stage light-gas gun. Although the ionic contribution is approximately linear with temperature in this regime, it is more difficult to calculate than the electronic contribution. Fortunately, our GPT method fills this need.

Figure 5 compares experimental results and theoretical pressure-density calculations for aluminum. We used muffin-tin band theory to obtain the zero-temperature and electronic contributions to the pressure.¹² The GPT computation adds the ionic contribution, and the combined result, obtained entirely from first-principles theory with no adjustable parameters, is in good agreement with the experimental data.

Fig. 4

Experimental (black) and theoretical (blue) zero-temperature pressure-volume curves in xenon, lanthanum, and aluminum (three very dissimilar elements) as a function of relative atomic volume. The experimental results have been reduced to zero temperature from measurements taken at room temperature (experimental curves and data points from the literature, see Ref. 11). The theoretical results are our calculations from first-principles muffin-tin band theory.

Fig. 5

Our theoretical shock-compression curve in aluminum as a function of density. The experimental results represent data obtained from the literature (open dots)¹³ and from our two-stage light-gas gun (solid dots).¹⁴ The theoretical curve represents the combined results obtained with first-principles muffin-tin and GPT calculations.

Phase Stability

The application of electron-band theory to the general problem of phase stability in condensed matter and the calculation of temperature-pressure phase diagrams is comparatively new and shows great promise for the future. At low temperatures, most simple and transition metals and many insulators occur in one of three common crystal structures: face-centered cubic (fcc), body-centered cubic (bcc), or hexagonal close-packed (hcp). One challenge in calculations of phase stability is to differentiate among these structures on the basis of the tiny total energy differences between them (often 1% or less of the energy difference between isolated free atoms and the solid). For

many years, in fact, it was debatable whether band-theory methods could ever be accurate enough to predict the stable structures of the elements.

There is now a growing body of evidence that this can be done with rather good reliability. For example, at zero temperature, both perturbative methods, such as GPT, and muffin-tin methods, such as LMTO, now give consistent results for simple metals. Figure 6a displays our LMTO calculations of total energy differences for the bcc and the hcp structures with respect to the fcc structure in aluminum as a function of volume; Fig. 6b shows our parallel GPT calculations.¹⁵ Both methods correctly identify the observed fcc structure as stable (i.e., the one of lowest energy) at zero compression. Both methods predict a sequence of pressure-induced phase transitions from fcc to hcp to bcc. In this case however, the predicted phase transitions, occur above 100 GPa, beyond the range of current experiments.

However, subsequent LMTO calculations for the heavy alkaline earth metals, carried out elsewhere,¹⁶ have predicted sequences of structural transitions at lower pressures, in striking agreement with findings of recent diamond-anvil experiments.¹⁷ Furthermore, another application of electron-band theory has yielded very close agreement with experimental results for the low-pressure transitions in silicon and germanium.¹⁸

Corresponding temperature-induced phase transitions at constant pressure also can be calculated from first principles with the GPT method. Many of the alkali and alkaline-earth metals, for example, undergo a transition from either hcp or fcc to bcc upon increasing temperature. This occurs because the bcc structure has lower vibrational frequencies than the others (it is less tightly packed and, hence, softer than either an fcc or hcp lattice). Thus, raising the temperature and thereby creating phonons will lower the bcc free energy relative to the other two, making a phase transition possible.

Figure 7 compares our theoretical GPT and the experimental phase diagram in

solid calcium to 3 GPa. The low-temperature fcc phase and high-temperature bcc phase are correctly predicted, as is the approximate location of the phase line separating them. Localized d-electron effects, explicitly incorporated by the GPT, are crucial to this agreement. This agreement between theory and experiment is truly remarkable given the extremely small structural energy differences that must be calculated to make these predictions.

Our GPT method also permits calculation of the thermodynamic properties of the liquid state, including the melting curve on the phase diagram. This is possible because the ion-ion pair potential computed at any given density applies just as much to the liquid as to the solid state.

In the liquid, however, we also must have information about the statistical distribution of ion positions in space. This information is embodied in the structure factor (pair-correlation function) for the ions and in the entropy of the

Fig. 6

Variation of the zero-temperature total energy of the bcc (black) and hcp (blue) crystal structures in aluminum with respect to that of the observed fcc structure (horizontal line) as a function of relative atomic volume, as calculated by (a) the linear muffin-tin orbital (LMTO) method and (b) our generalized pseudopotential theory (GPT). Although the pressures involved are beyond the present range of experimental verification, both theoretical methods predict pressure-induced phase transitions from fcc to hcp to bcc as each, in turn, becomes the phase of minimum energy.

fluid, both of which can be obtained, either analytically or from Monte Carlo calculations, by replacing the exact pair potential between atoms with a simple but closely related model form called the reference pair potential.^{19,20} This potential usually contains a single variational parameter that is constrained to minimize the free energy of the real liquid, thereby making the method quantitatively accurate.

The major hurdle in applying this fluid variational theory is the

identification of a satisfactory reference system for the metal of interest. Present experience is very limited in this regard. One metal for which a good choice appears to be available is aluminum,²⁰ and we are currently investigating others of theoretical and practical importance.

The most demanding test of the reference system, and of our GPT method itself, is in the calculation of the melting curve. (Again, this calculation involves very tiny energy differences.) Figure 8 shows the full GPT-calculated low-pressure phase diagram of aluminum, together with the experimentally observed melting curve. The predicted melting curve deviates from the experimental data by only about 10%.

Summary

Many of LNL's programs require accurate and detailed information about the phase diagrams and the equations of state of various materials over ranges of temperature and density that are beyond the reach of laboratory experiment and, hence, must be calculated from theoretical considerations. Dramatic advances in electron-band theory enable us to calculate reliably, for many materials, these thermodynamic properties from first principles using two new calculational approaches, the linear muffin-tin orbital (LMTO) method and our generalized pseudopotential theory (GPT). The LMTO method is particularly suited for calculating phase stability and equations of state at low temperature and applies equally well to simple, transition, and actinide metals as well as to many insulators. The strength of the complementary GPT formulation is that it applies equally to the whole range of condensed matter, from perfect crystals at absolute zero to completely disordered liquid metals, allowing us to calculate phase diagrams at finite temperature, thermal contributions to the equation of state, and liquid thermodynamic properties. The agreement we have been able to achieve between our calculations and experimental results bodes well for the future of band-theory methods in calculating phase diagrams and equations of state. □

Fig. 7
Theoretical and experimental pressure-temperature phase diagram in solid calcium. We obtained the theoretical result by first-principles calculations with the GPT.

Fig. 8
Theoretical (blue) and experimental (black) pressure-temperature phase diagram in aluminum, including the melting curve. This theoretical result was obtained by first-principles calculations with the GPT.

Key Words: diamond-anvil compression; electron-band theory; equation of state; generalized pseudopotential theory (GPT); linear muffin-tin orbitals (LMTO); phase transition; pseudopotential theory; shock compression; two-stage light-gas gun.

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Silicone Cushions for Engineering Applications

Designing cellular silicone cushions that can function in adverse environments is a complex, iterative process. We must study material properties to produce cushions that are tailored to satisfy various engineering requirements.

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The performance of a complex system depends on the ability of its internal parts to retain their shapes and relative positions, even though they may be made of materials with widely differing thermal-expansion properties. Some systems may remain in relatively stable environments but others must function over a wide temperature range. To meet these conditions, we use cellular silicone cushions to relieve and distribute stresses.

Support cushions, in addition to accommodating differential thermal expansion, serve (in increasing order of importance) to:

- Damp out shock and vibrational impulses.
- Take up dimensional tolerances in components.
- Distribute or attenuate loads.
- Maintain part relationships by exerting positive stress.
- Accommodate component separation during thermal cycling.
- Accommodate irreversible thermal and nonthermal distortions.

Design and Properties

Cushions, in their role as buffers, act as organic springs. The crucial

parameters characterizing a cushion are its stiffness (modulus) and its stroke (amount of possible compression). If the cushion obeyed Hooke's Law, its stress-strain curve would be a straight line (Fig. 1). However, the stress-strain curve is nonlinear; the cushion exhibits hysteresis and transient effects, as well. The stress-strain curve for loading and unloading are different, and the first load-unload cycle is different from all subsequent cycles (see Fig. 1).

Designing a cushion to meet engineering requirements involves three interrelated parameters: load, stroke, and thickness. For example, a soft cushion can provide a large stroke but will not support a large load unless it is prohibitively thick. In contrast, a stiff thin cushion can support a large load but, because it will have little stroke, can build up destructive stresses during thermal cycling. Thus, cushion design is a complex, iterative process, and flexibility in altering materials properties to match different engineering demands is an important requirement for a prospective cushion material.

The ideal cushion material must have:

- Long term stability.
- Elastomeric properties over a wide temperature range.

- **Low compression set** (i.e., the ability to recover its original dimensions after an applied load is released).
- **Load retention** (i.e., the ability to continue to support a given stress at a given deformation).
- **Convenient control of the effective modulus.**

The first cushions were solid "waffle" elastomers or polyurethane foams, but these materials proved unsatisfactory, having poor load-bearing properties and deteriorating very rapidly. Silicone cushions are superior to other elastomers and foams in terms of thermal properties, long-term stability, and lower compression set. Cellular silicone cushions are better than blown silicone foams because they provide greater flexibility for designing material properties to match various engineering requirements.

We began to develop cellular silicone cushions in 1961. Initially, Union Carbide Corporation provided the cellular silicone material and Bendix, Kansas City, molded it into cushion parts. In 1978, Union Carbide stopped supplying both the cellular silicone molding compound and the raw materials from which it was made. This forced Bendix to develop its

own cushion-manufacturing activities; Bendix now buys the starting materials from various commercial sources and processes them into finished cushion parts.

Manufacture

Figure 2 illustrates the complex sequence of steps for processing the starting materials into finished cellular silicone cushions.¹ First, the raw silicone gum is mixed with an inert filler (silica)² and a processing aid (a silicone compound) that promotes favorable gum-filler interactions. The resulting

Fig. 1

Although silicone cushions function as organic springs, they violate Hooke's law (the behavior shown by the straight lines for various stiffnesses), exhibiting nonlinear behavior in a stress-strain test, hysteresis on every load-unload cycle, and a transient effect on the first load cycle. These material properties are important in cushion design.

Fig. 2

Steps in the manufacture of cellular silicone cushions. Silicone gum and silica are mixed, milled, extruded, and bin aged for one week. A catalyst, the cure initiator, and urea, the temporary filler, are then added, and

parts are molded in a heated, high-pressure press. The urea is dissolved by washing the part in water, producing the open-pore structure characteristic of cellular silicone cushions. Postcure baking, testing, packaging, and shipping complete the manufacturing process.

reinforced gum is milled, extruded, and aged for one week. It is then mixed with a cure initiator³ and a temporary filler (urea).⁴ The resulting molding compound is shaped into parts or test slabs in a high-pressure hot mold. The part is then washed in water to dissolve the urea and produce the open-pore cushion. Subsequent postcure baking completes the polymerization.

Both Bendix and LLNL have the capability for manufacturing cellular silicone cushions, although parts currently are made exclusively at Bendix. Process development is primarily the province of Bendix,⁵ while we continue to do the materials development.

Materials Development

The primary objective of our cushion project is to understand the materials needed to fulfill programmatic requirements for both present and future applications. Our effort, therefore, is directed toward three major goals:

- Developing sources of well-characterized cushion material.
- Determining how to adjust cushion properties by changes in both materials and processing.
- Improving and predicting the long-term chemical and physical stability of cushion materials.

The accomplishment of these goals requires efforts in synthesis, analytical development, materials formulation, processing and characterization, life testing, and modeling. We interact with Bendix at each step.

Synthesis

Synthesis involves the design of chemical polymers to obtain desired physical and chemical properties.^{6,7} The silicone gum used in cushions is a terpolymer consisting of about 86% dimethylsiloxane, 13.5% diphenylsiloxane, and 0.5% methylvinylsiloxane.⁸ Dimethylsiloxane, the major component, provides thermal stability and chemical inertness. Diphenylsiloxane lowers the glass-transition temperature of the material by disrupting the crystallinity of the polymer, thus extending the service temperature to below -55°C . Methylvinylsiloxane,

although present at a very low concentration, is probably the most critical component. Because the "catalyst" or cure initiator we use is vinyl specific, the vinyl group in this chemical component is responsible for hooking the linear polymer chains into the final cross-linked network.

There are three general ways to link these chemical components together into a linear polymer: (1) randomly, (2) as a triblock polymer consisting of distinct repeating units, and (3) as a hybrid of the first two (Fig. 3). All cellular silicone cushions (including those to be developed in the near future) are based on a random terpolymer reinforced with silica. Indeed, the cushion material of the future may well be the block polymer without the inert filler (and hence the processing aid) because it would simplify the manufacturing process, possibly enhance longer-term stability, and eliminate the biggest gap in our understanding of cushion materials.

The raw silicone gum currently being used (SE-54) has a molecular weight of about 600 000, a fixed methylvinylsiloxane content of only 0.2%, and trimethylsiloxane groups terminating both ends of the linear terpolymer. We are developing a new gum (L97) of similar molecular weight that has a variable vinyl content, is terminated at the ends by dimethylvinylsiloxane, and can be synthesized with transient "catalysts" that leave no chemically active residue.

Because we can vary the vinyl content, we can tailor the cushion's load-bearing mechanical properties to meet engineering requirements. For example, a higher vinyl content means a more tightly cross-linked polymer and, hence, a stiffer cushion. Furthermore, a vinyl content of more than about 0.3% by weight produces cushions with a substantially lower compression set than those containing 0.2% or less. The vinyl groups terminating the linear chains provide an additional decrease in compression set, apparently because this feature chemically incorporates the chain ends into the polymer network by cross-linking specifically through the vinyl groups. Cushions based on L97 gum

typically are a factor of two or three more resilient (i.e., have lower compression sets) than cushions based on SE-54 gum.

There is evidence that the traditional catalyst used in polymerizing the three components into the final gum leaves a harmful ionic residue. As part of our synthesis program, we have developed transient catalysts whose neutral residues are easily removed. Thermogravimetric analysis shows that L97 silicone gums synthesized using the transient catalysts have even greater thermal stability than those made of SE-54. The final assessment, however, will depend on life tests, both short-term tests at high temperature (accelerated aging) and long-term tests at lower temperatures.

Analytical Development

We have interacted closely with Bendix to coordinate analytical methods and specifications for materials acceptance before production.⁹ Initially, there was no accurate and precise analysis for vinyl content. Development of a suitable analytic method has required considerable work because the vinyl concentration is so low.

We have developed two techniques for analyzing vinyl content to better than ± 0.02 wt%. One technique uses Fourier-transform nuclear magnetic resonance and determines the vinyl content by measuring the relative concentration of vinyl protons.¹⁰ The other involves acid digestion with cleavage of the vinyl group, followed by gas-chromatographic analysis of the resulting ethene. The excellent agreement between these two widely dissimilar techniques, coupled with analyses of standards, gives us confidence in both the accuracy and the precision of our analysis. These techniques, now being implemented, will make it possible to routinely analyze silicone gums for vinyl content.

Formulation, Processing, and Characterization

Previously, the only way to adjust the material properties of cushions was to change their porosity (where porosity is defined to be one minus the ratio of cushion density to the density of the

corresponding solid silicone rubber). Figure 4 compares the load-compression curves for a specific vinyl content and varying porosity with the curves for a specific porosity and varying vinyl content. It is apparent that a given load-compression requirement can be met by varying either the vinyl content or the porosity.

Figure 4 also illustrates the tradeoffs among load, stroke, and thickness. Engineering requirements are often expressed in terms of stroke (e.g., ± 0.5 mm) and load at a specific gap (e.g., 100 kPa at 2 mm). For a given vinyl content and porosity (e.g., 0.4 wt% vinyl and 56% porosity), such requirements correspond to a compression of 27% in Fig. 4. This, in turn, implies a specific thickness of $2/(1 - 0.27) = 2.74$ mm to meet the load-at-gap requirement. However, at a thickness of 1.5 mm (the stroke requirement), the cushion is compressed to 45% (i.e., $1 - 1.5/2.74$) and, therefore, has a much higher load value (275 kPa).

Silicone gum L97 is a vinyl-terminated linear polymer:

L97 consists of three major chemical components:

Component A   Component B   Component C

They are linked together in one of three ways:

- (1) randomly, A A B C B A C C B, forming a random terpolymer,

- (2) in ordered groups, A A A A A — B B B B B B B — A A A A A forming a triblock polymer,

- (3) in a mixture of the two modes, A A A A A — B C A B A A C, forming a hybrid random block copolymer.

Fig. 3

The polymer architecture of silicone gums is based on three siloxanes: dimethylsiloxane, diphenylsiloxane, and methylvinylsiloxane (abbreviated A, B, and C, respectively). These three components are mixed in a variable but specific ratio and linked together chemically into a vinyl-terminated linear polymer. Currently, these three components are anionically polymerized to produce a random terpolymer. We are investigating triblock polymers consisting of distinct, well-defined repeating units because they appear to have superior properties.

Fig. 4

Load-compression curves showing what can be done in tailoring the properties of cellular silicone cushions to meet engineering requirements (dashed lines; see text for discussion). The three critical parameters in designing cushions are vinyl content, porosity, and thickness. Increasing the vinyl content with a fixed porosity (56% in this case, blue curves) increases the cushion stiffness by promoting cross-linking in the polymer network. Increasing the porosity with a fixed vinyl content (0.7% in this case, black curves) decreases the cushion stiffness by making the cell walls thinner in the final cushion.

If the load value at the maximum or minimum requirement of the stroke is too high or too low, it is possible to change one or more of the variables (thickness, porosity, or vinyl content). For example, the load at 1.5 mm gap can be decreased by using a thinner cushion, by increasing the porosity, by decreasing the vinyl content, or by any combination of the three. In practice, all three variables are adjusted to meet the load requirements at the nominal and compressed thicknesses (2 and 1.5 mm, respectively).

Adjusting the porosity during cushion formulation is easier than adjusting the vinyl content of the gum during

polymer synthesis. However, we have demonstrated that blending two silicone gums of different vinyl content produces a gum of intermediate properties. We can envision a system in which a silicone gum similar to L97 will exist in two forms, one high in vinyl and one low. Load requirements for different programs will be met by blending appropriate amounts of the two and formulating the cushion to a specific porosity.

We have identified a commercial vendor who will synthesize L97 to our specifications. A great deal of work remains to be done, however, before this material can be substituted for SE-54. Many of the processing variables (e.g., formulation variables, molding time and temperature, and postcure time and temperature) must be optimized with respect to the mechanical properties of the finished cushion (e.g., load and compression set). We can do the initial work but, because of the uncertainties associated with the hundredfold scaleup from laboratory to production quantities, final processing optimization will take place at Bendix.

Life Testing

The mechanical properties of cushions degenerate over time. Therefore, we must make time-temperature compatibility studies of the cushion materials. Furthermore, although silicone cushions are quite inert, it is important to know whether they will adversely affect any other components in the system (occasionally, we must solve compatibility problems that arise from synergistic chemical effects). The purpose of the life test is twofold: to minimize degeneration resulting from the introduction of new materials and to predict future properties of materials presently being used.

The lifetime of many mechanical systems is more than 20 years. Obviously, it is impractical to actually test a material for this long before using it in production. Consequently, life testing takes one of two experimental approaches: a short-term (days to weeks) accelerated-aging test at elevated temperatures or a longer-term (months to a few years) test at realistic service-

temperature limits followed by modeling and extrapolation. Of course, life testing may continue while a material is in production or in use; Union Carbide cushion material more than 10 years old is still being tested.¹¹

We are pursuing both of these experimental approaches to life testing. There currently is no good accelerated-aging test for cellular silicone cushion material. Most of the results of past short-term testing of this material at 150°C correlated poorly with tests conducted at lower temperatures, although, paradoxically, the results of short-term testing of hydrogen-blown silicone cushions correlated well.

We studied this anomalous behavior using chemiluminescence¹² and found two distinct chemical mechanisms operating in both materials between room temperature and 200°C (Fig. 5). For cellular silicone cushions, the high-temperature mechanism dominated at temperatures greater than 110°C, whereas for the hydrogen-blown silicone cushions, the high-temperature mechanism remained insignificant below 150°C. In other words, with cellular silicone cushions, the short-term testing promotes a chemical degradation reaction that does not occur at service temperatures, skewing the test results. Figure 5 also illustrates the correspondence between the chemiluminescence data, which represent a microscopic and molecular process, and the compression-set data, which represent a macroscopic, bulk measurement.

Because of these results, we are in the process of redefining the accelerated-aging test procedures for cellular silicone materials. Our ultimate goal is to obtain a procedure and associated criteria that can realistically serve as a quality-control test during the manufacture of cellular silicone cushions.

The second approach to life testing, long-term testing at realistic service temperatures, is a coordinated effort that is much larger in scope than the short-term testing program. The two major types of long-term life testing are a straight load-retention test (done at Bendix) and a combined load-retention

and compatibility test. Our function is the assimilation and reduction of data.

In the first of these tests, cushion samples are placed in fixtures at a predetermined strain level (i.e., percent compression) and held at various temperatures (23, 50, and 70°C) for up to two years. The samples are tested periodically during this interval to determine the percent load retention (i.e., the change in load at a given gap after a given time at a given temperature).

In our analyses, we use an empirical model to describe the data. We express the total cushion-response curve as a sum of three contributions: static, hysteretic, and transient. One goal of the modeling is to determine how the parameters in the model evolve with treatment (i.e., stored compression, time, and temperature). The other is to assess

Fig. 5

Arrhenius plot of the relative rate of compression set and chemiluminescence vs inverse temperature for cellular silicone cushions and hydrogen-blown silicone cushions. The change in degradation mechanism at higher temperature is apparent from the nonlinear nature of the plot. The correlation between the molecular measurements (chemiluminescence) and bulk measurements (compression set) is evident and was the basis for redesigning the test procedure.

the reliability of extrapolating the model to longer times to predict the mechanical properties of cushions after years of storage.

Two things are apparent in a typical response surface (Fig. 6). First, the model is essentially linear in time or temperature after the first two months. This linear behavior also has been seen in cushions made of older materials. Second, the largest change in the percent load retention occurs in the first two months; in fact, it has been shown that this change occurs primarily in the first few days. This observation supports the idea of using a very short test (just a few days) as a quality control procedure during cushion manufacture.

Future substitution of any new material for current materials will be conditioned by available improvements in processing and immediate mechanical properties as well as in the relative performance of the new material during life testing.

Theoretical Modeling

We have made a modest effort in theoretically modeling the properties of

cushions, both to provide a guideline for designing cushions (processing and manufacture) and for interpreting some of the results of the empirical modeling, starting with the static portion of the load-compression curve. We were able to relate the stress, strain, and degree of porosity from first principles, achieving excellent agreement with experimental results.¹³ We have also extended this model to relate the porosity and vinyl content to a specified load-at-gap engineering requirement.¹⁴ Currently, we are attempting to interpret and describe the hysteresis effect and to use that description to design better quality control and life tests. One potential new test being evaluated this year is a long-term creep test, which provides complementary information to the stress relaxation test and is easier to model.

Conclusion

We are working to provide better cushion materials to meet engineering requirements. The development of improved materials arises from coordinated efforts in research, process development, and improved

Fig. 6

Three-dimensional response surface illustrating the dependence of percent load retention on time and temperature (the stored compression is fixed). The surface starts at 100% load retention at time zero and then decays rapidly in the first two months. Subsequently, the surface can be described quite well by a level plane. Additional experiments have shown that the initial decrease in load retention occurs primarily within the first few days. Because different materials exhibit a different initial decrease, we are interested in using this test for production quality control.

characterization. Success in developing new silicone gums, understanding filler-gum interactions, and interpreting the results from life tests will assure us of cushion materials that can meet future engineering requirements. ■

Key Words: cellular silicone; cushion; life testing; material properties.

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Synchrotron-Radiation Research Project (Brief)

Construction has begun on a two-beam-line synchrotron-radiation research facility at the Stanford Synchrotron Radiation Laboratory. This facility will provide highly collimated x rays with very desirable characteristics for research in many scientific disciplines, including biology, chemistry, and atomic and x-ray physics. The facility will use a wiggler, i.e., a multimagnet array that produces synchrotron radiation of unusually high intensity. Photon energies at the various experiment stations will range from 5 eV to 50 keV. The building is to be completed and the beam-line components ready for installation by mid-1985.

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Raman Spectroscopy of Shocked Water (Brief)

A combination of shock-wave techniques with sensitive spectroscopy is yielding new information about the dynamic chemical processes occurring in materials shocked to high pressures. We have made the first measurements of spontaneous Raman spectra emitted from water shocked to 7 GPa. The Raman spectrum of shocked water differs noticeably from that of unshocked water, particularly in the width of the OH-stretch band, which is about 20% narrower.

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The Strength of Ice

In order to model the evolution and current state of Callisto and Ganymede (Jupiter's two largest moons), which are similar in mass, density, temperature, and apparent composition (about 75% ice by volume) but different in appearance, we are studying the flow properties of ice under extreme conditions. With our new testing apparatus, we have determined that ice is very much weaker at low temperatures (below 160 K) than had been believed. This finding partially explains some of the unusual features found on these Jovian moons, although many questions are still being investigated.

Contact: William B. Durham (415) 422-7046 or Hugh C. Heard (415) 422-7088.

LLNL in the Developing Livermore Valley

A series of aerial photographs highlights fifty years of development in the Livermore Valley and illustrates the trend of urban encroachment into the land surrounding the Laboratory.

Contact: David Shikany (415) 422-1914.

First-Principles Calculations of Materials Properties

Many Laboratory programs require accurate and detailed information about the thermodynamic properties of materials over ranges of temperature and density that are experimentally inaccessible. Dramatic advances in electron-band theory (the quantum-mechanical theory of electrons in solids and liquids) enable us to calculate reliably, for many materials, these thermodynamic properties from first principles.

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Silicone Cushions for Engineering Applications

When a complex system composed of materials of very different properties is subjected to varying temperature, differential thermal expansion and contraction will produce intolerable stresses unless the parts are separated by suitable cushions. In addition to accommodating differential thermal expansion and contraction, these cushions must absorb shock and vibration, take up dimensional tolerances in the parts, and distribute and attenuate applied loads. We are studying cellular silicone cushions, starting with raw materials and polymer manufacture, to analysis of mechanical and chemical properties, through short- and long-term life testing, in order to tailor cushions to various specific engineering requirements.

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Past Titles

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temperature limits followed by modeling and extrapolation. Of course, life testing may continue while a material is in production or in use; Union Carbide cushion material more than 10 years old is still being tested.¹¹

We are pursuing both of these experimental approaches to life testing. There currently is no good accelerated-aging test for cellular silicone cushion material. Most of the results of past short-term testing of this material at 150°C correlated poorly with tests conducted at lower temperatures, although, paradoxically, the results of short-term testing of hydrogen-blown silicone cushions correlated well.

We studied this anomalous behavior using chemiluminescence¹² and found two distinct chemical mechanisms operating in both materials between room temperature and 200°C (Fig. 5). For cellular silicone cushions, the high-temperature mechanism dominated at temperatures greater than 110°C, whereas for the hydrogen-blown silicone cushions, the high-temperature mechanism remained insignificant below 150°C. In other words, with cellular silicone cushions, the short-term testing promotes a chemical degradation reaction that does not occur at service temperatures, skewing the test results. Figure 5 also illustrates the correspondence between the chemiluminescence data, which represent a microscopic and molecular process, and the compression-set data, which represent a macroscopic, bulk measurement.

Because of these results, we are in the process of redefining the accelerated-aging test procedures for cellular silicone materials. Our ultimate goal is to obtain a procedure and associated criteria that can realistically serve as a quality-control test during the manufacture of cellular silicone cushions.

The second approach to life testing, long-term testing at realistic service temperatures, is a coordinated effort that is much larger in scope than the short-term testing program. The two major types of long-term life testing are a straight load-retention test (done at Bendix) and a combined load-retention

and compatibility test. Our function is the assimilation and reduction of data.

In the first of these tests, cushion samples are placed in fixtures at a predetermined strain level (i.e., percent compression) and held at various temperatures (23, 50, and 70°C) for up to two years. The samples are tested periodically during this interval to determine the percent load retention (i.e., the change in load at a given gap after a given time at a given temperature).

In our analyses, we use an empirical model to describe the data. We express the total cushion-response curve as a sum of three contributions: static, hysteretic, and transient. One goal of the modeling is to determine how the parameters in the model evolve with treatment (i.e., stored compression, time, and temperature). The other is to assess

Fig. 5

Arrhenius plot of the relative rate of compression set and chemiluminescence vs inverse temperature for cellular silicone cushions and hydrogen-blown silicone cushions. The change in degradation mechanism at higher temperature is apparent from the nonlinear nature of the plot. The correlation between the molecular measurements (chemiluminescence) and bulk measurements (compression set) is evident and was the basis for redesigning the test procedure.